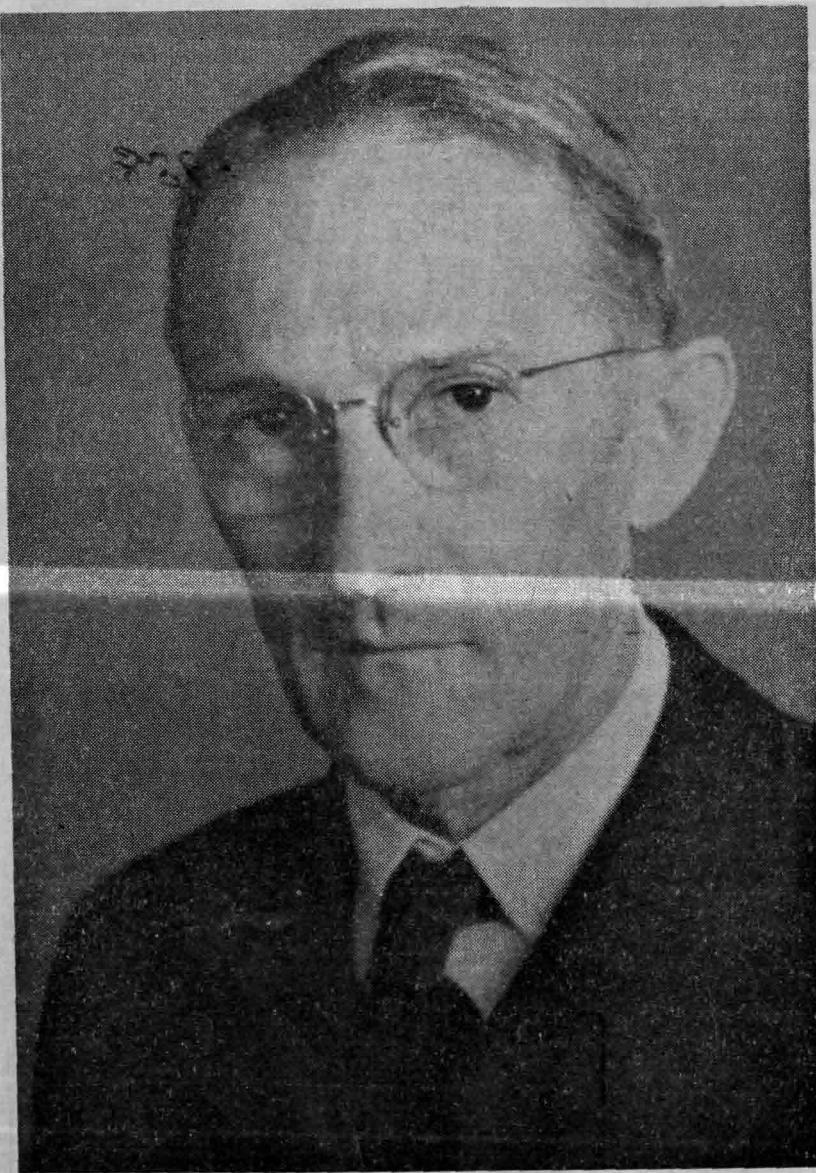


ESSENTIALS OF PHYSICAL CHEMISTRY



J. Heyrovsky

who has been awarded Nobel Prize in 1959 for devising "Polarographic analysis" using dropping-mercury electrode. "Oscillographic polarography" has proved very useful in ore analysis and in the determination of the purity of samples of pharmaceutical products; such as vitamins, hormones and antibiotics.

ESSENTIALS OF PHYSICAL CHEMISTRY

(A Text Book for B.Sc. Students of Indian Universities)

By

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PREFACE TO THE TENTH EDITION

In presenting the tenth edition of the book, the authors have utilised the opportunity to add some more topics so that the three-year degree course may be fully covered. A discussion of 'Dipole moments' has been included in Chapter II. In Chapters XXIV and XXV, the following topics have been included : Enthalpy, Kirchoff's equation ; Joule-Thomson effect ; Entropy ; Free energy and maximum work ; Van't Hoff Isotherm and Van't Hoff Isochore ; Glass electrode ; Redox potential, etc.

Nearly all the line diagrams have been redrawn and a new fronticepiece given. The problems at the end of various chapters have been reinforced by the addition of latest questions set in the B. Sc. examinations of Indian Universities.

It is hoped that with these additions, the book will serve a more useful purpose. To all those who sent us valuable suggestions for the improvement of the book, we extend our heartfelt thanks. Any suggestions for further improvement of the book will be gratefully received.

May 28, 1960.

THE AUTHORS

EXTRACT FROM PREFACE TO THE FIRST EDITION

The important role played by Physical Chemistry in the development of modern scientific ideas and chemical industries is now well recognised and for some time past, this branch of Chemistry has been receiving increased attention at the hands of the educators all over the country. At the same time there is a general feeling that very few really good books are available which can help the Indian students to clearly grasp the fundamentals of the subject. The authors seek justification for presenting the present volume in the honest and sincere attempt they have made to remove this deficiency.

The book not only provides a complete course of Physical Chemistry for B. Sc. Pass students of the Indian Universities but will also be found useful by the Honours students.

A special feature of the book is provision of a historical background which will enable the student to appreciate the spirit with which a scientist views all, new and old, ideas, viz., "No theory is more than a special way of looking at things, a variable formula expressing invariable phenomena."

The inclusion of a variety of solved and unsolved numerical examples will greatly help the student to grasp the basic principles.

While inviting criticism from fellow teachers for the improvement of the subject matter, we desire to express our sincere thanks to our colleagues for the kindly interest that they have taken during the progress of the book in the press.

June 20, 1943

THE AUTHORS

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CHAPTER I

FUNDAMENTAL PRINCIPLES

WHAT IS PHYSICAL CHEMISTRY ?

The distinction between the various branches of Science gradually disappears with their all-round progressive advance and it becomes very difficult to outline the boundary of any one of them. This is true more particularly of Physics and Chemistry. Chemistry deals with the changes which matter undergoes by the interaction of its various forms and in a broad sense studies the structure of matter by analysis and synthesis. Physics on the other hand, is concerned with the general properties of matter (kinetic, thermal, electrical, etc.) and with processes in which matter suffers no chemical change. **Physical Chemistry** embraces both of the above problems viz., structure and properties of matter and provides a common ground between the two sister sciences. Besides, Physical Chemistry endeavours to penetrate more deeply into the structure of atoms and molecules and their different states of aggregation. It also studies the physical characteristics of chemical reactions with respect to electrical, thermal, kinetic, photo-chemical and such other properties.

The close relation as regards the subject-matter between Physics and Chemistry is further emphasised by the fact that both in apparatus and in methods of measurement, the experimental technique of Physical Chemistry derives partly from Physics and partly from Chemistry. The same is true of the theoretical aspect of the subject. Physical Chemistry draws its facts from Physics on one side and all branches of Chemistry on the other and in turn helps them by correlating these facts.

FORMS OF MATTER—ELEMENTS AND COMPOUNDS

A brief examination of the substances around us will show that matter exists in two forms. Substances such as gold, copper or sulphur when heated or subjected to the action of an electric current or treated with acids or alkalies, are either unaffected or they produce new chemical substances of which they form only a part without losing their individuality. *Such substances which cannot be broken down to anything simpler* are termed **Elements**. The other substances when subjected to a similar treatment break down to give two or more elements. For example, sodium chloride when fused and electrolysed forms the elements sodium and chlorine. This class of *chemical substances which may be broken down to produce more than one element* are known as **Compounds**.

The simple definition of an element given above is questionable. Although elements have resisted decomposition by ordinary physical and chemical means, we have got instances of radio-active elements which disintegrate spontaneously to form new elements. Moreover, it has now been established that by bombarding ordinary stable elements with α , β or other high speed particles they can be made to yield new elements. In the face of these facts we must seek for a more

exact definition of an element. As we will study later, the *atomic number* has been now shown to be the most fundamental property of an element and this corresponds to its position in the periodic table. An element must have a definite atomic number and it must occupy a place in the periodic table. Hence, an **Element** can very well be defined as a **simple chemical individual which has a definite atomic number and occupies a position in the periodic table.** This definition covers all the stable and radio-elements.

LAWS OF CHEMICAL COMBINATION

The laws governing the formation of chemical compounds from elements are :

- (1) the Law of Conservation of Mass ;
- (2) the Law of Constant Composition or Definite Proportions ;
- (3) the Law of Multiple Proportions ;
- (4) the Law of Reciprocal Proportions or Equivalent Weights ; and
- (5) the Law of Gaseous Volumes.

The first four laws concern the combination of elements by weight and the last deals with the volumes of combining gases.

✓ Law of Conservation of Mass. (*Lomonossoff, 1756*). The law of conservation of mass states that :

When a chemical change occurs, the total mass of the products is the same as the total mass of the reacting substances.

Landolt (1900—1908) carried out a series of experiments which firmly established the truth of the law. For his experiments he selected reactions in which the evolution of heat is small. Two of such reactions are :—

- (i) sodium sulphite + iodine = sodium sulphate + sodium iodide,
- (ii) iodic acid + hydriodic acid = iodine + water.

Solutions of the two reactants were placed in the two limbs of the H-tube which was then sealed. The tube was counterpoised on a sensitive balance and inverted when the solutions mixed and the reaction took place. The tube was allowed to stand and come back to room temperature. The weight of the tube remained unchanged showing thereby that mass remains unaffected during a chemical reaction.

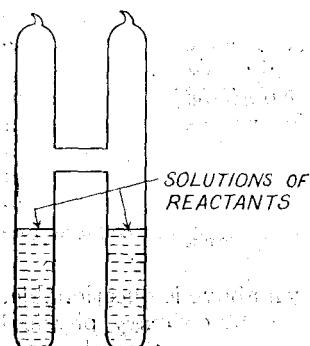


Fig. 1. Landolt's Tube.

Modern research has, however, indicated that the law of conservation of mass is true only to a very high degree of approximation. Almost all the reactions are attended by a loss of energy which according to Einstein's Theory of Relativity should be accompanied by a loss of mass ; since the loss of mass by conversion

to energy is too small to be detected even by the most sensitive balance, it is convenient to continue to stick to the old definition of the

law of conservation of mass although it is no longer true to state that mass cannot be destroyed by a chemical change.

Law of Constant Composition or Definite Proportions. (Proust, 1799). This law states that :

The same compound always contains the same elements combined together in the same fixed proportion by weight.

It is an established fact that no matter by what method a chemical compound is prepared, it always has the same composition. Let us take the example of carbon dioxide. This gas can be obtained by (i) burning carbon, (ii) heating sodium bicarbonate, (iii) heating calcium carbonate, and (iv) action of sulphuric acid on calcium carbonate. Samples of carbon dioxide obtained by these different methods on analysis show that they contain carbon and oxygen combined together in the ratio of 12 grams of carbon to 32 grams of oxygen.

In the same way whichever compound is analysed its composition is always found to be the same irrespective of its method of preparation or the source from which it has been obtained. No compound has ever been known to possess a variable composition.

The discovery of *isotopes** has, however, shown that the law of definite proportions is not of absolutely universal application. Lead, for example, has two isotopes having atomic weight 206 and 208 and the molecular weights of lead chloride obtained from these would be $(206 + 2 \times 35.5) = 277$ and $(208 + 2 \times 35.5) = 279$ respectively. The combining ratio by weight of lead and chlorine in the two samples of lead chloride would be different. This goes against the law of constant composition.

The law would, therefore, apply rigidly only to compounds obtained from the same isotope or a mixture of isotopes in the same definite proportions.

Law of Multiple Proportions. (Dalton, 1803). The law of multiple proportions states that :

When two elements combine to form two or more different compounds, the weights of one element which combine with a fixed weight of the other, bear a simple ratio to one another.

Hydrogen combines with oxygen to form two different compounds, water and hydrogen peroxide.

	Composition by weight	
	Hydrogen	Oxygen
Water (H_2O)	2	16
Hydrogen peroxide (H_2O_2)	2	32

The proportion of oxygen combining with a constant weight 20 of hydrogen is 16 : 32 or 1 : 2.

***Isotopes** are the different forms of an element which possess similar chemical properties and yet differ in mass. They have same atomic number and different atomic weights.

Nitrogen forms as many as five stable oxides.

	Composition by weight	
	Nitrogen	Oxygen
Nitrogen monoxide (N_2O)	28	16×1
Nitrogen dioxide (NO)	28	16×2
Nitrogen trioxide (N_2O_3)	28	16×3
Nitrogen tetroxide (N_2O_4)	28	16×4
Nitrogen pentoxide (N_2O_5)	28	16×5
Nitrogen hexoxide (N_2O_6)	28	16×6

It is clear from the above figures that the weights of oxygen in combinations with a fixed weight, 28 gms. of nitrogen are in the ratio $1 : 2 : 3 : 4 : 5 : 6$.

The two examples given above fully illustrate the law of multiple proportions. It must, however, be borne in mind that this law is strictly applicable only if we consider such compounds which are formed from the same isotope of an element or from a mixture of isotopes of fixed composition. In many organic compounds e.g., Stearin $C_{57}H_{110}O_6$, the ratio in which the atoms combine is far from simple.

Law of Reciprocal Proportions or Equivalent Weights. (Richter, 1792). The law of reciprocal proportions states that :

If an element A combines with an element B and also combines with an element C, then if B and C combine together, the proportion by weight in which they do so will be simply related to the weights of B and C which combine with a constant weight of A.

Hydrogen combines with sulphur forming hydrogen sulphide (H_2S) and also it combines with oxygen forming water (H_2O). Here

2 gms. of hydrogen combine with 32 gms. of sulphur and 16 gm. of oxygen. Now if sulphur and oxygen combine at all, they

must do so in the ratio $\frac{32}{16}$, or a ratio which is simply related to it. Actually

sulphur combines with oxygen forming sulphur dioxide (SO_2) in the ratio $\frac{32}{32}$.

Fig. 2. Thus we find that the ratio $\frac{32}{32}$ is simply

related to the ratio $\frac{32}{16}$, for $\frac{32}{32} : \frac{32}{16} : 1 : 2$.

The weights of two elements combining with a constant weight of a third element are referred to as 'equivalent weights'. Since hydrogen combines with a large number of elements, we can express the equivalent weights of elements in terms of that of hydrogen as 1. Thus the equivalent weight of Na = 23, Cl = 35.5, O = 8, S = 16,

$N = \frac{14}{3}$, $P = \frac{31}{3}$. Since hydrogen does not combine with many

elements, its equivalent weight is taken as unity.

elements which may, however, combine with oxygen or chlorine, the **Equivalent weight** of an element may be defined as *the number of parts by weight of it that will combine with or displace, directly or indirectly, one part by weight of hydrogen* or 8 parts by weight of oxygen or 35·5 parts by weight of chlorine.*

In the light of the above definition, the law of reciprocal proportions may also be stated as :—

"Substances react in the ratio of their equivalent weights".

Law of Gaseous Volumes. (Gay Lussac, 1898). The law of Gaseous Volumes states that :

When gases react together, they do so in volumes which bear a simple ratio to one another and the volumes of the products, if these are gaseous, all volumes being measured under the same conditions of temperature and pressure.

The law is illustrated by the following examples in which, of course, all the gas volumes are measured under identical conditions.

1 volume of nitrogen + 3 volumes of hydrogen = 2 volumes of ammonia.
1 volume of oxygen + 2 volumes of hydrogen = 2 volumes of water vapour.

Unlike the preceding laws of chemical combinations, Gay Lussac's law is not exact but only approximately correct under ordinary conditions. For example, recent determinations have shown that at normal temperature and pressure 2·0027 volumes of hydrogen combine with one volume of oxygen to form water. This and such other deviations from the law of gaseous volumes can, of course, be understood when the approximate character of the gas laws is taken into consideration.

DALTON'S ATOMIC THEORY

The idea that substances are made up of infinitely small particles was held by the ancient Greek and Indian Philosophers. Dalton, however, was the first to utilise this conception to provide a simple and logical explanation of the laws of chemical combination. The theory of atoms as put forth by Dalton in 1903 postulates :

- (1) An element is composed of a number of extremely small particles called 'ATOMS' which are not subdivided in the course of a chemical change.
- (2) Atoms can neither be created nor destroyed.
- (3) Atoms of the same element are similar to one another in all respects and have equal weights. Atoms of different elements have different properties and different weights.
- (4) Compounds are formed by the combination of atoms of different elements in simple ratios, 1 : 1, 1 : 2, 1 : 3, 1 : 4 etc.

* To be more exact, 1·008 parts by weight of hydrogen.

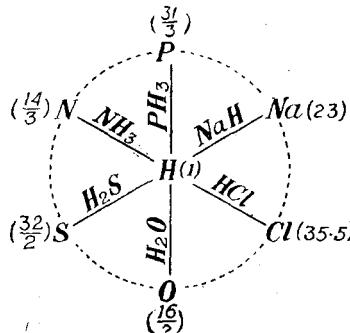


Fig. 3. Equivalent Weights.

Explanation of the Laws of Chemical Combination by Weight

The laws of chemical combination by weight can be explained in a simple manner with the help of Dalton's theory.

(i) The Law of Conservation of Mass.

Since, according to Dalton, atoms cannot be created, destroyed, or sub-divided during a chemical change, the total number of atoms and their mass before and after a reaction remains the same.

(ii) The Law of Constant Composition.

A chemical compound, since it is always formed by the union of a definite number of different atoms each of which has a definite weight, must essentially be of invariable composition.

(iii) The Law of Multiple Proportions.

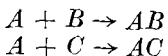
If two elements, A and B, combine to form more than one compound, let the formulae of these compounds be AB_1 , AB_2 , AB_3 , etc. Now if a and b are the atomic weights of A and B respectively, the weight of the molecules of compounds would be

$$\begin{aligned} & a + 1b \\ & a + 2b \\ & a + 3b \end{aligned}$$

It is clear that the weights, $1b$, $2b$, $3b$, of element B which combine with a constant weight a of A, bear a ratio $1 : 2 : 3$.

(iv) The Law of Reciprocal Proportions.

Let A, B, C, represent three elements with atomic weights a , b and c respectively. Now suppose,



If B and C combine together, then *atoms being indivisible*, the resulting compound molecule will consist of

either 1 atom of B + 1 atom of C,
or atom of B + 2 atoms of C,
or atom of B + 3 atoms of C, etc.

In these cases the ratio of the weight of B and C which combine would be $\frac{c}{b}$, $\frac{2c}{b}$, $\frac{3c}{b}$, etc. Thus the proportions by weight in which B and C combine together must be simply related to the ratio $\frac{c}{b}$ of weights of C and B which combine with a constant weight a of A. This is the law of reciprocal proportions.

Present Position of Dalton's Theory

Let us now examine the various postulates of Dalton's theory in the light of our modern knowledge of the structure of the atom.

(i) Atoms are now known to be composed of outer electrons and a nucleus. Chemical combination takes place by the transference of electrons from one atom to the other. Strictly speaking, therefore, the atom is not indivisible even in a chemical change but since the transference of electrons does not produce any appreciable change in the weight or the individuality of the atom, the postulate No. 1 of Dalton's theory regarding the individuality of the atom is not seriously affected.

(ii) The second postulate that '*the atoms can neither be created nor destroyed*' requires a little consideration. It is true that atoms cannot be created out of nothing but the modern research has shown that new atoms can be produced by the artificial disintegration of heavier atoms*. This, however, does not change the position as the postulate is quite correct while considering ordinary chemical changes.

(iii) The third postulate that '*the atoms of the same element are equal in weight*' surely requires a modification as the discovery of isotopes has proved beyond doubt that the atoms of the same element having different weights may exist. If by the word 'element' as given in Dalton's theory we may understand '*the same isotope*' of an element, it would be all right.

✓ AVOGADRO'S LAW

According to Dalton's theory, *elements combine in simple ratio by atoms* and according to Gay Lussac's law *gases react in simple ratio by volumes*. Surely, this points to some simple relation between the number of atoms in equal volumes of different gases under identical physical conditions. Berzelius favoured the supposition that '*equal volumes of all gases under the same conditions of temperature and pressure contain the same number of atoms*.' It was, however, soon discovered that this supposition was untenable. Avogadro suggested that the ultimate particle of a gas is not a single atom but a 'combination of atoms' which he named as *molecules*. A **molecule** may thus be defined as *the smallest particle of an element or compound which is capable of independent existence*.

In 1811, Amadeo Avogadro put forward a generalisation which gave a relation between volumes of gases and the number of molecules. As it was merely an intelligent guess, the relationship was originally named **Avogadro's Hypothesis**. It states that :

Equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules.

In 1860, Cannizzaro applied this hypothesis to the study of gases. Since then Avogadro's hypothesis assumed the status of a law. Like other gas laws, Avogadro's law is also an approximate law and it would be more correct to say '*approximately equal number of molecules*' instead of '*equal number of molecules*' in the statement of the law.

Importance and Usefulness of Avogadro's Law

Avogadro's Law has played an important part in the development of Chemistry. Some of the points in connection with this law are given below :—

- (1) *It has placed Dalton's atomic theory on a firm footing* by making clear the distinction between atoms and molecules.
- (2) *It has offered an explanation of Gay Lussac's Law of Gaseous Volumes.*

* See Chapter X on Radioactivity.

Thus in the case of hydrogen-chlorine combination :

1 volume of hydrogen + 1 volume of chlorine = 2 volumes of hydrochloric acid.

Applying Avogadro's law

n molecules of hydrogen + n molecules of chlorine = $2n$ molecules of hydrochloric acid.

It means one molecule of hydrochloric acid contains $\frac{1}{2}$ molecule of hydrogen and $\frac{1}{2}$ molecule of chlorine. This is quite understandable as according to Avogadro's law a molecule may consist of two or more than two atoms and can be divided.

(3) It has helped in the deduction of the atomicity* of elementary gases.

DETERMINATION OF ATOMICITY OF HYDROGEN

We have shown in (2) that one molecule of hydrochloric acid contains $\frac{1}{2}$ molecule of hydrogen + $\frac{1}{2}$ molecule of chlorine. This means that it is possible to get half a molecule of hydrogen and hence it follows that a molecule of hydrogen must contain 2, 4, 6, or an even number of atoms.

The number of sodium salts that can be obtained from an acid depends on the replaceable hydrogen atoms present in its molecule.



Thus sulphuric acid which yields two sodium salts has 2 hydrogen atoms and phosphoric acid which yields 3 sodium salts has 3 hydrogen atoms. Now in the case of hydrochloric acid only one sodium salt is obtained which indicates that a molecule of this acid contains only one hydrogen atom. Therefore, half a molecule of hydrogen gas contains 1 atom. Or, one molecule contains 2 atoms i.e., hydrogen is diatomic.

(4) It has helped in deducing the relationship

$$\text{M. Wt.} = 2 \text{ V.D.}$$

The Vapour Density of a gas is the ratio of the weight of a certain volume of that substance to the weight of the same volume of hydrogen, both volumes being measured under identical conditions of temperature and pressure.

$\text{V.D.} = \frac{\text{Wt. of certain volume of the substance}}{\text{Wt. of the same volume of Hydrogen}}$ (under same temperature and pressure).

Applying Avogadro's Hypothesis we have,

$$\begin{aligned} \text{V.D.} &= \frac{\text{Wt. of } n \text{ molecules of the substance}}{\text{Wt. of } n \text{ molecules of Hydrogen}} \\ &= \frac{\text{Wt. of 1 molecule of the substance}}{\text{Wt. of 1 molecule of Hydrogen}} \quad \dots (i) \end{aligned}$$

Now by definition :

$$\text{M. Wt.} = \frac{\text{Wt. of 1 molecule of the substance}}{\text{Wt. of 1 atom of Hydrogen}} \quad \dots (ii)$$

Dividing (ii) by (i)

$$\frac{\text{M. Wt.}}{\text{V.D.}} = \frac{\text{Wt. of 1 molecule of Hydrogen}}{\text{Wt. of 1 atom of Hydrogen}}$$

Since, 1 molecule of Hydrogen contains 2 atoms

$$\frac{\text{M. Wt.}}{\text{V.D.}} = 2, \text{ or M. Wt.} = 2 \text{ V.D.}$$

This relation is very useful in the determination of molecular weights.

*Atomicity of an element is the number of atoms present in its molecule.

(5) *Avogadro's Law has led to the deduction :*

22·4 litres of any gas at N.T.P. will contain its molecular weight in grams.

It has been found experimentally that 22·4 litres of hydrogen at N.T.P. weigh equal to 2 grams, i.e., its molecular weight in grams. According to Avogadro's law, equal volumes of all gases under the same conditions of temperature and pressure contain equal number of molecules, and hence it follows that:

22·4 litres of any gas at N.T.P. will contain 1 gram molecule or its molecular weight in grams. This relation also helps us in the determination of molecular weights.

(6) *This law helps in the calculation of the molecular formulae of gases and is useful in Gas Analysis.*

If the volumes of the reactants and the products are known, the molecular formula can be found out without further data.

For Example :—

1 volume of Nitrogen + 3 volumes of Hydrogen \rightarrow 2 volumes of ammonia.

If n be the number of molecules in 1 volume, according to Avogadro's law:

n molecules of Nitrogen + $3n$ molecules of Hydrogen \rightarrow $2n$ molecules of ammonia.

Or, 1 molecule of Nitrogen + 3 molecules of Hydrogen \rightarrow 2 molecules of ammonia.

Since Nitrogen and Hydrogen are diatomic, 2 atoms of Nitrogen + 6 atoms of Hydrogen \rightarrow 2 molecules of ammonia.

. . . . 1 molecule of ammonia contains 1 atom of Nitrogen and 3 atoms of Hydrogen. Hence, the molecular formula of ammonia is NH_3 .

(7) *Avogadro's law helps in the determination of Atomic Weights.*

MOLECULAR WEIGHTS

The **molecular weight** of a substance is *the weight of a molecule of that substance as compared to the weight of an atom of oxygen taken as 16**.

One **gram molecule** or **mol.** of a substance is its *molecular weight expressed in grams*.

The molecular weight of a non-volatile substance is generally determined by measuring the elevation of boiling point, the depression of freezing point or the lowering of vapour pressure of a pure solvent caused by the addition of a solute to it. These methods will be considered in Chapter VI.

Determination of Molecular Weights of Gases

(1) **Regnault's Method.** In this method the weight of a known volume of the given gas is determined and from this the weight of 22·4 litres of the gas at N.T.P. is calculated. This gives the molecular weight.

The apparatus which is employed was devised by Regnault

*Originally the **molecular weight** was defined as the weight of a molecule of a substance as compared to the weight of an atom of hydrogen. The International Atomic Weight Committee has, however, decided to adopt oxygen as the standard, the atomic weight of which is taken as 16.

(1842) and is indicated in Fig. 4. It consists of two glass globes of exactly the same size and capacity suspended by the two sides of a balance. The globe B is filled with air under normal pressure and closed, while the second globe A is evacuated. Weights are added to the left-hand pan (not shown in the figure) until A is counterpoised. The globe A is then filled with the gas whose molecular weight is to be determined and the weights now added to the right-hand pan (Fig. 4) to restore the balance to equilibrium evidently give the weight of a known volume of gas under a definite pressure and temperature.

From this we can calculate the weight of 22.4 litres of the gas at N.T.P. which gives the molecular weight of the given gas.

Example. In a determination of the molecular weight of argon by Regnault's method the volume of the globe was 32.762 c.cs. The weight of gas filling it at 19.05°C and 535.1 m.m. was 0.03786 gm. Calculate the molecular weight of argon.

The volume of the gas = 32.762 c.c. at 19.05°C and 535.1 m.m.

$$\begin{aligned} \text{Volume at N.T.P.} &= \frac{535.1 \times 32.762 \times 273}{292.05 \times 760} \\ &= 21.57 \text{ c.cs.} \end{aligned}$$

Now, 21.57 c.cs. of the gas weigh 0.03786 gm.

$$\therefore \text{Wt. of 22.4 litres of the gas} = \frac{0.03786 \times 22.4 \times 1000}{21.57} = 39.01.$$

Hence, the molecular wt. of argon is 39.31.

(2) The Diffusion Method. Graham's Law of Diffusion states that the rates of diffusion of gases through an aperture are inversely proportional to the square roots of their densities.

$$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}}$$

where r_1 and r_2 are the rates of diffusion and d_1 and d_2 the densities of two different gases respectively under the same conditions. Since the density of a gas is proportional to its molecular weight (M) we can write

$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

In certain cases the times taken for diffusion of the same volume of gases are noted and the molecular weight determined from the relation,

$$\frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$$

where t_2 and t_1 are the time taken for the diffusion of the same volume of gases with molecular weights M_2 and M_1 respectively.

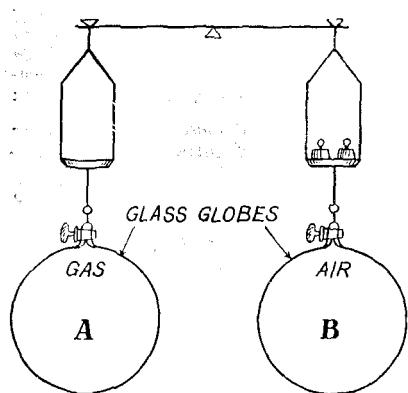


Fig. 4. Regnault's apparatus for the determination for the molecular weights of gases.

Example. 10 c.cs. each of oxygen and carbon dioxide were made to diffuse through a porous partition. The times taken were found to be in the ratio 1 : 1.18. Calculate the molecular weight of carbon dioxide, that of oxygen being 32.

Here

$$\begin{aligned} t_1 &= 1 \\ M_1 &= 32 \end{aligned}$$

$$\begin{aligned} t_2 &= 1.18 \\ M_2 &= x \end{aligned}$$

Substituting these values in the relation $\frac{t_2}{t_1} = \sqrt{\frac{M_2}{M_1}}$ we have

$$\frac{1.18}{1} = \sqrt{\frac{x}{32}}$$

$$\begin{aligned} x &= 32 \times 1.18 \times 1.18 \\ &= 44.5 \end{aligned}$$

or

Determination of Molecular weights of volatile substances

The molecular weight of a volatile liquid or solid can be calculated from its vapour density by using the relation $M.$ Wt. = 2 = V. D. deduced earlier from a consideration of Avogadro's Law or by calculating the weight of 22.4 litres of the vapour at N.T.P.

(1) **Victor Meyer's Method.** In Victor Meyer's method a known weight of the liquid or solid is caused to vaporise very rapidly and the volume of air displaced by it is measured with the help of the apparatus shown in Fig. 5.

The Victor Meyer's tube is raised to a temperature about 30°C higher than the volatilisation temperature of the substance by placing it in the jacket containing the boiling liquid. When no more air escapes from the side tube, a graduated tube filled with water is inverted over the side tube, dipping in a trough full of water. A small quantity of the substance is accurately weighed in a small stoppered bottle and quickly dropped in the heated Victor Meyer tube and the cork immediately replaced. The bottle drops on the asbestos pad placed at the bottom of the Victor Meyer tube and its contents suddenly change to vapour, blow out the stopper and displace an equal volume of air which collects in the graduated tube full of water. When no more air bubbles come out, the volume of air collected is noted after careful levelling. This gives us the volume of vapour occupied by the weight of the substance taken, under atmospheric pressure and temperature. This is reduced to N.T.P. and the weight of 22.4 litres of the vapour calculated.

Example. In a Victor Meyer determination, 0.292 gm. of a substance displaced 61 c.cs. of air at 22°C and 755 m.m. pressure. Calculate the molecular weight of the substance.

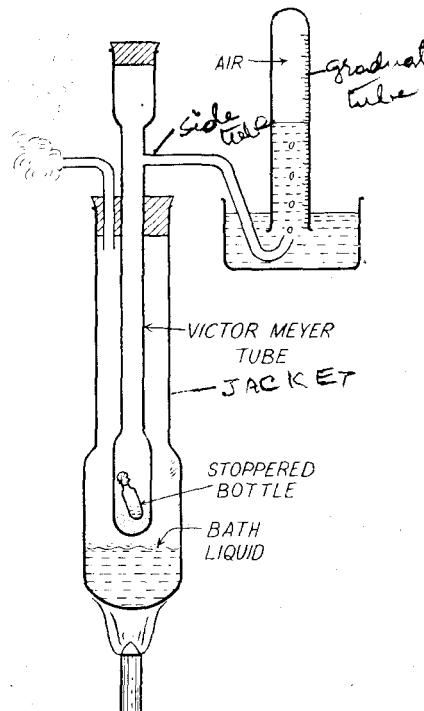


Fig. 5. Victor Meyer's apparatus for the determination of molecular weights of volatile substances.

(Aq. tension at 22°C = 20 m.m.)

$$\begin{aligned} \text{Volume of air} &= 61 \text{ c.cs.} \\ \text{Temperature} &= 22 + 273 = 295^{\circ}\text{ Abs.} \\ \text{Pressure} &= 755 - 20 = 735 \text{ m.m.} \end{aligned}$$

\therefore Volume of vapour at N.T.P.

$$\begin{aligned} &= \frac{61 \times 273 \times 735}{295 \times 760} \\ &= 54.6 \text{ c.cs.} \end{aligned}$$

Wt. of the substance = 0.292 gm.

Molecular weight is the weight of 22.4 litres of the vapour at N.T.P.

$$\therefore \text{Molecular weight} = \frac{0.292}{45.6} \times 22400 = 119.8.$$

(2) **Duma's Method.** A few c.c. of the liquid is placed in a bulb with a narrow drawn-out neck (*Duma's bulb*). The bulb is now

placed in a heating bath and when the liquid in it has evaporated completely its mouth is sealed with a blowpipe flame. This bulb is now weighed and the weight of the vapour present in it is found by subtracting the weight of the empty bulb. To find its volume, the sealed end is broken under water when the water rushes in and fills it up completely. From the weight of water filling the bulb its volume can be calculated. Knowing the weight of vapour and its volume at the temperature of the bath and atmospheric pressure, the molecular weight of the liquid can be calculated as shown in the example solved above.

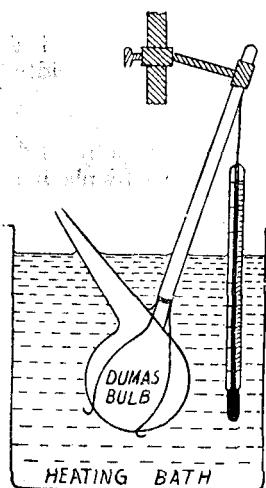


Fig. 6. Duma's apparatus for the determination of molecular weights of volatile liquids.

EQUIVALENT WEIGHTS

The **equivalent weight** of a substance is the number of parts by weight of it which combine with or displace 8 parts by weight of oxygen or 1.008 parts by weight of hydrogen.

The **gram equivalent weight** of a substance is its equivalent weight expressed in grams.

Determination of Equivalent Weights

The exact determination of equivalent weights is of very great importance because substances react in the ratio of their equivalent weights and most of the atomic weights are derived from their exact values. Some of the common methods employed for the determination of equivalent weights are described below :—

(1) **Hydrogen displacement method.** Many metals react with dilute acids with the evolution of hydrogen, e.g., iron, magnesium, zinc etc. In certain cases hydrogen is evolved by the action of water or alcohol, e.g., sodium, potassium, calcium etc. The equivalents of such metals can be determined by finding out the weight of the metal which would give rise to 1.008 parts by weight of hydrogen.

An air-tight apparatus of the type shown in Fig. 7 is fitted up. An accurately weighed quantity of the metal is placed in the conical flask along with a little water. A test tube containing dilute HCl is now lowered in, taking care that no acid flows out from the tube till the apparatus has been completely fitted and the graduated tube full of water placed in position. The flask is now tilted. The acid reacts with the metal and the hydrogen produced collects in the graduated tube. Knowing the volume of hydrogen evolved at N.T.P. and thus its weight and the weight of the metal taken, the equivalent weight of the latter can be determined by applying the relation :

$$\frac{\text{Eqvt. wt. of the metal}}{\text{Eqvt. wt. of hydrogen i.e., } 1.008} = \frac{\text{Wt. of the metal taken}}{\text{Wt. of hydrogen evolved}}$$

(2) **Oxide formation method.** (a) *Direct oxidation.* A weighed quantity of the element is converted into its oxide by heating it in a current of oxygen. After cooling, the oxide is weighed and the weight of combined oxygen calculated. Then

$$\frac{\text{Eqvt. wt. of the metal}}{\text{Eqvt. wt. of oxygen } (=8)} = \frac{\text{Wt. of the metal}}{\text{Wt. of oxygen}}$$

This method has been applied for the determination of the equivalent weights of magnesium, carbon, phosphorus etc.

(b) *Indirect oxidation.* The equivalent weights of metals like bismuth, zinc, copper, tin and iron have been determined by dissolving a known weight of the metal in concentrated nitric acid, evaporating the solution to dryness and strongly heating the solid nitrate thus produced. The weight of the oxide left behind is determined and calculations made as outlined above.

(3) **Reduction of an Oxide.** A weighed quantity of the oxide (prepared by heating the nitrate, carbonate, or hydroxide of the metal) is heated and reduced in a current of hydrogen. The weight of the metal left behind is determined and the equivalent weight calculated by finding the weight of the metal that combines with 8 parts by weight of oxygen.

(4) **Combination with Chlorine.** Certain elements like gold, silver, phosphorus, antimony, etc. easily combine with chlorine to form chlorides. In such cases the equivalent weight is found by forming the chloride and calculating the weight of the element combining with 35·46 parts by weight of the chlorine.

(5) **Metal displacement method.** Metals like zinc and iron which are high up in the electromotive series, i.e., more electropositive, displace the less electropositive metals from their salt solutions

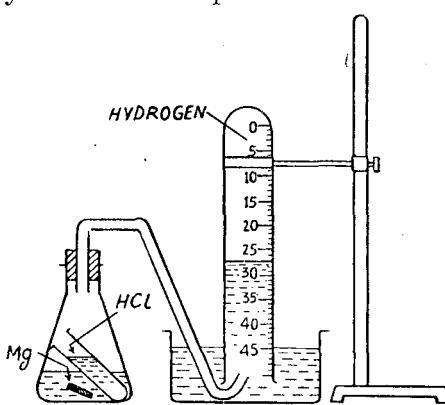


Fig. 7. Equivalent weight by hydrogen displacement.

quantitatively. Thus copper is displaced from copper sulphate solution by the addition of iron. If the equivalent weight of iron is known, that of copper can be calculated by finding out the weight of copper deposited and the weight of iron dissolved.

$$\frac{\text{Wt. of copper}}{\text{Wt. of iron}} = \frac{\text{Eqvt. wt. of copper}}{\text{Eqvt. wt. of iron}}$$

(6) **By double decomposition.** If a compound can be quantitatively converted into another by precipitation or otherwise, the equivalent weight of any one of the three radicals involved can be calculated provided the equivalent weights of the other two are known. Thus in the change $\text{AB} + \text{CD} = \text{AD} + \text{CB}$, if we know the weights of AB and AD and the equivalents of A and D, the equivalent weight of B can be calculated from the relation :

$$\frac{\text{Wt. of AB}}{\text{Wt. of AD}} = \frac{\text{Eqvt. of A} + \text{Eqvt. of B}}{\text{Eqvt. of A} + \text{Eqvt. of D}}$$

(7) **By electrolysis.** According to Faraday's second law of electrolysis, if the same current is passed for the same time through a number of solutions of different electrolytes, the weights of the different substances, liberated at the electrodes are proportional to their chemical equivalents.

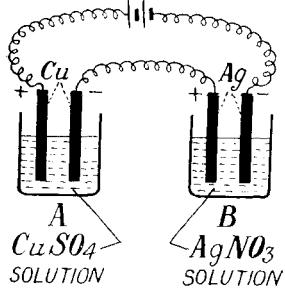


Fig. 8. Determination of equivalent weight by electrolysis.

dried and weighed. The equivalent weight of copper is determined from the relation :

$$\frac{\text{Increase in wt. of copper cathode}}{\text{Increase in wt. of silver cathode}} = \frac{\text{Eqvt. of copper}}{\text{Eqvt. of silver (given)}}$$

ATOMIC WEIGHTS

The atomic weight of an element is the weight of its atom as compared with the weight of an atom of oxygen taken as 16.*

Nearly all the chemically determined atomic weights are the average of the weights of two or more isotopes and since these isotopes are present in an almost fixed ratio, the average atomic weight as experimentally determined is always a constant quantity, (See Chapter IX).

*Originally hydrogen atom with its weight equal to one, was the standard of comparison. Since 1908, however, the **oxygen standard** has been adopted for the following reasons :—(i) Hydrogen does not in general form well-defined compounds with metals whose atomic weights must therefore be determined through the medium of some non-metal as oxygen, (ii) Atomic weights of most of the elements become approximately whole numbers, (iii) Hydrogen is so very light compared with the atoms of the majority of the elements that a small experimental error is likely to cause a sufficiently magnified error.

Determination of Atomic Weights

(1) **By the application of Avogadro's Law (Cannizzaro's Method).** The molecular weights of a number of compounds in which a particular element occurs, are first determined by methods based on Avogadro's law. Each compound is analysed and the weight of the particular element in one molecular weight of the compound is calculated. The smallest weight of the element present in the molecular weight of any of these compounds will most probably be the atomic weight of the element because out of all the compounds examined some at least might be containing one atom only of the given element per molecule.

(2) **By determination of specific heats.** The method is based on **Dulong and Petit's Law** according to which *the product of the atomic weight and the specific heat of an element in the solid state is approximately equal to 6·4.*

Atomic wt. \times Specific heat is equal to 6·4 approx.

$$\therefore \text{Approx. Atomic weight} = \frac{6\cdot4}{\text{Specific heat}}$$

$$\text{But Atomic weight} = \frac{\text{Equivalent weight} \times \text{Valency}}{\text{Atomic weight}}$$

$$\text{or Valency} = \frac{\text{Equivalent weight}}{\text{Atomic weight}}$$

The approximate value of atomic weight obtained from Dulong and Petit's Law is divided by equivalent weight and the valency obtained is changed to the nearest whole number. The accurate value of atomic weight is then found out by multiplying the equivalent weight by valency. An example will make the point clear.

Example. 1·02 gm. of a metal formed 1·31 gms. of its oxide. The specific heat of the metal is 0·056. Find its exact atomic weight.

$$\text{Wt. of the metal} = 1\cdot02 \text{ gm.}$$

$$\text{Wt. } , , \text{ oxide} = 1\cdot31 \text{ gm.}$$

$$\text{Wt. of oxygen} = 0\cdot29 \text{ gm.}$$

$$\therefore \text{Equivalent weight of the metal} = \frac{1\cdot02}{0\cdot29} \times 8$$

$$= 28\cdot12.$$

$$\therefore \text{Approx. Atomic weight} = \frac{6\cdot0}{0\cdot056} = 114\cdot29$$

$$\therefore \text{Valency} = \frac{114\cdot29}{28\cdot14} = 4 \text{ (to the nearest whole number)}$$

$$\therefore \text{Accurate atomic wt.} = \text{Eqvt. wt.} \times 4 = 28\cdot12 \times 4 \\ = 112\cdot48.$$

(3) **By the application of the Law of Isomorphism.** Mitscherlich noticed in 1819 that crystals of some substances are similar in shape and that the crystals of one such substance can grow in a saturated solution of the other. Such substances are said to be **Isomorphous**, (*having the same shape*) and this phenomenon is known as **Isomorphism**.

He also enunciated the law (**Mitscherlich's Law**) that "*Isomorphous substances possess an equal number of atoms united in a similar way*". This law is also sometimes very useful in deciding the atomic weight of an element. Suppose the atomic weight of

chromium is to be determined. We know that chrome alum, $K_2SO_4 \cdot Cr_2(SO_4)_3 \cdot 24H_2O$, is isomorphous with potash alum, $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$, i.e., chromium in chrome alum has the same position as aluminium in potash alum. If the valency of aluminium is 3 that of chromium must also be the same. We can thus get the atomic weight of chromium by multiplying its equivalent weight by 3. The following solved example will illustrate the method more clearly :—

Example. Barium sulphate is isomorphous with strontium sulphate which contains 47.7% of strontium. Calculate the atomic weight of strontium.

Formula of barium sulphate is $BaSO_4$.

Since strontium sulphate is isomorphous with $BaSO_4$, it contains the same number of atoms united in the same way and its formula would be $SrSO_4$.

Let the atomic weight of strontium be x .

$$\therefore \text{Its mol. wt.} = x + 32 + 64$$

and percentage of strontium in it = $\frac{x}{x + 96} \times 100$

But the given percentage is = 47.7

$$\therefore \frac{x + 100}{x + 96} = 47.7$$

$$\text{Whence } x = 87.56.$$

\therefore Atomic weight of strontium is 87.55.

(4) From a study of the Periodic Table. (See Chapter VII).

(5) With the help of Aston's Mass Spectrograph (See Chapter IX).

QUESTIONS AND PROBLEMS

1. Explain clearly the distinction between elements and compounds. How would you define an element in the light of modern researches?

2. State and explain the laws of chemical combination. Three oxides of lead were found to contain respectively 92.83%, 90.65% and 86.62% of lead and 7.17%, 9.35% and 13.38% of oxygen. Show that these figures illustrate the law of multiple proportions.

3. Give a short account of Dalton's Atomic Theory and discuss its present position.

4. State briefly Dalton's Atomic Theory and the chemical evidence on which it is based.

5. State Avogadro's Law and discuss its importance in Chemistry.

6. State Graham's Law of diffusion and explain how it can be utilised in the determination of molecular weights of gases.

Calculate the molecular weight of a gas which under precisely similar conditions takes 1.117 times as long as oxygen to diffuse through an aperture.

7. Starting from Avogadro's Law deduce a relationship between the molecular weight and the vapour density of a substance.

8. Describe Victor Meyer's method for determining the molecular weight of a volatile substance.

0.2 gm. of a substance when vaporised, displaced 62.0 c.cs. of air measured over water at 16°C and 771 m.m. pressure. Calculate the molecular weight of the substance.

9. Briefly describe the general methods for the determination of equivalent weights. How would you experimentally determine the equivalent weight of magnesium?

10. 0.0396 gm. of a metal was completely dissolved in HCl and the hydrogen evolved mixed with oxygen and sparked. 13.75 c.cs. of dry oxygen measured at 27°C and 680 m.m. pressure were required for complete combustion. Calculate the equivalent weight of the metal.

FUNDAMENTAL PRINCIPLES

11. State Dulong and Petit's Law and discuss its applications. Determine the atomic weight of an element from the following data :—

Sp. heat 0·119 ; 10 gms. of the element combines with 4·298 gms. of oxygen ; 8·0 gms. of the element combines with 10·159 gms. chlorine.

12. Outline briefly the method that you would follow for determining the atomic weight of a newly discovered element.

The chloride of an element contains 37·322 per cent of chlorine. The vapour density of the chloride is 190 ($H=1$). The specific heat of the element is 0·0276. Find the atomic weight of the element and the formula of the choride.

13. State Mitscherlich's law of isomorphism and point its importance in atomic weight determination.

14. An element A forms a chloride which contains 29·34 per cent by weight of chlorine and is isomorphous with potassium chloride. Calculate the atomic weight of A and explain clearly the theoretical principles you use in your calculation. What other experiments you would suggest to confirm the value of the atomic weight ?

15. Describe methods for determining the equivalent weight of metals and discuss in detail one such method.

1·5 gms. of the iodide of a metal dissolved in water was mixed with 150 c.cs. of N/10 $AgNO_3$ solution. The excess of $AgNO_3$ left required 75·5 c.cs. of N/15·1 KCl solution. What is the equivalent weight of the metal ?

16. 0·2 gm. of the chloride of an element was dissolved in water and treated with $AgNO_3$ solution. 0·47 gm. of $AgCl$ is precipitated. One litre of vêpours of original chloride weighed 6 gm. at 100°C and 760 m.m. Find the atomic weight of the element and the molecular formula of the chloride.

17. What is isomorphism ? What are the criteria determining it ? How is the principle of isomorphism utilised in Physico-chemical measurements ?
(Nagpur B.Sc., 1953)

18. Write an essay on the principle underlying the determination of atomic weights of elements.
(Nagpur B.Sc., 1953)

19. Give an account of the accurate determination of atomic weights by chemical means.
(Annamalai B.Sc., 1954)

20. Describe a method for determining the molecular weight of a volatile substance.
(Gauhati B.Sc., 1954)

21. Name various methods of finding out the molecular weight of a substance and describe in detail any one method which is applicable to gases.

Calculate the volume occupied by 5 gms. of a substance at N.T.P. of which the molecular weight is 200.
(Lucknow B.Sc., 1955)

22. Describe with all essential details one method of determining the vapour density of vapour.
(Travancore B.Sc., 1956)

23. Describe the Victor Meyer's method of determining the molecular weight of a vaporisable liquid.

In a Victor Meyer experiment, 0·2335 gm. of a liquid was vaporised and the displaced air occupied 37·1 c.cs. at 29°C and 740 m.m. pressure. Calculate the molecular weight of the liquid. The vapour pressure of water at 29°C is 26·3 m.m.
(Travancore B.Sc., 1957)

24. Write notes on the following :—

- (a) Dulong and Petit's Law.
- (b) Avogadro's Hypothesis.
- (c) Isotopes.

(Rajputana B.Sc., 1958)

25. Describe the determination of the vapour density of a volatile liquid by Victor Meyer's method.

0·512 gm. of a volatile liquid when vaporised in Victor Meyer's apparatus displaced 77·8 c.cs. of air collected over water at 15°C and 750 m.m. pressure.

Vapour pressure of water at 15°C is 12 m.m. Calculate the molecular weight of the compound.

($R=0.08205$ litre-atmosphere) (Rangoon B.Sc., 1958)

26. Name the various methods of determining molecular weights of substances from vapour density measurements. Describe one method.

(Venkateswara B.Sc., 1959)

27. What do you understand by the equivalent weight of a substance?

What will be the equivalent weight of a metal, 65.4 gms. of which liberate from a dilute solution of an acid, 22.4 litres of hydrogen gas at N.T.P.? What will be the atomic weight of the metal if it forms a volatile chloride of vapour density 68.2? ($\text{Cl}=35.5$) (Rajasthan B.Sc., 1959)

28. What is meant by the terms atomic weight and equivalent weight of an element? Describe any two methods for the determination of the equivalent weight of a metal.

0.5595 gm. of a metal when changed into its chloride weighs 0.717 gm. The specific heat of the metal is 0.059 calories. What is the correct atomic weight of the metal? ($\text{Cl}=35.5$) (Marathwada, B.Sc., 1959)

ANSWERS

6. 39.9

8. 75.39

10. 19.80

11. 55.83 ; 53.96

12. At. Wt.=238.56 ; Formula MCl_4

14. 85.5

15. 23

16. 76.8 ; MCl_3

21. 560 c.c.

23. 166.1

25. 71.63

27. 32.7 ; 65.4

28. 126.1

CHAPTER II

PHYSICAL PROPERTIES AND CHEMICAL CONSTITUTION

INTRODUCTION

The importance of physical measurements like density, refractive index, viscosity, surface tension, etc., has considerably increased during the recent years because of their great usefulness in elucidating the composition and the structure of molecules. The various physical properties based upon these measurements which have been utilised for this purpose can be divided into four classes :

(1) **Additive Properties.** These are properties of the individual atoms and remain unchanged, no matter in what physical or chemical state they exist. Thus the *mass* or *weight* of an atom does not alter and we can find out the molecular weight of a substance by simply adding up the atomic weights of the various atoms present in the molecule. Similarly the molecular heat of a compound is the sum of the atomic heats of the atoms present in it. Radioactivity is another additive property.

(2) **Constitutive and Additive Properties.** These are additive properties but the additive character is modified by the manner in which the atoms are linked together. Thus, the *atomic volume of oxygen* in hydroxyl group (OH) is 7.8 while in the ketonic group (>CO) it is 12.2. Parachor, molecular refractivity and molecular viscosity are some other examples of this type.

(3) **Purely Constitutive Properties.** These depend entirely upon the arrangement of atoms in the molecule and not on their number. Thus *optical activity* is the property of the asymmetry of the molecule and occurs in all compounds containing an asymmetric carbon atom.

(4) **Colligative Properties.** These depend only on the number of molecules present, their nature or magnitude playing no part. Thus, 1 gram molecule of *any* gas at N.T.P. will occupy a volume equal to 22.4 litres, gaseous volume being a colligative property. Other such properties are *Osmotic pressure*, *Depression of freezing point*, *Elevation of boiling point* and the *Lowering of vapour pressure* (See Chapter V).

Some properties of classes (2) and (3) which depend upon the arrangement of atoms in the molecules will be discussed in this Chapter because it is only properties of this kind that can throw light on the constitution of molecules.

MOLECULAR VOLUME

The **Molecular Volume** of a substance is *the volume in cubic centimetres occupied by the molecular weight in grams.*

$$\text{Molecular volume} = \frac{\text{Molecular weight}}{\text{Density}}$$

The molecular weight can be accurately determined by any of the methods described in Chapter I or V while for accurate determinations of density, some form of *density bottle* (commonly known as

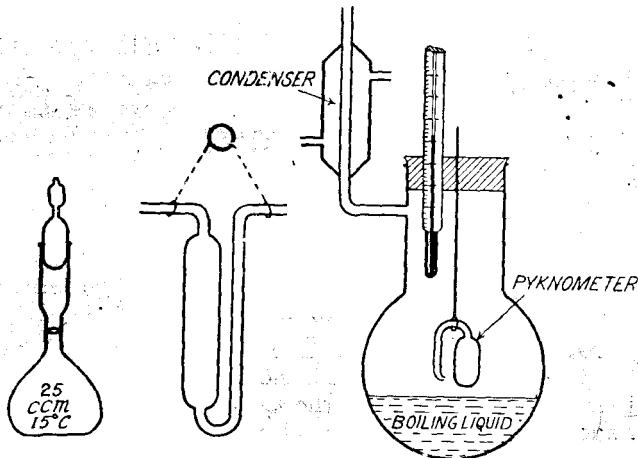


Fig. 9.

Density bottle
for volatile
liquids

Ordinary
Pyknometer

Pyknometer method
for density at
boiling points

specific gravity bottle) or *pyknometer* is employed. The bottle or the pyknometer is filled with water and weighed. Then it is filled with the liquid and weighed again. Knowing the weights in the two cases and subtracting the weight of the empty vessel, we can know the weights of water and liquid occupying the same volume.

Thus, Density = $\frac{\text{Wt. of the liquid}}{\text{Wt. of water}} \times \text{Density of water at that temperature.}$

Density bottle is very convenient for the determination of density at ordinary temperatures. Pyknometer, on the other hand, can be suspended in a *thermostat** and is used for the determination of density at various temperatures.

Molar Volume and Chemical Constitution

Let us consider a homologous series of normal primary saturated alcohols.

The difference of CH_2 between the molecules of any two adjacent members, with the exception of the second value corresponds to a continuous decrease in the difference of density as we go down. *The regularity exhibited by the molar volumes is much more striking than that displayed by densities* as the difference of CH_2 corresponds to a constant difference of 16·2.

The volume of organic liquids is usually affected greatly by temperature. Kopp (1855) found that *the molar volume of a liquid determined at its own boiling point, is approximately equal to the sum of the volumes of its constituent atoms*. This is usually called **Kopp's Law.**

***Thermostat.** It is a constant temperature bath. It has a heating arrangement with automatic control to keep the temperature of the bath constant.

Formula of Alcohol	Density at 0°C (d)	Difference for Adjacent Members	Molar Volumes ($\frac{M}{d}$)	Difference for Adjacent Members
CH_3OH	0.812	...	39.4	
$\text{CH}_3\text{CH}_2\text{OH}$	0.806	-0.006	57.1	17.7
$\text{CH}_3(\text{CH}_2)\text{CH}_2\text{OH}$	0.817	0.011	73.4	16.3
$\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{OH}$	0.823	0.006	89.9	16.5
$\text{CH}_3(\text{CH}_2)_3\text{CH}_2\text{OH}$	0.829	0.006	106.1	16.2
$\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{OH}$	0.833	0.004	122.5	16.4
$\text{CH}_3(\text{CH}_2)_5\text{CH}_2\text{OH}$	0.836	0.003	138.7	16.2
$\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{OH}$	0.839	0.003	154.9	16.2
$\text{CH}_3(\text{CH}_2)_7\text{CH}_2\text{OH}$	0.842	0.003	171.1	16.2

From a study of different compounds, Kopp devised a set of *atomic volumes* but these were shown to be for the most part inaccurate by Le Bas (1906). Le Bas also pointed out that constitutional and structural influences introduce marked variations in molar volumes (see oxygen and nitrogen in the Table below) and gave the following as some of his volume equivalents.

Carbon	= 14.8	Nitrogen = 15.6
Hydrogen	= 3.7	= 10.5 (in primary amines).
Chlorine	= 22.2	= 12.0 (in sec. amines).
Bromine	= 27.0	Oxygen (O") = 7.4 (aldehydes, ketones).
Iodine	= 37.0	Oxygen (O') = 9.1 (methyl esters).
Sulphur	= 25.6	= 11.0 (higher esters).
Benzene ring	= -15.0	= 12.0 (acids).

From such data, it is possible to calculate the molar volume of any organic substance.

For example, consider ethyl acetate $\text{CH}_3\text{C}(\text{O})\text{OC}_2\text{H}_5$
 4C gives a volume of $14.8 \times 4 = 59.2$
 8H " " " $3.7 \times 8 = 29.6$
 O in CO " " " $7.4 \times 1 = 7.4$
 O in higher esters " " $11.0 \times 1 = 11.0$
 Total = 107.2

The experimental value 106.4 is quite near the calculated value. It is found, however, that in a large number of cases, such an agreement does not exist.

To improve matters, Sugden suggested in 1924 another form of molar volume called the **parachor** which is described below under surface tension.

SURFACE TENSION

Let us consider two molecules P and Q one of them, P well below the surface and the other Q, just on the surface of the liquid. Due to molecular attraction, P is pulled equally on all sides by the neighbouring molecules whereas Q is pulled downwards and laterally only. The resultant force acting on P is zero but Q on the other hand, is subject to an

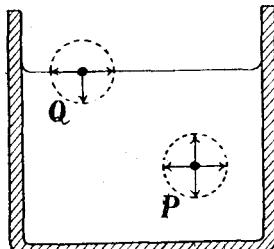


Fig. 10. Unbalanced force of attraction is the cause of surface tension.

unbalanced force acting inwards at right angles. Similar is the case with all other molecules present in the surface. The surface of a liquid, therefore, is the seat of a special force as a result of which molecules in the surface are bound together to form something like a stretched membrane tending to compress the molecules below to the smallest possible volume. This force responsible for the tension of the surface of a liquid is termed **Surface Tension**. It is defined as *the force in dynes acting upon a line of 1 cm. length on the surface of the liquid.*

Determination of Surface Tension

The most frequently used methods for the determination of surface tension are: (1) *Capillary height method*, (2) *Drop weight method*, (3) *Ring method*, and (4) *Maximum bubble pressure method*.

A brief description of each is given below.

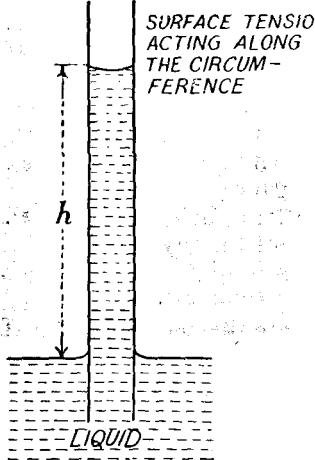


Fig. 11. Rise of a liquid in a Capillary Tube.

(1) **The Capillary Height Method.** (a) *Single Capillary Method.* When the end of a capillary tube is placed in a liquid which wets the tube, the liquid is drawn up the capillary to a certain height h . This column of the liquid is supported by the surface tension acting along the circumference of the tube which is equal to $\gamma \cdot 2\pi r$, where γ is the surface tension of the liquid and r the radius of the tube. The weight of the liquid thus supported is $\pi r^2 \cdot hdg$, where d is the density of the liquid and g the acceleration due to gravity at the place where the experiment is being performed.

$$\text{Hence } \gamma \cdot 2\pi r = \pi r^2 \cdot hdg.$$

$$\text{Or } \gamma = \frac{1}{2}r \cdot hdg.$$

In order to know the value of γ , it is necessary to determine the value of h , r and d .

For accurate determinations, it is necessary to add to the weight of the liquid supported $\pi r^2 \cdot hdg$, the weight of the liquid constituting the meniscus. For capillary tube of small diameters, quite accurate results are obtained if in the above formula, the observed height h is increased by $r/2$.

(b) *Double Capillary Method.* In the single capillary method, it is difficult to determine the level of the flat surface of the liquid unless it is present in a large quantity. It has been shown by Richards and Coombs that the diameter of the reference tube must be *at least 3.8 cms.* and when, therefore, the liquid is available in a small amount, it is difficult, to get correct results. The difficulty is overcome by using a double capillary.

If two capillary tubes of radii r_1 and r_2 respectively be immersed to the same level in a liquid of density d , the surface tension γ

of the liquid can be calculated by observing the difference in height ΔH to which the liquid rises in the two tubes.

If the correction for the dimensions of the meniscus is neglected, the surface tension is given by the relation :

$$\gamma = \frac{g}{2 \left(\frac{1}{r_1} - \frac{1}{r_2} \right)} d. \Delta H$$

The apparatus as shown in Fig. 12 consists of two capillary tubes of uniform bore 2 mm. and 0.5 mm. respectively joined together in the form of a U-tube with a small hole blown at the lowest point. This U-tube capillary is fused in a vertical position in a thin walled glass tube containing the liquid and the height in the two capillaries is determined with the help of a cathetometer of accuracy 0.002 cm.

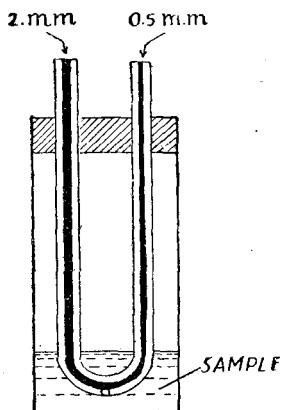


Fig. 12. Capillary U-tube.

(2) **The Drop Method.** When a liquid is allowed to flow very slowly through a capillary tube a drop will form which will increase up to a certain point and then fall. If the radius of the end of the tube be r , the total surface tension supporting the drop will be $\gamma \cdot 2\pi r$. The drop falls down when its weight W is just equal to this force. Hence we have

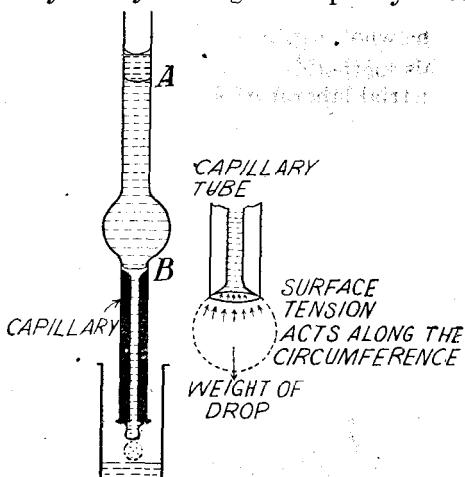


Fig. 13. The drop pipette.

about 20, are received in a weighing bottle and weighed. In this way we can find the weight of a single drop and calculate the surface tension of the liquid from the expression $\gamma \cdot 2\pi r = W$.

For relative determinations, instead of determining the weight of the drop, it is easier to count the number of drops formed by a given volume of the two liquids. Suppose we want to compare the surface tension of some oil with that of water. Water is first sucked up the tube and the drops counted as the meniscus falls from A to B. Then the drop pipette is dried and filled with the oil under examination. Now the number of drops formed by the oil, as the meniscus travels from A to B is recorded. Since the same drop pipette has

$$\gamma \cdot 2\pi r = W.$$

The apparatus used in these determinations consists of a bulb fused with a capillary tube and is called a **drop pipette**. The liquid under examination is sucked up the capillary, say up to the etched mark A. Then a definite number of drops,

been used in the two cases, the same volume of liquids ($V_A \rightarrow B$) has yielded a different number of drops, say n_1 and n_2 for the oil and water, respectively. But we know

$$\gamma \cdot 2\pi r = W = mg = Vdg$$

where m is the mass of one drop, V its volume, d the density, and g the acceleration due to gravity.

$$\text{Therefore for oil, } \gamma \cdot 2\pi r = \frac{V_{A \rightarrow B}}{n_1} d.g \quad \dots (1)$$

$$\text{For water } \gamma_w \cdot 2\pi r = \frac{V_{A \rightarrow B}}{n_2} d_w.g \quad \dots (2)$$

From (1) and (2)

$$\frac{\gamma}{\gamma_w} = \frac{n_2}{n_1} \times \frac{d}{d_w}$$

Hence by simply counting the number of drops for the oil and water and knowing their density, we can find the relative surface tension of the oil. If we are given the surface tension of water under the conditions of the experiment, the absolute surface tension of oil can be calculated.

The advantages of the drop-pipette method are that it is very convenient and quick. It can also be employed for determinations at different temperatures by placing the whole apparatus in a thermostat.

(3) **The Ring Method.** This method is used very conveniently for rapid determinations in industrial laboratories, more especially when the quantity of the liquid available is very small, say one c.c.

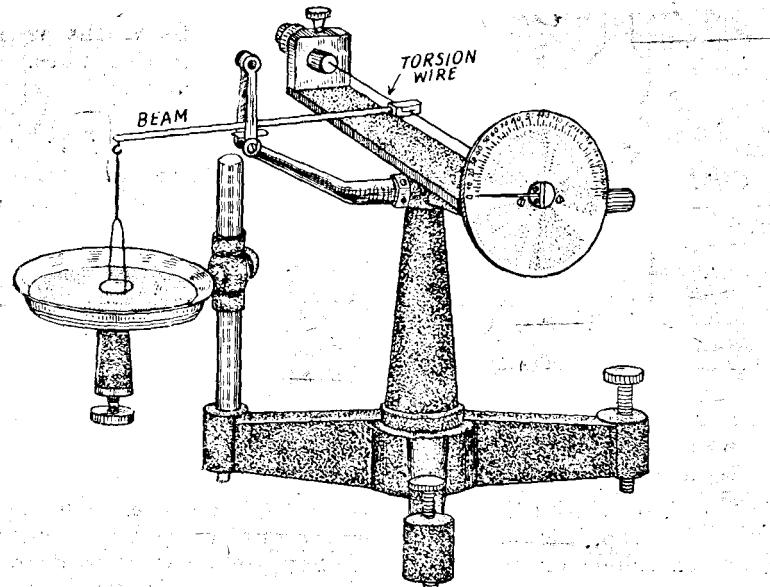


Fig. 14. Du Nouy's Torsion Balance.

The apparatus employed is called the **Torsion balance** or Du Nouy's balance. A platinum ring, about 4 cms. in circumference hangs

from the end of the beam of torsion balance. The force required to lift it up from the surface of the liquid is measured by the angle through which the pointer has to be moved on the graduated disc. The angle of torsion δ will be proportional to the downward pull on the ring due to the surface tension of the liquid acting on it. Total surface tension acting on the ring is $\gamma \cdot 2\pi r$, where r is the radius of the ring. Thus for the liquid under examination,

$$\text{and for water } \gamma_w \propto \delta_w$$

$$\text{Therefore, } \frac{\gamma}{\gamma_w} = \frac{\delta}{\delta_w}$$

Knowing the value of γ_w we can at once give the value of γ .

(4) **Maximum Bubble Pressure Method.** It was shown by Sugden (1924) that if two capillary tubes of different radii are immersed to the same depth in a liquid and the pressure required to liberate bubbles from each is measured, the surface tension can be calculated from the difference of these pressures. If r_1 is less than 0·01 cm. and r_2 not greater than 0·2 cm., the surface tension γ is given by the relation

$$\gamma = AP \left(1 + 0.69r_2 \frac{gD}{P} \right)$$

where A is the apparatus constant determined with a standard liquid, r_2 is the radius of the bigger capillary, D the density of the liquid and P the difference in pressure.

To measure the value of P , the apparatus shown in Fig. 15 is employed. When the stop-cock S is open, bubbles will form only at the larger capillary as the mercury flows down from the dropping funnel D . Note the maximum pressure required for this purpose with the help of the manometer. Now close the stop-cock S and let the mercury run. Bubbles will now form at the lower capillary end. Note the maximum pressure. The difference of these pressures gives the value of P .

Surface Tension and Chemical Constitution—The Parachor

Surface tension is due to an inward force acting on the molecules at the surface. We look to surface tension, therefore, to throw some light on the structure of molecules.

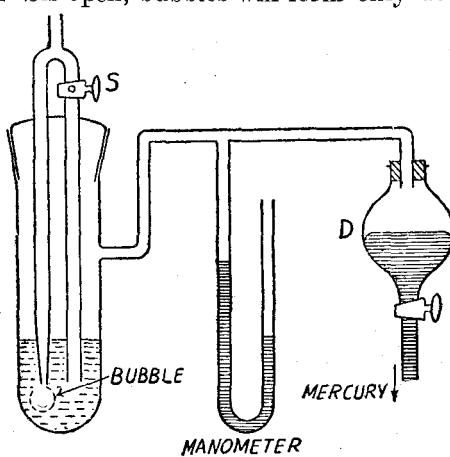


Fig. 15. Surface tension by maximum bubble pressure method.

Macleod (1923) discovered an interesting relationship between surface tension and density for normal liquids.

It may be stated as

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

where γ is the surface tension of the liquid, D its density and d the density of the vapour at the temperature of the experiment. C is a constant. Macleod's equation holds over a wide range of temperatures. Sugden (1924) pointed out that the expression

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

should also be valid. In this expression M is the molecular weight and [P] is called the **Parachor**. At ordinary temperature (far removed from the critical) d is negligible as compared with D, and we obtain the relation

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

where $\frac{M}{D}$ is the molecular volume.

For two liquids 1 and 2 :

$$[P_1] = \frac{M_1 \gamma_1^{\frac{1}{4}}}{D_1} \quad \dots (i)$$

$$\text{and} \quad [P_2] = \frac{M_2 \gamma_2^{\frac{1}{4}}}{D_2} \quad \dots (ii)$$

Dividing (i) by (ii), we have

$$\frac{[P_1]}{[P_2]} = \frac{M_1 \gamma_1^{\frac{1}{4}}}{D_1} : \frac{M_2 \gamma_2^{\frac{1}{4}}}{D_2}$$

If $\gamma_1^{\frac{1}{4}}$ be equal to $\gamma_2^{\frac{1}{4}}$

$$\frac{[P_1]}{[P_2]} = \frac{M_1}{D_1} : \frac{M_2}{D_2}$$

A comparison of parachors means, therefore, a comparison of molecular volumes under equal conditions of surface tension.

It was shown by Sugden that parachor is both additive and constitutive and its value for any compound can be expressed as the sum of two sets of constants, one depending upon the atoms present and the other upon the structural factors. The former are known as **Atomic parachors** and the latter as **Structural parachors**.

The values of atomic and structural parachors given by Sugden were revised by Mumford and Phillips in 1929. A further revision of these values has been carried out by Vogel (1948) on the basis of more accurate measurements on purer samples of the compounds. These

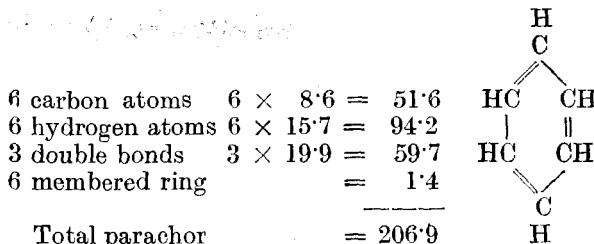
differ considerably from the original values of Sugden as shown in the Table below :

TABLE. *Atomic and Structural Parachors*

Atom, Group or Linkage	PARACHOR VALUE		
	Sugden (1924)	Mumford and Phillips (1929)	Vogel (1948)
Carbon	4·8	9·2	8·6
Hydrogen	17·1	15·4	15·7
Oxygen	20·0	20·0	19·8
Nitrogen	12·5	17·5	—
Chlorine	54·3	55·5	55·2
Bromine	68·0	69·0	68·8
Iodine	91·0	90·0	90·3
>C=O	—	—	44·4
-OH	—	—	30·2
-COOH	—	—	73·7
-NO ₂	—	—	73·8
Double Bond	23·2	19·0	19·9
Triple Bond	46·6	38·0	40·6
3 membered ring	17·0	12·5	12·3
4 ", "	11·6	6·0	10·0
5 ", "	8·5	3·0	4·6
6 ", "	6·1	0·8	1·4

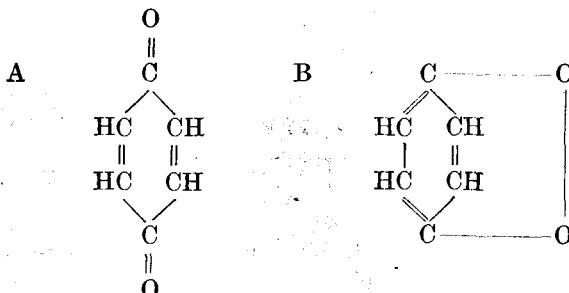
With the help of these atomic and structural parachors, the parachor of a compound can easily be calculated and this value may be used to draw conclusions regarding the structure of its molecule. The parachor has proved of great value in solving problems of chemical constitution.

Uses of Parachor. (i) *Deciding Constitution.* In the case of benzene, C₆H₆, if we adopt Kekule's formula, the value of the parachor may be calculated as follows using the latest data of Vogel.



The observed value for benzene is 206·2. The parachor value, therefore, is in harmony with Kekule's formula.

The following two structures have been proposed for quinone.



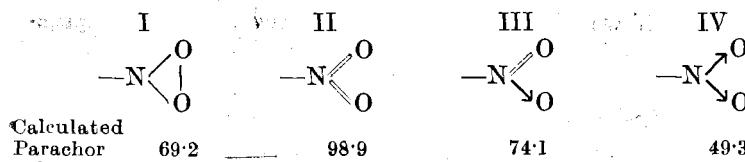
Calculated value of the parachor :—

FOR STRUCTURE A		FOR STRUCTURE B	
6C	$6 \times 8.6 = 51.6$	6C	$6 \times 8.6 = 51.6$
4H	$4 \times 15.7 = 62.8$	4H	$4 \times 15.7 = 62.8$
2O	$2 \times 19.8 = 39.6$	2O	$2 \times 19.8 = 39.6$
4 double bonds	$4 \times 19.9 = 79.6$	3 double bonds	$3 \times 19.9 = 59.7$
1 six membered ring	$1.4 = 1.4$	2 six membered rings	$= 2.8$
Total = 235.0		Total = 216.5	

The observed value for quinone is 236.8 and the formula A, therefore, represents correctly the structure of its molecule.

(ii) *Deciding the nature of valency.* The concept of parachor has given very valuable information regarding the nature of linkages in compounds of nitrogen, phosphorus and sulphur.

In *nitro group* the various atoms may be linked together in four different ways and the calculated parachor values would be different for the four structures.



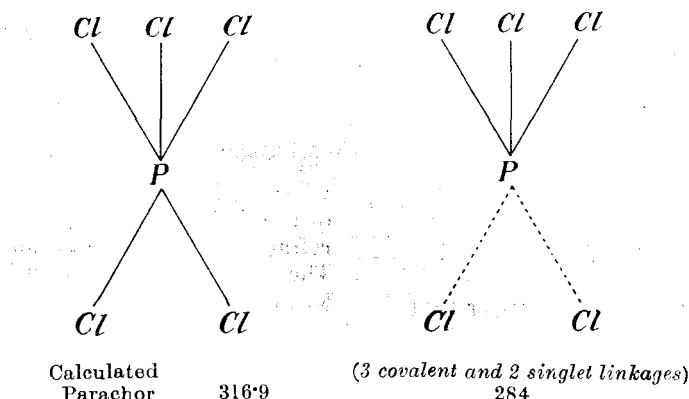
From the study of a large number of nitro compounds, the parachor value of NO_2 group has been found to be 73.0. Hence structure III gives a true picture of the arrangement of atoms in nitro group.

The value of parachor for
a triple bond (\equiv) involving 6 electrons is.....46.6
a double bond (=) involving 2 electrons is.....23.2
a single covalent linkage (-) involving 2 electrons.....0
(arbitrary)

*Singlet-linkage** involving one electron will, therefore, contribute (-11.6) to the parachor.

* See Chapter XI on Electronic Theory of Valency.

The evidence for the existence of singlet linkages has been confirmed by the parachor theory. Phosphorus pentachloride may have the following structural formulae :—



Experimental value of the parachor of phosphorus pentachloride is 282.5 being practically the same as the calculated value for the structural formula containing 2 singlets. This confirms the existence of single electron linkages in phosphorus pentachloride molecule.

REFRACHOR

By associating refractive index with the parachor, a new physical constant known as **Refrachor** has recently been obtained by Joshi and Tuli (*Jour. Chem. Sec.* 1951, 837-838). It is denoted by the symbol [F] and is given by the relation

$$[F] = - P \log (nD^{20} - 1)$$

In addition to the usual applications of the parachor, the new constant has been formed to be especially useful in :

(i) *Determining the percentage composition of a keto-enol tautomeric mixture.* The calculated refrachors of the keto and enol forms differ by as many as 12.4 units, such difference being 1.4 in case of parachor and 1.08 in case of molecular refractivity.

(ii) *Distinguishing between stably linked and reactive halogen atoms, and*

(iii) *the study of structural isomeric compounds.*

REFRACTIVE INDEX

When a ray of light passes from air into a denser medium, say a liquid, it is bent or refracted towards the normal. The ratio of the sine of the angle of incidence and that of refraction is constant and characteristic of that liquid (*Snell's law*). The constant ratio n is called the **Refractive index** of the liquid and may be written as

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

According to the wave theory of light, the ratio of the sines of the angles of incidence and refraction is identical with the ratio of the

velocities of light in the two media. Thus :

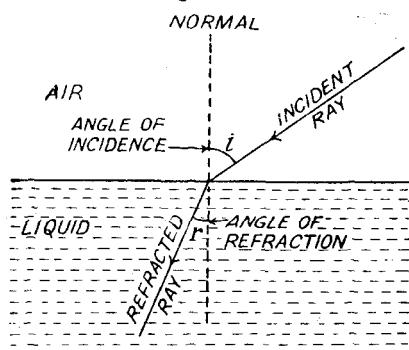


Fig. 16. Refraction of light.

in that case is reduced to

$$\sin r = \frac{n_1}{n_2}$$

or $\sin 90^\circ = 1$.

Determination of Refractive Index

For the convenient and rapid determination of the refractive index of liquids a number of instruments have been constructed. These instruments are called *refractometers*. We give below a brief account of the most prominent amongst them which are (i) the Pulfrich refractometer, and (ii) the Abbe refractometer.

Pulfrich Refractometer. Pulfrich refractometer is very accurate and simple in principle. It is indicated diagrammatically in

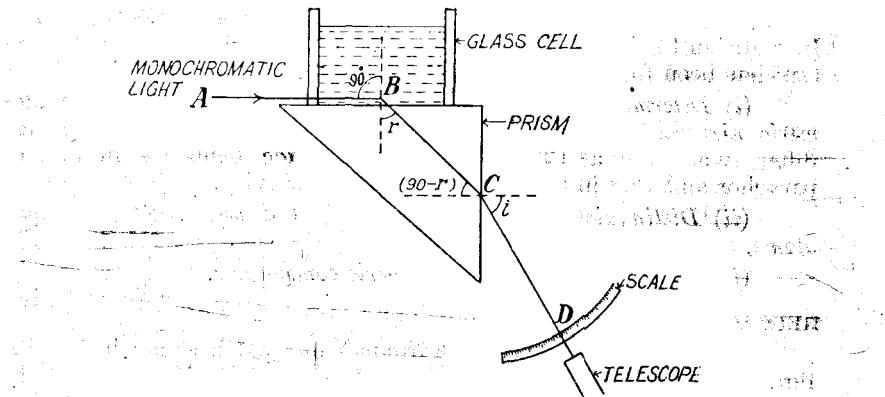


Fig. 17. The optical system of Pulfrich Refractometer.

Fig. 17. The essential part of the instrument is a right angled glass prism with a small glass cell cemented to its top. The liquid to be examined is placed in the cell and a beam of monochromatic light is made to enter the liquid at 'grazing incidence' along the surface between the liquid and the prism. It follows the path of ABCD and is observed in a telescope at D. If the telescope is moved to make an

$$n = \frac{\sin i}{\sin r} = \frac{\text{Velocity in air}}{\text{Velocity in liquid}}$$

When a ray of light passes from a rarer to denser medium it can be shown from the law of refraction that

$$\frac{\sin i}{\sin r} = \frac{n_2}{n_1}$$

where n_1 is the index of refraction of the rarer and n_2 the index of refraction of the denser medium. The angle of incidence can never be evidently greater than 90° and when it is 90° the above equation

angle with the horizontal which is less than i , no light can reach it. A very accurate determination can, therefore, be made of the angle i at which a sharp boundary between a dark and a bright field can be seen through the telescope.

For a ray of light passing from the liquid into the prism, if r be the angle of reflection when the angle of incidence is 90° , we have already stated

$$\sin r = \frac{n_1}{n_2} \quad \dots (1)$$

when n_1 is the refractive index of the liquid and n_2 is that of the glass prism. It is also clear from the diagram that

$$\frac{\sin i}{\sin (90-r)} = n_2 \quad \dots (2)$$

but since $\sin (90-r) = \cos r$, we have

$$\frac{\sin i}{\cos r} = n_2 \quad \dots (3)$$

$$\text{Or } \cos r = \frac{\sin i}{n_2} \quad \dots (4)$$

$$\text{But } \sin r = \sqrt{1 - \cos^2 r}$$

Substituting the value of $\cos r$ from (4) we get

$$\sin r = \sqrt{1 - \frac{\sin^2 i}{n_2^2}} \quad \dots (5)$$

and from (1)

$$n_1 = n_2 \sin r$$

$$\text{Hence } n_1 = \sqrt{n_2^2 - \sin^2 i}$$

If the refractive index n_2 of the glass is known and angle i is measured, then n_1 , the refractive index of the liquid, can be calculated. In actual practice, however, it is not necessary to go through the above calculations since the makers of the instrument supply tables giving refractive indices (n_1) corresponding to different values of i .

The index of refraction is dependent upon the wavelength of light employed, the index for the red rays being less than that for the violet rays. Measurements of the refractive index referred to D-line of sodium are commonly indicated by the symbol n_D .

Abbe Refractometer. The principle of this instrument is the same as that used in the Pulfrich refractometer. This instrument is, however, less accurate than the Pulfrich refractometer. It is principally designed for *quick determinations of the refractive index of small quantities of liquids*.

CONSTRUCTION. A general idea of the construction of this instrument is given in Fig. 18. A and B are two glass prisms. The hypotenuse surface of B is polished while that of A is finely ground. The two prisms are housed in metal casings hinged at H. The two prism faces can be held in contact with clamp C. A and B can be rotated about a horizontal axis immediately beneath a telescope T. To the metal case carrying the prism, is attached an arm R which moves along a graduated scale S, the reading on which gives directly the refractive index.

WORKING. A drop of the liquid is placed upon the surface of prism A. On clamping the two prisms A and B a film of the liquid spreads between them. Light reflected by a mirror M is then directed towards the prism system.

On reaching the ground surface of A it is scattered into the liquid film. No ray can, however, enter B with a greater angle of refraction than that of the ray corresponding to 'grazing incidence'. Hence when viewed through a telescope, just as in the case of Puifrich refractometer the field of view is divided into bright and dark portions. The edge of the bright portion when coincided with the cross-wire of the telescope gives the refractive index on the scale. If white light is employed, as is the case in practice, a diffused coloured border is seen in the telescope. This is made sharp and the colours are removed by the adjustment of two prisms (not shown in the diagram) attached at the nose of the telescope.

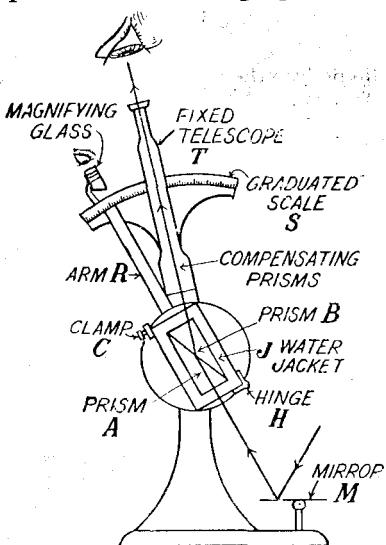


Fig. 18. Optical system of Abbe Refractometer.

Since temperature control is of great importance in determining the refractive index of liquids, the prisms A and B are enclosed in a water jacket J in order to maintain constancy of temperature.

Refractive index and Chemical constitution—Refractivity

Refractive index of a liquid changes not only with the wavelength of light but also with the temperature. It cannot, therefore, provide a satisfactory comparison of refractive powers of different liquids relative to their constitution. To eliminate the effect of temperature, Lorenz and Lorentz (1880) showed purely from theoretical considerations that

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

where n is the refractive index, d the density and R is a constant which they defined as the **Specific refraction** or **Refractivity**. In order to compare the refractive powers of different liquids the specific refractions are multiplied by their respective molecular weights, the resulting products being termed the **Molecular Refraction** or **Molecular Refractivity**. Thus,

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

where M is the molecular weight and RM is the molecular refraction or molecular refractivity. The value of molecular refraction is characteristic of a liquid and remains constant at different temperatures.

Molecular refraction is essentially an additive property as is shown by the fact that the increase in molecular refraction of successive members of an homologous series is nearly constant.

TABLE : Molar Refraction of homologous series of normal alcohols.

Formula	R _M for D-line	Difference
CH ₃ OH	8.218	—
CH ₃ CH ₂ OH	12.839	4.621
CH ₃ CH ₂ CH ₂ OH	17.515	4.676
CH ₃ (CH ₂) ₂ CH ₂ OH	22.130	4.615
CH ₃ (CH ₂) ₃ CH ₂ OH	26.744	4.614

Owing to the additive nature of molecular refraction, it is possible from a study of molecular refractions of different compounds of known constitution to work out a series of constants representing the *atomic refractions* (atomic weight \times specific refraction) of various elements.

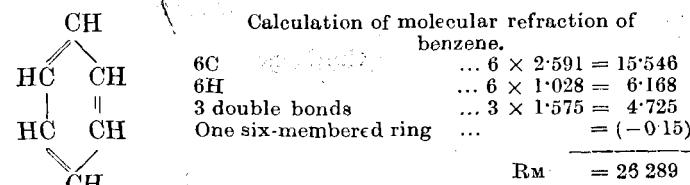
Like the parachor, molar refraction is constitutive as well and is influenced by the arrangement of atoms in the molecule or by such factors as unsaturation, ring closure, etc.

The atomic refraction of oxygen, for example, has different values in alcohols, ethers and ketones. Most of these atomic and structural molar contributions were determined by Eisenlohr but have recently been revised by Vogel (1948). In the table below are given some of his values.

TABLE : Molar Refraction contributions for D-line. (Vogel 1848)

CH ₄ increment	4.647	C=O	4.601
Hydrogen	1.028	—OH	2.546
Carbon	2.591	—COOH	7.226
Chlorine	5.844	—NO ₂	6.713
Bromine	8.741	Double Bond	1.575
Iodine	13.954	Triple Bond	1.977
Oxygen	1.764	6 Carbon ring	-0.15
Methyl radical	5.653	5 "	-0.19
Ethyl ,,	10.300	4 "	0.317

How the constant given above can be employed to confirm the structure of a compound may be illustrated by taking the example of benzene (C₆H₆).



The experimentally determined value 25.93 is in good agreement with the calculated value, which lends support to Kekulé's formula for benzene. Thus the determination of molecular refractions of liquids affords an easy means of ascertaining its chemical constitution.

Optical Exaltation. When a compound contains more than one double bond, the molecular refraction depends not only on the number of double bonds but also on their relative position in the molecule. Two double bonds when separated from each other by one single bond (*conjugated system of double bonds*) cause a marked increase in the observed molecular refraction. Thus two isomeric hydrocarbons of the formula C_6H_{10} with the following structures have different molecular refractions.

		R _M observed	R _M calculated
(a)	$CH_3=CH-CH_2-CH_2-CH=CH_2$	28.77	28.99
(b)	$CH_3-CH=CH-CH=CH-CH_3$	29.87	28.99

The observed value for hydrocarbon (b) and similar other compounds containing conjugated double bonds is abnormally high and this behaviour is spoken of as *optical exaltation*. It is, however, found that conjugated double bonds when present in a ring compound like benzene do not give rise to optical exaltation.

Additivity of Molar Refraction. For mixtures of neutral molecules which do not exert strong forces on each other, the molecular refraction of the mixture ($R_{1,2}$) is given by the expression

$$R_{1,2} = \frac{n^2 - 1}{n^2 + 2} \times \frac{x_1 M_1 + (1 - x_1) M_2}{d},$$

where n is the observed refractive index and d is the density of the mixture, x_1 is molar fraction of the component 1 and M_1 and M_2 the molecular weights of component 1 and 2 respectively. $R_{1,2}$ is then related to individual molar refractions R_1 and R_2 by the expression

$$R_{1,2} = x_1 R_1 + (1 - x_1) R_2.$$

This relation may be used to study solid-liquid mixtures as well.

VISCOSITY

Flowing is one of the characteristic properties of liquids. Some liquids flow more readily than others. Thus ether will move over a glass plate much more quickly than glycerol. The rate of flow depends on the nature of the liquid and on the force which produces the flow. Let us examine the motion of a liquid on a glass plate. The liquid may be considered to be consisting of a number of molecular layers arranged one over the other. The layer in contact

..... 4 } Layers of the liquid on a glass plate.
..... 3 } molecules of the liquid on a glass plate.
..... 2 } the liquid on a glass plate.
..... 1 } glass plate.

Fig. 19. Motion of a liquid on a glass plate.

with the glass plate remains stationary, the second layer moves slowly, the third one moves a little quicker than the second and the velocity of the fourth is maximum. There is thus a movement of different layers past one another in the direction of the flow. The displacement of different layers relative to one another is opposed by the internal friction or viscosity of the liquid. When the flow of the liquid becomes steady,

another in the direction of the flow. The displacement of different layers relative to one another is opposed by the internal friction or viscosity of the liquid. When the flow of the liquid becomes steady,

there will be a constant difference in the velocity between two different layers. It has been found that force per unit area required to maintain this condition is directly proportional to the difference of velocity v , of two adjacent layers, and inversely proportional to their distance, x , apart, i.e.,

$$\text{Force} \propto \frac{v}{x} \text{ or } F = \eta \times \frac{v}{x}$$

where η is the **Co-efficient of Viscosity** which may be defined as *the force per unit area required to maintain unit difference of velocity between two parallel layers in the liquid, one centimetre apart.* The co-efficient of viscosity is expressed in dynes per square centimetre.

The reciprocal of the co-efficient of viscosity is called **Fluidity**.

$$\text{Fluidity} = \frac{1}{\eta}.$$

Determination of Viscosity

The direct experimental measurement of absolute viscosity offers considerable difficulty. *The relative viscosity* of a liquid with respect to, say water, is all that is required for most purposes. It can be determined conveniently with the help of an apparatus called **Ostwald Viscometer**. The apparatus is shown in Fig. 20. A definite quantity of the liquid under examination is put into the wide limb and sucked up the right limb C, slightly above the etched mark A. The quantity of the liquid should be enough to fill the viscometer between C and C' approximately. The liquid is now allowed to flow back and the time taken for the meniscus to fall from A to B is noted. The liquid passes through the capillary tube BD and it is clear that the time of flow t , will be directly proportional to the co-efficient of viscosity. It is also inversely proportional to the density, d , of the liquid,

$$t \propto \frac{\eta}{d}, \eta \propto dt, \text{ or } \eta = k dt. \quad \dots (1)$$

The whole process is then repeated for water, exactly under the same conditions and taking about the same volume. Then

$$\eta_w = k d_w t_w \quad \dots (2)$$

where η_w , d_w and t_w are the co-efficient of viscosity, density and time of flow of water respectively.

From (1) and (2)

$$\frac{\eta}{\eta_w} = \frac{dt}{d_w t_w} \quad \dots (3)$$

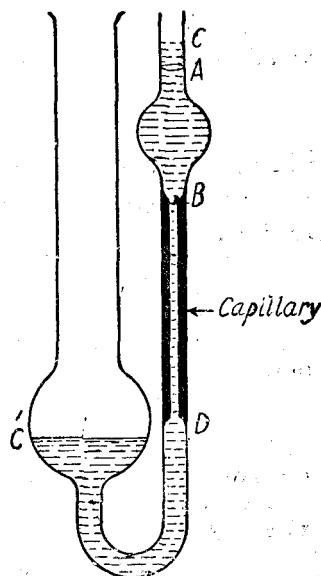


Fig. 20. The Ostwald Viscometer.

Taking the viscosity of water under the experimental conditions as unity

$$\frac{\eta}{1} = \frac{dt}{d_w t_w}$$

η is then the **Relative Viscosity** of the liquid. The absolute value can be calculated by substituting the value of absolute viscosity of water in the equation (3).

Ostwald Viscometer is a very convenient apparatus for determination of viscosity at higher temperatures as it can easily be suspended in a thermostat.

Viscosity and Chemical Constitution

Since viscosity depends on resistance offered when a molecular layer moves over another, some relationship between viscosity and constitution is to be anticipated. The following general rules have been discovered:

(i) In a homologous series, the increase in viscosity per CH_2 group is approximately constant.

(ii) An interesting relationship between viscosity and molecular volume discovered by Dunstan (1909) may be stated as

$$\frac{d}{M} \times \eta \times 10^6 = 40 \text{ to } 60,$$

where d is the density and M is the molecular weight.

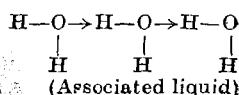
This expression is true only for non-associated liquids¹ whereas for associated liquids the number is considerably greater than 60. Dunstan's relation has been employed to know whether a given liquid is associated or not. For example, the value of the expression for benzene and water is 73 and 559 respectively, which is taken to mean that benzene is a normal liquid whereas water is an associated one.

Since $\frac{M}{d}$ represents the molecular volume, $\left(\frac{M}{d}\right)^{\frac{2}{3}}$ represents the area over which one gram-molecule of the liquid is distributed, i.e., molecular surface. The product of molecular surface and viscosity is termed **Molecular Viscosity**. Thus :

$$\text{Molecular viscosity} = \text{Molecular surface} \times \text{Viscosity}$$

$$= \left(\frac{M}{d}\right)^{\frac{2}{3}} \times \eta.$$

1. The molecules of **non-associated liquids** are present in normal state whereas molecules of **associated liquids** are linked to each other and are present in abnormal state.

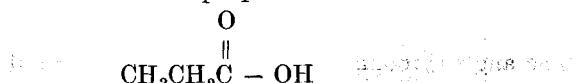


Thorpe and Rodger (1894) found that molecular viscosity is an additive property at the boiling point. The following constants were arrived at :—

Element of group	H	C	O (in — OH)	O (in : CO)	S
Corresponding Molecular viscosity	80	-98	196	248	155

From these constants the molecular viscosities of substances of known constitution could be calculated. If the calculated and experimental values come out to be the same this is taken as a confirmation of the constitution of the substance. Let us take the case of propionic acid for illustration.

The structural formula of propionic acid can be written as



Using the constants from the above table, its molecular viscosity can be calculated as follows :

$$\begin{array}{rcl}
 6\text{H} & \dots \dots \dots & 6 \times 80 = 480 \\
 \text{O} \text{ (in CO)} & \dots \dots \dots & = 248 \\
 \text{O} \text{ (in OH)} & \dots \dots \dots & = 196 \\
 3\text{C} & \dots \dots \dots & 3 \times (-98) = -294 \\
 \\
 \text{Total molecular viscosity} & = & 630
 \end{array}$$

The molecular viscosity of propionic acid as determined experimentally is also 630. The calculated and experimental values being the same, the structural formula assigned to propionic acid is correct.

(iii) Logarithm of the co-efficient of viscosity has also been Found to be an additive property.

(iv) **Rheochor.** It has been shown by Newton Friend that if molecular volume be multiplied by the eighth root of the co-efficient of viscosity, it leads to a constant to which he has given the name *Rheochor*.

$$R = \frac{M}{D} \times \eta^{\frac{1}{8}}$$

Rheochor may be regarded as *the molar volume of the liquid at the temperature at which its viscosity is unity*. Friend has shown it to be both additive and constitutive.

It must, however, be admitted that the relationships described above have not proved of much use in solving structural problems.

OPTICAL ACTIVITY

Ordinary light consists of wave-motion taking place in different places at right angles to the direction of transmission of light. Light which consists of wave-motion in a single plane only is said to be *plane polarised*.

Some liquids and solutions when they are placed in the path of a polarised beam of light have the remarkable property of rotating its plane through a certain angle. The property itself is called **optical activity** and the substance possessing it, is said to be **optically active**. The rotation may take place either clockwise or anti-clockwise. Substances which give rise to clockwise rotation are called **dextro-rotatory** and those which give rise to anti-clockwise rotation are said to be **laevo-rotatory**.

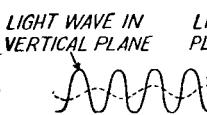


Fig. 21. Ordinary light consisting of wave motion in different planes.

LIGHT WAVE IN PLANE OF PAPER



Fig. 22. Plane polarised light consisting of wave motion in a single plane only.

The angle through which the plane of polarised light is rotated is determined by (i) the nature of the substance, (ii) the length of the layer through which the light has to pass, (iii) the density of the substance, (iv) the wave-length of the light employed, and (v) the temperature at which the observation is made. For purposes of comparison the results are usually expressed in terms of **specific rotation** which is given by the relation.

$$[\alpha]_{D_t} = \frac{\alpha}{l d}$$

where $[\alpha]_{D_t}$ the specific rotation at a temperature t , and for light provided by the sodium flame (D line), α is the observed angle of rotation, l is the length of the column of the liquid and d is the density.

The specific rotation of substances in solution is represented by a similar relation.

$$[\alpha]_{D_t} = \frac{100\alpha}{g l d}$$

where g is the number of grams of solute in 100 grams of the solution, d is the density of solution at temperature t , and α and l have the same significance as above.

Measurement of Optical Activity

Polarimeter. Accurate measurement of the angle of rotation can be made with the help of an instrument called *polarimeter*. It is commonly employed for finding the concentration of sugar in a given solution and when solely meant for this purpose the instrument is called a *Saccharimeter*.

PRINCIPLE AND WORKING. Imagine a long string passing through the slits S_1 and S_2 . By moving its end A up and down, waves are produced in the string which travel up to the other end B. Of course, the slit S_1 allows through it only those waves which are in a plane parallel to it. When the slit S_2 is also vertical, i.e., parallel to the slit S_1 , the waves which emerge from S_1 pass through it

unchecked. When S_2 is made horizontal, the wave motion is stopped by it (See Fig. 23).

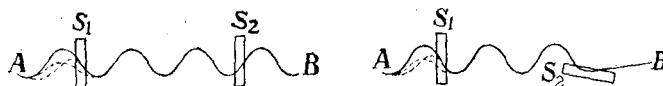


Fig. 23. Illustration of the principle of polarimeter.

The simplest polarimeter may be made of two *nicol* prisms P and A. P is fixed and A can be rotated. These prisms may be compared to the slits S_1 and S_2 in the above illustration and light

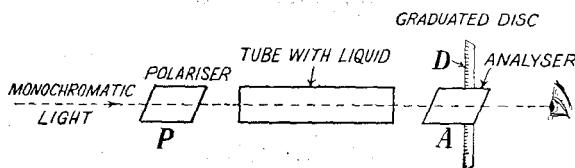
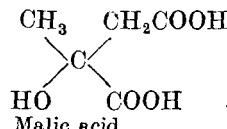
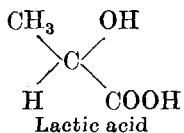


Fig. 24. Important parts of a polarimeter.

waves may be considered to correspond to waves in the string. The prism P, like the slit S_1 , allows only those light wave pass through it which move in a single plane. Since it causes the light to be plane polarised, it is called a *polariser*. When the prism A, the *analyser*, is in position similar to P, it allows the light waves coming from P to pass through it, but when it is rotated through the right angle no waves can pass through it and the field of view will be dark. If now a glass tube containing an optically active liquid is placed between these prisms, it rotates the plane of polarised light through a certain angle and therefore to get a dark field of view again, the prism A will have to be rotated through the same angle. This angle is measured with the help of a graduated disc at the centre of which is fixed the analyser A. This is the angle through which the plane of polarisation has been rotated by the active liquid. For greater accuracy modern polarimeters have many improvements over the simple type, the essentials of which have been described above.

Optical Activity and Chemical Constitution

Optical activity is purely a *constitutive property*, i.e., it depends entirely on the arrangement of atoms in the molecule. In the case of organic compounds, only those which contain an *asymmetric* carbon atom, that is, a carbon atom whose four valencies are satisfied by four different atoms or radicals, have the power of rotating the plane of polarised light. Lactic acid and malic acid both of which are known to exhibit optical activity, have the following structural formulae :



In these formulae no two groups attached to the central carbon atom are identical. A further remarkable fact is that an optically active substance like lactic acid always exists in two forms. While one form rotates the plane of polarisation to the left, the other rotates to the same extent but in the opposite direction, that is, to the right. The first is termed the *leavo*, or *l*-lactic acid and the second *dextro* or *d*-lactic acid.

Le Bel and Van't Hoff account for the above facts on the theory that the four different groups are not in the same plane as the carbon atom, but are supposed to be situated at the corners of a regular tetrahedron at the centre of which lies the carbon atom. According to this theory lactic acid molecule can be arranged in two different ways in space.

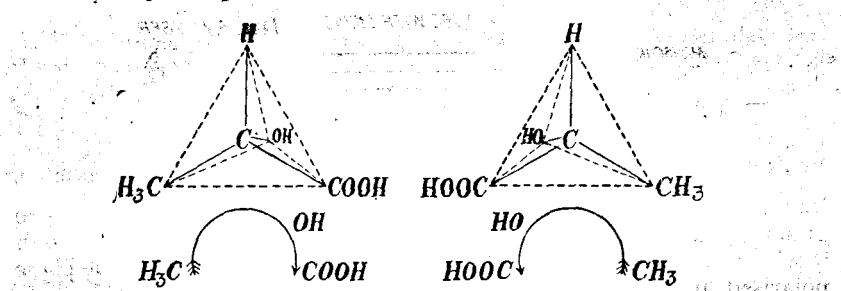


Fig. 25. Mirror-image forms of Lactic acid.

These two models are related to each other as an object to its mirror image and one cannot be superimposed over the other. One of these models corresponds to *l*-acid and the other to *d*-acid, but we can say exactly as to which model represents which form of the acid, as the internal mechanism by which a molecule rotates the plane of polarised light is not clearly understood. It may, however, be seen from the two models, that the groups in one case are arranged from left to right (clockwise) and in the other case from right to left (anti-clockwise) [See Fig. 25]. This probably explains that while one form rotates the plain of polarisation to the left, the other will rotate it to the right.

Optical activity is met with not only in compounds which contain an asymmetric carbon atom but also in compounds which contain other asymmetric atoms, e.g., silicon, nitrogen, etc. It is also displayed by compounds of which the molecule as a whole is asymmetric although it may not contain an asymmetric carbon atom. Thus, broadly speaking, the property of optical activity is linked with the asymmetry of molecules.

DIPOLE MOMENTS

When a covalent bond is formed between two unlike atoms, e.g., A : B, it is noteworthy that one atom is usually more electronegative than the other. If A is more electronegative than B, it has a greater tendency to attract electrons. Thus the shared pair of electrons is drawn near A, leaving a positive charge on the atom B and the molecule becomes dipolar ($A^- B^+$) on account of the relative displacement of centres of positive and negative electricity in it. In a

polar molecule, we have equal positive ($+q$) and negative ($-q$) charges separated by a distance r .

The **Dipole moment** of a molecule is defined as the vector equal in magnitude to the product of the electric charge q and the distance r , having the direction of the line joining the positive and negative centres.

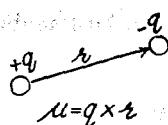
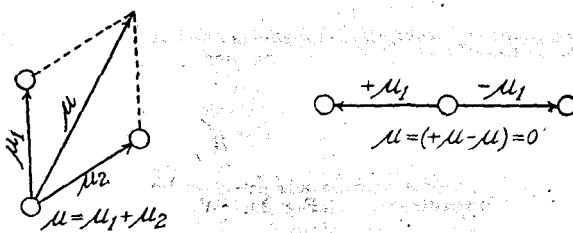


Fig. 26. Definition of dipole moment.

If a polyatomic molecule contains two or more bonds, the net dipole moment is the resultant of the vector addition of the individual moments. In a linear molecule, the individual bond moments may exactly cancel each other on vector addition, and the dipole moment would be zero.



(in a triangular molecule)

(in a linear molecule)

Fig. 27. Vector addition of dipole moments.

In expressing dipole moments, the charge is generally given in electrostatic units (esu) and distances in angstrom units ($1\text{A} = 10^{-8}\text{cm.}$) Thus an electron separated from a unit positive charge by a distance of 1A , would have a dipole moment of $(4.80 \times 10^{-10} esu)$. (10^{-8} cm.) $= 4.80 \times 10^{-18} esu$ per cm. or 4.8 debyes, the unit $10^{-18} esu$ cm. being called the *debye*.

The dipole moments can be determined experimentally by noting the influence on the movement of the molecules of the substance under examination through dielectrics when placed in electric field. The discussion of the procedure and the mathematical treatment are beyond the scope of this book. The dipole moments of some typical substances are given below :

COMPOUND	MOMENT (debyes)	COMPOUND	MOMENT (debyes)
HCl	1.03	CH ₄	0
HBr	0.78	CH ₃ Cl	1.45
HI	0.38	CH ₃ Br	1.85
H ₂ O	1.85	CH ₃ I	1.35
H ₂ S	0.95	CH ₃ OH	1.68
NH ₃	1.49	(C ₂ H ₅) ₂ O	1.14
SO ₂	1.61	C ₆ H ₅ OH	1.70
CO ₂	0	C ₆ H ₅ NO ₂	4.08

Dipole moments and Molecular structure. The determination of dipole moment of a substance gives two types of information regarding its molecular structure: (i) The extent to which a bond is ionised; and (ii) the geometrical shape of the molecule, particularly with regard to the angles between its bonds. The following examples are given for illustration.

(1) The dipole moment of HCl as determined experimentally is 1.303. If the molecule were completely ionised (H^+Cl^-), the moment would be

$$\mu = r \times e = 1.26 \times 4.80 = 6.05 \text{ d.}$$

1.26 being the distance H — Cl found by spectrum analysis. Therefore, we infer that ionic character of the bond between H and Cl is equivalent to a separation charge of about $\frac{1}{6}e$.

(2) Despite the difference in electronegativity between carbon and oxygen, carbon dioxide has no dipole moment. This is possible only if the molecule is linear, C — C — O, and the moments due to the two C — O bonds exactly cancel each other on vector addition.

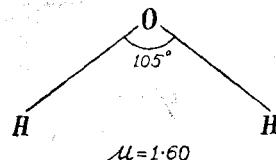
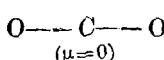


Fig. 28. CO_2 molecule is linear.

Fig. 29. Water molecule is triangular.

(3) Unlike carbon dioxide, water, H — O — H has dipole moment of 1.85 d, which obviously rules out linear structure. It has been estimated that each O — H bond has a moment of 1.60 d and hence the bond angle is about 105°.

(4) The dipole moment of *p*-dichlorobenzene is zero, while that of *o*-dichlorobenzene is 2.54. This shows that benzene ring is planer and in *p*-C₆H₄Cl₂ the C — Cl bonds are also directed in the plane of the ring, thus adding to zero. In *o*-C₆H₄Cl₂, the two bonds C — Cl contain an angle of 60° and their dipole moments on vector addition give a higher dipole moment.

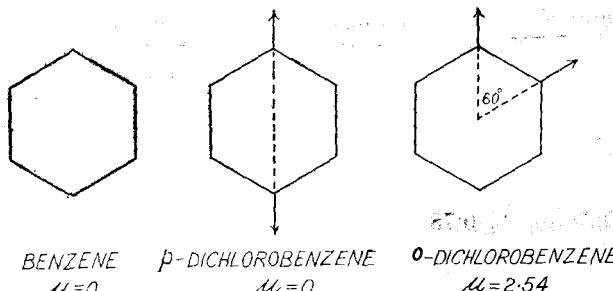


Fig. 30.

(5) For geometrical isomers, the dipole moment of the *cis*-isomer

has a higher value than the more symmetrical *trans* isomer. Thus :



Hence the determination of dipole moments is useful in identifying the *cis* and *trans* isomers.

QUESTIONS AND PROBLEMS

1. What is meant by colligative, additive and constitutive properties ? Give examples of each and explain briefly how they are related to the composition and structure of molecules of substances. (*Travancore B.Sc., 1954*)

2. What do you understand by the term *molecular volume* ? Write a note on the work of Kopp in connection with molecular and atomic volumes.

3. Define the term *Co-efficient of viscosity*. Describe a simple method for determining it in case of a liquid. Has this property of liquids been of any help in solving problems of chemical constitution ?

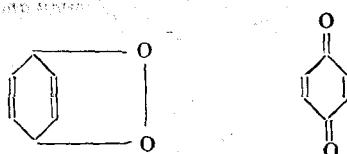
4. Describe briefly the various methods available for the determination of surface tension. Discuss how surface tension is related to chemical constitution ?

5. How is surface tension of a liquid measured ? Discuss the importance of surface tension measurements in the elucidation of problems in Physical Chemistry. (*Travancore B.Sc., 1954*)

6. How would you measure the surface tension of a liquid ? How is the value of parachor derived from it ? Discuss the applications of parachor in the elucidation of structure of organic molecules. (*Punjab B.Sc., 1954*)

7. Describe a method for measuring the surface tension of a liquid. How may surface tension be employed to detect "molecular association" in a liquid ? (*Andhra B.Sc., 1952*)

8. What do you understand by parachor ? How is it related to surface tension ? For quinone $\text{C}_6\text{H}_4\text{O}_2$, the following two constitutions have been proposed :



The experimental value for parachor for quinone is 237. (Parachor values for H = 17.1, C = 4.8, O = 20, for double bond 23.2, for a ring of six carbon atoms 6.1). Which constitution would you accept ?

(*Agra B.Sc., 1952*)

9. What do you understand by the term 'parachor' ? Illustrate the use of parachor measurements in the elucidation of molecular structures.

(*Ceylon Final, 1954*)

10. Explain clearly the term "Molar Parachor". How does it help in determining the constitution of an organic compound ? Illustrate by examples.

11. What do you understand by *Parachor* ? How is it related to surface tension ?

12. Explain what you understand by the following terms : Parachor ; Co-efficient of viscosity. Discuss the additive character of Parachor and its use in elucidating the constitution of organic compounds in doubtful cases.

13. Define the terms *specific refraction* and *molecular refraction*. What is the importance of the measurement of the refractive index of liquids?
14. How is optical activity accurately measured and what is the importance of this measurement in Chemistry? (Punjab B.Sc., 1944)
15. How would you determine accurately the refractivity of a liquid? What is the theoretical importance of this measurement?
16. Write an essay on molar refraction and its relation to molecular constitution of an organic compound. (Agra B.Sc., 1947)
17. Write notes on :—(a) Parachor, (b) Molecular refraction. (Madras B.Sc., 1953)
18. Discuss the relation between chemical constitution and physical properties. (Andhra B.Sc., 1953)
19. Write a short note on Parachor and chemical constitution. (Jammu and Kashmir B.Sc., 1954)
20. Write an essay on the relation between physical properties and chemical constitution. (Andhra B.Sc., 1955)
21. Explain "Molecular Refractivity". Give examples to illustrate its relation to chemical constitution. (Osmania B.Sc., 1955)
22. Write notes on : Determination of the surface tension and viscosity of liquids, optical activity, molecular volume and Parachor. (Rangoon B.Sc., 1956)
23. Write an essay on the relation between physical properties and chemical constitution. (Madras B.Sc., 1955)
24. Give a method of measuring surface tension of any liquid and point out how a study of this property can throw light on the degree of association of the liquid. (Lucknow B.Sc., 1955)
25. What are the different types of physical properties? How is parachor useful in determining the structures of organic compounds? (Baroda B.Sc., 1956)
26. Discuss the relations which have been found between some one property and chemical constitution. (Lahore B.Sc., 1956)
27. Write a note on : Viscosity in relation to chemical constitution. (Jammu and Kashmir B.Sc., 1958)
28. What is a polar molecule? How is its dipole moment determined? What information can dipole moments furnish about the structure of molecules? Give examples. (Kerala B.Sc., 1957)
29. What do you understand by parachor and dipole moment of molecules? What is their importance in the study of chemical structure? (Aligarh B.Sc., 1958)
30. Write notes on the following with special reference to their significance in molecular structure: (i) Parachor; (ii) Optical rotation. (Lahore B.Sc., 1958)
31. What is meant by 'parachor'? How is its determination helpful in the elucidation of molecular structure? (Punjab B.Sc., 1959)
32. Discuss the relation between surface tension and chemical constitution. (Rajasthan B.Sc., 1959)
33. Describe a method for measuring the surface tension of a liquid. In what ways does a knowledge of the surface tension assist in deciding chemical constitution? (Osmania B.Sc., 1959)
34. State McLeod's relation between surface tension and density of a liquid. Hence, bring out clearly the definition of parachor. Discuss the application of parachor. (Poona B.Sc., 1959)

CHAPTER III

THE GASEOUS STATE

THE SIMPLE GAS LAWS

Of the three states of matter, the solid, the liquid and the gaseous, the last is the one which is characterised by a simplicity and uniformity of behaviour. Among other characteristics of gases, the outstanding are the lack of a definite shape or volume, low density, slight viscosity and the ease with which they distribute themselves uniformly throughout the available space. *When the external conditions of temperature and pressure are altered the volume of all gases is affected to nearly the same extent irrespective of the nature of a gas.* Following are the laws which describe the behaviour of gases in general:—

✓ (1) **Boyle's Law.** Boyle's law states that :

If the temperature remains constant, the volume of a given mass of a gas varies inversely as the pressure to which it is subjected.

i.e., $V \propto \frac{1}{P}$, when T is constant,

or $PV = K$ (constant).

Thus we can also state Boyle's law as follows :

Temperature remaining the same, the product of pressure and volume of a given mass of gas is constant.

✓ (2) **Charles' Law.** The law states that :

If the pressure remains constant the volume of a given mass of a gas varies directly as its absolute temperature.

(Absolute temperature T = temperature on centigrade scale + 273)

i.e., $V \propto T$, when P is constant.

✓ (3) **Pressure-Temperature Law.** It states that :

If the volume remains constant the pressure of a given mass of a gas varies directly as its absolute temperature.

i.e., $P \propto T$, when V is constant.

THE GENERAL GAS EQUATION

The simple gas laws may be summed up in a single equation as follows :

$V \propto T$, when P is constant.....*Charles' law*
and $P \propto T$, when V is constant.....*Pressure-temperature law.*

Combining the two laws we have

i.e., $PV \propto T$, when P and V vary together
or $PV = kT$

where k is a constant. It can easily be realised that Boyle's law is also contained in this equation as when T itself becomes constant, $PV = kT = K$, another constant and this is Boyle's law.

In the equation $PV = kT$, k is a constant the value of which depends upon (i) the quantity of the gas, and (ii) the units in which

P, V and T are expressed. A more general form of the equation can be obtained by the application of *Avogadro's Law*. One gram-molecule of all gases under the same conditions of temperature and pressure occupies the same volume, so that the value of k will be the same for all gases if in every case **one gram-molecule** of the gas is considered. When this is done, k is replaced by R, and the equation $PV = kT$ becomes

$$PV = RT$$

This is known as the **Gas Equation** and the constant R is named the **Molar Gas Constant** or the **Gas Constant**. The above equation is applicable to 1 gm. mol. of the gas only. A more general form of the equation is

$$PV = nRT$$

where n is the number of gm. mols. of the gas taken when it occupies a volume V at the pressure P and temperature T.

The real **significance of R** will be readily understood when we examine the nature of the quantities of which it is made up.

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

But pressure is force per unit area

$$\begin{aligned}\therefore R &= \frac{\text{force}}{\text{area}} \times \frac{\text{volume}}{\text{temperature}} \\ &= \frac{\text{force}}{(\text{length})^2} \times \frac{(\text{length})^3}{\text{temperature}} = \frac{\text{force} \times \text{length}}{\text{temperature}} \\ &= \frac{\text{work}}{\text{temperature}}\end{aligned}$$

Hence R must be expressed in units of work divided by temperature. Thus in C.G.S. system (centimetre-gram-second system) the value of R will be expressed in *ergs per degree per mol.*

The numerical value of R can be calculated from the expression $R = \frac{PV}{T}$ making use of the fact that at 0°C , and at a pressure of 1 atmosphere, the volume occupied by 1 gram-molecule of the gas is 22.4 litres. Of course, the value will vary with the units in which P and V are expressed. Thus, if P and V are expressed in atmospheres and litres respectively, the value of R can be calculated as follows :

$$P = 1 \text{ atmosphere}; V = 22.4 \text{ litres}; T = 273^\circ \text{ Abs.}$$

$$\therefore R = \frac{PV}{T} = \frac{1 \times 22.4}{273} = 0.0821 \text{ litres-atmosphere per degree per mol.}$$

If P is expressed in dynes per square centimetre and V in c.c., we have

$$P = 76 \times 13.6 \times 981 \text{ dynes per sq. cm.}$$

$$V = 22,400 \text{ c.c.}$$

$$T = 273^\circ \text{ Abs.}$$

$$\therefore R = \frac{PV}{T} = \frac{76 \times 13.6 \times 981 \times 22400}{273} = 8.3 \times 10^7 \text{ ergs per degree mol}^{-1}$$

Since we know that 1 calorie = 4.18×10^7 ergs, the value of R may also be expressed in calories.

$$R = \frac{8.3 \times 10^7}{4.18 \times 10^7} = 1.99 \text{ or } 2 \text{ calories approximately per degree mol}^{-1}$$

Also, since 1 Joule = 10^7 ergs

$$R = 8.3 \text{ Joules degree}^{-1} \text{ mol}^{-1}.$$

KINETIC THEORY OF GASES

So far we have considered the gas laws which describe the general behaviour of gases. These laws are based on experiments quite independent of any theory of the nature of a gas. We will now proceed to see how they can be derived mathematically from the simple theory that a gas consists of a very large number of molecules in rapid motion in vacant space. This is the **Kinetic Theory of Gases** (*Kinesis*=motion).

The first attempt to explain the properties of gases was made as early as 1738 when Bernoulli pointed out that the pressure exerted by a gas is due to the impacts of the gas molecules on the walls of the containing vessel. His ideas were subsequently developed by Clausius and Kronig who in 1857 derived the 'Kinetic Equation' and proved from it the simple gas laws. The theory was further developed and extended by Maxwell, Kelvin, Boltzmann and others, who gave it the present form.

Postulates of the Kinetic Theory of Gases

(1) Every gas consists of a very large number of separate tiny particles called molecules. The actual volume of the molecules is negligible compared to the total volume of the gas.

(2) The molecules of a gas are in a state of constant rapid motion in all possible directions. They travel in straight lines until on collision with another molecule or the wall of the containing vessel the direction of motion is changed.

(3) The molecules exert no appreciable attraction on each other and behave as perfectly elastic bodies. Hence there is no loss of kinetic energy resulting from their collisions or mutual friction.

(4) The pressure which a gas exerts on the walls of the containing vessel is due to hits recorded by the moving molecules.

(5) The motion imparted to the molecules by gravity is negligible in comparison to the effect of the continued collisions between them.

(6) The absolute temperature of a gas is a measure of the average kinetic energy of all the molecules present in it. Or, the average kinetic energy of the gas molecules is proportional to the absolute temperature of the gas.

Kinetic Equation for Gases. Starting with the assumptions given above, it is possible to derive in a simple way an equation expressing the pressure exerted by a gas in terms of the number and velocity of the molecules. Let us imagine a definite mass of a gas contained in a cubical vessel (Fig. 31) and suppose that

the length of the edge of the cube is $= l$ cms.,

the total number of molecules is $= n$,

the mass of one molecule is $= m$,

and the average velocity¹ of the molecule = v .

Although the molecules are moving in every possible direction, the velocity of a molecule at any moment can be resolved into three directions X, Y, or Z parallel to the three edges of the cube. Since the molecules move in all directions and have no preference for any particular side, and as also the pressure exerted is the same on all sides, we may regard one-third ($n/3$) molecules moving parallel to any particular edge and striking the opposite faces again and again. Here we are, of course, neglecting the mutual collisions of the molecules but it is just the right thing because such collisions do not result in any decrease in the total energy.

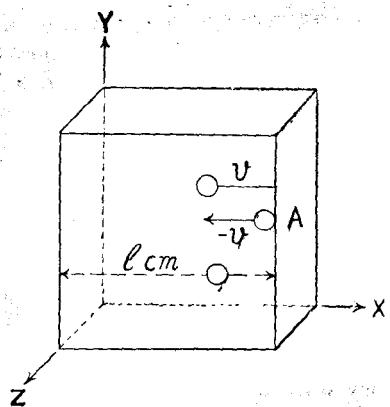


Fig. 31.

intervals. The velocity of the molecule before it strikes the face is v and since the molecules are perfectly elastic, it will rebound with the velocity $-v$. Thus,

momentum of the molecule before it strikes the face = mv

momentum of the molecule after the impact = $-mv$

hence the change in momentum at each impact = $mv - (-mv)$
= $2mv$

To hit the same face again the molecule has to move to the other face and back, i.e., a distance of $2l$ centimetres. It will impart impacts to the same face every $\frac{2l}{v}$ seconds, or that, the number of

impacts per second would be $\frac{v}{2l}$. But there are in all $n/3$ molecules

bombarding the two opposite faces and, therefore, the total change of momentum taking place per second at the face A is

$$\begin{aligned} &= \left\{ \text{Change of momentum at each impact} \right\} \times \left\{ \text{No. of impacts per sec. imparted by a single molecule} \right\} \times \left\{ \text{total number of molecules bombarding the face A} \right\} \\ &= 2mv \times \frac{v}{2l} \times \frac{n}{3} = \frac{1}{2} \frac{mnv^2}{l}. \end{aligned}$$

1. The 'average velocity' v , as considered here is in fact the **root mean-square (R.M.S.) velocity**, i.e., it is the under-root of the mean of the squares of velocities of all the n molecules.

$$v = \sqrt{\frac{v_1^2 + v_2^2 + v_3^2 + \dots + v_n^2}{n}}$$

If v may wrongly be considered as the average velocity in ordinary sense it should be equal to $v_1 + v_2 + v_3 + \dots + v_n/n$, but then the total kinetic energy calculated using this value would be altogether different from the actual one.

Since force is defined as the rate of change of momentum, $\frac{1}{2} \frac{mnv^2}{l}$ also represents the average force acting on A.

Pressure is force per unit area so that

$$P = \frac{\text{force}}{\text{area}} = \frac{1}{2} \frac{mnv^2}{l} \times \frac{1}{l^2} = \frac{1}{2} \frac{mnv^2}{l^3}.$$

But l^3 is the volume of the cube and we have

$$P = \frac{1}{2} \frac{mnv^2}{V}$$

or $PV = \frac{1}{2} mnv^2.$

This is the fundamental equation of the kinetic theory of gases and is often referred to as the **kinetic equation for gases**. It can also be expressed as

$$PV = \frac{1}{2} Mv^2, \text{ where } M \text{ is the total mass of the gas.}$$

Or $P = \frac{1}{2} \frac{M}{V} v^2$

$$= \frac{1}{2} Dv^2, \text{ where } D \text{ is the density of the gas.}$$

Although the kinetic equation has been derived for a cubical vessel, it is equally applicable to a vessel of any shape since the total volume may always be considered to be made up of a large number of extremely small cubes, for each of which the equation holds.

Deduction of Gas Laws from the Kinetic Equation

(a) Boyle's Law.

$$PV = \frac{1}{2} mnv^2 \quad \text{Kinetic Equation.}$$

According to the kinetic theory, there is a direct proportionality between absolute temperature and average kinetic energy of the molecules.

i.e., $\frac{1}{2} mnv^2 \propto T$

or $\frac{1}{2} mnv^2 = kT$

or $\frac{3}{2} \times \frac{1}{2} mnv^2 = kT$

or $\frac{3}{2} \frac{1}{2} mnv^2 = \frac{3}{2} kT.$

Substituting the above value in the kinetic equation, we have

$$PV = \frac{2}{3} kT.$$

The product PV, therefore, will have a constant value at a constant temperature.

(b) Charles' Law.

According to this law, the volume of a gas is directly proportional to the absolute temperature at constant pressure.

As derived above :

$$PV = \frac{2}{3} kT$$

Or $V = \frac{2k}{3P} T$

At constant pressure :

$$V = KT$$

Or $V \propto T$

(c) Avogadro's Hypothesis.

If equal volumes of two gases be considered at the same pressure, then

$$PV = \frac{1}{2}m_1n_1v_1^2 \dots \text{Kinetic Equation as applied to one gas}$$

$$PV = \frac{1}{2}m_2n_2v_2^2 \dots \text{Kinetic Equation as applied to 2nd gas}$$

$$\therefore \frac{1}{2}m_1n_1v_1^2 = \frac{1}{2}m_2n_2v_2^2 \dots (1)$$

When the temperature of both the gases is the same, their mean kinetic energy per molecule will also be the same.

$$\text{i.e., } \frac{1}{2}m_1v_1^2 = \frac{1}{2}m_2v_2^2 \dots (2)$$

Dividing (1) by (2), we have

$$n_1 = n_2$$

Or, under the same conditions of temperature and pressure, equal volumes of the two gases contain the same number of molecules. This is Avogadro's Hypothesis.

(d) Graham's Law of Diffusion.

$$PV = \frac{1}{2}mnv^2 \dots \text{Kinetic Equation}$$

$= \frac{1}{3}Mv^2$, where M is the total mass of the gas.

$$v^2 = \frac{3PV}{M}$$

$$= \frac{3P}{D}, \text{ where } D \text{ is the density of the gas.}$$

Hence

$$v = \sqrt{\frac{3P}{D}}.$$

Now the rate of the diffusion (r) of a gas certainly depends on the velocity of molecules; the greater the velocity the higher will be the rate of diffusion, i.e., $r \propto v$. Thus we have

$$r \propto \sqrt{\frac{3P}{D}}$$

Or

$$r \propto \sqrt{\frac{1}{D}}, \text{ if P be maintained constant}$$

Or, in words, the rate of diffusion of a gas is inversely proportional to the square root of its density if the pressure remains constant. This is *Graham's Law*.

Calculation of Kinetic Energy

The average kinetic energy of translation of the moving molecules may be calculated by the use of the kinetic equation as follows:—

$$PV = \frac{1}{2}mnv^2$$

$$\text{But } PV = nRT \text{ (For an ideal gas)}$$

$$\therefore \frac{1}{2}mnv^2 = nRT$$

$$\text{or } \frac{2}{3} \times \frac{1}{2}mnv^2 = nRT$$

But $\frac{1}{2}mnv^2$ is the Kinetic Energy

$$\therefore \frac{2}{3} \times K. E. = nRT$$

$$\text{or } K. E. = \frac{3}{2}nRT$$

It is evident that kinetic energy of translation of an ideal gas is independent of the nature of the gas or its pressure and depends only upon the temperature.

Calculation of Molecular Velocities

The kinetic theory not only affords a mathematical background of the previous gas laws, but also helps in calculating certain molecular constants. Thus, with its aid we can calculate the velocity of gas molecules.

The molecular velocities are very high indeed. The fastest moving gas molecules are those of hydrogen. The hydrogen molecule moves much faster than the fastest aeroplane or rifle bullet.

Record aeroplane speed 7·8 miles per minute.

Velocity of rifle bullet 31 miles per minute.

Velocity of Hydrogen molecule . . . 68 miles per minute.

The exceptionally high molecular velocities which might seem impossible to measure, can easily be calculated from the Kinetic gas equation. Several cases may arise according to available data and the conditions of the experiment.

CASE 1. Calculation of Velocity when temperature alone is given.

$$PV = \frac{1}{3}mnv^2 \quad \dots\dots\dots \text{Kinetic Equation}$$

$$\therefore v = \sqrt{\frac{3PV}{mn}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3RT}{M}}$$

If M, the total mass of the gas is equal to one gram molecule.

$R = 0.8315 \times 10^8$ ergs. Therefore,

$$v = \sqrt{\frac{3 \times 0.8315 \times 10^8 \times T}{M}} \text{ cms. per second}$$

Thus

$$v = 1.58 \sqrt{\frac{T}{M}} \times 10^4 \text{ cms. per second}$$

where T = absolute temperature, and M = molecular weight.

Example. Calculate the velocity of a molecule of carbon dioxide at 1000°C .

We know from the kinetic equation that

$$v = 1.58 \sqrt{\frac{T}{M}} \times 10^4 \text{ cms. per second.}$$

In this example

$$T = 273 + 1000 = 1273^\circ \text{ Abs.}$$

$$M = 44$$

$$\therefore v = 1.58 \sqrt{\frac{1273}{44}} \times 10^4 \text{ cms. per sec.}$$

$$= 84,988 \text{ cms. per sec.}$$

The velocity of carbon dioxide at 1000° is **84,988 cms. per sec.**

Note. It should be clearly understood that the value of v obtained with the help of the kinetic equation is in reality the root-mean-square velocity. The root-mean-square velocity is not identical with the average velocity.

If we suppose that equal number of molecules are moving at 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 cms. per second respectively, then, the root-mean-square velocity

$$v = \sqrt{\frac{1^2 + 2^2 + 3^2 + 4^2 + 5^2 + 6^2 + 7^2 + 8^2 + 9^2 + 10^2}{10}} = 6.2$$

and the average velocity of the molecules

$$= \frac{1+2+3+4+5+6+7+8+9+10}{10} = 5.5.$$

Maxwell has shown that these quantities are related as below :

$$\text{Average velocity} = 0.9213 \times \text{Root mean square velocity.}$$

CASE 2. Calculation of molecular velocity when temperature and pressure both are given.

Example. Calculate the velocity of chlorine molecules at 12°C and 78 cms. pressure.

From the kinetic equation it can be shown that

$$v = \sqrt{\frac{3PV}{M}}$$

where P = pressure, V = volume and M is the total mass of the gas.

Considering 1 gram-molecule (71 grams) of chlorine, its volume (V) at 12° and 78 cms. can be calculated.

$$V_{12} = \frac{P_n V_n T_{12}}{T_n P_{12}} = \frac{76 \times 22400 \times 285}{273 \times 78} \text{ c.c.}$$

Pressure at 12° in absolute units

$$= 78 \times 13.6 \times 981 \text{ dynes per square cm.}$$

Now substituting the values of P and V in the equation

$$v = \sqrt{\frac{3PV}{M}}, \text{ we have}$$

$$v = \sqrt{\frac{3 \times 78 \times 13.6 \times 981 \times 76 \times 22400 \times 285}{273 \times 71 \times 78}}$$

$$= 31,640 \text{ cms. per sec.}$$

CASE 3. Calculation of molecular velocity at N.T.P.

Example. Calculate the average velocity of a molecule of nitrogen at N.T.P.

We know from Kinetic equation

$$v = \sqrt{\frac{3PV}{M}}$$

For one gram-molecule (28 grams) of nitrogen under normal conditions

$$P = 76 \times 13.6 \times 981 \text{ dynes per sq. cm.}$$

$$V = 22,400 \text{ c.c.}$$

Substituting these values we have

$$v = \sqrt{\frac{3 \times 76 \times 13.6 \times 981 \times 22400}{28}}$$

$$= 49,330 \text{ cm. per second}$$

$$\therefore \text{Average velocity} = 0.9213 \times 49330 \text{ cms. per second}$$

$$= 45,447 \text{ cms. per second.}$$

CASE 4. Calculation of molecular velocity when pressure and density are given.

Example. Oxygen at 1 atmosphere pressure and 0°C has a density of 1.4290 grams per litre. Find the R.M.S. velocity of oxygen molecule.

$$PV = \frac{4}{3}mnv^2 = \frac{4}{3}Mv^2 \dots \dots \text{Kinetic Equation}$$

$$v = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{D}}$$

In the present case,

$$P = 1 \text{ atmosphere}$$

$$= 76 \times 13.6 \times 981 \text{ dynes per sq. cm.}$$

$$D = 1.429 \text{ grams per litre} = 0.001429 \text{ gm./c.c.}$$

$$v = \sqrt{\frac{3 \times 76 \times 13.6 \times 981}{0.001429}} = 46,100 \text{ cms. per sec.}$$

$$= 0.3 \text{ miles per sec.}$$

Note. It must be remembered that if the velocity is to be found in cms. per sec. (C.G.S. units), the pressure and density must be expressed in C.G.S. units.

THE MEAN FREE PATH

At a given temperature, the distance through which a molecule moves before collision with another molecule varies with the density, or so to say, the pressure of the gas. At low pressures, the molecules are far apart and the chances of mutual collision are comparatively less whereas these chances increase when the density is greater or when the gas is compressed.

The mean distance traversed by a gas molecule without coming into collision with another is called its **mean free path**. It is denoted by the symbol L. Evidently, this mean free path is greater, the lower the pressure. It is also connected with the viscosity of the gas. If η represents the co-efficient of viscosity, P, the pressure and d the density of the gas, the mean free path L is given by the expression

$$L = \eta \sqrt{\frac{3}{Pd}}$$

From an observation of the viscosity, therefore, the mean free path can be calculated. At N.T.P., it is 1.78×10^{-5} cm. in hydrogen, 1.0×10^{-5} cm. in oxygen and 0.95×10^{-5} cm. in nitrogen.

The mean free path multiplied by the number of collisions per second gives the root mean square velocity. Consequently, if the mean free path is known as also the molecular velocity, the number of collisions per second can be calculated.

$$\text{No of collisions per second} = \frac{v}{L}$$

At N.T.P., v for hydrogen is 183,100 cms. per second and L is 1.78×10^{-5} cm.

$$\therefore \text{No. of collisions per second} = \frac{183,100}{1.78 \times 10^{-5}} \\ = 102,865 \times 10^5$$

SPECIFIC HEAT RATIO OF GASES

The *specific heat* is defined as the amount of heat required to raise the temperature of one gram of a substance through 1°C . It may be measured *at constant volume* or *at constant pressure* and though the difference in the two values is negligible in case of solids and liquids, it is appreciable in case of gases and a *ratio of the two values gives us valuable information about the atomicity of a gas molecule*.

Specific Heat at Constant Volume. It is the amount of heat required to raise the temperature of one gram of gas through 1°C while the volume is kept constant and the pressure allowed to increase. It is denoted by the symbol c_v . In Physical Chemistry, it is more common, however, to deal with one gram molecule of the gas and the heat required in such case is called **Molecular Heat** and is represented at constant volume by C_v .

It is possible to calculate its value by making use of the Kinetic Theory.

Consider one gram molecule of a gas at the temperature T . Its kinetic energy is $\frac{1}{2} mnv^2$. From the kinetic equation :

$$\begin{aligned} PV &= \frac{1}{2} mnv^2 \\ &= \frac{3}{2} \times \frac{1}{2} mnv^2 = RT \end{aligned}$$

or $\frac{1}{2} mnv^2 (= \text{K.E.}) = \frac{3}{2} RT$

If the temperature is raised by 1°C or $(T+1)^{\circ}\text{Abs.}$, the kinetic energy becomes $\frac{3}{2} R(T+1)$.

$$\therefore \text{Increase in kinetic energy} = \frac{3}{2} R(T+1) - \frac{3}{2} RT \\ = \frac{3}{2} R$$

If, therefore, it be assumed that the heat supplied to a gas at constant volume is used up entirely in increasing the kinetic energy of the moving molecules, and consequently increasing the temperature the value of C_v , should be equal to $\frac{3}{2} R$. It is actually so for monoatomic gases and vapours because such molecules can execute only translatory motion along the three co-ordinate axes. But in the case of diatomic and polyatomic molecules, the heat supplied may not only increase this **kinetic energy of translation** of the molecules as a whole but also cause an increase in the energy in the inside of the molecules which we may call as **intramolecular energy**. This intramolecular energy may be the **vibrational energy**, i.e., energy of the atoms executing vibrations with respect to each other along their line of centres or **rotational energy** which manifests itself in the rotation of the molecules about axes perpendicular to the line of centres.

Consequently in such cases the molecular heat will be greater than $\frac{3}{2} R$ by a factor x

or $C_v = \frac{3}{2} R + x$.

The value of x varies from gas to gas and is zero for monoatomic molecules.

Specific Heat at Constant Pressure. It may be defined as the amount of heat required to raise the temperature of one gram of gas through 1°C , the pressure remaining constant *while the volume is allowed to increase*. It is written as c_p and the Molecular Heat in this case is represented as C_p .

Now, whenever a gas expands, it has to do work against external pressure. It means that when a gas is heated under constant pressure, the heat supplied is utilized in two ways :

(i) *In increasing the kinetic energy of the moving molecules*, and this has already been shown equal to $\frac{3}{2} R + x$ cals.

(ii) In performing external work done by the expanding gas. - The work done by the gas is equivalent to the product of the pressure and the change in volume. Let this change in volume be ΔV when the constant pressure is P and the initial volume is V.

For 1 gm. mol. of the gas at temperature T,

$$PV = RT \quad \dots (i)$$

At temperature $(T+1)^\circ$ Abs.

$$P(V + \Delta V) = R(T+1) \quad \dots (ii)$$

Subtracting (i) from (ii),

$$P \times \Delta V = R$$

Hence, R cals. must be added to the value $\frac{3}{2}R$ cals. in order to get the thermal equivalent of the energy supplied to one gram molecule of the gas in the form of heat when its temperature is raised by $1^\circ C$.

$$\therefore C_p = \frac{3}{2}R + R = \frac{5}{2}R \text{ (for mono-atomic molecules)}$$

For di- and poly-atomic molecules, it will be $\frac{5}{2}R + x$.

Specific Heat Ratio. The ratio of the molecular heats will be the same as the ratio of the specific heats. It is represented by the symbol γ .

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R + x}{\frac{5}{2}R + v}$$

For mono-atomic molecules, $x = 0$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R}{\frac{5}{2}R + v} = \frac{5}{3} = 1.667.$$

For di-atomic molecules in most cases, $x = R$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{7}{2}R}{\frac{7}{2}R + v} = \frac{7}{5} = 1.40.$$

For poly-atomic molecules, very often $x = \frac{3}{2}R$

$$\gamma = \frac{C_p}{C_v} = \frac{\frac{5}{2}R + \frac{3}{2}R}{\frac{5}{2}R + \frac{3}{2}R + v} = \frac{8}{6} = 1.33.$$

These results are found to be in accord with experimental observations at $15^\circ C$ given in the Table that follows and thus *specific heat ratio helps us to determine the atomicity of gas molecules*. The theoretical difference between C_p and C_v as calculated above is R and its observed value also shown in the Table below comes out to be about 2 calories.

Gas	C_p	C_v	$C_p - C_v = R$	$\gamma = C_p/C_v$	Atomicity
Helium	4.99	3.00	1.99	1.663	1
Argon	5.00	3.01	1.99	1.661	1
Mercury vapour	4.97	2.98	1.99	1.667	1
Nitrogen	6.93	4.94	1.99	1.40	2
Oxygen	6.95	4.96	1.99	1.40	2
Hydrogen	6.82	4.83	1.99	1.41	2
Carbon dioxide	8.75	6.71	2.04	1.30	3
Hydrogen sulphide	8.62	6.53	2.09	1.32	3

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THE IDEAL OR PERFECT GAS

The gas which obeys Boyle's and Charles' Law rigidly for all values of temperature and pressure is called a **Perfect gas**. In other words, a perfect gas is one which strictly follows the general gas equation $PV=RT$, since both the gas laws are contained in it. Actually no gas is perfect. They approach perfection as the temperature gets farther from their boiling points, so that at ordinary temperatures the most nearly perfect gases are those like nitrogen and hydrogen which have very low boiling points.

DEVIATIONS FROM GAS LAWS

For a perfect gas $PV=RT$. The equation may be tested for ordinary gases, by studying the variations in V produced by changes in pressure when the product PV should be constant provided, of course, the temperature T is kept constant throughout (Boyle's Law).

Deviations from Boyle's Law. Boyle's experiments upon the results of which his law is based were all performed at ordinary temperatures and pressures.

As experimental measurements extended to high pressures and low temperatures it was revealed that the law was applicable only as an approximation. The results of later experiments performed by Lord Rayleigh (1905) are depicted in Fig. 32 to illustrate the exactness of the law under different conditions.

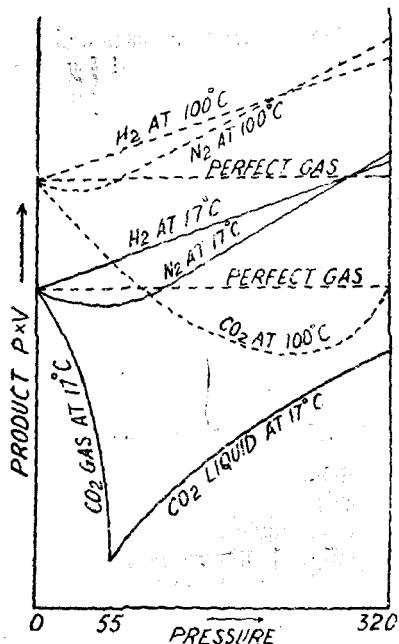


Fig. 32. Deviations from Boyle's law.

that PV for hydrogen increases continuously with the rise of pressure. In the case of nitrogen and carbon dioxide, however, PV first decreases, passes through a minimum where it remains constant for a while, and then rises. At very high pressures the curves are seen to pass up the ideal gas curve. Thus at high pressures, PV for all the gases including hydrogen has a higher value than expected of an ideal gas.

(c) **Effect of temperature** on deviations from Boyle's law becomes apparent from the relative study of the two sets of curves

(a) **At low pressures** the deviations are represented by the left-hand ends of the curves. For hydrogen PV increases as P increases while for nitrogen and carbon dioxide PV decreases as P increases. This means that in general at low pressures PV for all gases, excepting hydrogen, has a lower value than expected of an ideal gas.

(b) **At high pressures** the deviations are indicated by the right-hand ends of the curves. It can be seen from the diagram

at 17° and 100° . At 17° the curve for nitrogen has a more clearly marked minimum than at 100° . This effect is still more clear in the case of carbon dioxide, which shows a deep depression at 100° , while at 17° a sudden fall occurs at 55 atmospheres, at which pressure the gas liquefies. Thus at lower temperatures the deviations become more pronounced with the fall of temperature till at the approach of the conditions of liquefaction the curve records a sharp break.

Explanation of the Deviations from Gas Laws—Van der Waals' Equation.

The kinetic theory attributes the deviations from gas laws to faulty assumptions in the simple form of the theory. In deducing the gas laws from the kinetic theory two simplifying assumptions have been made :

(i) *the actual volume of the molecules themselves is negligibly small as compared with total space.* This space is called the volume of the gas.

(ii) *the molecules of a gas do not exert any attractive force on each other.*

In a gas confined at high pressure and low temperature these assumptions cease to be tenable and account must be taken both of the actual volume and of the mutual attractions of the molecules.

(a) **Volume correction due to the finite size of the molecules.** To allow for the volume occupied by the molecules themselves the total volume V of the gas should be reduced by a constant amount b . Instead of V , therefore, we write $(V - b)$. Strictly speaking b is not the actual volume of the gas molecules and has been theoretically shown to be roughly equal to 4 times their volume and may be called the *vibratory volume* or the *effective volume* of the gas particles.

(b) **Pressure correction due to the mutual attraction of the molecules.** The attractive forces between the molecules come into play when the molecules are brought closer together by compressing the gas. A molecule in the body of the gas is attracted in all the directions when the forces acting in opposite directions cancel out but a molecule in the boundary of the gas is subject to an inward pull due to unbalanced molecular attraction (Fig. 33).

When the pressure is high, the molecules come closer and this force of attraction is sufficient enough to cause an error if not taken into consideration. Now, the effect of this attraction is an inward pull on the molecule about to strike the wall of the vessel and some of the energy of its outward motion will be used up in overcoming this inward pull. It will not strike the opposite face, therefore, with the same force if it were not being dragged back. The observed pressure consequently will be less than the ideal pressure. Or, the ideal pressure (P_i) is equal to the observed pressure P plus a pressure correction P' depending upon this attractive force.

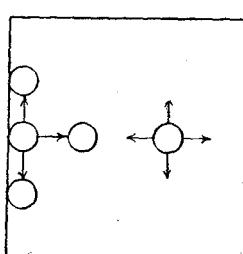


Fig. 33. Showing unbalanced molecular forces at the boundary.

$$P_i = (P + P')$$

This attractive force will be greater, the larger the number of molecules attracting them. Since the number about to strike at any instant is also proportional to the number present, this attractive force is proportional to the square of the density.

$\therefore P' \propto (\text{density of the gas})^2 \propto \frac{1}{V^2}$ where V is the volume of the gas

or $P' = \frac{a}{V^2}$

where a is the coefficient of attraction, i.e., attraction per unit volume and is constant for a particular gas.

$$\therefore \text{Ideal pressure} = \left(P + \frac{a}{V^2} \right).$$

Making both the pressure and volume corrections, the gas equation, $PV = RT$, may be written as

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

This equation first put forward by Van der Waal in 1879, is called **Van der Waal's Equation** and represents the behaviour of a gas over wide ranges of temperature and pressure with much greater accuracy than does the ordinary gas equation.

The deviations from Boyle's Law which we have already described can satisfactorily be explained with the help of Van der Waal's equation. On multiplication and neglecting very small fractions, Van der Waal's equation takes the form

$$PV - Pb + \frac{a}{V} = P'V' \quad \dots (1)$$

where P' and V' is the pressure and volume respectively of the gas if the gas were ideal.

(a) At low pressure the term $\frac{a}{V}$ representing the effect of attraction between the molecules overweighs the Pb factor and therefore neglecting Pb , equation (1) may be written as

$$PV + \frac{a}{V} = RT = P'V'$$

or $PV = P'V' - \frac{a}{V}$

that is the observed product PV at low pressure is less than $P'V'$, the product of pressure and volume if the gas were ideal.

(b) At high pressure the term Pb overweighs the term $\frac{a}{V}$

when the equation (1) may be written as

$$PV - Pb = RT = P'V'$$

or

$$PV = P'V' + Pb$$

that is, the observed product PV is greater than P'V', the product of pressure and volume if the gas were ideal.

It may be noted that the two factors $\frac{a}{V}$ and Pb act in opposite directions. While $\frac{a}{V}$ overweighs at low pressures, Pb overweighs at high pressures and thus it becomes obvious that at some medium pressure one will exactly balance the other. This explains the minimum points on the curves in the diagram (Fig. 32). At these points Van der Waal's equation becomes identical with the gas equation and the Boyle's Law is strictly obeyed.

(c) **At high temperatures**, as V is large, b and $\frac{a}{V}$ will be

negligibly small. Hence in this case Van der Waal's equation is almost reduced to $PV = RT$ indicating that at high temperatures the behaviour of the gas more nearly agrees with Boyle's Law.

(d) **Exceptional behaviour of Hydrogen** is attributed to the very small mass of the hydrogen molecules due to which the forces of attraction between the molecules are almost negligible. Therefore, neglecting the term $\frac{a}{V}$ in the equation (1), we have

$$PV - Pb = RT = P'V'$$

or

$$PV = P'V' + Pb.$$

In the case of hydrogen, therefore, even at low pressures PV is greater than P'V', the product of pressure and volume if the gas were ideal.

ISOTHERMS OF CARBON DIOXIDE—CRITICAL PHENOMENA

The curves representing the variations of volume and pressure at constant temperature are called **isotherms** (Greek, *isos* = equal, *thermos* = warm). For an ideal gas the product PV is constant and hence the isotherms would be rectangular hyperbolae (Fig. 34).

Andrews (1869) determined the isotherms of CO_2 at different temperatures. It can be seen from the diagram that the isotherm of CO_2 at 50° is nearly of the form required of an ideal gas. The isotherm at 31° remains horizontal for a short while at the point F, thus showing a great decrease of volume for a small change of pressure. This deformity in the curve is

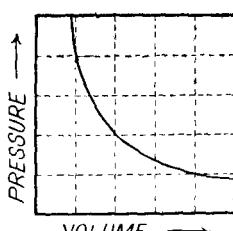


Fig. 34. Isotherm of an ideal gas.

coincident with the appearance of liquid CO_2 . At still lower temperatures the horizontal portions of the curves are much more pronounced. Let us study the isotherm at 21° . The portion AB represents the compression of CO_2 vapour ; at B, liquefaction commences and the curve BC remains horizontal while the gas is changing to liquid at constant pressure ; at C the liquefaction is complete, and the curve CD rises almost vertically, indicating a small decrease of volume with increase of pressure which is the characteristic of a liquid. It is evident from these considerations that at any point within the parabolic area indicated by the dotted line, both vapour and liquid are present, while outside this area either liquid or vapour only is present.

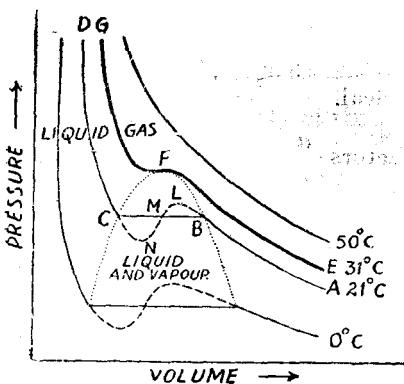


Fig. 35. Isotherms of CO_2 at different temperatures.

The isotherm EFG marks the boundary between gas and vapour. At the point F, the distinction between liquid and vapour states disappears and CO_2 exists in a state called the *critical state*. The point F is then called the *critical point*, the isotherm passing through this point is called the *critical isotherm*, and the temperature corresponding to this isotherm (31°C) is called the *critical temperature*.

The critical phenomenon observed by Andrews in connection with carbon dioxide may be observed with any other gas. The **critical temperature** is characteristic of a gas and may be defined as that temperature below which the continuous increase of pressure on a gas ultimately brings about liquefaction and above which no liquefaction can take place no matter how great be the pressure applied. The pressure required to liquefy the gas at the critical temperature is called the **critical pressure**, and the volume occupied by a mol. of the gas under these conditions is called the **critical volume**.

Application of Van der Waal's equation to critical phenomena.

Van der Waal's equation

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

on multiplication and arranging in powers of V, can be written as

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

This is a cubic equation in V and as such it may have three real roots, or one real and two imaginary roots. In other words, for given values of P and T, V may either have three real values or only one real value. This behaviour predicted by Van der Waal's equation will readily be understood from the isotherms of CO_2 given in Fig. 35. At 50° there is only one volume for each pressure. At 21° there are two different values of V, corresponding to the points

B and C at the same pressure, but the third volume demanded by Van der Waal's equation is missing. Further light on the point was thrown by Thomson in 1871. He substituted the experimental values of a and b in equation (2) and worked out values of V for different values of P at known temperatures. He further plotted a graph between P and V , and thus got theoretical isotherms of CO_2 . Isotherms obtained in this way are exactly of the form shown in Fig. 35. The theoretical isotherms below the critical point have no sharp breaks, the horizontal portions of the experimental curves being replaced by the wave-like portions of the theoretical curves indicated by the dotted line in the diagram. For example, the theoretical isotherm at 21° is represented by the continuous curve ABLMNCD. When such is the case it is obvious that at any temperature below the critical point there will be three volumes corresponding to a single pressure which in the case of the isotherm at 21° are shown by the points B, M and C. As the temperature rises, the wavy portion of the curve gets smaller and the three volumes get closer and closer until finally they merge into a single point F. Here the three roots of Van der Waal's equation become identical, the volume of the liquid becomes equal to the volume of the substance as gas, and there is no longer any distinction between the liquid and the gaseous states. In short the substance at this point is in critical condition. The values of T , P , and V at this point will, therefore, be critical temperature, pressure, and volume respectively. Hence by making use of the condition that at the critical point Van der Waal's equation should have equal roots, **calculation of critical constants** should be possible.

At the critical point the three roots of Van der Waal's equation are identical and equal to V_c (the critical volume), i.e.,

$$V = V_c$$

and $(V - V_c)^3 = 0$

or $(V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3) = 0 \quad \dots (3)$

This equation must be identical with the Van der Waal's equation (2) when $T = T_c$ (critical temperature), $P = P_c$ (critical pressure). Thus we have

$$V^3 - \left(b + \frac{RT_c}{P_c} \right) V^2 + \frac{aV}{P_c} - \frac{ab}{P_c} = 0 \quad \dots (4)$$

Equating the powers of V in equations (3) and (4)

$$3V_c = b + \frac{RT_c}{P_c} \quad \dots (5)$$

$$3V_c^2 = \frac{a}{P_c} \quad \dots (6)$$

$$V_c^3 = \frac{ab}{P_c} \quad \dots (7)$$

From (6) and (7)

$$V_c = 3b \quad \dots (8)$$

Substituting the value in (6)

$$P_c = \frac{a}{27b^2} \quad \dots \quad (9)$$

Substituting the value of V_c and P_c in (5)

$$T_c = \frac{8a}{27Rb} \quad \dots \quad (10)$$

Knowing a and b which can be deduced from the deviations from gas laws, the critical constants can easily be calculated. Conversely, since P_c and T_c can often be determined experimentally with comparative ease, these values may be employed to calculate the constants a and b .

$$a = 3V_c^2 P_c; \quad b = \frac{V_c}{3}$$

Experimental determination of Critical Constants

The actual determination of critical constants of a substance is often a task of considerable difficulty. Of these the critical temperature and critical pressure can be measured relatively easily with the help of Cagniard de la Tour's apparatus. It consists of a stout glass U-tube blown into a bulb at the lower end. The liquid under examination is contained in the bulb and the rest of the apparatus is filled with mercury. The upper end of the U-tube is sealed leaving a little air in it so that this can be used as a manometer.

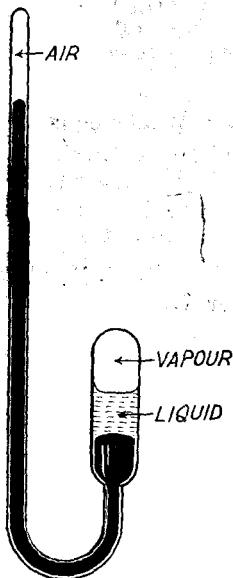


Fig. 36. Cagniard de la

Tour's apparatus.

The critical volume is the volume at critical temperature and critical pressure. It is much more difficult to measure since even a slight change in temperature or pressure at the critical point produces a large change in volume.

The most accurate method of determining the critical volume was given by Amagat. It consists of measuring the densities of liquid and its vapour at a number of temperatures near the critical point, and plotting these two densities against the temperature. When the two curves representing the densities of the liquid and vapour thus drawn are extended, they naturally meet at the critical temperature because here the density of liquid and vapour becomes identical. The mean values of densities of liquid and vapour are plotted so as to give the curve AB, which will obviously pass through the critical temperature. The intersection of AB with the abscissa at the critical temperature, will give the critical density. From this value the critical volume can be immediately calculated.

The following table gives the critical temperatures and critical pressures of a few substances.

Substance	Critical Temp. ($^{\circ}$)	Critical Pressure (Atmos.)
Helium	-268	2.3
Hydrogen	-241	11
Nitrogen	-146	35
Oxygen	-119	51
Carbon dioxide	+31	73
Ammonia	+131	113
Water	+374	217
Ether	+194	35

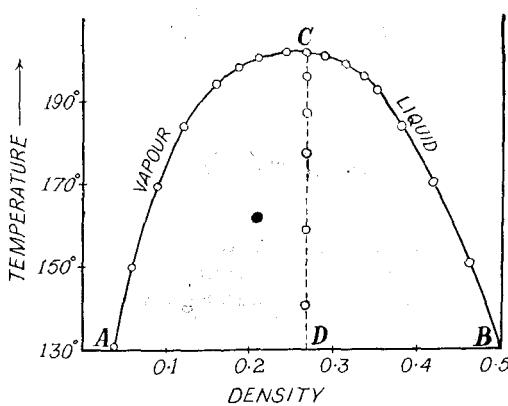


Fig. 37. Illustration of the determination of critical volume drawn from *n*-pentane.

LAW OF CORRESPONDING STATES

If the values of pressure, volume and temperature be expressed as fractions of the corresponding critical values, we have

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

where π , ϕ , and θ are termed the **reduced pressure**, the **reduced volume**, and the **reduced temperature** respectively.

If now we replace P , V and T by πP_c , ϕV_c , and θT_c respectively in Van der Waal's equation.

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

we have

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

Substituting the value of P_c , V_c and T_c in terms of a , b , and R as given in equations (8), (9) and (10), we get

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

Dividing this equation throughout by $\frac{a}{27b}$, we get,

$$\left(\pi + \frac{3}{\phi^2} \right) (3\phi - 1) = 8\theta \quad \dots (11)$$

This is known as Van der Waal's **reduced equation of state**. In this equation the quantities a , b , P_c , T_c , V_c which are characteristic of a given gas, have cancelled out, thus making it applicable to all substances in the liquid or gaseous state irrespective of their specific nature. From equation (11) it is clear that when two substances have the same reduced temperature and pressure, they will have the same reduced volume. Thus when two or more substances are at the same reduced temperature and pressure, they are said to be in **corresponding states**. In practice this means that the properties of liquids should be determined at the same reduced temperature because pressure has very slight effect on them. Since it has been found that boiling points of liquids are approximately $\frac{2}{3}$ of the critical temperature, it follows that liquids at their boiling points (in degrees absolute) are approximately in corresponding states. Therefore, in studying the relation between the physical properties of liquid and the chemical constitution, the physical properties may be conveniently determined at the boiling points of liquids.

LIQUEFACTION OF GASES

Liquefaction is the reverse of the process of vaporisation. The two conditions which tend to change a gas to the liquid state are *low temperature* and *high pressure*.

(1) **Faraday's Method.** Faraday (1823) succeeded in liquefying a number of gases such as sulphur dioxide, carbon dioxide, nitric oxide, chlorine, etc. He employed a V-shaped tube, in one arm of which the gas was prepared while in the other it was liquefied under its own pressure and with the help of external cooling.

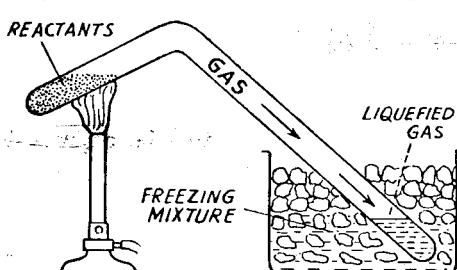


Fig. 38. Faraday's method for the liquefaction of gases.

gases became clear in 1869 when Andrews showed that each substance has a characteristic temperature, its *critical temperature*, above which it cannot be liquefied, however great the pressure may be. Faraday's success in the liquefaction of gases was due to the fact that the critical temperature of the gases examined by him happened to be

above or just below the ordinary atmospheric temperature. The discovery of the critical temperature emphasised the necessity of more effective cooling agents to liquefy other gases which resisted liquefaction.

(2) **Linde's Method.** Linde (1895) liquefied air making use of the fact that a compressed gas on free expansion produces intense cooling. In a gas at high pressure the molecules are very close to each other and, therefore, the molecular attraction is appreciable. When it is allowed to escape through a jet into a region of low pressure, the molecules move apart. In doing so, the intramolecular attraction must be overcome and energy is needed for it. This energy is taken from the gas itself which is thereby cooled. An apparatus worked on the above principle is shown in the diagram (Fig. 39). Air compressed to above 200 atmospheres is passed through a water-cooled pipe where the heat of compression is removed. Compressed air is then passed through a spiral pipe with a jet at the end through which the air issues. The free expansion of gases at the jet results in a considerable drop of temperature. The cooled air which is now approximately at atmospheric pressure passes up, cooling the incoming compressed gas of the spiral tube, and goes again to the compression pump. By repeated compression and expansion a temperature low enough to liquefy air is reached.

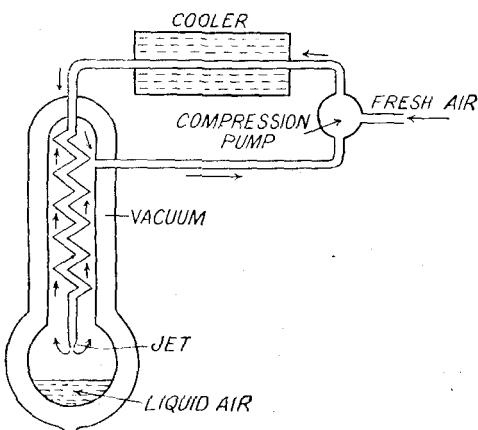


Fig. 39. Linde's method for the liquefaction of air.

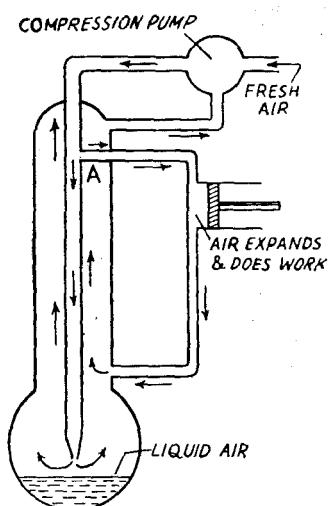


Fig. 40. Claude's Method. Another method for producing low temperature is due to Claude. In this method the compressed air is allowed to do mechanical work by expanding in the cylinder of an engine. Here the cooling produced is greater than in Linde's method as the gas does work not only in overcoming the intramolecular forces but also in driving the engine. By means of this method all known gases have now been liquefied. Helium, the last to succumb, was liquefied by Kammerlingh Onnes in 1908. For a more detailed discussion refer to a text-book on Physics.

An illustration of Claude's method is shown in Fig. 40. Compressed gas is passed through a pipe which bifurcates at A. A part of it goes into the expansion cylinder where it expands and does work by driving the piston back and the gas thus cooled goes up the liquefying chamber and cools the downcoming compressed gas which when released at the jet suffers a further cooling and liquefies. The gas escaping liquefaction goes back to the compression pump and the whole process is repeated over and over again.

QUESTIONS AND PROBLEMS

A. Gas Constant

1. What is the nature of R in the equation $PV=RT$? Calculate the numerical value of R in litre-atmospheres per degree and in calories per degree. (Agra B.Sc., 1959)

2. Calculate the numerical value of the gas constant in (a) litre-atmospheres, (b) ergs, and (c) calories per degree ($g=981$; density of Hg=13.6 gms./c.c.; calorie=4.183 $\times 10^7$ ergs). (Bombay B.Sc., 1949)

3. Calculate the value of the gas constant in (a) litre-atmospheres, (b) ergs and in (c) calories (per degree).

- ($g=981$ cms. per sec.; Density of Hg=13.6 gms. per c.c.; calorie=4.18 $\times 10^7$ ergs). (Poona B.Sc., 1955)

4. What is the nature of R in the general gas equation $PV=RT$? Calculate its value in ergs per degree per gram mol. (Agra B.Sc., 1959)

B. Kinetic Gas Equation

1. Explain the fundamental postulates of the Kinetic Theory of gases. Derive from Kinetic Theory the Gas law $PV=RT$ and the Graham's law of Diffusion. (Annamalai B.Sc., 1953)

2. State the main assumptions of the Kinetic Theory of Gases. Deduce Boyle's law from the assumptions.

- Calculate the root mean square velocity of oxygen molecule at 27°C and 740 mm. pressure. (Osmania B.Sc., 1953)

3. State the fundamental assumptions of the Kinetic theory of gases. Show how the theory supports Graham's Law of Diffusion.

- The density of hydrogen at 0°C and 760 mm. pressure is 0.00009 gm. per c.c. Find the root mean square velocity of hydrogen molecule. (Density of mercury is 13.5 and gravitational force is 981 dynes per sq. cm.) (Punjab B.Sc., 1954)

4. Derive an expression for the pressure of a perfect gas. Determine the root mean square velocity of nitrogen at N.T.P. Density of nitrogen at N.T.P. is 0.00125 gm. per c.c. (Banaras B.Sc., 1953)

5. State how Kinetic equation may be utilised to calculate the velocity of a gaseous molecule.

What is the average velocity of methane (CH_4) molecule at 500°C?

6. What is the R.M.S. velocity of molecules of CO_2 at 18°C and 800 mm. pressure? How does this value differ from the average velocity?

7. Calculate the R.M.S. velocity of the molecules of oxygen (a) at 0°C (b) at 100°C.

8. Find the R.M.S. velocity of oxygen molecules at 15°C and 770 mm. pressure.

9. How would you deduce Graham's Law of Diffusion from Kinetic assumptions about the structure of a gas.

- Calculate the R.M.S. velocity of oxygen molecules at a temperature of 27°C and a pressure of 740 mm.

10. The average velocity of the molecules of a certain gas at 0°C is 299 metres/sec. Calculate the molecular weight of the gas.

11. On the basis of Kinetic Theory deduce the relations between the pressure of a gas and the velocity and density of its molecules.

Calculate the molecular weight of a gas which takes 1.117 times as long as oxygen to diffuse under similar conditions through an aperture.

(Nagpur B.Sc., 1953)

12. Derive Boyle's law from the Kinetic Theory and prove Avogadro's Hypothesis from these considerations. (Allahabad B.Sc., 1954)

13. Calculate the speed of a hydrogen molecule given $P = 76$ cms. and a gram-molecule of hydrogen occupies 22.4 litres at N.T.P.

(Delhi B.Sc., 1956 Agra B.Sc., 1953)

14. What are the assumptions of Kinetic Theory? Deduce the kinetic expression for the pressure of a gas. Calculate the velocity of an oxygen molecule at 0°C.

(Nagpur B.Sc., 1955)

15. Give an account of the Kinetic Theory of Gases and how it supports (a) Avogadro's Hypothesis (b) Graham's law of diffusion.

(Banaras B.Sc., 1954; Osmania 1955; Allahabad 1955; Lucknow 1956)

16. Explain the assumptions underlying the Kinetic Theory of Gases and show that from them it is possible to deduce Boyle's law. (Banaras B.Sc., 1956)

17. Under constant pressure the time required for the effusion of hydrogen and of two gases A and B were respectively 2 seconds, 7.5 seconds and 9.9 seconds, the volume effusing being the same. What are the molecular weights of A and B? (Travancore B.Sc., 1956)

18. What are the assumptions of the Kinetic Theory of Gases and how far are they justified?

Calculate the root mean square velocity of the molecules of oxygen at N.T.P.

Density of oxygen = 0.001427 gm./c.c. at N.T.P.

Density of mercury = 13.6 gms./c.c.

'g' = 981 cms./sec².

(Poona B.Sc., 1956)

19. Give a short account of the Kinetic Theory of Gases. Show how the theory supports the gas laws and Graham's law of Gaseous Diffusion.

The speeds of diffusion of carbon dioxide and ozone are found to be 0.58 : 0.55. Find the molecular weight of ozone if that of carbon dioxide is known to be 44. (Delhi B.Sc., 1957)

20. Give the postulates of the Kinetic Theory of Gases. Derive an expression for the pressure of an ideal gas. Hence deduce (i) Boyle's law, (ii) Avogadro's Hypothesis and (iii) Graham's Law of Diffusion.

(Lahore B.Sc., 1958)

21. Write a short essay on the Kinetic Theory of Gases.

(Utkal B.Sc., 1959)

22. State the postulates of the Kinetic Theory of Gases and write the Kinetic Equation. Derive Graham's Law of Diffusion from it.

The relative densities of two Gases (A) and (B) are 1 and 1.05 respectively. Find the volume of (B) which would diffuse in the same time in which 150 c.c. of (A) would diffuse through a porous partition. (Marthwada B.Sc., 1959)

23. Write an account of the Kinetic Theory of Gases. How may laws of Boyle and Avagadro be derived on its basis? (Lucknow B.Sc., 1959)

C. Specific Heat Ratio

1. Describe the Kinetic Theory of Gases. With its help, deduce the ratio of the two specific heats of a monoatomic gas.

2. On the basis of the Kinetic Theory of Gases, calculate the ratio (C_p/C_v) of specific heat at constant pressure to constant volume, in the case of a monoatomic gas. How does C_p/C_v vary with the molecular complexity of gas?

(Baroda B.Sc., 1954)

3. Explain the difference between the specific heat at constant volume and specific heat at constant pressure of a gas. Deduce the ratio of the two specific heats of a gas from the Kinetic Theory.

The specific heat at constant pressure of argon is 0.075 and its molecular weight is 40. How many atoms are there in the molecule ?

(Gauhati B.Sc., 1955)

4. On the basis of the Kinetic Theory of Gases, calculate specific heat at constant pressure (C_p) and specific heat at constant volume (C_v) in the case of a monoatomic gas.

How does the ratio vary with the molecular complexity of the gas ?
(Baroda B.Sc., 1956)

5. Prove from the Kinetic Theory of Gases that the average kinetic energy of a gram-molecule of a perfect gas at temperature T (absolute) is given by $\frac{3}{2} RT$, where R is the gas constant. Calculate from this result the ratio of the specific heats at constant pressure and constant volume of a gas.

(Poona B.Sc., 1954)

6. What information concerning the atomicity of a gas can be obtained from a knowledge of its specific heats ?
(Osmania B.Sc., 1959)

7. Show with the help of the Kinetic Theory that the average kinetic energy of one gm. molecule of a gas is $\frac{3}{2} RT$ where R is gas constant and T is temperature. Further deduce the ratio of specific heats at constant pressure and constant volume. Comment on the ratio.
(Karnatak B.Sc., 1959)

D. Deviations from Gas Laws

1. What is an ideal gas ? How are deviations from ideal gas behaviour accounted for ?
(Nagpur B.Sc. 1953)

2. Deduce from the Kinetic Theory the expression $PV=RT$ for a perfect gas. Do real gases obey this equation ? Give reasons for your answer.
(Calcutta B.Sc., 1954)

3. State the assumptions of the Kinetic Theory of Gases. Give an account of deviations of gases from Boyle's law explaining (a) the nature of deviations, (b) the causes of deviations, (c) modifications suggested by Van der Waal in the gas equation.
(Mysore B.Sc., 1953)

4. Under what conditions do gases exhibit deviations from Boyle's law ? How are these deviations explained by the Kinetic Theory of Gases ?
(Madras B.Sc., 1955)

5. What are the postulates of the Kinetic Theory of Gases ? Discuss the deviations from the gas law, $PV=RT$ explaining the reason.
(Rajputana B.Sc., 1956)

6. Give an account of the deviations from the simple gas laws. How are these deviations explained by Van der Waal's equation ?
(Osmania B.Sc., 1956)

7. How do real gases deviate in their behaviour from ideal gases ? What explanation has been offered by Van der Waal for the deviations ?
(Mysore B.Sc., 1957)

8. Give a short account of the Kinetic Theory of Gases and derive the equation $PV=RT$. What are the limitations of this equation and what improvement has been suggested by Van der Waal ?
(Agra B.Sc., 1957)

9. What is an ideal gas ? In what respects does a real gas differ from an ideal gas ?
(Rajputana B.Sc., 1958)

10. Explain how real gases differ from an ideal gas. Discuss how best the Van der Waal's equation accounts for the behaviour of real gas.
(Karnatak B.Sc., 1959)

E. Van der Waal's Equation

1. Deduce the Van der Waal's equation and discuss its defects.
(Andhra B.Sc., 1954)

2. State the equation of Van der Waal as applied to real gases and indicate on a pv diagram the form of the corresponding isotherms. Deduce the relationship between the critical constants of a substance and the constants of the equation.
(Ceylon B.Sc., 1953)

3. Give an account of the Van der Waal's equation of state. What are its limitations ?
(Jammu & Kashmir B.Sc., 1954)

4. What do you understand by an equation of state? Why do real gases not obey the ideal equation of state? Calculate the critical constants of a gas from Van der Waal's equation. (*Osmania B.Sc., 1954*)

5. Discuss Van der Waal's equation and clearly explain the constants in the equation. Deduce critical constants in terms of constants in Van der Waal's equation.

Calculate the constants 'a' and 'b' for a gas obeying Van der Waal's equation of states if the critical temperature and critical pressure of the gas are 31°C and 72.8 atmospheres respectively. ($R=0.08206$ litre-atmospheres).

(*Bombay B.Sc., 1955*)

6. Deduce from Van der Waal's equation, expression for the critical pressure, volume and temperature of a gas. Discuss also the theory of corresponding states. (*Andhra B.Sc., 1956*)

7. Discuss Van der Waal's equation for real gases; give the relationship between the critical constants and Van der Waal's constants for gases.

(*Aligarh B.Sc., 1955*)

8. Derive the Van der Waal's equation and deduce from it the values of the critical constants of a gas in terms of the Van der Waal's constants 'a' and 'b'. (*Aligarh B.Sc., 1957*)

9. Explain clearly the Van der Waal's equation. Calculate the critical constants of a gas in terms of the Van der Waal's constants 'a' and 'b'. (*Jammu & Kashmir B.Sc., 1958*)

10. Van der Waal's constants in litre-atmospheres per mole for carbon dioxide are ' a ' = 3.6 and ' b ' = 4.28×10^{-2} . Calculate the critical temperature and critical volume of the gas.

($R=0.082$ litre-atmospheres). (*Poona B.Sc., 1957*)

11. Give a concise account of the arguments which led to Van der Waal's equation. State the equation and show how its constants are related to the critical constants. (*Gujarat B.Sc., 1956*)

12. Derive the relation $PV = \frac{1}{3} mnc^2$ for an ideal gas stating the assumptions involved. What modifications were introduced by Van der Waal in the case of real gases and why? (*Nagpur B.Sc., 1957*)

13. Define the law of "Corresponding States" and obtain the reduced equation of state. What is the limit of its applicability and to what use it has been put? (*Andhra B.Sc., 1953*)

14. What do you understand by the critical constants of a gas and the law of Corresponding States from Van der Waal's equation of gases. (*Rajputana B.Sc., 1957*)

15. How is Van der Waal's equation derived from the Gas Laws? Explain the terms 'critical temperature', 'critical pressure' and 'critical volume'. (*Allahabad B.Sc. 1958*)

16. Derive the Van der Waal's equation from the first principles. Find the value of the critical constants. (*Aligarh B.Sc., 1959*)

17. Give a derivation of Boyle's law from the Kinetic Theory of gases. Explain how Van der Waal accounted for the derivation of ordinary gases from the ideal behaviour. (*Venkateswara B.Sc., 1959*)

18. How far the gas equation $PV = RT$ is verified experimentally? What modifications have been suggested in this gas equation and how far the new equation is verified experimentally? (*Vikram B.Sc., 1959*)

F. Liquefaction of Gases

1. How can the law of "Corresponding States" be derived from the Van der Waal's equation?

Explain the significance of this law. Discuss the principles which are widely used to liquefy gases on the large scale. (*Rajputana B.Sc., 1954*)

2. Write an essay on liquefaction of gases. What do you mean by critical temperature and critical pressure in this connection? (*Banaras B.Sc., 1955 ; Delhi B.Sc., 1952*)

3. Comment briefly on the principles used in the liquefaction of air? (*Ceylon B.Sc., 1954*)

4. Give an account of liquefaction of air.
(Rangoon B.Sc., 1955; Madras B.Sc., 1955)
5. State the various methods of producing cold and show how these have been used in the liquefaction of gases.
(Delhi B.Sc., 1958)
6. What is meant by the law of "Corresponding States"? Obtain the reduced equation of state.
(Andhra B.Sc., 1958)
7. Write an account of the liquefaction of gases.
(Rangoon B.Sc., 1958)

ANSWERS

(A) GAS CONSTANT

- (1) 0.0821 litre-atmospheres per degree; calories.
- (2) 0.0321 litre-atmospheres per degree; 8.3×10^7 ergs per degree; 2 cals.
- (3) Same as for (2).

(B) KINETIC GAS EQUATION

- (2) 48387.5 cms./sec.
- (3) 183,900 cms./sec.
- (4) 49,330 cms./sec.
- (5) 10.98×10^4 cms./sec.
- (6) 40,620 cms./sec.
- (7) 46,160 cm. sec.
- (8) 53,950 cms./sec.
- (9) 47,410 cms./sec.
- (10) 48387.5 cms./sec.
- (11) 76.2
- (12) 39.91
- (13) 186,574 cms./sec.
- (14) 46,136 cms./sec.
- (15) 28.12
- (16) 49.0
- (17) 46,160 cms./sec.
- (18) 48.93
- (22) 146.4 c.c.

E. Van der Waal's EQUATION

- (5) $a = 0.0363$
- (6) 0.00043
- (10) 31°C ; 12.84×10^{-2} litres.

CHAPTER IV SOLUTIONS

INTRODUCTORY

So far we have restricted our study to pure elements and compounds in solid, liquid or gaseous state. Now we will proceed to discuss the properties of mixtures of chemical substances. A mixture of two or more chemical substances when it is homogeneous is called a **solution**. Since the substances mixed may originally be present as solid, liquid or gas, it is obvious that we can have in all nine **kinds of solution**. They are :

(i) Gas in Gas	(iv) Gas in Liquid	(vii) Gas in Liquid
(ii) Liquid in Gas	(v) Liquid in Liquid	(viii) Liquid in Solid
(iii) Solid in Gas	(vi) Solid in Liquid	(ix) Solid in Solid

Although examples of all these nine kinds of solutions are known, only the more important types will be considered here.

In the study of solutions it is customary to call the component present in a larger quantity as the **Solvent** and the one present in a smaller quantity as the **Solute**. When the solute is present in a very small quantity as compared with the solvent, the system is called a **Dilute Solution**. The laws governing the behaviour of dilute solutions are relatively simple and will be treated separately in the next chapter.

SOLUTIONS OF GASES IN GASES

When a gas is mixed with another gas a completely homogeneous solution results, provided of course they do not react chemically. It is obvious that such gaseous solutions will have the following characteristic properties :

(i) **Complete Miscibility.** According to the *Kinetic Theory* a gas consists of tiny molecules moving about in vacant space and thus when one gas is dissolved in another gas they form a homogenous solution quite readily. In such a gaseous mixture, the components can be present to an unlimited extent.

(ii) **Dalton's Law of Partial Pressures.** Since in a gaseous mixture the constituent molecules exist separately, it is obvious that the properties of the mixture will be the sum of properties of the components. Thus, Dalton (1802) was the first to show that *the total pressure exerted by a gaseous mixture is the sum of the individual or partial pressures of the component gases*. If $p_1, p_2, p_3 \dots$ be the partial pressures of the constituents, the total pressure P of the mixture is given by the expression :

$$P = p_1 + p_2 + p_3 + \dots$$

Like other gas laws, Dalton's law holds strictly only when the partial pressures are not too high. This law can be experimentally

tested by comparing the total pressure of a gaseous mixture with the sum of the individual pressure of each gas before mixing.

Example. At constant temperature, 250 c.cs. of nitrogen under 720 mm. pressure and 380 c.cs. of oxygen under 650 mm. pressure were put into a one-litre flask. What will be the final pressure of the mixture?

Since $PV = P'V'$ at constant temperature (Boyle's Law)

$$P \times 1000 = 720 \times 250 \quad \text{or} \quad P_{N_2} = 180 \text{ mm.}$$

$$P \times 10000 = 380 \times 650 \quad \text{or} \quad P_{O_2} = 247 \text{ mm.}$$

$$\text{Total pressure } P = P_{N_2} + P_{O_2} \quad (\text{Dalton's Law})$$

$$= 180 + 247 = 427 \text{ mm.}$$

SOLUTIONS OF GASES IN LIQUIDS

All gases are dissolved to a certain extent by all liquids, the amount dissolved depending upon the pressure, the temperature, the nature of the gas and the nature of the solvent. Thus, pressure has a marked influence on the solubility of a gas in a given solvent. Henry (1803) discovered a very simple relation between the pressure and solubility of a gas. This relation called **Henry's Law** may be stated as :

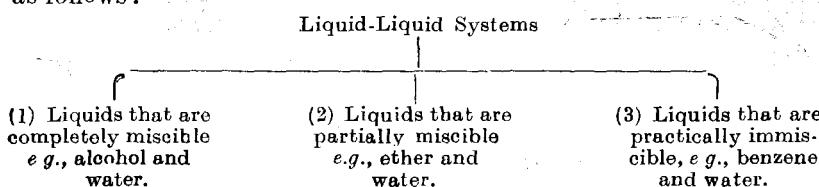
The solubility of a gas in a given solvent is directly proportional to the pressure to which the gas is subjected, provided, of course, the temperature remains the same, i.e.,

$$S \propto P \quad \text{or} \quad \frac{S}{P} = K \text{ (constant).}$$

Like most other laws of solutions, Henry's Law is not exact except in very dilute solutions. Thus if the gas is very soluble in the liquid, the law does not hold. Serious deviations from Henry's Law are also observed when the dissolved gas enters into chemical reaction with the solvent, for example, ammonia in water. In such a case the law applies only to the uncombined gas present in the liquid.

SOLUTIONS OF LIQUIDS IN LIQUIDS

Solutions of liquids in liquids may be divided into three classes as follows :



We will now proceed to consider the more important properties of these three classes of solutions.

Solubility of completely miscible liquids

Liquids like alcohol and ether mix in all proportions and in this respect they could be compared to gases. The properties of such solutions, however, are not strictly additive and, therefore, their

study has not proved of much interest. Generally, the volume decreases on mixing but in some cases it increases. Sometimes heat is evolved when they are mixed while in others it is absorbed. The separation of this type of solutions can be effected by fractional distillation.

Solubility of partially miscible liquids

A large number of liquids are known which dissolve in one another only to a limited extent, e.g., ether and water. The effect of temperature on the mutual solubility of these mixtures is of special interest. We will study this property with reference to three typical systems :—

- (i) the Phenol-Water System.
- (ii) the Triethylamine-Water System.
- (iii) the Nicotine-Water System.

The Phenol-Water System. Phenol and water when mixed in certain proportions from two separate layers, one consisting of a solution of phenol in water and the second of water in phenol. At higher temperatures the solubility of phenol in water (*1st layer*) gradually increases and so does the solubility of water in phenol

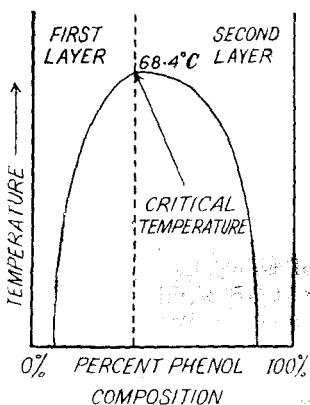


Fig. 41. Miscibility of Phenol and Water.

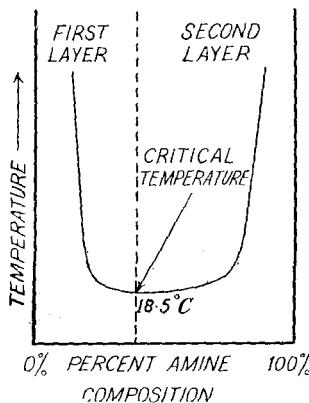


Fig. 42. Miscibility of Triethylamine and Water.

(*2nd layer*). At a certain maximum temperature (68.4°) the composition of two layers will thus become identical and one layer will result (Fig. 41). The temperature at which the two layers merge into one another resulting in one layer is called the **Critical Solution Temperature**. This temperature is characteristic for a particular system and is affected very much by the presence of impurities. The determination of critical-solution-temperature may, therefore, be used for testing the purity of phenol and other similar substances.

The Triethylamine-Water System. Unlike phenol and water, triethylamine and water are completely miscible at or below 18.5°C. At higher temperatures the mutual solubility decreases and they

separate into two layers. As is clear from the solubility curve of this system (Fig. 42) the behaviour in this case is just the reverse of phenol-water system.

The Nicotine-Water System. The behaviour of this type of system is as if it were a combination of the first two types. At ordinary temperature nicotine and water are completely miscible but at a higher temperature, the mutual solubility decreases and as the temperature is raised further the two liquids again become miscible. Thus, we have a closed solubility curve and the system has two critical-solution-temperatures, the upper 208°C and the lower 60.8°C .

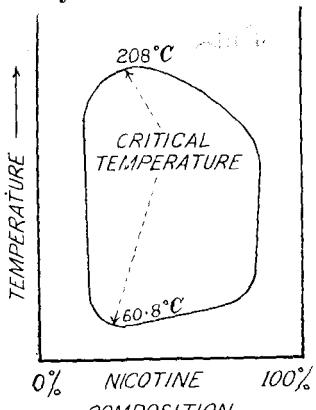


Fig. 43. Miscibility of Nicotine and Water.

The effect of pressure on this system is that the lower critical temperature is raised while the upper critical temperature is lowered gradually until finally they become one. At this point the liquids are miscible at all the temperatures (Fig. 43).

Vapour Pressures of Liquid-Liquid Solutions.

The study of the vapour pressures of mixtures of completely miscible liquids has proved of great help in the separation of the liquids by fractional distillation. The vapour pressures of two liquids with varying composition have been determined at constant temperature. By plotting the vapour pressures against composition it has been revealed that in general mixtures of the miscible liquids are of three types.

1st Type. For this type of solutions the vapour pressure curve exhibits a minimum. If we take a mixture which has an excess of X (more volatile component), we are somewhere at C on the curve. When this is distilled the vapour will contain excess of X and thus the remaining mixture will get richer in Y. Finally we reach the point D where vapour pressure is minimum and thus boiling point maximum. Here the mixture will distil unchanged in composition. Exactly similarly, if we take a mixture having a greater proportion of Y (point E), on distillation Y will pass over leaving the residue richer in X till in this way the minimum point D is again reached when the mixture will distil unchanged. It is obvious that *complete separation of this type of solutions into components is impossible*. At best it can be resolved into one pure component and the constant

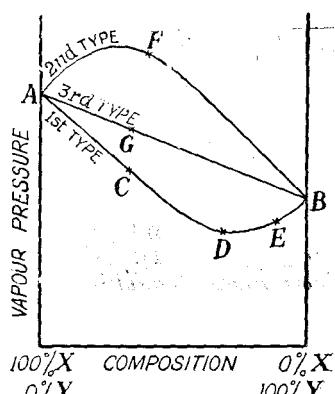


Fig. 44. Vapour pressure of liquids.

boiling mixture. The best known example of this type is presented by hydrochloric acid which forms a constant boiling mixture at 110°C and containing 20.24% of the acid. If a mixture of any other composition is distilled, either hydrochloric acid or water will pass over, the composition will move to the point of minimum vapour pressure when it distils without any change in composition.

2nd Type. In this case the vapour pressure curve records a maximum at F. At this point the mixture has the highest vapour pressure and, therefore, the lowest boiling point. Thus in this type of solutions the first fraction will consist of a constant boiling mixture with a fixed composition corresponding to the maximum point, until all of one component has been exhausted. After this the temperature will rise and the other component will pass over. In this kind of solutions also it is not possible to effect a complete separation by fractional distillation. At best we can resolve it into a constant-boiling mixture and one component in the pure state. Ethyl alcohol and water mixtures offer a good example of this type. Alcohol-water mixture containing 95.59 per cent alcohol boils at the minimum temperature 78.13° . Thus it is very difficult to obtain pure absolute alcohol by distillation. This difficulty has, however, been overcome by adding benzene which forms a low boiling mixture with water and on distillation it comes over leaving pure alcohol behind.

3rd Type. In this case the vapour pressures of mixtures always lie between the vapour pressures of pure components and thus the vapour-pressure-composition curve is a straight line. Suppose we have a mixture containing excess of Y which is represented by point G on the curve. On distillation X component being more volatile will be obtained in greater proportion in the distillate and we gradually travel along the curve AB. The later fractions will, of course, be poorer in X and richer in Y till we reach the 100 per cent Y-axis, when all the X will have passed over. By repeating the process of distillation with the fresh distillate which is now richer in X, we can get almost pure component X. Only in this type of solutions can we completely separate the components by fractional distillation. Thus methyl alcohol-water mixtures can be resolved into pure components by distillation.

The Theory of Fractional Distillation

We have discussed above the vapour-pressure-composition curves for the three types of solutions from a study of which we conclude that it is only in the case of the third type that a complete separation by distillation is possible. However, to understand the process of fractional distillation we must have an idea of the composition of the vapour phase and that of the liquid mixtures at different boiling temperatures. Thus for this purpose it is not the vapour-pressure-composition curve, but rather the temperature-composition curve that is important. If we plot the boiling point of liquid mixture against its composition and the composition of the vapour in contact with it, we get two separate curves for each type of solutions. The curves obtained for the third type are shown diagrammatically in Fig. 45.

The curves AEB and ADB are the temperature-composition curves for the vapour and liquid respectively. At any boiling

temperature C the composition of liquid mixture is represented by J and that of the vapour in equilibrium by K. Obviously the more volatile component Y is present in greater proportion in the vapour than the liquid mixture. Thus the condensed vapour or the distillate will be richer in X. If the distillate so obtained be now subjected to distillation, it will boil at F and the fresh distillate will have the composition L corresponding to I. Thus the proportion of Y in the second distillate is greater than in the first one. In this way by repeating the process of fractional distillation it is obvious that we can get almost pure Y.

[See also p. 11]

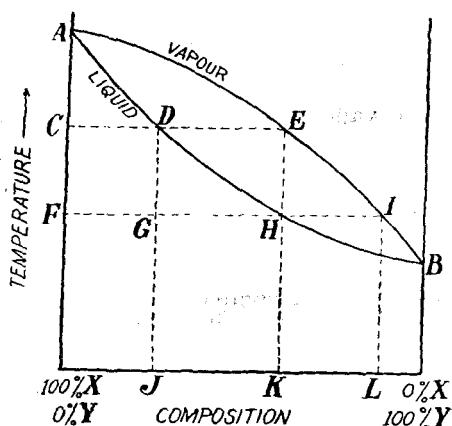


Fig. 45. Curves showing the composition of vapour and liquid at various boiling temperatures.

In first type of solutions (Fig. 46) if we have a boiling mixture represented by Y, its vapour will be poorer in Y than the liquid mixture and the boiling point would gradually rise till we reach the maximum point C where the composition of liquid and vapour is the same. Here the distillation proceeds without change of composition.

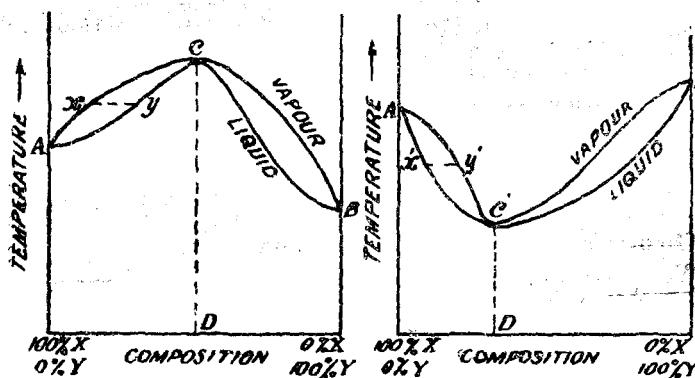


Fig. 46. Boiling point curves for 1st type of solutions.

Fig. 47. Boiling point curves for 2nd type of solutions.

Similarly in the second type, (Fig. 47) if we have a boiling mixture represented by the point X', the amount of Y in vapour is higher and gradually the boiling point falls to the minimum C' where the vapour and the liquid mixture have the same composition. At this temperature the mixture boils without any change in composition. Thus it is proved that the second and first type of solutions are not capable of being separated by fractional distillation.

The efficiency of the process of fractional distillation is considerably enhanced by the use of the so called **Fractionating columns**. These are of different designs. Usually they consist of a long tube blown into bulbs at intervals (Fig. 48) or a tube packed with beads. The fractionating column is fitted into the neck of the distillation flask so that the vapour of the boiling liquid passes up through it and is then delivered into the condenser. The vapour is rich in the more volatile component and in the fractionating column partial condensation of the less volatile component takes place. Thus the vapour leaving the

column becomes richer still in the more volatile component. Alternatively, it may be considered that the vapour is condensed by the first bulb and distilled into the second, each bulb of the column thus acting as a separate distillation unit. In this manner a sort of distillation and condensation goes on which results in the increase of the proportion of the volatile component in the outgoing vapour.

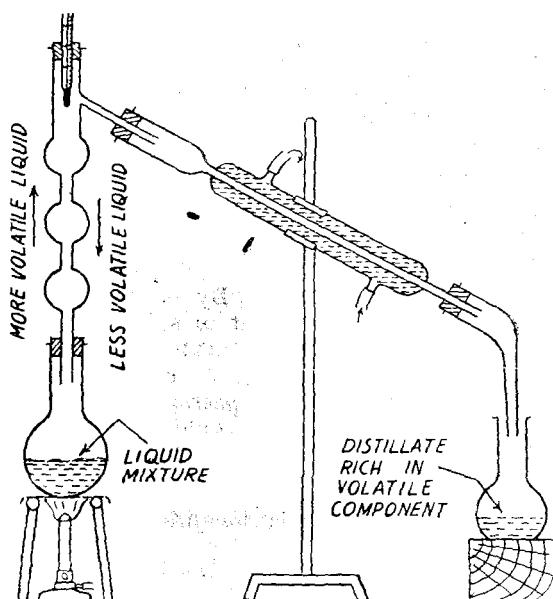
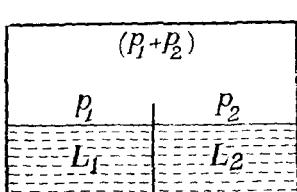


Fig. 48. Fractional Distillation with a fractionating column.

Vapour Pressure of mixtures of Non-miscible liquids

In a mixture of non-miscible liquids each component exerts its own vapour pressure independent of others and the total vapour pressure is thus equal to the sum of the individual vapour pressures of all the liquids.

In a mixture of non-miscible liquids L_1 and L_2 , the two liquids form separate layers and could be compared to the liquids contained in vessels with a common top (Fig. 49).



They exert their own vapour pressure independently and according to Dalton's law of partial pressures, the total vapour pressure will be equal to the sum of their individual vapour pressures. This generalisation which is the basic principle of steam distillation, has been tested experimentally in several cases. Some of the results obtained by Regnault are given on page 78.

Fig. 49. Vapour pressure of mixtures of non-miscible liquids.

Temperature	Vapour Pressure of Water	Vapour Pressure of Carbon disulphide	Sum	Vapour Pressure of Mixture (Observed)
12.07°	10.5 mm.	216.7 mm.	227.2 mm.	225.9 mm.
26.87°	26.3 mm.	388.7 mm.	415.0 mm.	412.3 mm.

The observed vapour pressure of the mixture is a little less than the sum of the individual vapour pressures of water and carbon disulphide and that is to be expected since each liquid is slightly soluble in the other.

Steam Distillation. By steam-distillation we mean the distillation carried in a current of steam. A mixture of water and a high boiling organic liquid is heated by means of a current of steam. *The mixture would boil when the combined vapour pressure of the two liquids is equal to the atmospheric pressure.* Naturally the boiling temperature of the mixture would be less than the boiling temperature of the pure organic liquid when the vapour pressure of the liquid alone would be equal to the atmospheric pressure.

Steam-distillation is done in preference to ordinary distillation in the following cases :—

(1) For the purification of an organic liquid when the impurities are difficult to be removed by other methods.

(2) When the given impure liquid is decomposed at high temperature and must, therefore, be distilled at a temperature lower than its boiling point.

(3) Steam-distillation is of service in separating compounds from others not volatile in it.

Experimental details of Steam-Distillation. The apparatus used for steam distillation is shown in Fig. 50. It consists of a

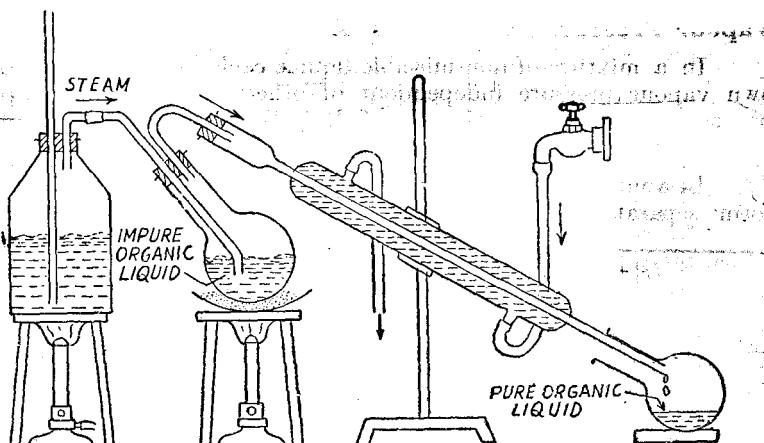


Fig. 50. Steam-Distillation.

metallic can C in which steam is continuously raised by boiling water. The steam from the can is passed into a large flask F containing the impure organic liquid. This is connected to a water condenser which has a receiver R placed below its lower end. Steam and vapours of the organic liquid from the flask are condensed and received in R. In the receiver we have water and organic liquid forming two separate layers which can be easily separated by means of a separating funnel. The organic liquid is then dried and redistilled.

Relative amounts of water and organic liquid distilling over. The amount of an organic liquid distilling in steam depends on
 (i) its partial pressure, and
 (ii) its vapour density.

as compared with the values of these physical constants for water. Thus :

$$\frac{\text{Organic liquid}}{\text{Water}} = \frac{P_o \times d_0}{P_w \times d_w}$$

where P_o and P_w represent the vapour pressures and d_0 and d_w are vapour densities of the oil and water at the boiling point.

Since densities of vapours are proportional to their molecular weights, the ratio of distilling liquids is given by the relation :

$$\frac{\text{Organic Substance}}{\text{Water}} = \frac{P_o \times M_o}{P_w \times 18}$$

Example. At a pressure of 760 mm. a mixture of nitrobenzene ($C_6H_5NO_2$) and water boils at 99°. The vapour pressure of water at this temperature is 733 mm. Find the proportion of water in benzene in the distillate obtained from the boiling mixture.

Molecular weight of water = 18

" " Nitrobenzene, $C_6H_5NO_2 = 12 \times 6 + 5 + 14 + 16 \times 2 = 123$.

Vapour pressure of water $P_w = 733$ mm.

" " of $C_6H_5NO_2$, $P_o = 760 - 733 = 27$ mm.

Putting the values in the relation

$$\frac{\text{Nitrobenzene}}{\text{Water}} = \frac{123 \times 27}{18 \times 733} = \frac{1}{3.97}$$

∴ the proportion of water to nitrobenzene in the distillate is approximately as 4 : 1.

SOLUTIONS OF SOLIDS IN LIQUIDS

All solids are soluble in all liquids but their solubility varies greatly with the nature of the solute and the solvent. The most striking characteristic of solution of solids in liquids is that there is a limit to the solubility of every solid in any liquid. The point at which a liquid cannot take up more of the solute at a given temperature is called the *Saturation point* and such a solution is known as **Saturated Solution**. A solution may sometimes hold more solute than even if it were saturated and such a solution is called a **Super-saturated Solution**.

Determination of Solubility. The solubility of a substance is defined as *the weight of it dissolved in 100 grams of its saturated solution*

at a given temperature. Thus, solubility can be determined by preparing a saturated solution of the solid and then analysing it by evaporation or by a suitable chemical method.

Saturated solution of a solid substance may be prepared by shaking excess of it with the solvent in a vessel placed in a constant-temperature-bath and filtering the clear solution. A known volume of this saturated solution is evaporated in a china dish and from the weight of the residue the solubility can easily be calculated. This method, though simple, does not yield accurate results. During filtration, cooling would take place and thus some solid may be deposited on the filter paper or in the stem of the funnel. However, this method is quite good for the determination of solubility at room temperature. The evaporation of a liquid is a highly undesirable operation as it is not possible to avoid loss of the liquid caused by spouting. This difficulty can, however, be overcome whenever a chemical method of analysis is available. Another defect in this method is that it takes a long time to establish the equilibrium between the solid and the solution so that the preparation of saturated solution by simple agitation with the solvent is delayed. This difficulty may be overcome by first preparing the saturated solution at a higher temperature and then to cool it to the desired temperature at which solubility is to be determined.

Solubility Curve. A curve drawn between solubility and temperature is termed a **Solubility Curve**. It shows the effect of temperature on the solubility of a substance. The solubility curves of substances like calcium acetate and calcium butyrate show decrease in solubility with increase of temperature while there are others like those of potassium nitrate and lead nitrate which show a considerable increase of solubility with temperature. The solubility curve of sodium chloride shows very little rise with increase of temperature. In general the solubility curves are of two types.

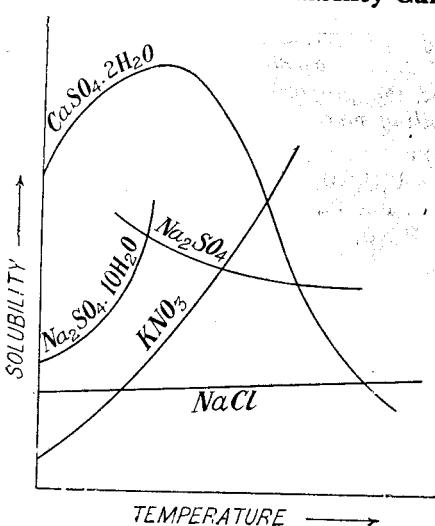


Fig. 51. Different types of solubility curves.

(1) *Continuous solubility curves*, and

(2) *Discontinuous solubility curves*.

Solubility curves of calcium salts of fatty acids, potassium chloride, lead nitrate, and sodium chloride are **Continuous Solubility Curves** as they show no sharp breaks anywhere. In case of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, no doubt, the curve first shows a rise and then a fall but it remains continuous at the maximum point. Sometimes the solubility curves exhibit sudden changes of direction and these

curves are, therefore, called **Discontinuous Solubility Curves**. The popular examples of substances which show discontinuous solubility curves are sodium sulphate, ferric chloride, ammonium nitrate, etc. In fact at the break a new solid phase appears and another solubility curve of that new phase begins. The break in a solubility curve thus shows a point where the two different curves meet each other. The solubility curves of sodium sulphate and ferric chloride will be discussed in detail in Chapter XVIII.

SOLUTIONS OF SOLIDS IN SOLIDS

Solution of a solid in another solid can be prepared by melting them together and subsequent cooling of the mixture. For example, gold and silver when mixed together, melted, and then cooled, yield solid solutions which are perfectly homogeneous. Sometimes solid solutions may be obtained by simply pressing together the two metals and thus establishing better contact when one metal would diffuse into the other. Solutions of gold and lead have been obtained by this method. The study of solutions of solids in solids is of great practical importance in metallurgy.

The formation of solid solutions is not limited to metals only. Organic substances like naphthalene and β -naphthol when melted together form the so-called 'mixed crystals' on cooling which are a solid solution of one of them in the other.

QUESTIONS AND PROBLEMS

1. Describe the various kinds of solutions giving two examples in each case.
 2. State and illustrate :—
 - (a) Dalton's Law of Partial Pressures.
 - (b) Henry's Law.
 3. State and explain Henry's Law regarding the solubility of a gas in a liquid. *(Jammu and Kashmir B.Sc., 1953)*
 4. Enunciate Henry's Law relating to solubility of gases in liquids and apply it to the case of soda-water bottle.
- A mixture of nitrobenzene and water boils at 99°C . If the vapour pressure of water at this temperature is 733 mm. of mercury, calculate the proportion of nitrobenzene in the distillate. *(Osmania B.Sc., 1953)*
5. Write notes on :—
 - (i) Critical solution temperature.
 - (ii) Azeotropic mixture. *(Travancore B.Sc., 1954)*
 6. Describe the methods you would use to separate two liquids from one another in a solution. State their limitations. Illustrate with examples and sketches of the apparatus employed.
 7. How do mixtures of liquids behave when they are subjected to distillation ? Give examples.
 8. Discuss the vapour-pressure-composition curves of systems containing mixtures of liquids which are (i) immiscible, and (ii) miscible in all proportions. *(Madras B.Sc., 1947)*
 9. Discuss the distillation under constant pressure of completely miscible binary liquid mixtures having a boiling point maximum. *(Osmania B.Sc., 1954)*
 10. Discuss the importance of 'Distillation' as a method of separating binary liquid mixtures with special reference to phase diagrams. *(Karnatak B.Sc., 1954)*

11. What is fractional distillation ? Discuss the theory on which it is based.
12. Explain the principle underlying the process of steam-distillation. (*Calcutta B.Sc., 1940*)
13. Write a note on steam distillation. (*Mysore B.Sc., 1954*)
14. Naphthalene ($C_{10}H_8$) distills in steam at $98.3^\circ C$ under a pressure of 753 mm. The vapour pressure of water at this temperature is 715 mm. Calculate the proportions of naphthalene and water in the distillate.
15. A mixture of bromobenzene and water boils at $95.2^\circ C$ under normal atmospheric pressure. At this temperature, vapour pressure of bromo-benzene is 119 mm. of mercury. Calculate the proportion of the two liquids in the distillate. ($Br=79.92$; $C=12$; $H=1$) (*Baroda B.Sc., 1953*)
16. Explain the principle underlying the process of steam distillation. Nitrobenzene can be distilled with steam under one atmospheric pressure at a temperature of $99.2^\circ C$. Calculate the amount of steam necessary to distil 100 gms. of nitrobenzene. The vapour pressure of water at $99.2^\circ C$ is 739 mm. of mercury. (*Poona B.Sc., 1954*)
17. Define the solubility of a substance. Illustrate the different types of solubility curves and explain their shapes.
18. Discuss the principle of :
 (i) Steam distillation.
 (ii) Fractional distillation of miscible liquid pair. (*Delhi B.Sc., 1954*)
19. Describe the vapour pressure properties of a system of two immiscible liquids. How are the facts utilised to estimate the molecular weight of a liquid by steam distillation ?
- A mixture of chlorobenzene and water, which are virtually immiscible, boils at $90.3^\circ C$ at an external pressure of 740.2 mm. The vapour pressure of pure water at $90.3^\circ C$ is 530.1 mm. Calculate the weight composition of the distillate. (Molecular weights : $C_6H_5Cl=112.5$ and $H_2O=18.02$)
 (Ans. 9 : 1 approx.) (*Baroda B.Sc., 1955*)
20. Describe the vapour pressure curves of mixtures of completely miscible liquids and explain their behaviour on distillation. (*Osmania B.Sc., 1955*)
21. Describe the behaviour of two liquids when a mixture of the two is distilled at atmospheric pressure. Indicate how you can determine the critical solution temperature of a mixture of phenol and water. (*Travancore B.Sc., 1956*)
22. Discuss the principles involved in the separation of the components of a mixture of two completely miscible liquids by distillation. Examine how far these principles are applicable to the separation of (a) nitrogen from liquid air, and (b) ethyl alcohol from its aqueous solution. (*Mysore B.Sc., 1956*)
23. Discuss fully the distillation of a mixture of two liquids. Illustrate your answer with examples and the vapour-pressure composition curves. (*Poona B.Sc., 1959*)
24. Discuss the distillation of those binary liquids which exhibit a maximum in their boiling point curve. (*Lucknow B.Sc., 1959*)
25. What is fractional distillation ? Discuss the principle underlying this process. (*Marthwada B.Sc., 1959*)
26. Explain Dalton's Law of Partial Pressures. Discuss the steam distillation of a non-miscible liquid like aniline. (*Delhi B.Sc., 1959*)

CHAPTER V

THEORY OF DILUTE SOLUTIONS

When the solute is present in a very small quantity as compared to the solvent, the system is called a **Dilute Solution**. Although the general laws discussed in this chapter are applicable to all types of dilute solutions, for a detailed study we select the ordinary popular type viz., the solution of a solid in a liquid.

THE DIFFUSION OF THE SOLUTE

One of the most important properties of gases is the property of diffusion by virtue of which a gas can distribute itself uniformly throughout the whole space offered. The molecules of a liquid or a substance in solution also possess this property but the process of diffusion in a liquid takes place much more slowly than in a gas, for the molecules of a liquid are more closely crowded together.

The diffusion of solute particles through a solvent can nicely be illustrated by slipping a layer of conc. solution of potassium permanganate at the bottom of a cylinder full of water, with the help of a thistle funnel. The coloured potassium permanganate can actually be seen diffusing up through water.

The process of diffusion of the solute in a solvent is due to (i) motion of solute molecules from a concentrated solution into the solvent, and (ii) motion of solvent molecules into the concentrated solution. The process of diffusion continues till the solute is distributed uniformly throughout the solvent (Fig. 52).

SEMI-PERMEABLE MEMBRANES

When a conc. solution and solvent are separated from each other by a special type of membrane, the movement of the solute

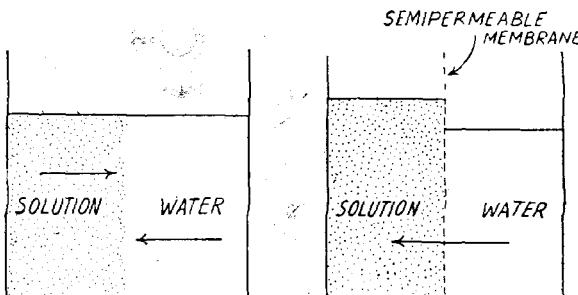


Fig. 52. Diffusion of solute in a solvent.
(Diagrammatic)

Fig. 53. Solvent molecules pass through a semi-permeable membrane whereas solute particles are held up by it.
(Diagrammatic)

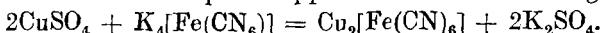
particles from the conc. solution into solvent is prevented but the flow of the solvent into it is allowed to continue. Such a membrane

which permits the solvent but not the solute to pass through it is known as a **Semi-permeable Membrane** (Fig. 53).

Semi-permeable membranes are common in living organisms. The membranes surrounding the plant cells and animal cells are semi-permeable but not completely so. Various gelatinous inorganic substances such as calcium phosphate and copper ferrocyanide are better and the latter is perhaps the best for this purpose.

Preparation of a Copper Ferrocyanide Semi-permeable Membrane. Semi-permeable membranes, commonly used in laboratory experiments, are usually constructed by depositing copper ferrocyanide in the porous walls of a battery pot. The membrane formed in each pore or capillary of the pot has a very small cross-section and can consequently withstand comparatively high pressure, in some cases upto 150 atmospheres.

The porous pot in which the membrane is to be deposited is thoroughly cleansed by washing successively with acid solution, water, alkali and finally with distilled water. The air bubbles enclosed in the pores are then removed by soaking the pot in distilled water for a few hours or better by forcing water through the pot under pressure. The pot is now filled with a 2·5 per cent solution of copper sulphate and allowed to stand in a solution of potassium ferrocyanide of similar strength (Fig. 54). The two solutions permeate the walls of the pot in opposite directions and a gelatinous



precipitate of copper ferrocyanide is formed in the interior of the pot where the two solutions meet. After the precipitation of the membrane, the pot is removed and carefully washed repeatedly with distilled water.

As a matter of fact this deposit does not occur exactly in the middle of the wall because there is a difference in the speeds with which the Cu^{++} ions and the ferrocyanide ions move, the copper ions moving faster. So, if a deposit is desired towards the inner wall of the cell as in Pfeffer's method, copper sulphate solution should be placed in the outer vessel and potassium ferrocyanide in the

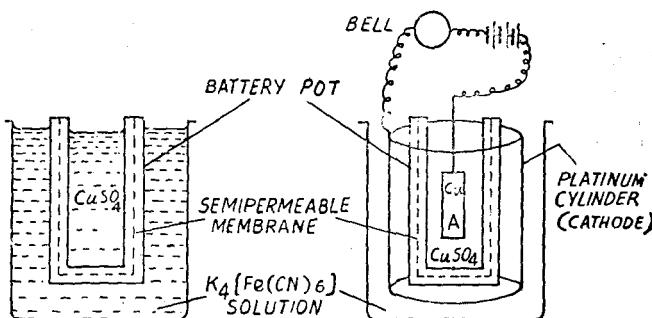


Fig. 54. Preparation of semi-permeable membrane.

Fig. 55. Electrical deposition of semi-permeable membrane.

cell itself. But as the methods frequently used now are those of Morse and Frazer or Berkeley and Hartley, the cell is prepared as described above by putting CuSO_4 in the cell and potassium ferrocyanide outside.

The formation of a semi-permeable membrane as described above, takes a long time and has now been replaced by the **Electrical method** which gives a more compact and stout membrane in a short time. In this method (Fig. 55) the diffusion of two salts is hastened up under electric force by passing current from the platinum plate A dipping in the pot, to a platinum cylinder surrounding it. The electrical resistance of the cell rises as the membrane is being formed and finally reaches a maximum value when on completion of the membrane the current is stopped and the bell B rings no more.

The Action of Semi-permeable Membranes. Several theories have been put forward to explain the action of semi-permeable membranes. It is most probable that each explanation given below may be correct within limits.

(1) *The Sieve Theory.* According to this theory, due to Traube, membrane is regarded as containing a large number of small pores and acts like a sieve. These pores are so small that only the water molecules can pass through them while the bigger solute molecules cannot. This theory may be said to have passed completely out of favour because cases of semi-permeability are known where the solute molecules are even smaller than the solvent molecules.

(2) *The Solution Theory.* This theory is widely accepted. According to this view the membrane is permeable to those substances which dissolve in it. For example, a layer of phenol slipped between a solution of calcium nitrate and water has been found to act as a semi-permeable membrane, calcium nitrate being insoluble in phenol cannot pass through it whereas water, which is soluble, passes through.

(3) *The Vapour Pressure Theory.* It is assumed that the semi-permeable membrane which separates a solution from a solvent has pores of such a nature that neither liquid can flow through, but the vapour of the solvent can pass through it. Since the vapour pressure of a solution is always lower than that of the pure solvent, the solvent molecules pass through the membrane into the solution. The theory furnishes a satisfactory explanation of osmosis.

OSMOSIS AND OSMOTIC PRESSURE

We have already pointed out that if a solution be separated from the pure solvent by a semi-permeable membrane, the membrane permits the solvent molecules through it but prevents that of the solute. Thus to have uniform concentration on both sides of the membrane, the solvent flows into solution.

*The spontaneous flow of solvent through a semi-permeable membrane from a solution of low concentration to one of higher concentration is termed **Osmosis** (Greek *osmos* = a push). It differs from diffusion in the sense that the flow of particles is in one direction only.*

Osmosis can be demonstrated* by means of the apparatus shown in Fig. 56. A battery pot with a copper ferrocyanide membrane deposited in its walls is filled with a 1% solution of cane sugar, and a rubber stopper with a long glass tube is firmly inserted into the mouth of the pot so that no air is enclosed with the sugar solution. The pot is now immersed in a beaker of distilled water. Osmosis takes place and the diffusion of water through the semi-permeable membrane causes the level of solution in the glass tube to rise. In the course of a few days the level of the solution will attain a definite maximum value. When this condition of equilibrium is reached, the hydrostatic pressure of the column of solution is just sufficient to prevent the entry of more solvent into the solution. This hydrostatic pressure, since it is produced by a process of osmosis, is termed the osmotic pressure of the solution.

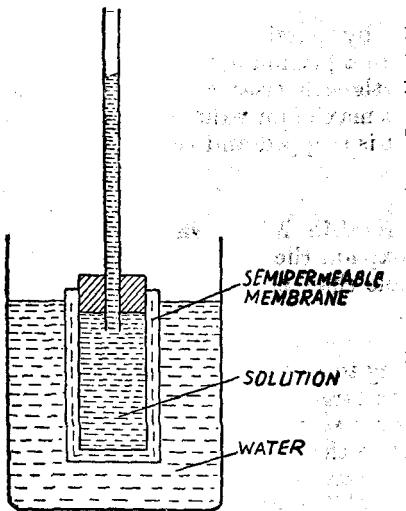


Fig. 56. Demonstration of Osmosis.

Supposing we were to have an apparatus of the type shown in Fig. 57 consisting of a chamber divided into two water-tight compartments (S and W) by a semi-permeable membrane and fitted with water-tight pistons P and P'. On placing the solution in compartment S and water in the compartment W, the piston P will be displaced upwards owing to the movement of water from W to S. To stop this movement of water, we apply mechanical pressure on solution and the pressure just sufficient to stop osmosis will be the osmotic pressure.

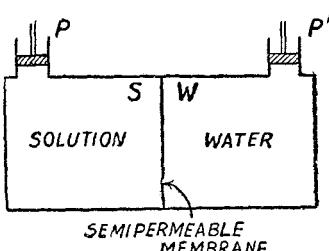


Fig. 57.

*Osmosis can also be demonstrated by the following interesting experiment. Take two eggs of equal size and remove their outer shell by dissolving in dilute hydrochloric acid. Now put one of them in distilled water and the other in saturated salt solution. After a few hours it will be noted that the egg placed in water swells and the one in salt solution shrinks.

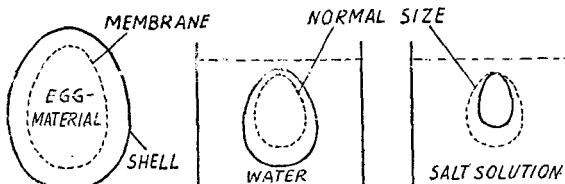


Fig. 58. (a) Egg.

Fig. 58. (b) Showing swelling of egg in water.

Fig. 58. (c) Showing shrinkage of egg in salt solution.

The **Osmotic Pressure** of a solution may thus be defined as the equivalent of excess pressure which must be applied to the solution in order to prevent the passage of solvent into it through a semi-permeable membrane separating the two.

Isotonic Solutions. When two solutions are separated by a semi-permeable membrane, the solvent will flow from the solution of lower osmotic pressure to the solution of higher osmotic pressure until both solutions have an equal osmotic pressure. Such a pair of solutions which produce no flow through a semi-permeable membrane are said to be 'isotonic' and are described as **Isotonic Solutions**.

Another Definition of Osmotic Pressure

When a solution and the solvent are separated by air under reduced pressure (Fig. 59), the vapour pressure of the solvent being higher than that of the solution, there is a flow of solvent to the solution. This phenomenon is akin to osmosis and here the solution-air interface acts as a semi-permeable membrane. The osmosis will be stopped when the vapour pressures of the solution and the solvent become equal. This can be done by applying pressure externally on the solution.* This affords

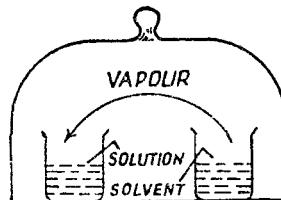


Fig. 59.

another definition of osmotic pressure. The **Osmotic Pressure** of a given solution is the excess pressure which must be applied to it in order to increase the vapour pressure of the solution until it becomes equal to that of the solvent.

This concept of osmotic pressure offers the best explanation of the mechanism of osmosis through a semi-permeable membrane. It follows from it that the isotonic solutions will have the same vapour pressure.

MEASUREMENT OF OSMOTIC PRESSURE

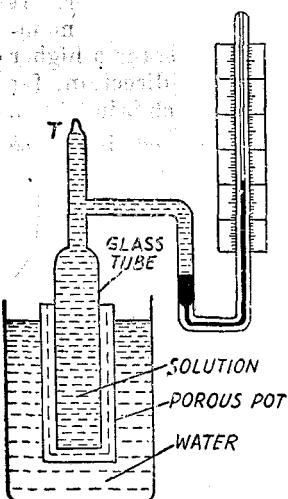


Fig. 60. Pfeffer's apparatus for osmotic pressure measurement.

(1) **Pfeffer's Method.** In the earlier experiments for the quantitative measurement of osmotic pressure, Pfeffer (1887) employed a very simple apparatus which is shown diagrammatically in Fig. 53. A battery pot with a semi-permeable membrane deposited in its walls is cemented to a wide glass tube which ends in a thin tube T at the top and carries a manometer in the side. The solution under investigation is introduced in the pot through the tube T. The apparatus is then made air-tight by sealing off at T. The manometer contains mercury and is closed at the upper end.

*Just as the vapour pressure of a liquid changes with changing temperature, it has been established that vapour pressure changes with changing total pressure on the liquid at constant temperature.

A portion of the pot is immersed in distilled water kept at constant temperature. In the course of a few days the manometer registers the maximum pressure which is the osmotic pressure of the solution.

Defects in Pfeffer's Method

(a) The osmotic pressure developed even in very dilute solutions are considerable and the great pressures set up often burst the membrane.

(b) It takes a long time for the establishment of the final equilibrium. The manometer thus records the maximum pressure only after a number of days have elapsed.

(2) **Morse and Frazer's Method.** These workers (1905) improved upon Pfeffer's method in several details. They obtained

a uniform, compact and stout membrane by depositing copper ferrocyanide *electrically* in the walls of a battery pot. For the measurement of high osmotic pressures they employed the apparatus indicated in Fig. 61. The porous pot with the semi-permeable membrane in its walls is firmly fitted in a stout bronze cylinder to the other end of which a manometer is securely fixed. Water is placed in the porous pot while the solution is present in the bronze cylinder. It can easily be realised that the membrane would be able to stand a higher pressure in the reverse direction, for there the principle of arch is involved.

The results obtained by these workers are accepted ones. They determined the osmotic pressure of sugar solutions up to 91 per cent strength, the strongest solution giving

the osmotic pressure of 273 atmospheres.

(3) **Berkeley and Hartley's Method.** Both the difficulties met with in Pfeffer's methods were overcome successfully by Berkeley and Hartley (1904). They used the method of applying to the solution a pressure which was just sufficient to stop osmosis. Fig. 62 shows the essential features of their apparatus. The porcelain pot containing the copper ferrocyanide membrane in its walls, is sealed into the outer bronze cylinder which is fitted with a piston and a manometer. Water is placed in the pot so that it stands upon a certain level in the side-tube T and the solution under examination is placed between the pot and the outer vessel. Water tends to pass through the pot into the solution and this is indicated by the downward motion of the water meniscus in the side-tube T. This flow or osmosis of water into the solution can be stopped by the application of external pressure on the solution with the help of the piston and

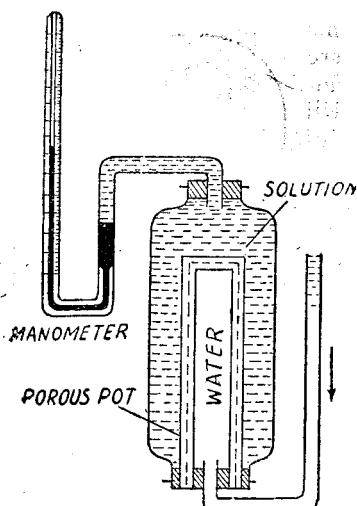


Fig. 61. Morse and Frazer's apparatus for high osmotic pressure.

this would be indicated when the water meniscus in the side-tube becomes stationary. The pressure so applied is equal to the osmotic pressure which can be read on the mercury manometer.

In this method, since the osmotic pressure is balanced by the external pressure, the strain on the membrane is removed and thus the danger of its bursting is eliminated. The time taken in these determinations will evidently be much less compared to the older method of Pfeffer. Moreover since the equilibrium is established rapidly, the concentration of the solution is not altered by dilution with the incoming solvent.

(4) **The Townend's Porous Disc Method.** This method was suggested by Townends in 1928 and improved by Martin and Schulz in 1931. It is based on the definition of osmotic pressure given on page 87 and the fact that the vapour phase acts as a perfect semi-permeable membrane permitting the passage of the solvent molecules only.

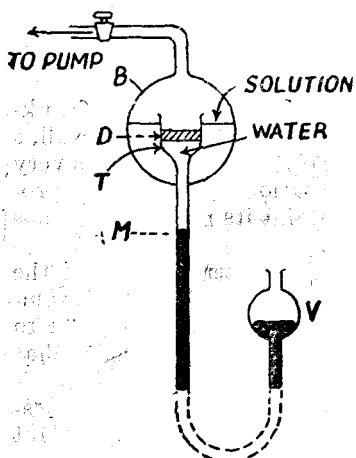


Fig. 63. Townend's Porous Disc Method.

With the help of a pump, air is completely removed from the apparatus.

By raising or lowering the mercury bulb V, a tension can be applied on the solvent. As the vapour pressure of the solvent is higher than that of the solution there will be a tendency for the solvent to distil in the outer bulb followed by an upward movement of the mercury meniscus M. But as the change of pressure on a liquid can alter its vapour pressure, the rate of movement of this meniscus will depend upon the tension applied.

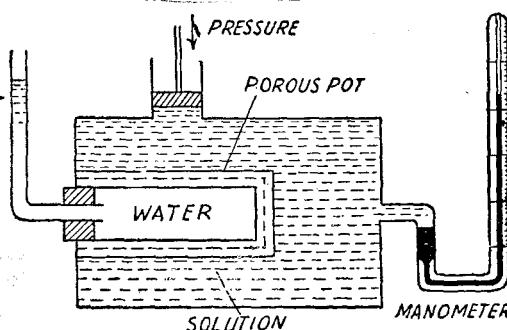


Fig. 62. Berkeley and Hartley's apparatus (Diagrammatic)

By observing the rate of movement up or down of this meniscus when different tensions are applied, the value is found by extrapolation for which there is no movement of the meniscus. In other words, the osmotic pressure is the "negative pressure" which must be applied to the solvent in order to reduce its vapour pressure to that of the solution.

SUPERIORITY OF TOWNEND'S METHOD

Townend's method of measuring osmotic pressure is superior to that of Berkeley and Hartley in two respects :

- 'i) It eliminates the use of a copper ferrocyanide membrane which is rather difficult to prepare and handle.
- (ii) This method is particularly useful in the case of non-aqueous solvents where the copper ferrocyanide membrane does not work at all.

(5) De Vries Method. This method depends on the fact that the protoplasmic layer of plant cells is composed of semi-permeable

materials through which only water can pass. Normally the protoplasmic layer, surrounding the cell sap is pressing against the cell wall (Fig. 64) but when placed in a solution of higher osmotic pressure than the cell sap, water is withdrawn from the cell and the protoplasm shrinks away from the cell wall, a

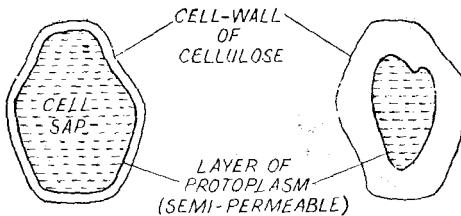


Fig. 64. Section of a normal Plant Cell.

Fig. 65. Section of a Plant Cell placed in a strong salt solution.

phenomenon known as *plasmolysis*. (Fig. 65). This change can very well be noted under a microscope. A solution in which the protoplasmic layer does not shrink and maintains its normal shape has the same osmotic pressure as the cell sap.

De Vries applied these principles to the determination of the osmotic pressures by placing plant cells in two solutions to be compared and noting as to how much each had to be diluted in order to give a solution of which the osmotic pressure was the same as that inside the cells.

A similar method for the comparison of osmotic pressure is described by Hamburger, who used red blood corpuscles instead of plant cells.

(6) Deduction of Osmotic Pressure from other Properties. Osmotic pressure can be deduced indirectly from certain other properties of solutions, such as the lowering of vapour pressure, the depression of freezing point and the elevation of boiling point.

VAN'T HOFF'S THEORY OF DILUTE SOLUTIONS

Pfeffer's investigations were originally undertaken for botanical purposes. Later Van't Hoff, a physical chemist, analysed the data obtained by Pfeffer and perceived the existence of striking parallelism between the properties of gases and the properties of solutions. In 1885, he put forth his **Theory of Solutions** according to which a substance in solution behaves exactly like a gas and the osmotic pressure of a dilute solution is equal to the pressure which the solute would exert if it were a gas at the same temperature and occupying the same volume

as the solution. Van't Hoff further gave a number of surprisingly simple laws obeyed by substances in solution. These laws for solutions are exactly parallel to gas laws.

(1) **Boyle-Van't Hoff Law for Solutions.** Van't Hoff pointed out that if a dissolved substance be regarded as analogous to a gas, the osmotic pressure could be considered to be produced by the bombardment of the semi-permeable membrane by the solute particles. The osmotic pressure will, therefore, be directly proportional to the number of solute molecules or the concentration of the solute at constant temperature. If P be the osmotic pressure, C the concentration and V the volume of the dilute solution, then

$$P \propto C = \frac{1}{V}$$

Or $P = \text{constant} \times \frac{1}{V}$

Or $PV = \text{constant}$, if temperature be kept constant.

Thus, for dilute solutions the product of osmotic pressure and volume is constant, provided the temperature is kept constant. This law is exactly similar to Boyle's law for gases and is known as **Boyle-Vant's Hoff Law for Solutions**. The table given below shows some experimental results of Berkeley and Hartley illustrating the constancy of the product PV .

Table. Relation between the osmotic pressure and concentration of the sugar solutions at 0°C

Concentration of sugar in solution (Grams per litre)	Osmotic Pressure P (Atmospheres)	Volume containing 1 gram molecule of sugar (V litres)	PV
2·02	0·134	169·3	22·7
10·0	0·66	34·2	22·6
20·0	1·32	17·1	22·6
45·0	2·97	7·60	22·6
93·75	0·18	36·5	22·5

(2) **Pressure-Temperature Law for Solutions.** The velocity of the solute molecules and, therefore, their bombardments on the semi-permeable membrane are directly proportional to the absolute temperature. Hence, if the number of solute molecules or the concentration remains the same, osmotic pressure will be directly proportional to absolute temperature. But since the concentration and volume are interdependent and volume changes in liquids by rise of temperature are negligible, we can say that the osmotic pressure of a dilute solution is directly proportional to absolute temperature. This is quite similar to Charles' Law of Gases and is known as **Pressure-**

Table. Relation between osmotic pressure and absolute temperature with reference to a cane-sugar solution containing 32 grams per litre.

Temperature °C	Temperature absolute (T)	Osmotic pressure in atmospheres (P)	$\frac{P}{T} \times 10^3$
5	278	2·45	8·81
10	283	2·50	8·83
15	288	2·54	8·82
20	293	2·59	8·84
25	298	2·63	8·84

Temperature Law for Solutions. This law deduced theoretically is borne out by the following data due to Morse and Frazer :—

(3) **General Equation for Solutions**

$$\text{Since osmotic pressure } \propto C \propto \frac{1}{V}$$

$$\therefore P \propto \frac{1}{V}$$

also

$$P \propto T$$

$$\therefore \propto \frac{T}{V}, \text{ or } PV \propto T$$

$$\text{Hence } PV = ST,$$

where S is a constant equivalent to gas constant and is usually named as *Solution Constant*. This expression which is exactly similar to the general gas equation is called the **General Equation for Solutions**. This relation has received confirmation from the data obtained by Barkeley and Hartley shown in the table above. The mean value of $PV = 22.6$ litre-atmospheres from that table, when divided by 273 gives the value of $R \left(= \frac{PV}{T} \right)$ as 0.0827, which agrees well with the value of $R (= 0.0821)$ in the gas equation.

(4) **Avogadro-Vant's Hoff Law for Solutions**

For a given solution,

$$PV = ST \quad \dots \quad \text{where } V \text{ is the volume containing 1 gram molecule of solute.}$$

For another solution,

$$P'V' = ST' \quad \dots \quad \text{where } V' \text{ is the volume containing one gram-molecule of the second substance.}$$

Now if $P = P'$, and $T = T'$ then it follows that $V = V'$.

Hence, pressure and temperature being the same, equal volumes of solutions would contain equal number of molecules of the solute. This is exactly similar to Avogadro's Law for gases and is, therefore, called **Avogadro-Van't Hoff Law for Solutions**.

The close analogy between gases and dilute solutions traced by Van't Hoff may now be summarised as follows :—

GASES	SOLUTIONS
(i) $P \propto \frac{1}{V}$, if T is constant <i>(Boyle's Law)</i>	$P \propto C \propto \frac{1}{V}$, or $P \propto \frac{1}{V}$, if T is constant. <i>(Boyle-Van't Hoff Law)</i>
(ii) $P \propto T$, if V is constant <i>(Pressure-Temp. Law)</i>	$P \propto T$, V, of course remains constant <i>(Pressure-Temp. Law)</i>
(iii) $PV = RT$ <i>(General Equation for gases)</i>	$PV = ST$ <i>(General Equation for solutions)</i>
(iv) P and T being the same, equal volumes of gases contain equal number of molecules. <i>(Avogadro's Law)</i>	P and T being the same, equal volumes of solutions contain equal number of molecules of the solute. <i>(Avogadro-Van't Hoff Law)</i>

PROBLEMS ON OSMOTIC PRESSURE

The analogy between gases and solutions is so complete that all the gas laws may be considered to apply to solutions rigidly. This gives an easy solution of problems concerning the behaviour of substances in solution.

(1) Calculation of Solution Constant

Example. A solution of cane-sugar ($C_{12}H_{22}O_{11}$) containing 34.2 grams per litre has an osmotic pressure of 2.4 atmospheres at 20°C. Calculate the solution constant R . [C=12, H=1, O=16]

$$\text{Molecular weight of cane-sugar } (C_{12}H_{22}O_{11}) \\ = 12 \times 12 + 22 \times 1 + 11 \times 16 = 342$$

$R = \frac{PV}{T}$... General Equation for solutions, where P = osmotic pressure, V = volume of solution containing 1 gram-molecule of solute, T = absolute temperature.

In the present case,

$$P = 2.4 \text{ atmospheres.}$$

V :—

34.2 gram of sugar is dissolved in 1 litre.
342 gram (1 mole.) of sugar is dissolved in 10 litres

$$\therefore V = 10 \text{ litres}$$

$$T = 273 + 20 = 293.$$

Substituting the values, P, V and T in $R = \frac{PV}{T}$, we have

$$R = \frac{2.4 \times 10}{293} = 0.0819 \text{ litre-atmosphere.}$$

(2) Calculation of Osmotic Pressure

Example 1. Calculate the osmotic pressure of a 5% solution of glucose ($C_6H_{12}O_6$) at 18°C.

$$\frac{PV}{T} = R \text{ ... General Equation for solutions}$$

$$R = 0.0821 \text{ litre-atmosphere.}$$

$$T = 273 + 18 = 291$$

V :—

5 gms. of glucose is dissolved in 100 c.c. of solution

$$180 \text{ " } \quad \text{ " } \quad \text{ " } \quad \text{ " } \quad \frac{100}{5} \times 180 \text{ " }$$

$$\therefore V = 3600 \text{ c.c.} \\ = 3.6 \text{ litres.}$$

or

Substituting in equation $\frac{PV}{T} = R$,

$$\text{we have } \frac{P \times 3.6}{291} = 0.0821$$

$$\therefore P = \frac{0.0821 \times 291}{3.6} = 6.64 \text{ atmospheres.}$$

Example 2. Calculate the osmotic pressure in millimetres of mercury at 15°C of a solution of naphthalene ($C_{10}H_8$) in benzene containing 14 gms. of naphthalene per litre of solution,

$$PV = RT$$

$$R = 0.0821 \text{ litre-atmospheres.}$$

$$T = 15 + 273 = 288^\circ \text{ Abs.}$$

V = Volume in liters containing 1 gm. mole.

$$= \frac{128}{14} \text{ litres.}$$

$$V = \frac{0.0821 \times 288}{128}$$

= 2.586 atmospheres.

$$= 2.586 \times 760 = 1965 \text{ mm.}$$

Example 3. Calculate the osmotic pressure of solution obtained by mixing (a) 100 c.cs. of 3.4 per cent solution of urea (m. wt. 60), and (b) 100 c.cs. of 1.6 per cent solution of cane-sugar (m. wt. 342), at 20°C.

After mixing, the volume for each of the solutions = 200 c.cs.

Osmotic Pressure of urea :—

3.4 gms. urea is dissolved in 200 c.cs.

$$60 \quad , \quad , \quad , \quad \frac{200 \times 60}{3.4} \text{ c.c.}$$

$$= \frac{200 \times 60}{3.4 \times 1000} = \frac{12}{3.4} \text{ litres.}$$

$$\therefore P = \frac{RT}{V} = \frac{0.0821 \times (273 + 20) \times 3.4}{12} = 6.81 \text{ atm.}$$

Osmotic pressure of cane-sugar :—

1.6 gms. of sugar is dissolved in 200 c.cs.

$$342 \quad , \quad , \quad , \quad \frac{200}{1.6} \times \frac{342}{1000} = \frac{342}{8} \text{ litres}$$

$$\therefore P = \frac{RT}{V} = \frac{0.0821 \times (273 + 20) \times 8}{342} = 0.56 \text{ atm.}$$

Since the dissolved substances behave like gases, the total osmotic pressure will be equal to the sum of the individual osmotic pressures of the two solutions (*Dalton's Law*).

∴ Osmotic pressure of the mixture = 6.81 + 0.56 = 7.37 atm.

(3) Calculation of Molecular Weight from Osmotic Pressure

Example 1. A solution of glycol containing 1.82 grams per litre has an osmotic pressure of 51.8 cms. of mercury at 10°. What is the molecular weight of glycol?

Suppose M is the molecular weight of glycol

1.82 gms. of glycol are present in 1 litre

1 gm. of glycol is present in $\frac{1}{1.82}$ litre

M gms. of glycol is present in $\frac{M}{1.82}$ litres

Thus, in the present case, we have

$$V = \frac{M}{1.82} \text{ litres}$$

$$P = 51.8 \text{ cms. or } \frac{51.8}{76} \text{ atmospheres.}$$

$$T = 273 + 10 = 283.$$

Substituting these values in the equation $\frac{PV}{T} = R$

$$\frac{\frac{51.8}{76} \times \frac{M}{1.82}}{283} = 0.0821$$

$$\text{Hence, } M = 0.0821 \times 283 \times \frac{76}{51.8} \times 1.82 = 62.$$

Example 2. Morse and Frazer observed that a solution of glucose containing 18 grams per litre had an osmotic pressure of 2.39 atmospheres at 23°C. Find the molecular weight of glucose.

Let M be the molecular weight of glucose.

18 gms. of glucose is present in 1 litre

1 gm. of glucose is present in $\frac{1}{18}$ litre

M gms. of glucose is present in $\frac{M}{18}$ litres

Thus, in the present case

$$V = \frac{M}{18} \text{ litres}$$

$$P = 2.39 \text{ atmospheres}$$

$$T = 273 + 23 = 296$$

Substituting these values in the equation $\frac{PV}{T} = R$, we have

$$\frac{2.39}{296} \times \frac{M}{18} = 0.0821$$

$$\therefore M = 0.821 \times \frac{296}{2.39} \times 18 \\ = 183.$$

(4) Calculation of Molecular Weight by Comparison of Osmotic Pressure

Example 1. A 5% solution of cane-sugar (m. wt. = 342) is isotonic with 0.877% solution of urea. Find the molecular weight of urea.

For isotonic solutions at the same temperature, molar concentrations are equal (*Avogadro's Law*)

$$\text{Molar concentration of cane-sugar} = \frac{5}{342} \text{ per 100 c.c.}$$

$$\text{Molar concentration of urea} = \frac{0.877}{M} \text{ per 100 c.c., where } M \text{ is the molecular weight of urea.}$$

Comparing the molar concentrations in the two cases

$$\frac{5}{342} = \frac{0.877}{M}$$

$$\text{or } M = \frac{0.877 \times 342}{5} = 59.98.$$

Example 2. Solutions containing 20 grams of sucrose ($C_{12}H_{22}O_{11}$) per litre and 1.63 grams of the boric acid in 450 c.cs. respectively are isotonic. Find the molecular weight of the boric acid.

$$\text{Concentration of sucrose} = \frac{20}{342} \text{ gm. molecules per litre}$$

$$\text{Concentration of boric acid} = \frac{1.63 \times 1000}{M \times 450} \text{ gm. molecules per litre}$$

Comparing molar concentration

$$\frac{20}{342} = \frac{1.63 \times 1000}{450 \times M}$$

$$\therefore M = \frac{1.63 \times 1000}{450} \times \frac{342}{20} = 61.94$$

ABNORMAL OSMOTIC PRESSURES

Measurements of the osmotic pressure of electrolytes give results considerably higher than those calculated from their formulae.

This is due to the fact that such compounds dissociate and break down in solution into ions. The osmotic pressure of a solution depends on the number of particles present in a given volume. If each molecule dissociates into two more ions, the number of particles exceeds the normal number and the osmotic pressure is consequently higher. The abnormal osmotic pressure noted experimentally was once employed to calculate the degree of dissociation and vice versa.

It must be pointed out that these calculations are now more or less of historical significance in view of the Theory of Strong Electrolytes according to which strong electrolytes are completely dissociated at all dilutions and any differences between the values of the osmotic pressure of the strong electrolytes must be ascribed to different inter-ionic attractions rather than to partial dissociations.

The ratio of the observed osmotic pressure to what it would be if dissociations were complete is now known as the **Osmotic Co-efficient** and is denoted by the symbol g . For a fully ionised electrolyte showing no inter-ionic attraction, g should be equal to 1. Since the observed value of g is found to be less than one, the value $(1-g)$ is a measure of either inter-ionic attraction or partial dissociation or both.

Example 1. A solution containing 7.45 gms. of potassium chloride per litre was found to exert an osmotic pressure of 4.44 atmospheres at 17°C. Calculate the degree of dissociation of the dissolved salt.

Molecular weight of potassium chloride = $39 + 35.5 = 74.5$.

7.45 gms. of pot. chloride are dissolved in 1 litre

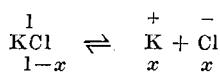
74.5 gms. (i.e., 1 gm. molecule) of chloride are dissolved in 10 litres. Thus

$$V = 10 \text{ litres.} \quad T = 273 + 17 = 290.$$

By substituting these values in $\frac{PV}{T} = 0.0821$, we can get the value of normal osmotic pressure.

$$\text{Normal osmotic pressure} = \frac{0.0821 \times 290}{10} = 2.3809 \text{ atmospheres.}$$

If x is the degree of dissociation (fraction of molecules which dissociate),



One molecule of potassium chloride will give x potassium ions and x chloride ions leaving behind $(1-x)$ ions undissociated. Total number of particles after dissociation is, therefore, $1-x+x+x=1+x$ as compared to one normal molecule, had no dissociation taken place. Since osmotic pressure is proportional to number of particles in solution,

$$\frac{\text{Observed osmotic pressure}}{\text{Normal osmotic pressure}} = \frac{\text{Number of particles after dissociation}}{\text{Normal number of particles}}$$

$$\frac{4.44}{2.38} = \frac{1+x}{1}$$

$$x = \frac{2.38}{2.38} - 1 = 0.8648.$$

Hence, potassium chloride is 86.48% dissociated.

Example 2. A 1% solution of potassium chloride is dissociated to the extent of 82%. What would be its osmotic pressure at 18°C?

Molecular weight of KCl = $39 + 35.4 = 74.5$

One gm. of KCl is dissolved in 100 cc. or $\frac{1}{10}$ litres

$$74.5 \text{ " " " } \frac{1}{10} \times 74.5 = 7.45 \text{ litre.}$$

Thus $V = 7.45 \text{ litres}$

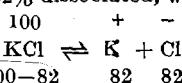
$$T = 273 + 18 = 91$$

$$R = .0821$$

Normal osmotic pressure P :

$$P = \frac{RT}{V} = \frac{.0821 \times 91}{7.45} = 3.20 \text{ atmospheres.}$$

When KCl is 82% dissociated, we have



Thus, if the number of particles before dissociation is 100, after dissociation it would be 182.

Applying the relationship :—

$$\frac{\text{Observed osmotic pressure}}{\text{Normal osmotic pressure}} = \frac{\text{No. of particles after dissociation}}{\text{No. of particles before dissociation}}$$

$$\therefore \text{Obs. osmotic pressure} = \frac{182}{100} \times \text{Normal osmotic pressure.}$$

$$\frac{182}{100} \times 3.20 = 5.82 \text{ atmospheres.}$$

MOLECULAR WEIGHT OF DISSOLVED SUBSTANCES

We have just seen that the molecular weight of a dissolved substance can readily be calculated from the osmotic pressure of its solution. Unfortunately the measurement of osmotic pressure requires an elaborate apparatus and cannot be carried out as an ordinary laboratory process. Therefore, we have to look to some other properties of a solution related to osmotic pressure, which can be determined with moderate ease. Three of such properties which are frequently employed for the determination of molecular weight in solution are

- (i) the lowering of vapour pressure,
- (ii) the elevation of the boiling-point, and
- (iii) the depression of the freezing point.

of the pure solvent, caused by the addition of a solute to it.

Lowering of Vapour Pressure and Molecular Weight

It has long been known that the vapour pressure of a liquid is diminished when a non-volatile substance is dissolved in it and the decrease is proportional to the amount of solute dissolved. Suppose the pure liquid has a vapour pressure p and that a solution of known concentration has a vapour pressure p_s , the lowering being $(p - p_s)$. It was shown as early as 1848 by Von Babo that although the value of p increases rapidly with the temperature, the ratio $(p - p_s)/p$ is the same at all temperature for a given dilute solution. This ratio of the decrease of vapour pressure to the vapour pressure of the pure solvent is termed the **relative lowering of the vapour pressure**.

Raoult's Law. The fundamental law governing the vapour pressure of dilute solutions was established in 1887 by Raoult through

exhaustive experimental investigations following the earlier work of Von Babo and Wullner. According to **Raoult's Law**, the relative lowering of the vapour pressure is equal to the ratio of the molecules of the solute and the total number of molecules in the solution i.e., the **molar fraction** of the solute. This law may be put in the form

$$\frac{p - p_s}{p} = \frac{n}{n + N}$$

where n and N represent the number of molecules of the solute and solvent respectively.

Raoult's Law can be derived in the following simple way. If the vapour pressure p_s of molecules of solvent above a solution is considered, it is clear that it must be proportional to the fraction of molecules of this kind i.e., molar fraction of the solvent in solution,

$\frac{N}{n + N}$ where n and N are, of course, gram molecules of solute and solvent respectively.

$$p_s \propto \frac{N}{n + N} \text{ or } p_s = k \frac{N}{n + N}, \text{ where } k \text{ is a constant.}$$

In the case of the pure solvent $n=0$ and the fraction $\frac{N}{n + N}=1$.

$$\therefore \text{the vapour pressure } p = k.$$

The expression for the vapour pressure of the solution now becomes

$$\begin{aligned} p_s &= p \frac{N}{n + N} \\ \text{or} \quad \frac{p_s}{p} &= \frac{N}{n + N} \\ \text{or} \quad 1 - \frac{p_s}{p} &= 1 - \frac{N}{n + N} \\ \frac{p - p_s}{p} &= \frac{n}{n + N} \end{aligned}$$

This is Raoult's Law.

If in a determination, w = weight of solute, W = weight of pure solvent, m = molecular weight of solute, and M = molecular weight of solvent

$$\frac{p - p_s}{p} = \frac{n}{n + N} = \frac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}}$$

Since for dilute solutions $\frac{w}{m}$ is small it can be neglected in the denominator. Thus Raoult's Law would now be written as

$$\frac{p - p_s}{p} = \frac{wM}{mW}$$

This expression enables us to calculate the molecular weights of the dissolved substances when the relative lowering of vapour pressure produced by a known weight of the solute in a known weight of a given solvent is known.

Relation between Vapour Pressure and Osmotic Pressure.

The great theoretical importance of Raoult's Law was demonstrated in 1887 by Van't Hoff who showed that the lowering of the vapour pressure of a solution was directly related to its osmotic pressure and the relative lowering of vapour pressure may be deduced in the following simple way :

Fig. 66 shows a solution contained in a tube separated by a semi-permeable membrane, and exerting its full osmotic pressure which is balanced by the hydrostatic pressure of the column of solution, the larger outer vessel being supposed to be evacuated.

The pressure of vapour at the level of the surface a , of the solution must be the same inside and outside the tube. If p is the vapour pressure of the pure solvent, and p_s the vapour pressure of the solvent over the solution, the difference between them is equal to the hydrostatic pressure of the vapour column of height h . That is,

$$p - p_s = h.g.d. \quad \dots (i)$$

where d is the density of the vapour acting over unit cross-section.

Let M be molecular weight of the solvent, then the volume occupied by M grams of vapour at a pressure p and at absolute temperature T is

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

\therefore the vapour density

$$d = \frac{M}{V} = \frac{Mp}{RT}, \quad \dots (ii)$$

Since the density of a dilute solution can be taken as equal to the density of the pure solvent S , the osmotic pressure P of the solution is given by the relation

$$P = h.g.S \text{ or } h = \frac{P}{S.g} \quad \dots (iii)$$

Substituting the values of h and d from (ii) and (iii) in the expression (i) we have

$$p - p_s = \frac{P}{S.g} \times \frac{Mp}{RT} g$$

$$\text{or } \frac{p - p_s}{p} = \frac{M}{RST} P \quad \dots (iv)$$

where M is the molecular weight of solvent in the form of vapour and S its density. This expression gives a relation between the lowering of vapour pressure and the osmotic pressure. At a fixed temperature, say the freezing or boiling-point, p and S have a definite constant value and, therefore, it follows that $(p - p_s) \propto P$.

Hence the lowering of vapour pressure is proportional to the osmotic pressure of the solution.

We can derive Raoult's Law from the relation as follows :

If V' is the volume of solvent containing one gram molecule of the solute,

$$P = n \frac{RT}{V'}, \text{ where } n \text{ stands for number of gram molecules of solute.}$$

Since $V' = \frac{MN}{S}$ when N = number of gram-molecules of solvent :

$$P = \frac{nRTS}{MN}.$$

Substituting this value of P in relation (iv) we get

$$\frac{p - p_s}{p} = \frac{M}{SRT} \times \frac{nRTS}{MN} = \frac{n}{N}$$

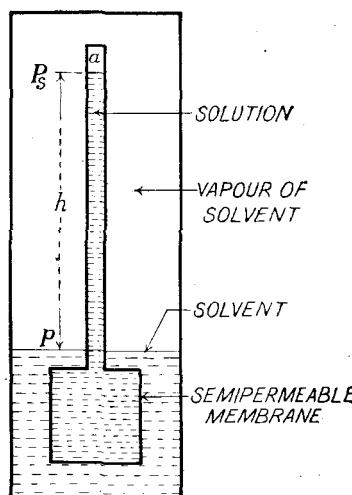


Fig. 66. Osmotic pressure and vapour pressure.

This is a modified form of Raoult's Law, in which n , which is small compared with N , is neglected in the denominator when the solution is dilute.

Determination of the Lowering of Vapour Pressure

There are two types of experiments for the measurement of the lowering of vapour pressure. The first is static, and the second dynamic in nature. We will describe methods of each type.

(1) **The Barometric Method.** It is a typical static method. A long barometric tube filled with mercury is inverted in a dish containing mercury. The mercury falls into the tube until the pressure due to the column of mercury is equal to the atmospheric pressure and there is a vacuum produced at the top of the tube. A small quantity of the pure solvent is then introduced into the vacuum with the help of a bent dropper as shown in the diagram, Fig. 67. The solvent vaporises and due to its pressure the mercury column is pressed down. This depression measured in millimetres or centimetres of mercury represents the vapour pressure (p) of the solvent at the temperature of the experiment. The experiment is repeated with the solution and the difference found in the two heights; this represents the amount by which the vapour pressure of the pure solvent (p) and the solution (p_s) differ.

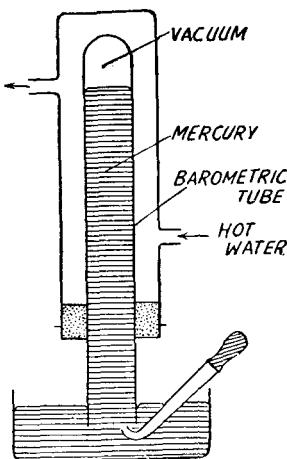


Fig. 67.
Barometric method for
measuring vapour pressure.

Usually this method cannot be applied for the accurate determination of molecular weights because the depressions of vapour pressure are too small to cause difference in mercury level which could be measured accurately.

Isotenoscope Method. This method is due to Smith and Menzies. The *isotenoscope* consists of a bulb A (Fig. 68) of about 2 cm.

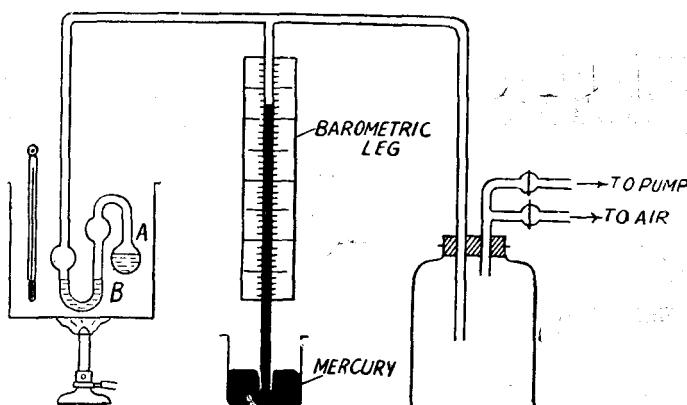


Fig. 68. Isotenoscope method for measuring the vapour pressure.

diameter which is fused to a bulbed U-tube B with limbs about 3-4 cms. long. The bulb is a little more than half filled with the liquid under examination and 3 to 4 c.cs. of the liquid are also placed in the U-tube B. The isoteniscope is then attached to the rest of the apparatus as shown in Fig. 68 and placed in a constant temperature bath.

On evacuation, the liquid in the bulb A begins to boil and expels all the air. The pressure is then cautiously restored by admitting air so that the level of the liquid in the two limbs of the U-tube becomes equal.

Under these conditions the pressure read on the barometric leg when subtracted from the atmospheric pressure gives the vapour pressure of the liquid at the temperature of the experiment because the pressure of the vapour in the bulb A is balanced by the pressure of air introduced to bring the liquid in the two limbs of the U-tube at the same level.

Example. Raoult found that a solution of 11.346 gms. of turpentine in 100 gms. of ether (m. wt. 74) had a vapour pressure of 360.1 mm. At the temperature of the experiment the vapour pressure of pure ether was 383 mm. Calculate the molecular weight of turpentine.

$$p_s \text{, the vapour pressure of pure solvent} = 383 \text{ mm.}$$

$$p_s \text{, the vapour pressure of solution} = 360.1 \text{ mm.}$$

Substituting in Raoult's equation we have

$$\frac{p - p_s}{p} = \frac{n}{N + n}$$

$$\text{or } \frac{p - p_s}{p} = \frac{N}{N + n} = \frac{N}{n} + 1$$

$$\text{or } \frac{383}{383 - 360.1} - 1 = \frac{N}{n} \text{ or } \frac{383 - 22.9}{22.9} = \frac{N}{n} = \frac{m \times 100}{11.346 \times 74}$$

$$\text{Whence } m = 132.$$

(3) The Manometric Method. The apparatus used in this method is illustrated in Fig. 69. The manometric liquid is *n*-butyl phthalate because of its low density and low volatility. The apparatus is filled with solvent and solution as indicated, and evacuated. The difference in the height of the liquid in the two limbs of the manometer gives the difference between the vapour pressure of the pure solvent and the solution. This method suffers from the same disadvantages as the Barometric method. The differences of vapour pressure are too small to cause appreciable differences in the level of the liquid in the two limbs. However, the method works well with strong solutions and at high temperatures when the vapour pressures are also high. The entire apparatus can be conveniently placed in a hot bath and the determination made at any temperature.

(4) Walker and Ostwald's Dynamic Method. In this method a current of dry air drawn through two sets of bulbs A and B (Fig. 70) containing respectively (i) the

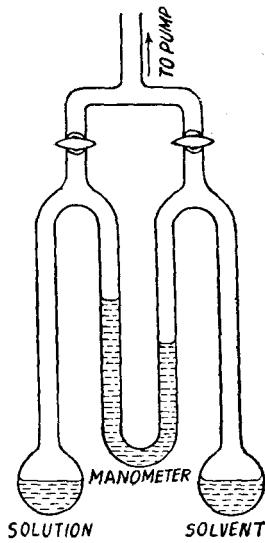


Fig. 69. Manometric method.

solution (vap. pressure p), and (ii) the pure solvent (vap. pressure p_s) it passes through the solution in bulbs A, the air becomes saturated

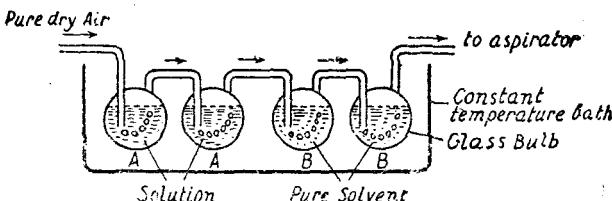


Fig. 70. Walker and Ostwald's method.

with vapour of the solvent. The amount of vapour the air takes up here is proportional to the vapour pressure p_s of the solution. But the vapour pressure of the solvent in bulbs B is greater than that in bulbs A by $(p - p_s)$. Hence as the air passes through the bulbs B it takes up more vapour, the amount being proportional to $(p - p_s)$. There will thus be a loss in weight of B which will be proportional to $(p - p_s)$. After passing through both the sets of bulbs the air gets saturated with an amount of solvent and the total loss in weight of A and B will, therefore, be proportional to p .

$$\text{Loss in weight of B} \propto (p - p_s).$$

$$\text{Loss in weight of A + B} \propto p$$

$$\therefore \frac{\text{Loss in weight of B}}{\text{Loss in weight of A + B}} = \frac{p - p_s}{p}$$

As the relative lowering of vapour pressure is independent of the temperature, it is not essential to carry out the experiment at any particular temperature. All parts of the apparatus must, of course, be kept at constant temperature.

As a check on the value of total loss in the two sets of bulbs, a set of calcium chloride tubes may be fixed at the end of the apparatus, if water is the solvent. These absorb all the water from the issuing air, and the increase in weight will be equal to the total loss in weight of A and B. In such a case

$$\frac{\text{Loss in weight of B}}{\text{Gain in weight of calcium chloride tubes}} = \frac{p - p_s}{p}$$

Walker and Ostwald's method has been extensively employed for the determination of molecular weights. It yields quite accurate results.

Example 1. A current of dry air was passed through a series of bulbs containing a solution of 3.458 gms. of a substance is 100 gms. of ethyl alcohol, and then through a series of bulbs containing pure alcohol. The loss of weight in the former series of bulbs was 0.9675 gm. and in the latter series 0.0255 gm. Calculate the molecular weight of the solute.

$$\text{Loss of weight in the first set of bulbs} = 0.9675 \text{ gm.}$$

$$\text{, " , second ,} = 0.0255 \text{ "}$$

$$\text{, " , two sets ,} = 0.9930 \text{ "}$$

$$\frac{p - p_s}{p} = \frac{\text{Loss of weight in second set}}{\text{Total loss of weight in the two sets}} = \frac{0.0255}{0.9930}$$

Since according to Raoult's Law :

$$\frac{p - p_s}{p} = \frac{wM}{mW}$$

$$\frac{0.0255}{0.9930} = \frac{3.458 \times 46}{m \times 100}$$

$$\therefore m = \frac{3.458 \times 46 \times 0.9930}{100 \times 0.0255} = 62$$

Example 2. Air was drawn through a solution containing 38·0 gms. of solute in 100 gms. of water and through water. The loss of weight of water was 0·0551 gm. and the total weight of water absorbed in a sulphuric acid tube was 2·2117 gms. What is the molecular weight of the dissolved substance?

In this case

$$\frac{p - p_s}{p} = \frac{\text{Loss of weight of water}}{\text{Gain in weight of } H_2SO_4 \text{ tube}}$$

$$= \frac{0.0551}{2.2117}$$

Since the solution is not very dilute we shall use Raoult's Law in the form

$$\frac{p - p_s}{p} = \frac{w}{m + \frac{W}{M}}$$

$$\frac{0.0551}{2.2117} = \frac{38}{m + \frac{100}{18}}$$

$$= \frac{38 \times 18}{(38 \times 18) 100m}$$

$$\text{or } (2.2117 - 0.0551) \times 38 \times 18 = 0.0551 \times 100 \times m$$

$$\text{or } 2.1566 \times 38 \times 18 = 5.51 m$$

$$\text{Whence } m = 267.7.$$

Elevation of Boiling Point and Molecular Weights

Any liquid boils at the temperature at which its vapour pressure is equal to that of the atmosphere and since the vapour pressure of a solution is always less than the vapour pressure of the pure solvent it follows that the boiling-point of a solution will always be higher than that of the pure solvent. If we plot the vapour pressure of the solvent and of two solutions of different concentrations against the temperature, a series of regular curves as shown in Fig. 71 are obtained. If the line PC represents the atmospheric

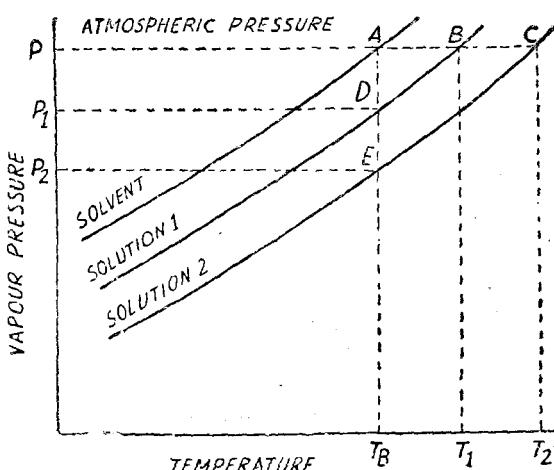


Fig. 71. Relation between vapour pressure and boiling-point.

pressure, the temperature T_B will be the boiling-point of the solvent and T_1 and T_2 that of the solution 1 and solution 2 respectively.

For very dilute solutions the curves are approximately parallel straight lines. Thus the triangles ACE and ABD are similar and

$$\frac{AC}{AB} = \frac{AE}{AD}$$

or

$$\frac{T_2 - T_B}{T_1 - T_B} = \frac{p - p_2}{p - p_1}$$

where p is the vapour pressure of the solvent, p_1 and p_2 that of the solutions 1 and 2 respectively.

If ΔT and Δp represent the elevation of boiling-point and the lowering of vapour pressure as compared with the pure solvent, it follows

$$\frac{\Delta T_2}{\Delta T_1} = \frac{\Delta p_2}{\Delta p_1}$$

that is, the elevation of boiling-point is proportional to the lowering of vapour pressure or $\Delta T \propto \Delta p$.

But

$$\frac{\Delta p}{p} = \frac{wM}{mW} \quad \dots\dots \text{Raoult's equation}$$

∴

$$\Delta p = pM \frac{w}{mW}.$$

For the same solvent, M is constant and p , the vapour pressure at the boiling-point is also constant.

$$\Delta p \propto \frac{w}{mW}$$

But we have shown that $\Delta T \propto \Delta p$

$$\Delta T \propto \frac{w}{mW}$$

or

$$\Delta T = k \frac{w}{mW}$$

The constant k is called the *boiling-point constant* for the solvent.

When $\frac{w}{m} = 1$ and $W = 1$, the expression

$$\Delta T = k \frac{w}{mW} \text{ is reduced to } \Delta T = k.$$

Thus the boiling-point constant is equal to the elevation of boiling-point which would theoretically be produced if 1 gram molecule of a non-volatile solute were dissolved in one gram of the solvent.

Ordinarily, the **molecular elevation constant** or the **boiling-point constant** of a solvent is defined as the elevation of boiling point which would be produced by dissolving one gram molecule of the solute in 100 grams of the solvent.

In this case, since in the expression $\Delta T = k \frac{w}{mW}$

$$\frac{w}{m} = 1, \text{ and } W = 100,$$

$$\Delta T = \frac{k}{100} = K \text{ or } k = 100 K$$

Hence

$$\Delta T = 100 K - \frac{w}{Wm}$$

or

$$m = \frac{100 Kw}{\Delta TW}$$

where m = molecular weight of the solute ; K = molecular elevation constant ; w = weight of solute ; ΔT = elevation of boiling-point and W = weight of solvent.

Since the elevation of boiling-point can be determined with comparative ease in the laboratory, the above expression is employed for the calculation of molecular weights of dissolved substances.

Van't Hoff showed by the thermodynamical reasoning that

$$K = \frac{0.02T^2}{L},$$

where T is the boiling-point of the solvent on the absolute scale and L is the latent heat of vaporisation in calories per gram of solvent. Thus, for water $T = 373$ and $L = 537$

$$K = \frac{0.02 \times 373 \times 373}{537} = 5.18$$

Other solvents have different boiling-point constants.

Water	... 5.2°C	Benzene	... 26.7°C
Ethyl alcohol	... 11.5°C	Ether	... 21.0°C

Sometimes in the determination of molecular weight the amount of the solvent is noted not by weight but by volume. This makes no difference in the expression for the calculation of the molecular weight, except that a different elevation constant K is employed, which is equal to the ordinary boiling-point constant divided by the density of the solvent at its boiling-point.

Methods of determining the Elevation of Boiling-Point.

For determining the elevation of boiling-point the following methods are commonly employed :—

- (a) *Beckmann's method.*
- (b) *Landsberger's method.*
- (c) *Cottrell's method.*

Beckmann's Method. The solvent is boiled in the boiling tube (Fig. 72) which has a platinum wire fused through the bottom and contains a layer of glass beads to promote regular boiling and to prevent superheating of solvent. The boiling tube is surrounded by a glass outer jacket in which the same solvent is kept boiling. This prevents radiant heat from affecting the apparatus. Both the inner tube and the

outer jacket are fitted with condensers. The whole apparatus is heated on an asbestos box provided with chimneys for promoting convection currents. The box screens off the direct heat of the flame and thus avoids superheating of the solvent. The thermometer used to note the rise of boiling-point is of special type (Beckmann Thermometer) with a scale of 6° graduated to 0.01°C .

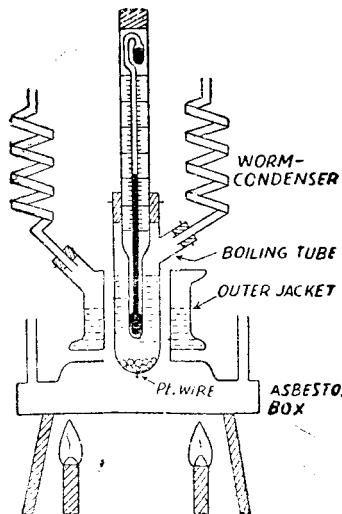


Fig. 72. Beckmann's Boiling-point apparatus.

In a determination, weighed quantity (20 grams) of solvent is placed in the boiling tube and heated gently until a steady temperature is reached. This is the boiling-point of the solvent. An accurately weighed quantity $0.2-0.5$ gram of the substance whose molecular weight is to be determined is then dropped into the solvent through the side tube and temperature again brought to steady state which indicates the boiling-point of the solution.

The older form of the apparatus described above, which was designed for heating by gas has largely been superseded by the apparatus designed for electrical heating. The new type of apparatus permits of results being obtained more rapidly and with greater accuracy.

Landsberger's Method. This method is the most convenient for the determination of the elevation of boiling-point in the laboratory. In this method the solution is heated by bubbling through it the vapour of the boiling solvent in an apparatus of the type shown in Fig. 73. It consists of (i) A *boiling flask* which sends vapour of the solvent into the inner tube. (ii) An *inner boiling tube* which has a bulb with a hole in the side, and is graduated in c.c.s. It is fitted with a Beckmann thermometer (or an ordinary thermometer graduated to 0.01°C) and a glass tube with a bulb blown at the end which has many holes in it. This *rose-head* ensures uniform distribution of the vapour through the solvent. The bulb reflects

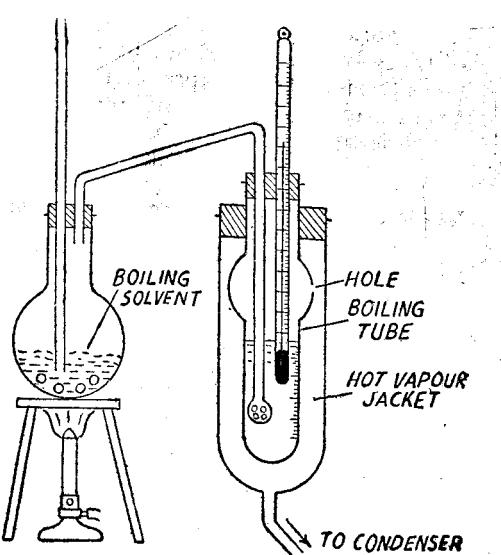


Fig. 73. Landsberger's apparatus.

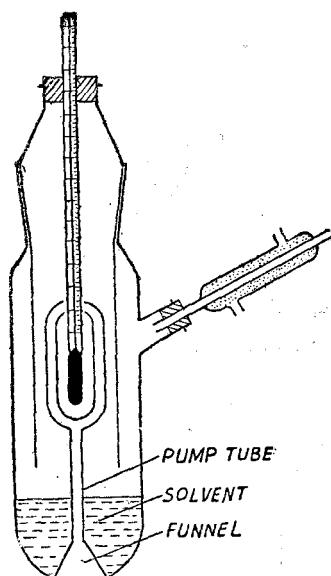
back any particles of the solvent which happen to fly about when the boiling becomes brisk. (iii) An outer covering-tube which receives hot vapour from the inner tube through the hole. This forms a protecting jacket round the boiling tube, prevents the loss of heat from it due to radiation and, in addition, protects it from draughts of air.

In an actual determination 5 to 7 c.cs. of solvent are placed in the inner tube and the vapour of the solvent passed through it. At the start the solvent vapour condenses and as more vapour is passed the liquid becomes warmer and in time boils. As soon as the temperature has become constant the thermometer reading is taken. This is the boiling-point of the pure solvent. Now the supply of solvent vapour is cut off temporarily and a weighed quantity (0·2-0·5 gram) of the substance whose molecular weight is to be determined is dropped into the solvent in the boiling tube. The boiling-point of the solution is then determined as before. Immediately after the temperature is read off, the thermometer and the rose head are carefully raised out of the solution and the volume of the solution noted. Further quantities of the substance can be added to the solution and the boiling-point determined after each addition.

Cottrell's Method. Cottrell (1919) designed an improved boiling-point apparatus (Fig. 74) which eliminates fluctuations of temperature and errors due to superheating. The apparatus consists of a boiling tube into the neck of which fits a hollow stopper. The lower edge of the stopper projects below the neck so as to form a cylinder enclosing the bulb of the thermometer and the branches of the pump-tube. This cylinder serves as a jacket for the thermometer and prevents the condensed liquid falling from the condenser from coming into contact with the thermometer.

At first a known amount of the solvent is made to boil by means of a gas flame, protected from draughts with the help of screens. As the solvent boils the bubbles of vapour which form under the funnel rise up in the tube carrying with them liquid which is projected against the stem of the thermometer. In this way the bulb of the thermometer is kept bathed in the boiling liquid. The constant temperature is soon obtained which gives the boiling-point of the pure solvent. Now a weighed amount of substance is dropped in the solvent and the boiling-point of the solution determined in the same way as for the solvent.

Example 1. The solution of 2·78 gms. of benzophenone in 55·6 gms. of acetone had its boiling-point raised by 0·472. Find the molecular weight of benzophenone. Elevation constant for acetone is 17·2°.



g. 74. Cottrell's Boiling-point apparatus.

$$\text{It has been shown that } m = \frac{100Kw}{\Delta TW}$$

where K = elevation constant, w = weight of solute.
 ΔT = elevation of boiling-point, W = weight of solvent.

In the present case

$$K = 17.2^\circ; w = 2.78 \text{ gms.}; W = 55.6 \text{ gms.}; \Delta T = 0.472^\circ$$

Substituting these values, we have

$$m = \frac{100Kw}{\Delta TW} = \frac{100 \times 17.2 \times 2.78}{5.56 \times 0.472} = 182.2$$

Example 2. The boiling-point of chloroform was raised by 0.323° when 0.5143 gm. of anthracene was dissolved in 35 gms. Calculate the molecular weight of anthracene. ($K = 39.0^\circ$).

From the definition of elevation constant we know that K is the elevation produced when 100 gms. of solvent contain m gm. where $m = m.$ wt. of solute.

In the present case, 100 gms. of chloroform contain

$$\frac{0.5143 \times 100}{35} \text{ gms. of anthracene}$$

Thus 0.322° elevation is produced when 100 gms. of

$$\text{chloroform contain } \frac{0.5143 \times 100}{35} \text{ gms. of anthracene}$$

39° (K) elevation is produced when 100 gms. of

$$\text{chloroform contain } \frac{0.5143 \times 100 \times 39}{35 \times 0.323} \text{ gms. of anthracene}$$

$$= 177.4 \text{ gms.}$$

∴ Molecular weight of anthracene = 177.4 .

Depression of Freezing Point and Molecular Weights.

A solvent and a solution each has a definite vapour pressure even at very low temperatures. A solid also has a vapour pressure

although it is extremely small. If we plot the vapour pressure curves for the solid solvent, liquid solvent, and two solutions of different concentrations, we obtain the diagram shown in Fig. 75. The freezing-point of the pure solvent is given by the temperature T_F when both the liquid and the solid solvents are in equilibrium. Since the vapour pressure of a solution is always less than the vapour pressure of the solvent, the

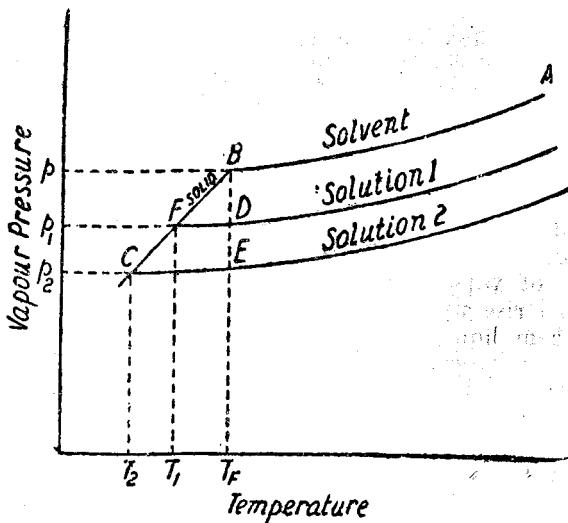


Fig. 75. Relation between vapour pressure and freezing-point.

vapour pressure curves of solutions will cut the vapour pressure curve

of solid solvent at lower temperatures T_1 and T_2 which represent the freezing-points of the solutions 1 and 2 respectively.

For very dilute solutions the curves FD and CE are almost parallel straight lines and CB is also approximately a straight line. Since the triangles BEC and BDF are similar.

we have $\frac{EC}{DF} = \frac{BE}{BD}$ or $\frac{T_F - T_2}{T_F - T_1} = \frac{p - p_2}{p - p_1}$

where p is the vapour pressure of the solvent, p_1 and p_2 that of solutions 1 and 2 respectively.

If ΔT and Δp represent the depression of freezing-point and the lowering of vapour pressure respectively as compared with the pure solvent, it follows

$$\frac{\Delta T_2}{\Delta T_1} = \frac{\Delta p_2}{\Delta p_1}$$

that is, **the depression of the freezing-point is proportional to the lowering of the vapour pressure, or**

$$\Delta T \propto \Delta p$$

But $\frac{\Delta p}{p} = \frac{wM}{mW}$...Raoult's Equation

Since for the same solvent, M is constant and its vapour pressure p at the freezing-point is also constant.

$$\Delta p \propto \frac{w}{mW}.$$

But we have already shown that $\Delta T \propto \Delta p$

$$\Delta T \propto \frac{w}{mW} \text{ or } \Delta T = k \frac{w}{mW}.$$

The constant k is called the *freezing-point constant* for the solvent.

When $\frac{w}{m} = 1$ and $W = 1$, the expression $\Delta T = k \frac{m}{mW}$ is reduced to $\Delta T = k$.

Thus, the freezing-point constant is equal to the depression of the freezing-point which would theoretically be produced if 1 gram-molecule of a non-volatile solute were dissolved in one gram of the solvent.

Ordinarily, the **molecular depression constant** or the **freezing-point constant** of a solvent is defined as the depression of freezing-point which would be produced by dissolving one gram-molecule of the solute in 100 grams of the solvent. In this case in the expression

$$\Delta T = k \frac{w}{Wm}, \quad \frac{w}{m} = 1 \text{ and } W = 100, \quad \Delta T = \frac{k}{100} = K$$

Hence,

$$\Delta T = \frac{100Kw}{mW}$$

Or

$$m = \frac{100Kw}{\Delta TW}.$$

where m = molecular weight of the solute.

K = freezing-point constant.

w = weight of the solute.

W = weight of solvent.

This expression is employed for calculating molecular weights of dissolved substances.

According to Van't Hoff, $K = \frac{0.02T^2}{L}$,

where T is the freezing-point of the solvent on absolute scale and L the latent heat of fusion in calories per gram.

Thus for water, $T = 273^\circ$, and $L = 80$ calories

$$K = \frac{0.02 \times 273 \times 273}{80} = 18.63$$

The value of K for some solvents is given

Water	... 18.6°C	Acetic acid	... 38.2°C
Benzene	... 51.2°C	Phenol	... 7.3°C

Methods of determining the Depression of Freezing-point.

Beckmann's Method. The apparatus which is almost exclusively employed for the determination of the lowering of freezing-point was designed by Beckmann (1838) and is shown in Fig. 76. It consists of (i) the inner *freezing-point tube* provided with a side tube for introducing the solute and fitted with Beckmann thermometer* and a platinum stirrer; (ii) the outer air-jacket surrounding the inner tube which ensures a slower and more uniform rate of cooling of the liquid; (iii) a stout glass or stone cylinder C which contains a suitable cooling mixture and is provided with a stirrer.

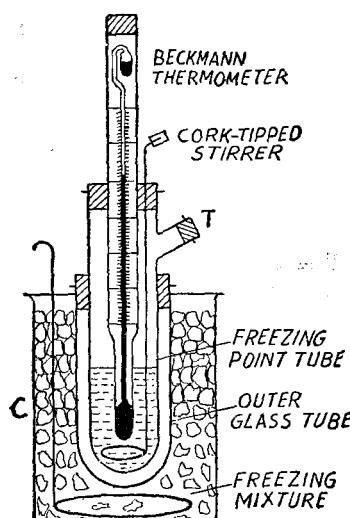


Fig. 76. Apparatus for the determination of the molecular weight of dissolved substance by the depression of the freezing-point.

point tube again in the freezing bath and allow the temperature to

In an actual determination 15—20 grams of the solvent is taken in the inner *freezing-point tube* and the apparatus set up as shown in the diagram, so that the bulb of the thermometer is completely immersed in the solvent. First determine the approximate freezing-point of the solvent by directly cooling the f. pt. tube in the cooling bath. When this has been done, melt the solvent and place the freezing-

***Beckmann Thermometer.** This is a very sensitive thermometer graduated in one hundredths of a degree over a range of 6 degrees. The unique feature of this thermometer, however, is the small mercury reservoir at the top. The amount of mercury in this reservoir can be decreased or increased by tapping the thermometer gently. In this way the thermometer is adjusted so that the top of mercury thread will rest at any desired point on the scale when the instrument is placed in the freezing solvent. This thermometer has proved of great service while noting small differences in temperature.

fall. When it has come down to within about a degree of the approximate f. pt. determined above, dry the tube and place it cautiously in the air jacket. Let the temperature fall slowly and when it has come down again to about 0.5° below the freezing-point, stir vigorously. This will cause the solid to separate and the temperature will rise owing to the latent heat set free. Note the highest temperature reached and repeat the process to get concordant value of freezing-point.

The freezing-point of the solvent having been accurately determined, the solvent is remelted by removing the tube from the bath, and a weighed amount (0.1-0.2 gm.) of the solute is introduced through the side tube T. Now the freezing-point of the solution is determined in the same way as that of the solvent. A further quantity of solute may then be added and another reading taken. Knowing the depression of the freezing-point, the molecular weight of the solute can be determined. This method gives accurate results, if the following precautions are observed :

- (i) The supercooling should not exceed 0.5°C .
- (ii) The stirring should be uniform at the rate of about one movement per second.
- (iii) The temperature of the cooling bath should not be 4° to 5° below the freezing-point of the liquid.

Rast's Camphor Method. Rast (1922) has devised a simple method which for practical purposes is very convenient. He makes use of the fact that camphor has a very high molecular depression. One gram-molecule of a substance dissolved in 100 grams of camphor produces a depression of 400°C . In this case depression is so great that it can easily be determined with an ordinary thermometer.

A definite weight of the substance whose molecular weight is to be determined is mixed intimately with a known weight of camphor and the melting point determined in the usual way in a capillary tube. This is equal to the freezing-point of the solution of the substance in camphor. The depression of freezing or melting point so found can be employed for calculating molecular weight.

Besides camphor, other substances have also been suggested for use as "solvents". These are camphorquinone (m. pt. 197.2°C , molecular depression 457°C), hexachloroethane (m. pt. 187°C , molecular depression 477°C) and tetrabromethane (m. pt. 93°C , molecular depression 86.7°). In the choice of the "solvent" the essential point is to see that the solute is *perfectly soluble* and not isomorphous with it.

The results obtained are approximate and are within 5% of the actual values. The method, however, is extremely useful when very small quantity of a substance soluble in camphor is available and which does not decompose when heated to the melting point of camphor.

Example 1. 5 grams of a substance dissolved in 50 grams of water lowered the freezing-point by 1.2°C . Calculate the molecular weight of the substance. The molecular depression for water is 18.5°C .

$$\text{We know that } m = \frac{100Kw}{\Delta TW},$$

where K = molecular depression for solvent, w = weight of solute.

ΔT = depression of freezing-point, W = weight of solvent.
In the present case, $K = 18.5^{\circ}$;

$$w = 5 \text{ gms.}; W = 50 \text{ gms. and } \Delta T = 1.2^{\circ}\text{C}.$$

Substituting these values we have,

$$m = \frac{100Kw}{\Delta TW} = \frac{100 \times 18.5 \times 5}{50 \times 1.2} = 154.2.$$

Example 2. 0.440 gm. of a substance dissolved in 22.2 gms. of benzene lowered the freezing-point of benzene by 0.567°. Calculate the molecular weight of the substance. ($K = 51.2^\circ$).

K is the depression of freezing-point when 100 gms. of solvent contain m gms., where m = molecular weight of the solute.

In this case 100 gms. of benzene contain $\frac{0.440 \times 100}{22.2}$ gms. of the substance

Thus 0.567° depression is produced when 100 gms. of

benzene contain $\frac{0.440 \times 100}{22.2}$ gms. of the substance

51.2°C (K) depression will be produced when 100 gms. of

benzene contain $\frac{0.440 \times 100 \times 51.2}{22.2 \times 0.567}$

= 178.9 gms. of the substance

∴ Molecular weight of the substance is 178.9.

ABNORMAL MOLECULAR WEIGHTS

When the molecular weights of certain substances are determined by one or more of the methods described above, the results obtained do not agree with the normal molecular weights calculated from their accepted chemical formulae. In some cases the values obtained are too large and in other cases they are too small.

The elevation of boiling point (ΔT) or the depression of freezing-point of a liquid by a dissolved substance is proportional to the lowering of vapour pressure and thus to the osmotic pressure of the solution. But the osmotic pressure of a solution depends on the number of solute particles in a given volume. Therefore,

$$\Delta T \propto \text{Osmotic Pressure} \propto \text{number of solute particles.}$$

$$\text{Since Molecular Weight} \propto \frac{1}{\Delta T} \dots \dots \dots m = \frac{100Kw}{\Delta TW}$$

$$\text{we may say that } M/Wt. \propto \frac{1}{\text{Number of solute particles.}}$$

For substances which dissociate or associate in solution the number of particles in solution differs from the normal number and this causes the molecular weight to be abnormal.

$$\frac{\text{Observed Mol. Wt.}}{\text{Normal Mol. Wt.}} = \frac{\text{Normal number of solute particles}}{\text{Number of solute particle after dissociation or association}}$$

Dissociation

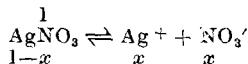
Soluble salts, acids and bases are known to ionise in solution. One normal molecule in this way yields two or more ions and thus the number of soluble particles increases than the normal number. **The observed molecular weights of substances which undergo dissociation in solution will, therefore, have a lower value than the normal molecular weights.**

Example 1. 0.3015 gm. of silver nitrate when dissolved in 28.40 gms. of water depressed the freezing point by 0.212°. To what extent is silver nitrate dissociated? (K for water = 18.5°)

$$\text{Observed Mol. Wt.} = \frac{100Kw}{\Delta TW} = \frac{100 \times 18.5 \times 0.3015}{0.212 \times 28.4} = 92.64$$

Normal Mol. Wt. calculated from the formula $\text{AgNO}_3 = 108 + 114 + 48 = 170$

If x is the degree of dissociation (fraction dissociated) of silver nitrate



One normal molecule in solution will yield x ions of silver and x ions of nitrate leaving behind $(1-x)$ molecules of silver nitrate undissociated. Thus the total number of particles in solution will be $(1-x) + x + x = 1 + x$ compared to one normal molecule if silver nitrate were undissociated.

$$\frac{\text{Normal Mol. Wt.}}{\text{Observed Mol. Wt.}} = \frac{\text{Number of particles after dissociation}}{\text{Normal number of solute particles}}$$

In the present case

$$\frac{170}{92.64} = \frac{1+x}{1} \text{ or } x = \frac{170}{92.64} - 1 = 0.835.$$

Hence silver nitrate is 83.5% dissociated.

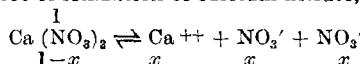
Example 2. A solution containing 1.23 gms. of calcium nitrate in 10 gms. of water boils at 100.975°C. Calculate the degree of ionization of the salt.

Molecular elevation of boiling-point of water = 5.2°C.

$$\text{Observed Mol. Wt.} = \frac{100Kw}{\Delta TW} = \frac{100 \times 5.2 \times 1.23}{0.975 \times 10} = 65.6.$$

$$\text{Normal Mol. Wt. calculated from formula, } \text{Ca}(\text{NO}_3)_2 = 40 + 2(14 + 48) \\ = 164$$

If x is the degree of ionization of calcium nitrate,



$$\frac{\text{Normal Mol. Wt.}}{\text{Observed Mol. Wt.}} = \frac{\text{Number of particles after dissociation}}{\text{Normal number of particles}}$$

$$\frac{164}{65.6} = \frac{1+2x}{1} \text{ or } 2x = \frac{164}{65.6} - 1.$$

$$\therefore x = 0.75$$

Hence calcium nitrate is 75% ionised.

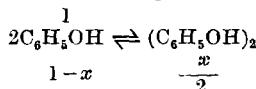
Association

Certain organic substances undergo association in aqueous solution. In such a case the number of solute particles decreases than the normal number and, therefore, the observed molecular weight is higher than the normal molecular weight.

Example. Phenol (C_6H_5OH) associates in water to double molecules. When 0.6677 gm. of phenol is dissolved in 35.5 gms. of water it depresses the freezing point by 0.215°. Calculate the degree of association of phenol. Molecular depression constant of water = 18.50°.

$$\text{Observed mol. wt. of phenol} = \frac{100Kw}{\Delta TW} = \frac{100 \times 18.5 \times 0.6677}{0.215 \times 35.5} = 161.84$$

Normal mol. wt. calculated from formula $C_6H_5OH = 6 \times 12 + 5 + 16 + 1 = 94$
Since phenol associates to give bi-molecules in solution



one normal molecule will yield $\frac{x}{2}$ bi-molecules leaving behind $(1-x)$ molecules of phenol unassociated. Thus the total number of particles in solution will be $(1-x) + \frac{x}{2} = 1 - \frac{x}{2}$ compared to 1 normal molecule if phenol were not associated.

$$\frac{\text{Normal mol. wt.}}{\text{Observed mol. wt.}} = \frac{\text{Number of particles after association}}{\text{Normal number of solute particles}}$$

$$\frac{94}{161.84} = \frac{1 - x/2}{1} \quad \text{or} \quad \frac{x}{2} = 1 - \frac{94}{161.84}$$

or $x = 0.838$.

Hence phenol is 83.8% associated.

Van't Hoff Factor *i*

If instead of examining the molecular weights, we note the values of the various colligative properties for solutions of electrolytes and non-electrolytes, we find that the osmotic pressure, depression of f. pt., lowering of vapour pressure and elevation of b. pt. are all higher for solutions of electrolytes than of non-electrolytes of the same molecular concentration.

The number of times a colligative property of an electrolyte is greater than that of a non-electrolyte of the same concentration is termed the **Van't Hoff Factor** and is denoted by the symbol *i*.

$$i = \frac{\text{observed value for an electrolyte}}{\text{normal value for non-electrolyte}}$$

QUESTIONS AND PROBLEMS

A. Osmotic Pressure

1. What is a semi-permeable membrane and how is it prepared? Explain the action of such a membrane.

2. How can a semi-permeable membrane be prepared and used for the determination of osmotic pressure of a solution of sucrose. Calculate the osmotic pressure of an aqueous solution of glucose ($C_6H_{12}O_6$) containing 60 gms. in 600 c.c. at $0^\circ C$. (Mysore B.Sc., 1953)

3. Explain what is meant by osmotic pressure. How can you measure it? At $24^\circ C$ the osmotic pressure of a cane sugar solution is 2.5 atmospheres. What is the concentration of the solution in gm. mols. per litre? (Allahabad B.Sc., 1938)

4. What is meant by osmotic pressure and how may this be used to determine the molecular weight of a substance? State the limitations of the method.

A solution containing 3.12 gms. of a substance per litre gives an osmotic pressure of 1.27 atmospheres at $25^\circ C$. Calculate the molecular weight of the substance. (Calcutta B.Sc., 1942)

5. What is osmotic pressure? How is it determined? Discuss the mechanism of osmosis. (Annamalai B.Sc., 1953; Agra B.Sc. 1957)

6. A 4 per cent solution of sugar gave an osmotic pressure of 208.2 cms. of mercury at $15^\circ C$. Find its molecular weight. (Aligarh B.Sc., 1954)

7. Calculate the osmotic pressure at $25^\circ C$ of a 3 per cent solution of urea, (Molecular weight of urea = 60). (Banaras B.Sc., 1952)

8. What is osmotic pressure and how is it used to determine the molecular weight of a substance?

A solution of glucose, containing 18 grams of the substance per litre, gave an osmotic pressure of 2.4 atmospheres at $27^\circ C$. Calculate the molecular weight of glucose. (Banaras B.Sc., 1953)

9. What is meant by osmotic pressure and how is it measured ? A solution of a non-electrolyte containing 0.220 gram. in 120 c.cs. of water gave an osmotic pressure of 56 cms. of Hg at 30°C. Calculate its molecular weight.

(Travancore B.Sc., 1954)

10. Explain the term 'osmotic pressure'. How is it determined ? What are isotonic solutions ? De Vries found that 3.42% solution of cane sugar was isotonic with a 5.96% solution of raffinose. Calculate the m. wt. of raffinose.

(Agra B.Sc., 1952)

11. Calculate the concentration of a solution of glucose that is isotonic, at the same temperature with solution containing 6.2 gms. of urea per litre.

(Delhi B.Sc., 1945)

12. Calculate the gas constant R in litre-atmospheres from the observations that a solution containing 34.2 gms. of cane sugar in 1 litre of water has an osmotic pressure of 2.522 atmospheres at 20°C.

13. Discuss the statement that a substance in very dilute solution behaves like a gas and show how the fact is made use of in the determination of molecular weights.

(Andhra B.Sc., 1952)

14. State the laws of osmotic pressure. Discuss its analogy to gas pressure. Explain how you would determine the molecular weight of a substance in solution from its osmotic pressure. Is the method applicable to all cases ?

(Calcutta B.Sc., 1954)

15. Discuss an experiment to determine the osmotic pressure of a solution. How can you explain the abnormal osmotic pressure observed in case of electrolytes ?

(Aligarh B.Sc., 1953)

16. What is the osmotic pressure of a solution and how is it measured ? Explain how the degree of dissociation of an electrolyte can be determined by the measurement of osmotic pressure.

(Agra B.Sc., 1948)

17. What is the osmotic pressure of a decinormal solution of sodium chloride at 27°C, assuming that the salt is 90 per cent dissociated at this dilution ?

(Punjab B.Sc., 1939)

18. "The behaviour of a solute in dilute solution is similar to its behaviour in the form of a gas occupying the same volume as the volume of the solution." Discuss fully the above statement.

The osmotic pressure of a 0.5N solution of NaCl is 20.29 atmospheres at 18°C. Calculate the degree of dissociation of the salt. (Na = 23 ; Cl = 35.5).

(Delhi B.Sc., 1939)

19. What is osmotic pressure and how is it measured ? Explain how the degree of dissociation of an electrolyte may be determined by osmotic pressure measurements.

(Nagpur B.Sc., 1953)

20. How can measurement of the osmotic pressure be employed for molecular weight determination ? What substances produce abnormal result and why ?

21. Discuss the properties of dilute solutions with special reference to the analogy between gases and dissolved substances. What is meant by Van't Hoff's 'i' and how is this explained ?

(Nagpur B.Sc., 1955)

22. Explain what is meant by osmotic pressure and describe in detail a method for its determination. State the laws of osmotic pressure and also the conditions under which these are true.

A solution containing 1.732 gms. of a compound in 100 c.cs. is isotonic with a solution of cane sugar containing 4.23 grams per 100 c.cs. Calculate the molecular weight of the compound.

(Patna B.Sc., 1955)

23. Describe a method for the direct determination of osmotic pressure of dilute solutions. How is this measurement used for finding out molecular weights ? Calculate the osmotic pressure of a 5 per cent urea solution at 0°C.

(Agra B.Sc., 1955)

24. What is meant by the osmotic pressure of a solution ? How will you determine the osmotic pressure of a solution ?

Find the osmotic pressure of a solution made by dissolving 6 grams of urea (CON_2H_4) in 1120 c.cs. of the solution in water at 27°C.

$$R = 0.08205 \text{ litre-atmospheres, } C = 12, O = 16, H = 1, N = 14.$$

(Rangoon B.Sc., 1956)

25. Describe a method for the direct determination of osmotic pressure of dilute solutions. How is this measurement used for finding out molecular weight?

Calculate the osmotic pressure in atmosphere of a N/10 solution of cane sugar at 0°C. [C = 12, H = 1, O = 16]. (Delhi B.Sc., 1956)

26. How is osmotic pressure of an aqueous solution determined? Calculate the osmotic pressure of a 5% solution of sucrose in water at 27°C. (Madras B.Sc., 1955)

27. Write a brief essay on the mechanism and measurement of osmotic pressure. (Osmania B.Sc., 1955)

28. State the laws of osmotic pressure and clearly bring about the analogy between the gas pressure and osmotic pressure. Indicate how the molecular weight of a non-volatile substance can be obtained from a knowledge of the osmotic pressure of its solution. (Mysore B.Sc., 1955)

29. What led Van't Hoff to introduce his factor 'i'? How is it determined experimentally?

A 3·4 per cent solution of BaCl_2 is isotonic with a 7·2 per cent solution of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$). Calculate the degree of dissociation and the Van't Hoff factor 'i' for the BaCl_2 solution.

$$(H = 1; C = 12; O = 16; Cl = 35·5; Ba = 137·3)$$

(Poona B.Sc., 1956)

30. Write a note on Van't Hoff theory of dilute solution.

A solution of cane sugar at 27°C produces an osmotic pressure of 4·93 atmospheres. Calculate the freezing point of this solution. (Molecular depression constant for 100 gms. of water = 18·6°C. (Lucknow B.Sc., 1956)

31. What do you understand by the term osmotic pressure? Describe an apparatus for the measurement of osmotic pressure of aqueous solutions.

0·1 N solution of sodium chloride is found to be electrolytically dissociated to the extent of 79% at 0°C. What is the osmotic pressure of the solution? (Bombay B.Sc., Subs. 1956)

32. What is osmotic pressure? Describe an accurate method of determining it experimentally. How do you explain the abnormal behaviour of electrolytes in osmotic pressure measurement? (Travancore B.Sc. 1957)

33. What do you understand by 'osmotic pressure' of a solution? Calculate the osmotic pressure of a 5 per cent solution of cane sugar at 15°C. (C = 12, H = 1, O = 16). (Allahabad B.Sc., 1958)

34. What is osmotic pressure of a solution and show how is it determined?

4·0 grams of a substance present in 100 c.cs. of its solution in water gave rise to an osmotic pressure of 5·1 atmospheres at 22°C. Calculate the molecular weight of the substance. (Aligarh B.Sc., 1957)

35. Describe a method for measuring the osmotic pressure of a concentrated solution.

Will 0·01 M solution of cane sugar and sodium chloride in water have the same osmotic pressure at a given temperature? Give reasons for your answer. (Jammu & Kashmir B.Sc., 1957)

36. How is osmotic pressure demonstrated? How is it measured? What is the function of the semi-permeable membrane? State the relationship between the lowering of vapour pressure and osmotic pressure and its application. (Delhi B.Sc., 1958)

37. What is a semi-permeable membrane? Give two examples of such a membrane. (Bombay B.Sc., 1958)

38. Describe in detail a method for determining the osmotic pressure of a concentrated solution of urea. Discuss the mechanism of osmotic pressure. (Andhra B.Sc., 1958)

39. Write an essay on Van't Hoff's contributions to the study of dilute solutions and the developments based on them. (Delhi B.Sc., 1959)

40. What do you understand by "Osmotic pressure of a solution"? Describe one method of determining it.

A solution of 10·2 gms. of glycerine per litre is isotonic with a solution of glucose containing 2 grams in 100 c.cs. Calculate the molecular weight of glycerine. The molecular weight of glucose is 180. (Poona B.Sc., 1959)

41. Discuss Osmotic Pressure. What is Van't Hoff's theory of dilute solutions ?

Calculate the concentration of that solution of glucose which is isotonic with a solution containing 6 gms. of urea per litre.

(Mol. Wt. of glucose = 180 ; Mol. Wt. of urea = 60)

B. Lowering of Vapour Pressure

1. Show how the lowering of vapour pressure caused by dissolving a non-volatile solute in a solvent is related to osmotic pressure of the solution.

2. Deduce a relation between the lowering of the vapour pressure of a solvent produced by the small amounts of a normal solute and the molecular weight of the solute. The vapour pressure of a 2·1% aqueous solution of a none-electrolyte at 100°C is 755 mm. Calculate the molecular weight of the solute.

3. What do you understand by 'relative lowering of vapour pressure' of a solvent by a solute ? Derive its relation to the molecular weights of the solvent and the solute. Describe an experiment to find the molecular weight of a solute by its help.

4. Show how the lowering of vapour pressure caused by dissolving a non-volatile solute in a solvent is related to the osmotic pressure of a solution.

The vapour pressure of ether at 20°C is 442 mm. and that of a solution of 6·1 gms. of benzoic acid in 50 gms. of ether is 410 mm. at the same temperature. Calculate the molecular weight of benzoic acid in ether.

(Nagpur B.Sc., 1953)

5. Define and illustrate osmosis. What is the relation between the lowering of the vapour pressure of a solution and its osmotic pressure ?

(Gauhati B.Sc., 1953)

6. Derive Raoult's equation for vapour pressure lowering. Discuss its applicability.

(Andhra B.Sc., 1954)

7. Derive an expression showing the relation between the relative lowering of the vapour pressure and the osmotic pressure of a dilute solution of a non-volatile solute in a solvent.

(Travancore B.Sc., 1953)

8. State Raoult's law. Explain how it can be used for determining molecular weight of a dissolved substance. The vapour pressure of a solution containing 13 gms. of solute in 100 gms. of H₂O at 28° is 27·371 mm. Calculate the molecular weight of the solute. The vapour pressure of water at this temperature is 28·065 mm.

(Gauhati B.Sc., 1953)

9. The vapour pressure of pure water at 0°C is 4·579 mm. of mercury. A solution of lactose (8·45 grams in 100 grams of water) has a vapour pressure of 4·559 mm. at the same temperature. Calculate the molecular weight of lactose.

(Delhi B.Sc., 1954)

10. Pure and dry nitrogen gas is slowly bubbled through a solution of 2·25 gms. of a non-volatile organic compound in 150 gms. of benzene, and then bubbled through pure benzene. The solution is found to be 2·1540 gms. lighter while the pure benzene suffered a loss in weight of 0·160 gms. Calculate the molecular weight of the dissolved substance.

(Calcutta, B.Sc., 1941)

11. A current of dry air was drawn through a solution containing 1·75 gms. of a non-volatile substance in 50 gms. ethyl alcohol (A). The same current was then bubbled through pure alcohol (B). The loss of weight of A was 0·8759 gm. when that of B was 0·0241 gm. Calculate the molecular weight of the dissolved substance. How far can the calculated molecular weight be regarded as the correct molecular weight ?

(Patna B.Sc., 1953)

12. Explain briefly the relationship between the decrease of vapour pressure of a solvent and the molecular weight of the solute dissolved in this solvent. Describe an experimental method of measuring this lowering of vapour pressure.

A current of dry air is passed through a solution containing 5 grams of phenol in 50 grams of water, and then through pure water. If the loss in weight

of the former is 1.85 grams and of latter is 0.036 gram, calculate the molecular weight of phenol. (Utkal B.Sc., 1954)

13. Derive Raoult equation for vapour pressure lowering and explain how this can be used to obtain the molecular weights of dissolved substances. (Andhra B.Sc., 1955)

14. Derive Raoult's Law and explain how the lowering of vapour pressure of a solvent can be employed to determine the molecular weight of the dissolved substance.

18.2 gms. of urea are dissolved in 100 grams of water at 50°C. The lowering of vapour pressure produced is 5 mm. Calculate the molecular weight of urea. The vapour pressure of water at 50°C is 92 mm. (Delhi B.Sc., 1955)

15. Derive the relationship between osmotic pressure and the lowering of vapour pressure of a solution. How did the study of vapour pressure lead Raoult to determine the molecular weight of a solute in a solvent? Describe the experiment for its determination. (Banaras B.Sc., 1955)

16. Derive the relationship between the lowering of vapour pressure of a solvent produced by the addition of a small amount of a normal solute and the molecular weight of the solute.

The vapour pressure of a 2.1 per cent aqueous solution of non-electrolyte at 100°C is 755 mm. Calculate the molecular weight of the solute. ($K = 18.5$) (Punjab B.Sc., 1955)

17. Air was drawn through a solution containing 38.0 gms. of solute in 100 gms. of water and through water. The loss in weight of water was 0.0551 gm. and the total weight of water absorbed in a sulphuric acid tube was 2.2117 gms. What is the molecular weight of the dissolved substance? (Rajputana B.Sc., 1955)

18. Deduce Raoult's law,

$$\frac{P_0 - P}{P_0} = \frac{n}{N + n}$$

and discuss its applicability. (Lucknow B.Sc., 1955)

19. Derive the relationship between the lowering of vapour pressure and the osmotic pressure. How can Raoult's law be obtained from the above relationship? (Aligarh B.Sc., 1955)

20. Discuss the relative merits of the different methods of determining the molecular weight of a soluble substance using dilute solutions. Describe the experimental determination, from the lowering in vapour pressure. (Travancore B.Sc., 1956)

21. Describe a method for the determination of molecular weights by the relative lowering in the vapour pressure of a pure solvent produced by a non-volatile solute.

At 0°C the vapour pressure of water = 4.62 mm. and that of a solution of 2.28 gms. of CaCl_2 in 100 gms. of water = 4.584 mm. Calculate the degree of dissociation of the salt. (Banaras B.Sc., 1956)

22. What do you understand by the relative lowering of osmotic pressure. Enunciate Raoult's law in this connection.

A current of dry air was bubbled through a bulb containing 26.66 g. of an organic substance in 200 g. of water; then through a bulb, at the same temperature, containing pure water and finally through a tube containing fused calcium chloride. The loss of weight of the water bulb = 0.0870 g. and the gain of weight of the calcium chloride tube = 2.036 g. Calculate the molecular weight of the organic substance in the solution. (Agra B.Sc., 1956)

23. Explain the cause of the lowering of freezing point and elevation of boiling point of solution by means of vapour pressure curves. What is Raoult's law of lowering of vapour pressures and how is it employed in determining the molecular weight of non-volatile solutes? (Rajputana B.Sc., 1956)

24. Describe a method of determining the vapour pressure of an aqueous solution.

When 2.47 grams of a substance are dissolved in 100 grams of benzene, the vapour pressure of the solution at 80°C is 7.42 mm., whereas at the same temperature, pure benzene has a vapour pressure of 751.8 mm. Find the molecular weight of the dissolved substance. (Osmania B.Sc., 1956)

25. State Raoult's law. Explain how it can be used for determining molecular weight of a dissolved substance. The vapour pressure of a solution containing 13 gms. of solute in 100 gms. of water at 28°C is 27.371 mm. Calculate the molecular weight of the solute. The vapour pressure of water at the temperature is 28.065 mm. (Nagpur B.Sc., 1957)

26. State Raoult's law for the lowering of the vapour pressure of a solvent by a solute.

The vapour pressure of a solvent at the room temperature is 450 mm. of Hg. When 100 gms. of a substance are dissolved in 500 gms. of the solvent the vapour pressure of the latter falls to 420 mm. of Hg. If the molecular weight of the solvent is 74, what is the molecular weight of the solute ?

(Rajputana B.Sc., 1958)

27. State Raoult's law of lowering of vapour pressure and derive the relation between the relative lowering of vapour pressure and the molecular weight of the solute. (Aligarh B.Sc., 1958)

28. What is Raoult's law ? Describe any one method for the determination of molecular weight of a dissolved substance. (Gauhati B.Sc., 1958)

29. Enumerate Raoult's law in connection with the relative lowering of vapour pressure.

A current of dry air is passed through a solution of 5 grams of A in 100 grams of water, and then through water alone. The loss of weight of the solution is 0.78 gram and that of water is 0.02 gram. Calculate the molecular weight of A. (Punjab B.Sc., 1959)

5. Freezing Point Method

1. Explain clearly what is meant by 'Cryoscopic constant (molecular depression of freezing point of a solvent)'. How is this constant determined experimentally for a solvent like water ? (Delhi B.Sc., 1954)

2. Explain how the depression of the freezing point of a solvent may be employed to determine the molecular weight of the dissolved substance.

1.355 gms. of a substance dissolved in 55 gms. of acetic acid produced a depression of 0.618°C in the freezing point. Calculate the molecular weight of the dissolved substance. The molecular depression is 38.5 (per 100 gm.)

3. Describe Backmann's method for determining the molecular weight of a substance by depression of freezing point. The solution obtained by dissolving 1.26 gms. of sodium chloride in 50 gms. water freezes at -1.53°C . Calculate the degree of dissociation of sodium chloride. ($K = 18.5$).

4. 15 gms. of a substance dissolved in 150 gms. of water produced a depression of 1.2°C in the freezing point. Calculate the molecular weight of the substance. K for water (100 gms.) is 18.5°C .

5. The freezing point of a solution of 3 gms. of cadmium iodide in 95 c.c.s. of water is -0.165°C . Calculate the apparent molecular weight of the substance. (K for water is 18.9).

6. How would you determine the molecular weight of a substance by the freezing point method ? Give the practical details. The freezing point of pure benzene is 5.40° and that of a solution containing 2.093 gms. of an organic substance in 100 grams of benzene, is 4.440° . Calculate the molecular weight of the substance in solution. K_{1000} for benzene = 5. (Banaras B.Sc., 1950)

7. Describe the freezing point method of determining the molecular weight of a substance. Discuss its limitations. What is Van't Hoff's factor ? (Aligarh B.Sc., 1954)

8. A solution containing 0.622 gm. of solute in 40 gms. of water froze at -0.51°C . What is the molecular weight of the solute ? (K for water is 18.58). (Andhra B.Sc., 1954)

9. Describe the freezing point method for the determination of molecular weight of a substance in solution. What is meant by the freezing point constant of a solvent ? Can you determine the molecular weight of sodium chloride by this method ? If not, explain why ? (Calcutta B.Sc., 1954)

10. Explain the term Cryoscopic constant. Explain Beckmann's freezing point method of determining the molecular weight of a substance. Indicate its limitations. (Mysore B.Sc., 1953)

11. Describe how you would determine the molecular weight of a non-volatile compound by observations of freezing points of its solution.

A solution of 8.55 gms. of cane sugar in 100 gms. of water froze at -0.472°C and a solution of 7.24 gms. of an unknown substance in 100 gms. of water froze at -0.930°C . Calculate the molecular weight of the unknown substance. (Nagpur B.Sc., 1953)

12. Describe the F. P. method of determining the molecular weight of a substance and discuss its limitations. What is Van't Hoff's factor? How would you determine the degree of dissociation of an electrolyte in aqueous solution from its F. P. depression?

13. An aqueous solution of cane sugar having a concentration of 1.71% freezes at -0.093°C . Calculate the freezing point of 5% solution of calcium nitrate in water, assuming the salt to be completely ionised at this concentration.

14. An aqueous solution develops an osmotic pressure of 2.463 atmospheres at 27°C . Calculate the freezing point of the solution. (Molecular depression for 1000 grams of water is 1.87) (Nagpur B.Sc., 1954)

15. 1 gm. of a dibasic organic acid when dissolved in 100 c.cs. of water caused a lowering in the freezing point by 0.15°C . 10 c.cs. of the acid solution when titrated against N/10 alkali required 12 c.cs. Calculate the degree of ionisation of the acid. K for water is 18.9.

16. Explain how the depression of freezing point of a solvent may be employed to determine the molecular weight of a dissolved substance. Discuss its limitations. What is Van't Hoff's factor? (Banaras B.Sc., 1954)

17. (a) What do you understand by the term 'molecular depression constant' for a solvent? How is it determined?

- (b) A solution of 1 gram of silver nitrate in 50 grams of water freezes at -0.348°C . Calculate to what extent the salt is ionized in solution. K for water = 18.6. (Allahabad B.Sc., 1954)

18. Describe the experimental method for the determination of the molecular weight of a substance by the depression of the freezing point.

The freezing point of benzene is 5.54°C and that of a solution containing 2.093 gms. of an organic compound in 100 gms. of benzene is 4.44°C . Calculate the molecular weight of the organic compound (freezing point constant for benzene is 5). (Utkal B.Sc., 1955)

19. Describe the cryoscopic method for determining the molecular weight of a substance. State the limitations of this method.

The freezing point of nitrobenzene is 3°C . A solution of 1.2 gms. of chloroform (CHCl_3) in 100 gms. of nitrobenzene freezes at 2.3°C . A solution of 0.6 gm. of acetic acid in 100 gms. of nitrobenzene freezes at 2.64°C . Calculate the apparent molecular weight of acetic acid and comment on the result obtained. (Patna B.Sc., 1955)

20. What is meant by Molecular Depression of freezing point of a solvent? Deduce the relationship between the concentration of a solution and the lowering of freezing point. (Nagpur B.Sc., 1955)

21. What is abnormal molecular weight obtained for certain substances by the freezing point method?

One gram of a monobasic acid when dissolved in 100 gms. of water lowers the freezing point by 0.168°C . 0.2000 gm. of the same acid when dissolved and titrated required 15.1 c.cs. of N/10 alkali. Calculate the degree of ionization of the acid. (K for water is 18.6). (Allahabad B.Sc., 1955)

22. Describe the determination of the molecular weight of a non-electrolyte by the depression of the freezing point of a solvent.

A solution made by dissolving 6.4 gms. of an organic substance in 25.6 gms. of benzene lowers the freezing point by 1°C . Molecular depression for 100 gms. of benzene is 51.2. Find the molecular weight of the substance. (Rangoon B.Sc., 1956)

23. (a) Describe one important method for the determination of the molecular weight of a non-electrolyte.

(b) 1.355 grams of a substance, dissolved in 55 grams of acetic acid produced a depression of 0.618°C in the freezing point. Calculate the molecular

weight of the dissolved substance. The molecular depression of the freezing point of acetic acid (100 grams) is 38.5°C . (Punjab B.Sc., 1956)

24. How will you determine the molecular weight of a substance soluble in water by the depression of freezing point?

The solution obtained by dissolving 1.26 gms. of sodium chloride in 50 gms. of water freezes at -1.53°C . Calculate the degree of dissociation of sodium chloride. The molar depression of the freezing point in 109 gms. water is 18.6.

[Na = 23, Cl = 35.5] (Delhi B.Sc., 1956)

25. Describe the method employed to determine the molecular weight of a substance by the freezing point method. Calculate the freezing point lowering of a 5% solution of cane sugar in water. (Molar freezing point depression of water = 18.6°C). (Madras B.Sc., 1955)

26. Describe Beckmann's freezing point apparatus for the determination of molecular weights of dissolved substances.

2.167 gms. of a substance dissolved in 100 gms. of benzene depressed the freezing point of benzene by 0.348°C . What is the molecular weight of the substance? (Assume molecular depression of freezing point of benzene to be 5 per 1000 gms. of solvent.) (Bombay B.Sc., Subs., 1956)

27. Explain how the molecular weight of a dissolved substance can be determined by the freezing point method. Describe briefly the experimental procedure involved in the determination. What are the errors that affect the measurements? (Mysore B.Sc., 1956)

28. Derive a relation between the freezing point depression of a solvent and the molecular weight of the solute.

The freezing point of a solution of 0.3210 gm. of naphthalene in 52.12 gms. of benzene is 5.155° whereas the freezing point of the pure solvent is 5.40° . If the molecular depression of freezing point per 100 gms. of the solvent be 51.2, find the molecular weight of naphthalene. (Agra B.Sc., 1957)

29. The freezing point of a solution of 0.684 gm. of cane sugar in 50 gms. of water is -0.074°C . If the freezing point of a solution of 0.2925 gm. of sodium chloride in 100 gms. of water is -0.17°C , calculate the apparent molecular weight and the degree of dissociation of sodium chloride.

(Allahabad B.Sc., 1958)

30. Describe the determination of the molecular weight of a none-electrolyte by the depression of the freezing point of a liquid.

A solution containing 136.8 gms. of a non-electrolyte in 420.2 of water froze at -1.95°C . Calculate the molecular weight of the compound. Molecular depression for 100 gms. of water is 18.5. (Rangoon B.Sc., 1958)

31. A solution of 0.8 gm. of a compound A in 400 gms. of acetic acid freezes at 16.4°C , the pure acid freezing at 16.5°C ; 200 gms. of the same specimen of acetic acid containing 4.46 gms. of another compound B freezes at 15.6°C . If the vapour density of A is 37, find the molecular weight of B. (Vikram B.Sc., 1959)

32. What is the freezing point constant of a solvent? How is it related to its latent heat of solidification?

10.0 gms. of a substance of molecular weight equal to 18.0, when dissolved in 100.0 gms. of water, lower the freezing point of the latter by 1.0°C . Calculate the freezing point constant of water. (Rajasthan B.Sc., 1959)

D. Boiling-Point Method

1. How is the boiling point elevation connected with the molecular concentration of a solution? Deduce the relationship with the help of Raoult's Law for dilute solutions. Describe an experiment to determine the molecular weight of a non-volatile solute with its help.

2. Explain clearly the principle underlying the determination of the molecular weight of a non-volatile solute in aqueous solution by the boiling point method. Describe the apparatus used in this method and indicate the precautions to be taken to ensure accuracy in measurement.

3. How is vapour pressure of a solution related to concentration? 1.55 gms. of urethane dissolved in 34.22 gms. of methyl alcohol raised the boiling

point by 0.320° . The elevation constant for methyl alcohol is 8.8. Calculate the molecular weight of urethane.

4. What is meant by the term 'Molecular Elevation Constant' of a solvent? How is the latent heat of vaporisation of a substance connected with molecular elevation? The heat of vaporisation of 1 gm. of carbon disulphide is 86.72 calories and the boiling point is 46°C . Calculate the molecular elevation constant.

5. What is meant by elevation of boiling-point? Describe an arrangement by which this elevation can be determined. From the elevation of the boiling-point of a solvent by a solute, how can the molecular weight of solute be determined?

6. A solution containing 0.5042 gm. of a non-volatile solute dissolved in 42.02 gms. of benzene boils at 80.38°C . Find the molecular weight of the solute given that the boiling point of benzene is 80.2°C and the its latent heat of evaporation is 94 calories per gram.

7. How may the molecular weight of a substance in solution be determined by the method of the elevation of boiling-point? What are the limitations of this method? A solution containing 0.7269 gm. of camphor (mol. wt. = 152) in 38.08 grams. of acetone (boiling at 56.30°C) boiled at 56.55°C . What is the molecular elevation of boiling-point and the latent heat of vaporisation of acetone?

(Rajputana B.Sc., 1954)

8. The boiling point of pure benzene is 80.000°C . If 0.5042 gm. of a substance dissolved in 42.02 gms. of benzene raises its boiling-point to 80.175°C and if the latent heat of evaporation of benzene is 94 calories per gm., what is the molecular weight of the solute?

(Karnatak B.Sc., 1954)

9. A solution containing 5 gms. of KCl per litre of water boils at 100.065°C at 760 mm. pressure. Determine the degree of dissociation of KCl. F. P. constant for water is 5.4 (per 100 gms.)

(Rajputana B.Sc., 1951)

10. Calculate the molecular elevation of the boiling-point of water (when one gram molecule of the solute is dissolved in 1000 gms. of the solvent) it being given that the latent heat of water is 539.9 calories per gram. (B. P. of water = 100°C ; R = 1.985 calories per degree per molecule).

(Baroda B.Sc., 1954)

11. Explain what is meant by the ebullioscopic constant of a liquid. A solution of 9.472 gms. of CdI_2 in 44.69 gms. of water boiled at 100.305°C . The latent heat of vaporisation of water is 536 calories per gram. What is the molecular weight of CdI_2 in the solution? What conclusion as to the state of CdI_2 in solution may be drawn from the result? ($\text{Cd} = 112.4$; I = 126.9)

(Osmania B.Sc., 1954)

12. Give a brief account of the principal methods employed for determining the molecular weight of a substance in solution, and discuss their relative merits.

(Andhra B.Sc., 1940)

13. Discuss critically the methods available for determining the molecular weights of substances in solution.

(Ceylon Final, 1953)

14. What are the different methods for the determination of the molecular weight of a substance in solution, giving the limitation, if any, for each method. Describe any one method in detail.

(Annamalai B.Sc., 1954)

15. Describe a method for determining the molecular weight of a non-electrolyte by the elevation of the boiling-point of a solvent.

A solution made by dissolving 1.5126 gms. of a substance in 21.01 gms. of benzene has a boiling-point 1.05°C higher than the boiling point of pure benzene. Find the molecular weight of the substance. Molecular elevation of boiling-point of 100 gms. of benzene is 25.70.

(Rangoon B.Sc., 1955)

16. Explain clearly the principle underlying the determination of the molecular weight of a non-volatile solute in aqueous solution by the boiling-point method. Describe the apparatus used in this method and indicate the precautions to be taken to ensure accuracy in the measurement.

3 gms. of camphor added to 25.2 gms. of chloroform raised the boiling-point of the solvent by 0.299°C . Calculate the molecular weight of camphor. (K for 1000 gms. of chloroform is 8.322)

(Patna B.Sc., 1956)

17. What is meant by the term 'molecular elevation constant'?

Describe the methods for determining the molecular weight of a non-volatile solute by the boiling-point method.

(Allahabad B.Sc., 1957)

18. Give a neat diagram and explain in detail Landsberger Ebullioscopic method for the determination of molecular weight.

A solution of 1.19 gms. iodine dissolved in 35 gms. of ether raised the boiling point of ether by 0.296°C . Calculate the molecular weight of iodine. The molecular elevation constant of ether for 100 gms. of solvent is 22.2°C .

(Delhi B.Sc., 1957)

19. Indicate the methods of calculating molecular weight of a substance from its ebullioscopic and osmotic pressure data. What is the explanation of abnormal molecular weights?

0.5 gm. of a substance dissolved in 20 gms. of water lowers its freezing point by 0.4°C . What is the molecular weight of the substance? The molecular depression constant for water is 18.5. (Mysore B.Sc., 1958)

20. An aqueous solution of a substance boils at 100.26°C . at atmospheric pressure. Calculate the freezing point of the same solution under identical conditions. Molar lowering of the freezing point for water is 1.85°C and molar elevation of the boiling point for water is 0.52°C . (Kerala B.Sc., 1957)

21. Describe the determination of the molecular weight of a non-electrolyte by the elevation of boiling-point of a liquid.

1.234 gms. of an organic compound when dissolved in 30.26 gms. of chloroform raised the boiling point by 1.210°C . Calculate the molecular weight of the organic compound. Molecular elevation of boiling point for 100 gms. of chloroform is 37.86. (Rangoon B.Sc., 1958)

22. Describe with the help of a neat diagram the working of Landsberger's apparatus for the determination of molecular weights. What are its limitations?

Calculate the boiling point of a solution containing 0.4560 gram of camphor (m. wt. = 152) dissolved in 34.4 grams of acetone (b. pt. 56.30°C), if the molecular elevation per 100 grams acetone is 17.2°C . (Agra B.Sc., 1959)

ANSWERS

A. OSMOTIC PRESSURE.

- | | | | |
|-----|--------------------|-----|--------------------------|
| 2. | 12.452 atmospheres | 3. | 0.103 gm. mols/lit. |
| 4. | 60.1 | 6. | 345.2 |
| 7. | 12.232 atmospheres | 8. | 184.7 |
| 9. | 61.87 | 10. | 596 |
| 11. | 18.6 gm./lit. | 12. | 0.086 litres atmospheres |
| 17. | 4.679 atmospheres | 18. | 69.79 per cent |
| 22. | 140 | 23. | 18.677 atmospheres |
| 24. | 2.19 atmospheres | 25. | 2.241 atmospheres |
| 26. | 3.6 atmospheres | 29. | 71.94 ; 2.44 |
| 30. | -0.372°C | 31. | 4.013 atmospheres |
| 33. | 3.45 atmospheres | 34. | 189.95 |
| 39. | 91.8 | 40. | 18 gm./litre |

B. LOWERING OF VAPOUR PRESSURE.

- | | | | |
|-----|-------|-----|--------|
| 2. | 57.46 | 4. | 124.69 |
| 8. | 94.61 | 9. | 348.2 |
| 10. | 16.9 | 11. | 60.1 |
| 12. | 94.3 | 14. | 60.3 |
| 16. | 57.46 | 17. | 274.5 |
| 21. | 55.38 | 22. | 56.15 |
| 24. | 147.8 | 25. | 94.61 |
| 26. | 214.4 | 29. | 36 |

C. FREEZING-POINT METHOD.

- | | | | |
|----|--------|----|---------------|
| 2. | 153.48 | 3. | 92.0 per cent |
| 4. | 154.17 | 5. | 361.72 |

- | | | | |
|-----|-----------------------|-----|----------------|
| 6. | 109.01 | 8. | 56.65 |
| 11. | 146.98 | 13. | -1.697 |
| 14. | -0.187°C | 15. | 16.13 per cent |
| 17. | 59.1 per cent | 18. | 9.514 |
| 19. | 116.2 | 21. | 0.203 |
| 22. | 1280 | 23. | 153.48 |
| 24. | 90.95 per cent | 25. | 0.272° |
| 26. | 31.13 | 28. | 128.7 |
| 29. | 31.83 ; 83.8 per cent | 30. | 308.86 |
| 31. | 91.68 | 32. | 1.80 |

D. BOILING-POINT METHOD.

- | | | | |
|-----|----------|-----|---------------|
| 3. | 124.6 | 4. | 23.47 |
| 6. | 177 | 7. | 19.91 ; 109.1 |
| 8. | 182 | 9. | 79.3 per cent |
| 10. | 5.14 | 11. | 360.6 ; 0.768 |
| 15. | 176.2 | 16. | 128.25 |
| 18. | 255.0 | 19. | 115.62 |
| 20. | -0.925°C | 21. | 127.6 |
| 22. | 56.45°C | | |

CHAPTER VI

THE COLLOIDAL STATE

INTRODUCTORY

Thomas Graham (1861) divided soluble substances into two classes, 'crystalloids' and 'colloids,' according to their powers of diffusion across vegetable or animal membranes. Substances such as salt, sugar and urea which diffuse rapidly were termed **Crystalloids** on account of the fact that they are readily obtained in the crystalline form. The other class includes many amorphous substances like gelatin, starch and gum which exhibit little or no tendency to diffuse through the membrane and were, because of their gluey nature, called **Colloids** (Greek *kolla* = glue and *eidos* = like).

Since the time of Graham our conception of colloids has undergone a radical change. The difference in the rate of diffusion of 'crystalloids' and 'colloids' through a membrane can only be explained by assuming that 'colloids' in the dissolved state yield bigger particles which cannot easily penetrate through the minute pores of the membrane whereas 'crystalloids' in solution are broken down to tiny molecules or even fragments of molecules (ions) which can diffuse through quickly. It is true that 'colloids' readily yield a particle size in solution which hinders their diffusion through a membrane but certainly it does not mean that other substances are debarred from being brought down to that particle size. Gold, copper and other metals which are ordinarily insoluble in water have all been obtained in the colloidal state. Sodium chloride, according to Graham, is a crystalloid but it has been obtained in the colloidal state in benzene. Soap behaves as a 'colloid' in water and a crystalloid in alcohol. In face of such facts Graham's distinction which implies that colloids and crystalloids are particular kind of substances, is no more tenable, for *all substances by employing suitable methods can be obtained in the colloidal condition.* We should thus speak of the **Colloidal state of matter** just as we speak of the liquid, solid and gaseous state of matter, rather than to call a particular material as colloid or crystalloid. Although the term colloid has lost its original significance, it is still used to describe such organic substances as gelatin, gum albumin, etc. which practically always readily yield colloidal solutions.

NATURE OF COLLOIDAL SOLUTIONS

In a true solution the solute particles are present as molecules or ions giving a homogeneous mixture which consists of a single phase. In a colloidal solution, on the other hand, the unit particles of the dissolved substance are either very large molecules (starch for example has m. wt. of about 32,000) or essentially aggregate of a large number of molecules. These particles even though they may consist of thousands of molecules are too small to be seen under the microscope. Thus to the naked eye there could be no difference between a colloidal solution or an ordinary solution.

However, if colloidal particles grow in size further, they become visible under the microscope and then we get what we call a 0.2×10^{-4} cm. 1×10^{-7} cm.

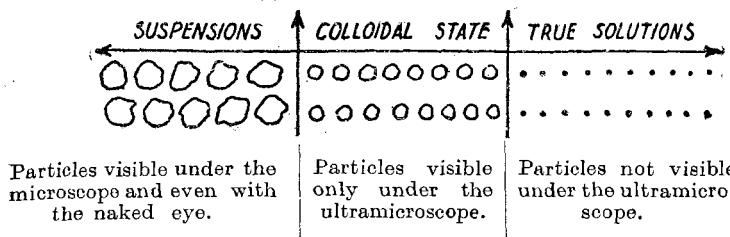


Fig. 77. Diameter of solute particles.

suspension. The particles of a coarse suspension are visible even with the naked eye. The colloidal state can thus be regarded as the intermediate stage between molecules and particles of a coarse suspension.

The true nature of colloidal solutions was revealed as a result of the invention of **ultramicroscope** by Zsigmondy (1903). An intense converging beam of light is thrown into the colloidal solution which is then examined through a microscope placed at right angles to the path of light (Fig. 78). Under these conditions, when a true solution is tested, the field revealed under the microscope remains quite dark as no direct light enters the microscope. The colloid particles, however, scatter light in all directions which also enters the microscope. Thus bright colloidal particles are observed against a dark background (Fig. 79). The particles which are too small to be seen in the most powerful microscope are detected by the halos of scattered light formed round them (Fig. 80). It must be clearly

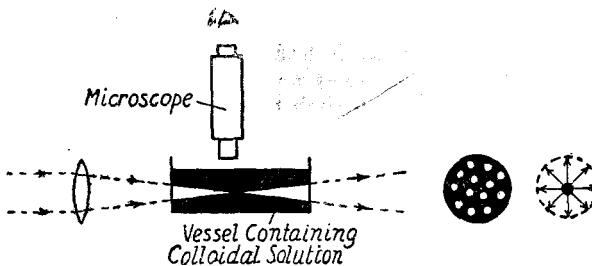


Fig. 78. Ultramicroscope.

Fig. 79. View Fig. 80. Halo of under ultra-scattered light microscope. round sol. particles.

realised that the ultramicroscope does not render visible the actual particles themselves. Only the light scattered by them is seen and thus no idea of the shape, colour, or relative size of the particles can be formed.

The ultramicroscope examination of colloidal solutions makes it abundantly clear that unlike true solutions they are heterogeneous systems consisting of two phases. One phase is present in the form of extremely small particles dispersed in a solvent and is termed the **dispersed phase** or **inner phase**. The other phase (solvent) in which the particles are dispersed is called the **dispersion medium** or **outer phase**.

CLASSIFICATION AND TERMINOLOGY

So far we have referred only to colloidal solutions which are diphasic systems with a solid as dispersed phase and a liquid as dispersion medium. In a diphasic system, however, each one of the two phases can either be a gas, liquid or solid. In all, eight such systems are possible.

Table : Types of Colloidal systems

SYSTEM	NAME	EXAMPLES
1. Gas dispersed in liquid	Foam	Foam on soap solution (soap lather).
2. Gas dispersed in solid	Solid foam	Pumice stone. Minerals with gaseous inclusions.
3. Liquid dispersed in gas	Mist, Fog, Cloud	Rain, Mist, Clouds.
4. Liquid dispersed in liquid	Emulsion	Milk, Water in benzene, Oil in water.
5. Liquid dispersed in Solid	Gel or Jelly	Precipitate of iron hydroxide obtained in analysis, Silicic acid gel.
6. Solid dispersed in gas	Aerosol	Coal smoke from chimney. Ammonium chloride fumes.
7. Solid dispersed in liquid	Sol, Colloidal solution.	Gold or Silver in water; Nickel in benzene.
8. Solid dispersed in solid	Solid Sol.	Coloured gems and glasses.

Colloidal systems of two gases cannot exist since the unit particles of a gas are simple molecules and are incapable of producing two phases. We shall, however, restrict our study mainly to colloidal solutions, which are frequently referred to as **sols**. Colloidal solutions in water are termed **hydrosols**. When the dispersion medium is alcohol or benzene, they are called **alcosols** and **benzosols** respectively.

Yet another classification exists. Gelatin, gum and certain other organic substances which directly pass into colloidal solution when brought in contact with water are called **hydrophilic** (water-loving) **colloids**. When once precipitated from the colloidal form they can be directly reconverted into the colloidal form and are for this reason termed **reversible colloids**.

Insoluble substances like metals, metal sulphides, metal hydroxides and other inorganic substances which do not readily yield colloidal solutions when brought in contact with water are called **hydrophobic** (water-hating) **colloids**. When once precipitated, they cannot be directly obtained back into the colloidal form and are, therefore, termed **irreversible colloids**.

More general terms than hydrophilic and hydrophobic are **lyophilic** and **lyophobic** respectively, *lyo* meaning solvent.

PREPARATION OF COLLOIDAL SOLUTIONS

Practically all substances can form colloidal solutions although not with the same ease. Gelatin, gum, starch, etc., for example, yield colloidal solutions on simple warming or agitation with water.

Metals and other inorganic substances, on the contrary, can be obtained in the colloidal form with difficulty and by the use of special devices.

To get a substance in colloidal form we can either start with the material in bulk and break it down into fine particles of colloidal dimensions (**Dispersion methods**), or we can bring about the union of a large number of atoms or molecules to form bigger particles of colloidal size (**Condensation methods**). Thus we have the following methods for the preparation of colloidal solutions :—

Dispersion Methods	Condensation Methods
<ul style="list-style-type: none"> (i) Mechanical dispersion. (ii) Electro-dispersion. (iii) Peptization. 	<ul style="list-style-type: none"> (i) Excessive cooling. (ii) Lowering of solubility by exchange of solvent. (iii) Passing vapour of an element into a liquid. (iv) Chemical action : <ul style="list-style-type: none"> (a) double decomposition. (b) oxidation. (c) reduction. and (d) hydrolysis.

Dispersion Methods :

(i) **Mechanical Dispersion.** The substance to be dispersed is ground as finely as possible by the usual methods. It is then

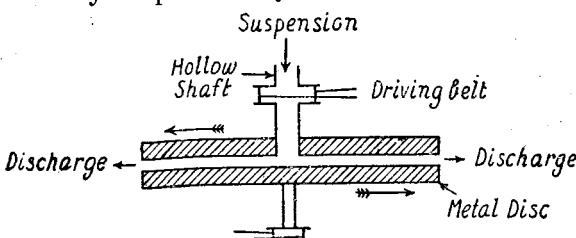


Fig. 81. Disc Mill.

shaken with the dispersion medium and thus obtained in the form of a coarse suspension. This suspension is then passed through a

Colloid Mill. The simplest type of Colloid Mill called **Disc Mill** consists of two metal discs nearly touching each other and rotating in opposite directions at a very high speed. The suspension passing through these rotating discs is exposed to a powerful shearing force (Fig. 81) and the suspended particles are torn apart to yield particles of colloidal size.

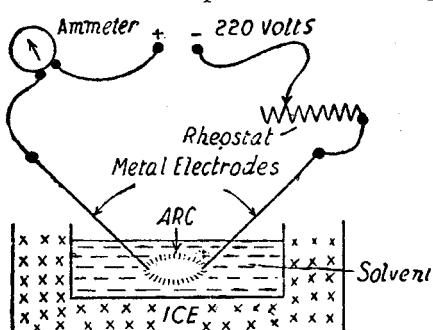


Fig. 82. Bredig's Arc Method.

(ii) **Electro-Dispersion, Bredig's Arc Method.** This

method consists in striking an arc between the electrodes of a metal which is to be obtained in colloidal form, the electrodes being immersed in the dispersion medium, commonly water (Fig. 82). The intense heat of the arc turns the metal into vapours which are immediately condensed by the surrounding ice-cold water to give particles of colloidal size. A slight trace of potassium hydroxide in water helps to stabilise the sol. The sol. is then filtered to free it from a few relatively bigger suspension particles eventually formed. This method of preparing sols. is of very wide application. Gold, platinum, silver, copper and such other metals can thus be obtained in the colloidal form.

The principle underlying the method is essentially one of condensation of the atoms of the metal to the aggregates of colloidal size but since we start from the metal in bulk and finally get the colloidal particles from it, the method has been treated as one of dispersion.

(iii) **Peptization.** Peptization is the converse of coagulation. *It is the process by which a stable colloidal solution can be produced from substances originally present in massive form when the colloidal particles pre-exist in the substance to be dispersed.* In other words, it is the redispersion of a coagulated sol. Freshly prepared ferric hydroxide on treatment with a small amount of ferric chloride solution (**peptizing agent**) at once forms a dark reddish brown sol. Another familiar example of peptization in qualitative analysis is the formation of colloidal solution of aluminium hydroxide by the addition of a small amount of dilute hydrochloric acid, not sufficient to form aluminium chloride solution.

Condensation or Aggregation Methods

(i) **Excessive Cooling.** The colloidal solution of ice in an organic solvent like chloroform or ether is obtained by freezing a solution of water in the solvent. The molecules of water which can no longer be held in solution gather together to form particles of colloidal size.

(ii) **Lowering of Solubility by Exchange of Solvent.** Substances like sulphur, rosin, etc., which are more soluble in alcohol than in water, give a hydrosol by pouring a small amount of their alcoholic solution in excess of water. The substance is present in the molecular state in alcohol but on transference to water, in which it is insoluble, molecules precipitate out to form particles of colloidal size.

The indicator phenolphthalein is soluble in alcohol but not in water and is, therefore, supplied to the laboratory in alcoholic solution. If water is added to this solution, a milky liquid is produced which contains phenolphthalein in the colloidal solution.

(iii) **Passing Vapour of an Element into a Liquid.** If the vapours of a boiling element are conducted into a liquid, condensation takes place, sometimes with the formation of a stable sol. Thus mercury sols. result on passing a stream of vapours from the boiling element into cold water containing suitable stabilizing electrolytes

such as ammonium salts or citrates. Sulphur sols, can easily be prepared by a similar procedure.

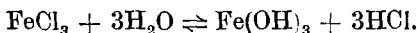
(iv) **Chemical Action.** When the solubility of the substance is sufficiently small, it may be obtained in the colloidal form by chemical precipitation. Before the actual precipitation commences the insoluble substance first of all appears in the molecular state but as the precipitation proceeds a large number of these molecules assemble and grow to the colloidal size. The various types of chemical reactions available for the purpose are :

(i) *Double decomposition.* Colloidal solution of *arsenious sulphide* may be obtained by the action of hydrogen sulphide on arsenious oxide ($\text{As}_2\text{O}_3 + 3\text{H}_2\text{S} \rightarrow \text{As}_2\text{S}_3 + 3\text{H}_2\text{O}$). One gram of arsenious oxide is dissolved in about 500 c.c. of water by keeping it boiling till the whole of the oxide goes in solution. It takes a pretty long time and during this interval the evaporated water should be made up by adding freshly prepared distilled water. The solution is then cooled and a slow stream of hydrogen sulphide gas is passed through. This is continued till the yellow colour of the colloidal solution attains maximum intensity. The excess of hydrogen sulphide gas is removed by boiling and testing with lead acetate paper. Alternatively a stream of hydrogen may be passed through the sol. to sweep away hydrogen sulphide gas which, if not removed, may precipitate the sol. to a certain extent.

(ii) *Oxidation.* A milky colloidal solution of *sulphur* is frequently formed during qualitative analysis by the action of hydrogen sulphide on the solution of an oxidising agent, say nitric acid ($\text{H}_2\text{S} + \text{O} \rightarrow \text{H}_2\text{O} + \text{S}$).

(iii) *Reduction.* A violet colloidal solution of *gold* can be obtained by the reduction of a gold chloride solution using stannous chloride solution ($2\text{AuCl}_3 + 3\text{SnCl}_2 \rightarrow 3\text{SnCl}_4 + 2\text{Au}$) as reducing agent. Colloidal silver may be obtained by reducing silver nitrate solution with tannic acid solution.

(iv) *Hydrolysis.* A deep red colloidal solution of *ferric hydroxide* can be prepared rapidly by the gradual addition of 2 or 3 c.c. of a 30% solution of ferric chloride to 500 c.c. of boiling water with constant stirring.



The neutral ferric chloride solution used as a reagent in the laboratory becomes dark red on standing. This change in colour is due to the formation of colloidal ferric hydroxide by partial hydrolysis.

PURIFICATION OF COLLOIDAL SOLUTIONS

Dialysis. It is found that substances in true solution will pass through parchment, collodion or animal membranes but colloidally dispersed particles cannot do so. This is due to the fact that membranes contain small pores through which dissolved molecules and ions can diffuse smoothly but colloidal particles by virtue of their magnitude and massive nature diffuse very slowly and are mostly kept back. This process of separating a 'crystallloid' from a 'colloid' by diffusion or 'filtration' through a membrane was named **Dialysis**.

(Greek, *to dissolve through*) by Graham and the apparatus employed to effect such a separation is called a **Dialyser**. Graham's dialyser consists of a shallow cylinder open at both ends, over one end of which a membrane is tied. The colloidal solution to be dialysed is placed in this cylinder which is then suspended in a large dish containing distilled water (Fig. S3). The distilled water is renewed from time to time, but it is preferable to use a continuous flow, as dialysis is greatly accelerated thereby. This may be done by allowing water to flow into the outer vessel and removing it by means of a syphon. Dialysis is a slow process and usually takes several hours, sometimes days for completion. The progress of dialysis can be noted from time to time by testing and estimating the soluble impurity present in the shallow cylinder.

When a solution of sodium silicate is added to an excess of hydrochloric acid and dialysed as explained above the resulting sodium chloride and hydrochloric acid diffuse away, leaving colloidal silicic acid behind.

The diffusion of the electrolyte through the membrane can be facilitated under the influence of the electric field and the process is

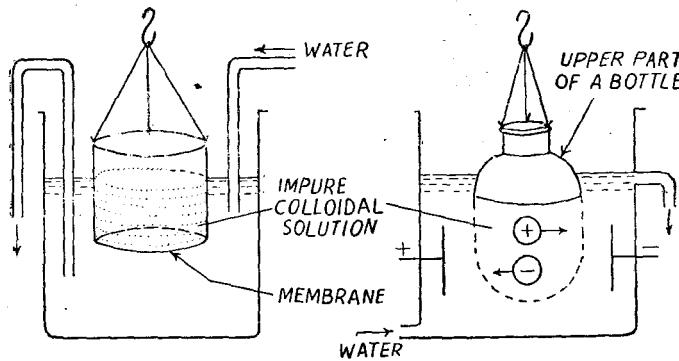


Fig. 83. Graham's
Dialyser.

Fig. 84. Electro-
dialysis.

then called **Electro-dialysis**. In this case the outer vessel containing pure water is fitted with two electrodes (Fig. 84). The electric field applied across the apparatus assists the motion of the ions of the electrolyte to the oppositely charged electrode. Electro-dialysis is evidently not meant for the removal of non-electrolytic impurities like sugar and urea.

Ultrafiltration. In *ultrafiltration* the liquid dispersion medium as well as the substance in true solution is removed from the colloidal material. Pressure is applied to the solution in a strong cylinder so as to force the liquid through the very small pores of a special membrane when the solid colloidal material is left behind. Ordinary filter papers can be used for ultrafiltration by impregnating them with solution of collodion in acetic acid. Graded filters of different effective pore size can be made by varying the concentration of the acid. By using such graded filters *pure* colloidal solution with uniform required particle size can be obtained when coarse bigger particles are held back.

Ultrafilters are useful in removing soluble impurities from colloids and they find extensive application in bacteriology as bacteria can generally be removed from solution by ultrafiltration.

PROPERTIES OF COLLOIDAL SOLUTIONS

1. Heterogeneity. A colloidal solution consists of tiny solid particles dispersed in a liquid. The particles, though invisible under the microscope, can be detected by the help of an ultramicroscope. The differential behaviour of colloidal solutions from true solutions is due to the difference in the size of the solute particles.

2. Osmotic Pressure. The osmotic pressure of colloidal solutions is usually very small. This is to be expected because a colloidal particle is an aggregate of about 1000 molecules as they exist in a true solution. Since osmotic pressure depends in dilute solutions on the number of particles, it becomes less when the same amount in true solution is colloidally dispersed to form aggregates containing about one thousand molecules per particle.

Attempts have been made to measure the molecular weights of colloids from a determination of their osmotic pressure. The molecular weights of colloids have been found to be very high, e.g., starch has an estimated m. wt. = 32,000.

3. Filtrability. The colloidal particles can easily pass through an ordinary filter paper, the size of their pores being too big to retain particles of colloidal dimensions. It is, however, possible to construct filters of unglazed porcelain (*ultra filters*) which will filter out a colloidally dispersed substance and let through any soluble material.

4. Faraday-Tyndall Phenomenon or Tyndall Effect. A beam of light entering a dark room lights up the dust particles floating in the air. We observe a similar phenomenon when the projection machine in a darkened cinema hall begins to throw the picture on the screen. Similarly, when a strong beam of light is concentrated on a

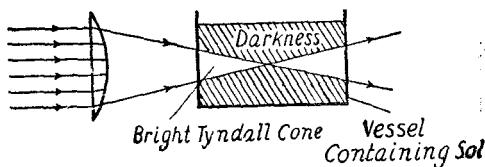


Fig. 85. The Tyndall Effect.

colloidal solution the path of the beam is illuminated by a bluish light (and becomes visible when observed from the side). This phenomenon discovered by Faraday and later studied by Tyndall has been named **Faraday-Tyndall Phenomenon** or simply **Tyndall Effect**. The cause of this phenomenon is the scattering of light by the colloidal particles. This scattering of light cannot be due to simple reflection because the size of the particles is smaller than the wave-lengths of visible light which are, therefore, unable to reflect light waves. This is why the colloidal particles cannot be seen directly under the microscope. In this phenomenon of 'scattering' the particles themselves become self-luminous due to the absorption of light energy which is then scattered as light of shorter waves. This accounts very well for the bluish **Tyndall Cone**.

Faraday-Tyndall phenomenon has been employed as the basic principle for the construction of ultramicroscope. It has been used to detect solid suspended impurities in solutions.

5. Colour. The colour of colloidal solutions is determined by the wave-length of the light scattered by the colloidal particles which again depends on the size and nature of the particles. This is fully borne out by the experimental data obtained in the case of silver sols.

COLOUR OF SILVER SOL.	DIAMETER OF PARTICLES
(i) Orange-yellow 6×10^{-5} m.m.
(ii) Orange red 9×10^{-5} m.m.
(iii) Purple 13×10^{-5} m.m.
(iv) Violet 15×10^{-5} m.m.

The colour changes produced by varying particle size have been observed in many other cases.

5. Brownian Movement. Careful ultramicroscopic examination of a colloidal solution reveals that the suspended particles are in constant rapid zig-zag motion (Fig. 86) called the **Brownian Movement**, after the name of its discoverer Sir Robert Brown (1827). The phenomenon is very striking in colloidal solutions and becomes less intense as the particles increase in size. It is detectable even with particles which are so large that they are visible under an ordinary microscope. Brown himself first noted this movement while examining pollen grains suspended in water under a microscope.

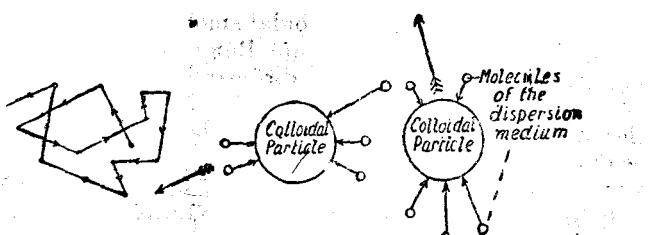


Fig. 86. Path of a particle undergoing Brownian movement.

Fig. 87. *Brownian motion.* The arrows indicate the direction of the impacts and their length corresponds to the strength of the impact. The resultant of all the impacts is indicated by long arrows shown separately. This shows the direction in which the particle moves.

The Kinetic Theory of molecular motion furnishes an ice explanation of the phenomenon. Let us consider a single colloidal particle suspended in water. It is surrounded by a large number of comparatively small molecules of the dispersion medium which are in constant irregular motion. The colloidal particle is knocked about as a result of its unequal bombardment by the molecules of the dispersion medium (Fig. 87).

With the increase of particle-size the probability of unequal bombardment diminishes. In coarse suspensions the impacts on different sides of the particle neutralise each other's effect and Brownian motion vanishes (Fig. 88).

The phenomenon of Brownian movement is an excellent proof of the existence of molecules and their ceaseless

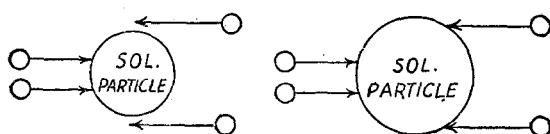


Fig. 88. Showing how Brownian motion vanishes with increase of particle's size.

motion in liquids. Brownian motion counteracts the force of gravity acting on the colloidal particles and is thus responsible to a certain extent for the stability of colloidal solutions.

7. Cataphoresis. An important property of colloidal solutions is that their particles carry an electric charge and, therefore, move

towards one or the other electrode when the solution is placed in an electric field. This migration of colloidal particles under the influence of electric field is called **Cataphoresis**. By noting the direction of the motion of colloidal particles under the influence of electric force, we find out the type of charge on them. **Cataphoresis is thus employed to determine the sign of the electric charge on the colloidal particles.** Some of the results of investigation on different sols. are mentioned below for reference.

Fig. 89. *Cataphoresis.* The colloidal particles of the sol. contained in the U-tube are negatively charged and, therefore, migrate to the positive electrode where they lose the charge and are deposited on it.

particles can under suitable conditions be 'electro-plated' on the surface of a metal, cloth or wood.

POSITIVE SOLS.	NEGATIVE SOLS.
(i) Oxides e.g., TiO_2 .	(i) Metals e.g., Ag, Cu, Au, etc.
(ii) Metallic hydroxides e.g., $Fe(OH)_3$, $Al(OH)_3$, $Cr(OH)_3$	(ii) Metallic sulphides e.g., As_2S_3 , Sb_2S_3 , CdS .
(iii) Basic dye-stuffs e.g., Bis-mark brown, methylene blue.	(iii) Acid dye-stuffs e.g., eosin. (iv) Gums, starch, etc.

8. Electro Osmosis. We have just seen that the particles of a colloidal solution are charged and move relatively to the dispersion medium under the influence of an electric field. It follows, therefore, that if the particles can be maintained stationary, the dispersion medium would move. This movement of the dispersion medium under the influence of the electric field is known as **Electro-osmosis** (*Osmosis* = diffusion through porous membranes). This can be observed by fixing a porous diaphragm made out of the material of the dispersed phase in a U-tube containing the dispersion medium as shown in the diagram (Fig. 90). When an electric field is set up across the ends of the tube, the dispersion medium is

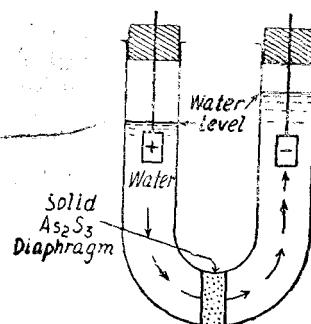
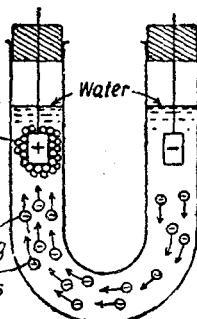


Fig. 90. Electro-osmosis.

seen to move towards one or the other electrode. The direction of motion is opposite to that which the diaphragm would follow if it were free to move.

Technically the phenomenon has been applied in the removal of water from peat, in dewatering moist clay and in drying dye pastes.

9. Precipitation or Coagulation. It is a remarkable fact that precipitation, or *coagulation*, of colloidal solutions can readily be brought about by the addition of small amounts of electrolytes. When for example, a few drops of barium chloride solution are added to a colloidal solution of arsenious sulphide, it immediately becomes turbid and in a short time the sulphide separates in the form of a precipitate. This can be explained in a very simple manner as follows : Originally, we know, the particles of As_2S_3 sol. carry negative charges and are kept apart due to their mutual electrical repulsions. Barium chloride in solution produces Ba^{++} and Cl' ions and arsenious sulphide particles being negatively charged will attract and absorb some of the Ba^{++} ions with the result that their negative charge gets neutralised. Robbed of their charge there remains nothing to keep the As_2S_3 particles away from each other. Under the influence of gravity they gather together to form bigger aggregates which finally settle down in the form of a precipitate. That the oppositely charged Ba^{++} ions take part in precipitating the As_2S_3 sol. is confirmed by the fact that these ions have actually been detected in the precipitate by analysis.

Since it is the charge on the ions which is responsible for the precipitation of the colloidal solution, it is not surprising that the power of an ion to coagulate a sol. depends on its valency. *The higher the valency of the active ion, the greater is its precipitating action.* This is known as the **Hardy-Schulze Law**. The precipitating action of the cations Na^+ , Mg^{++} , Al^{+++} on As_2S_3 sol. in conformity with the *Hardy-Schulze* law has been found to be in the order $\text{Al}^{+++} > \text{Mg}^{++} > \text{Na}^+$.

Table. *Coagulation of an As_2S_3 Sol. by Electrolytes.*

(Millimols per litre required to produce precipitation)				
NaCl	51·0	MgSO_4	0·81	$\text{Al}(\text{NO}_3)_3$ 0·095
KCl	49·5	BaCl_2	0·69	AlCl_3 0·093
		CaCl_2	0·65	

With a positively charged sol. such as ferric hydroxide, it is the negative ions which are active precipitants and it is the valency of these ions which is important. Thus it will be seen from the following Table that the bivalent SO_4'' ion is much more effective than the monovalent Cl' ion.

Table. *Coagulation of a Ferric Hydroxide Sol. by Electrolytes.*

(Millimols per litre required to produce coagulation)			
KCl	9·5	K_2SO_4	0·20
NaCl	9·3	MgSO_4	0·22
BaCl_2	9·6		

The **mutual coagulation of two sols.** can be effected by mixing provided the particles of one sol. bear positive and those of the other negative charge. Ferric hydroxide sol. and arsenious sulphide sol. form such a pair and when mixed in the correct proportions they are precipitated as a common 'absorption compound'.

Relative stability of Hydrophilic and Hydrophobic sols

In the case of hydrophobic sols, coagulation begins immediately if the charge on the particles is removed. With hydrophilic sols., however, no coagulation is noticed on the removal of the charge. The reason is that hydrophilic sol. particles are heavily hydrated and the water envelope surrounding them prevents their coming into intimate contact necessary for the occurrence of coagulation. It may, therefore, be concluded that a hydrophilic sol. is stabilized by two distinct factors, its charge and its hydration. In order to coagulate a hydrophilic sol., therefore, it is essential to remove both the causes of stability. It has actually been found that after the removal of charge from the hydrophilic sol. particles by an electrolyte if a dehydrating substance, say alcohol or acetone is added to the resulting sol., it causes the removal of hydration of the particles and coagulation sets in at once. This is illustrated in the diagram (Fig. 91).

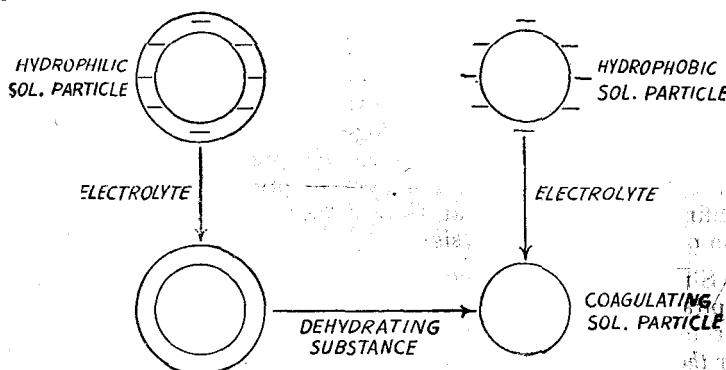


Fig. 91. Coagulation of a hydrophilic sol. particle.

10. Protection. Colloidal solutions such as those of metals like gold and silver can normally be precipitated by small amounts of electrolytes. This can be prevented, or at least retarded, by the previous addition of a more stable hydrophylic colloid like gelatin or albumin. For example, if a little gelatin is added to a gold sol. it is no longer precipitated on the addition of sodium chloride. The process by

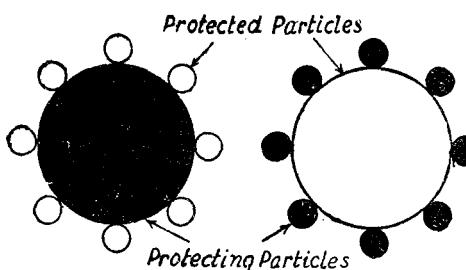


Fig. 92. When protected particles are smaller than protecting particles.

Fig. 93. When protected particles are bigger than protecting particles.

which the sol. particles are protected from precipitation by electrolytes due to the previous addition of some

hydrophilic colloid is termed **Protection** and the colloid which is added to achieve this is commonly called a **Protective colloid**.

The explanation of the protection of a sol. by a protective colloid, as usually given, is that the particles of the sol. absorb the protective colloid particles which thus form a *protective layer* about them. This protective layer prevents the precipitating ions from reaching the sol. particles which in this way are preserved from precipitation. According to a recent view the sol. acquires the stability of the protective colloid merely on account of the mutual adsorption of their particles and it is immaterial whether the sol. particles adsorb the protective colloid or *vice versa*. In fact it is reasonable to assume that if the protected particles are smaller than the protecting particles, the former will be adsorbed by the latter (Fig. 92) and if the protected particles are bigger than the protecting particles the latter will be adsorbed by the former (Fig. 93).

The hydrophylic colloids differ widely in their powers of protection. The protective power of a certain colloid is usually measured in terms of what is known as the 'gold number'. **Gold number** is the number of milligrams of protective colloid which just prevents the coagulation (accompanied by a change in the colour from red to blue) of 10 c.c. of a given gold sol. when 1 c.c. of a 10% solution of sodium chloride is added to it. The gold numbers of a few colloids are given below :

Gelatin	0·005	Starch	25
Egg albumin	0·08	Dextrin	6—123
Gum arabic	0·10	Colloidal Silica	Infinite

It will be seen from this table that gelatin and egg albumin are much more effective than starch and dextrin.

II. Adsorption. The particles at the surface of a solid or liquid are in a state of tension and in order to satisfy their residual valencies exhibit a tendency to attract on to and retain at their surface other particles with which they come into contact. This property causes the concentration of a substance at the interface or the separating surface of two phases and is known as **adsorption**. It is evident that the larger the surface for the same volume of an adsorbent, the larger will be the adsorption produced. In a colloidal solution a very small mass of the dispersed phase is present as a very large number of tiny particles. Thus the area of the surface of this phase is very large relative to the mass of the substance. Moreover when we break a substance into small particles the valencies of the separating atoms which were mutually satisfied are now set free (Fig. 95). *The large surface offered by colloidal particles and these free valencies are responsible for marked adsorption by colloids.*

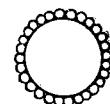


Fig. 94. Adsorption on a colloidal particle.

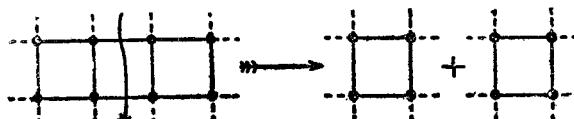


Fig. 95. Showing how breaking of a substance into two halves results in the increase of surface and free valencies.

This theory of adsorption explains why finely divided metals like nickel and platinum are so efficient catalysts.

The adsorption of materials from the dispersion medium plays an important part in colloid chemistry. The very **origin of the charge** on the sol. particles in most cases has been demonstrated to be due to the preferential adsorption of a certain type of ions present in the dispersion medium. The particles of a particular sol. are positive or negative according as the sol. has been prepared in an acidic or alkaline medium which can be explained to be due to the selective adsorption of H^+ or OH^- ions respectively present in excess in the dispersion medium.

It has been found that the ions precipitating a sol. are present in the coagulated mass which shows that it is the adsorption of these ions which results in the neutralisation of the charge on the colloidal particles.

Adsorption indicators. The use of certain dyestuffs like *casin*, *dichlorofluorescein* etc., in silver titrations is based on the phenomenon of adsorption. If silver nitrate be titrated with say, potassium bromide, we get a precipitate of silver bromide which can adsorb bromide ions in preference to Ag^+ . The silver ions are adsorbed only when there are no bromide ions left and these are adsorbed as silver salts of the dye possessing a different and deeper shade. If eosin (pinkish yellow) is used as indicator, the colour of the precipitate changes from yellow to brick red the moment there are any free Ag^+ in solution. The titrations can be performed with even very dilute solutions.

EMULSIONS

A dispersion of tiny droplets of one liquid in another liquid is known as an **emulsion**. Any two immiscible liquids can yield an emulsion.

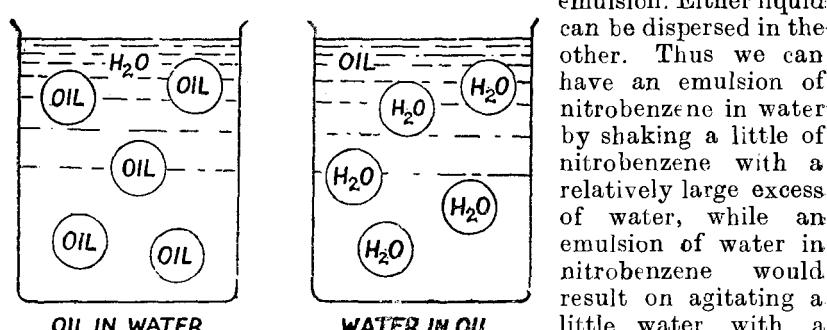


Fig. 96. Two types of emulsions.

there are two types of emulsions recognised :

- (1) Oil-in-Water emulsions, and
- (2) Water-in-Oil emulsions.

Water is usually one of the components and the other is an oil or a liquid insoluble in water which takes the place of oil.



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(21.2.1894—1.1. 1955)

Born at Bhera in West Punjab, he took his M.Sc. from Punjab University in 1919. After taking his D.Sc. from London University under Prof. Donnan he worked under Prof. Haber at Kaiser Wilhelm Institute, Berlin, and later under Prof. Freundlich, an expert on *Colloids*. Was sometimes Professor of Chemistry at Banaras Hindu University and from 1924-1940 worked as Director of the University Chemical Laboratories, Lahore. He was Director of Scientific and Industrial Research of the Government of India till his death. In 1943, he was made a Fellow of the Royal Society and was responsible for setting up a chain of National Research Laboratories in India.

The emulsions composed entirely of water and oil are not stable. The dispersed droplets at once come together (coalesce) and form a separate layer. To stabilise an emulsion the addition of a third substance, known as an **emulsifying agent** or **emulsifier**, is essential. The emulsifier concentrates at the oil-water interface and forms a film sufficiently tough to prevent the coalescence of the droplets. Soaps, gelatin, and gum are useful emulsifying agents. According to Bancroft, an emulsifier at the water-oil interface lowers the surface tension on the side of one liquid more than it does on the other and thus the interface will tend to curve around the second liquid which is dispersed as droplets.

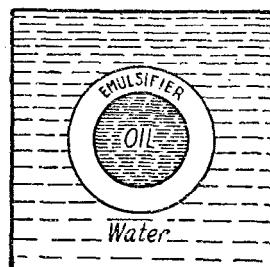


Fig. 97. Roll of emulsifier.

Preparation of Emulsions. (1) The oily substance is mixed with the emulsifying agent, say soap, and thoroughly ground in a mortar. This is then agitated with water to form an emulsion.

(2) The emulsifier is mixed with a little water and thoroughly ground. The oil is then added to it bit by bit and the liquid shaken.

(3) *Homogenizing.* This method is often applied for stabilising an already available emulsion. The emulsion is forced through capillary tubes under high pressure and the stream is allowed to break against a hard surface. Homogenized cream and milk are prepared by this method.

Properties of Emulsions. Emulsions show all the properties of sols.

1. *Cataphoresis.* Like sols., droplets in an emulsion are electrically charged. They migrate to the oppositely charged electrode under the influence of electric field.

2. *Demulsification.* The stability of an emulsion is determined by (*i*) the toughness of the film which prevents the droplets of the emulsoid particles from coalescing, and (*ii*) the electric charge borne by the emulsoid particles. Emulsions are, therefore, coagulated, broken or *demulsified* by the addition of a material that would destroy the emulsifier or by the addition of an electrolyte which destroys the charge.

Boiling, centrifuging and freezing also cause demulsification. When water is the dispersion medium, addition of a dehydrating agent or alcohol may cause the emulsion to break. Emulsions are coagulated, broken, or *demulsified* by the addition of an electrolyte or a material that would destroy the emulsifier. Heating, freezing or centrifuging may also cause demulsification.

3. *Dilution.* Emulsion can be diluted with any amount of the dispersion medium while the dispersed liquid when mixed with it will at once form a separate layer. This property of emulsions is used to detect the type of a given emulsion.

Examples and uses. Obviously, an emulsified substance is more effective than if it were in massive form. It offers much greater surface for action. Thus many pharmaceutical preparations are emulsions e.g., emulsions of Cod-liver oil and Halibut-liver oil. The emulsified oil is more readily acted upon by the digestive juices in the stomach and elsewhere. The disinfectants, phenyl and lysol, yield an emulsion of the oil-in-water type when poured into water.

GELS

Colloidal systems containing a liquid dispersed in a solid are called gels. Gels are obtained by the coagulation of certain colloidal sol-

tions when the coagulated material encloses the entire liquid medium yielding a semi-solid mass. For example, if a hot and sufficiently concentrated colloidal solution of gelatin is allowed to cool, it sets to a semi-solid mass. In the process of gel-formation or *gelation* the sol. particles come together and form bigger aggregates which finally grow so large that they touch each other. These aggregates continue to grow and form a continuous network which encloses the entire dispersion medium. Thus a gel is usually assumed to have a structure somewhat like a honeycomb.

Silicic acid gel may be formed by the addition of acid to sodium silicate in suitable concentrations when the resulting silicic acid forms stiff, transparent gel immediately.

The addition of alcohol to a saturated solution of calcium acetate in water first produces a calcium acetate sol. which then sets to a hard jelly called **solid alcohol**. It is the solid fuel commonly used for burning in specially designed lamps for military field service.

A large number of articles of common uses are gels. For example, soaps, boot polishes, animal tissues, and the various food-stuffs have all gel structure. The hydroxides of Al, Cr, and Fe usually precipitate as gels.

Properties of Gels. On standing, an inorganic gel loses water and shrinks. The shrinking of gel with the simultaneous exudation of the solvent from it is termed *Syneresis* or *weeping of the Gel*.

The gel structure offers little resistance to the diffusion of any substances dissolved in the sol. before setting.

APPLICATIONS OF COLLOID CHEMISTRY

Most of the substances we come across in our everyday life are colloids and we are mainly colloids ourselves. The food we eat, the

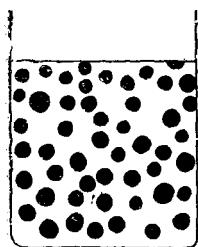


Fig. 98 (i). Black colloidal particles in suspension in water (white).

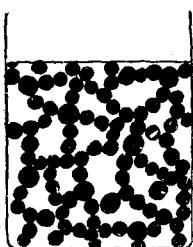


Fig. 98 (ii). The hydrated colloidal particles arranged in a network that encloses water to form a gel.

clothes and shoes we wear, the wooden furniture we use, the houses we live in, the very books and newspapers we read, are all largely composed of colloids. Let us examine our *dinner table* from this angle.

ARTICLE	TYPE OF COLLOIDAL SYSTEM
(i) <i>Halwa</i>	Gel structure.
(ii) Steaming hot food	Droplets of water dispersed in air.
(iii) Biscuits or <i>roti</i>	Air dispersed in water.
(iv) Milk	Fat globules dispersed in water.
(v) Butter	Water dispersed in fat.
(vi) Cheese	Fat dispersed in solid casein.
(vii) Smoke from cigarettes	Carbon dispersed in air.
(viii) Ice cream	Ice particles dispersed in cream.
(ix) Fruits	Juice dispersed in the solid tissue of the fruit.
(x) <i>Lassi</i>	Suspension of casein in water.

We will now discuss a few important applications of colloid chemistry.

(i) **Colloidal Medicines.** Colloidal medicines are more effective on account of their easy assimilation and adsorption.

(i) *Argyrol* and *protargol* are protected colloidal solutions of silver. They are used as a cure for granulations.

(ii) *Colloidal gold, manganese, calcium, etc.*, are used for intramuscular injections to raise the vitality of human system in diseases like tuberculosis and rickets.

(iii) *Colloidal Sulphur* is used as a germ killer, especially in plants.

(iv) *Colloidal antimony* has been shown to be effective in curing *kalazar*.

(2) **Smoke Precipitation.** Every day we see so much smoke coming out of the chimneys. Its production in big cities cannot be avoided due to the existing large number of factories which are an essential feature of modern civilisation. Now, smoke is a colloidal system consisting of carbon particles dispersed in air. The carbon particles remain in colloidal suspension because they carry an electrical charge which prevents them from settling. If somehow their charge could be removed, the smoke particles would precipitate.

To achieve this, Cottrell devised an **electrical precipitator** in which

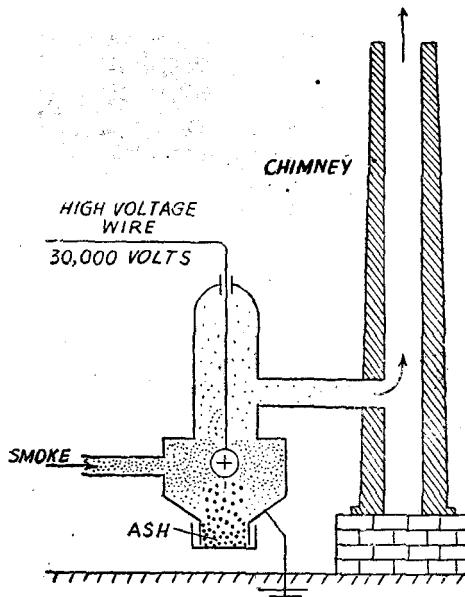


Fig. 99. Smoke precipitation.

the carbon particles in smoke are made to settle down by bringing them in direct contact with oppositely charged metallic plates. A modern form of this precipitator is shown in Fig. 99. The smoke is led through a chamber provided with a metallic knob charged to a very high potential. The charged particles are attracted to the knob, lose their charge and fall down, while the gases free from smoke pass up the chimney.

(3) **Sewage Disposal.** Dirt particles dispersed in water carry a charge on them and may be separated by *Cataphoresis*. A system

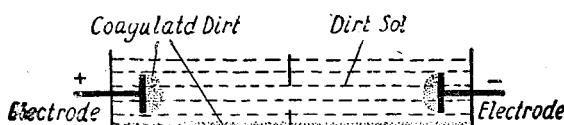
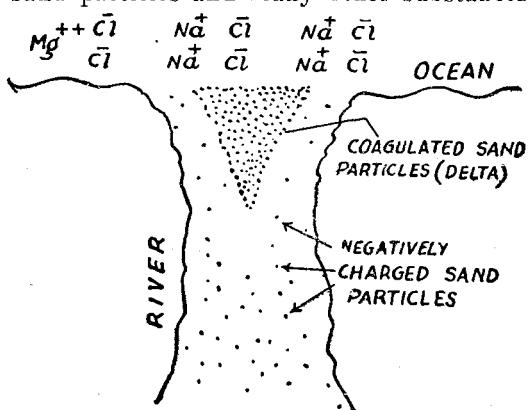


Fig. 100. Sewage disposal.

of two tanks fitted with metallic electrodes is used to effect the separation (Fig. 100.). The solid dirt particles dispersed in water are coagulated on the oppositely charged electrodes. The deposit thus obtained may be utilised as a manure.

(4) **Purification of Water.** Impure water contains clay particles and bacteria, etc., suspended in it. When alum is dissolved in such water, the coagulation of colloidal impurities takes place. Alum furnishes aluminium ions Al^{+++} in solution which discharge the negatively charged sol. particles and cause them to settle down. The clear water can then be decanted off.

(5) **Formation of Delta.** The river water carries with it sand particles and many other substances in the suspended state.



Sea-water on the other hand contains a number of electrolytes dissolved in it. When the river-water meets sea-water, the colloidal sand and other suspended materials present in the former are precipitated by the electrolytes of the latter and delta is formed.

(6) **Rubber Industry.**

Rubber is obtained from the sap of certain trees as an emulsion of negatively charged rubber particles in water (*Latex*). On boiling, the protective layer of the protein, naturally covering the particles, is broken and the rubber particles are exposed to the coagulating effect of salts present in the dispersion medium. The coagulated mass is *vulcanised* (treated with sulphur) and sold as rubber.

Metal and wooden articles can be "rubber plated" by *cataphoresis* when the negatively charged rubber particles are deposited on the article which is made the anode in such a process (*Anode process*).

(7) **Tanning.** Both hides and leather are gel structures containing proteins in the colloidal state. When hides are soaked in *tannin* which itself is a sol., the mutual coagulation of the positively charged particles of the hide and the negatively charged particles of tannin takes place. This process called **tanning** imparts hardness to leather which now has a less tendency to undergo putrefaction.

Among the material tanning agents, chromium salts are used with advantage for the precipitation of the hide material and the process is called *chrome tanning*.

(8) **Cleansing Action of Soap.** Action of soap is two-fold :—

- (a) It forms a colloidal solution in water and removes dirt by simple adsorption at the surface of the sol. particles ; and
- (b) It emulsifies the greasy or oily materials which are thereby detached from the body or cloth. Other substances which are usually sticking on account of the grease are also automatically released when the latter is emulsified.

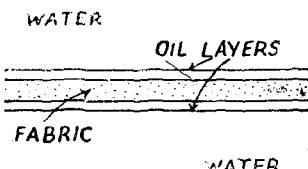


Fig. 102. Oil film on fabric in the presence of water.

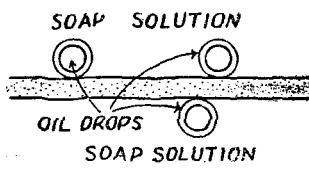


Fig. 103. Soap is adsorbed on the oil, lowers the interfacial tension between oil and water, and thus the former rolls into droplets.

(9) **Chemical Warfare.** Smoke or mist screens are formed by the dispersion of irritant or otherwise harmful substances by bombs, portable sprayers, etc.

Gas masks are essential to filter out irritant or toxic smokes which are adsorbed by a suitable adsorbent like colloidal animal charcoal.

(10) **Photographic Plates.** These are thin glass plates coated with gelatin containing a fine suspension of silver bromide. A solution of potassium bromide and gelatin is mixed with a solution of silver nitrate. Insoluble silver bromide appears in the form of a fine suspension protected by gelatin. This is then painted on the glass plates.

(11) **Colloids in Nature.** (i) **Rain.** When air saturated with water vapour reaches a cool region, colloidal particles of water in

air are formed due to condensation. Further condensation results in the formation of bigger drops of water which fall due to gravity. Sometimes oppositely charged clouds meet each other and mutual coagulation results in rainfall.

Bancroft succeeded in causing **artificial rain** by throwing electrified sand from an aeroplane and thus coagulating the mist hanging in the air. Mist is, of course, a colloidal system with water dispersed in air.

(ii) **Blue Colour of the Sky.** Under the ultra-microscope the colloidal particles appear to be bluish stars. Only blue light is scattered and the rest of it is absorbed. There are numerous dust and water particles floating about in the sky. They scatter blue light and make the sky look bluish. Without this scattering, sky would have been all dark.

(iii) **Tail of comets.** When a comet flies with tremendous velocity, some solid particles are left behind floating in air and produce *Tyndall Cone* which forms its tail.

(iv) **Blood.** Blood is a colloidal solution of an albuminoid substance and is coagulated to a clot by trivalent aluminium ions of alum or ferric ions of ferric chloride. This explains the *stoppage of bleeding* by the application of alum or ferric chloride.

The greater part of the oxygen taken up by blood in the lungs is adsorbed on the surface of colloidal red corpuscles and not dissolved in ordinary sense. Carbon monoxide gas is a deadly poison to human system because once the corpuscles adsorb this gas they cease to function as 'oxygen carriers'.

(v) **Milk.** Milk is an emulsion of fat in water, the emulsifying agents being albumin and casein. It is very easily digestible because emulsified fat offers large surface to the action of digestive juices secreted in the mouth, stomach and elsewhere inside the body.

(vi) **Soils.** Good soils should be colloidal in nature. They can then retain more moisture for emergency and moreover the nourishing materials are supplied to the plant by the process of adsorption. The decayed animal refuse *humus* serves as a protective colloid for the soil.

QUESTIONS AND PROBLEMS

1. Define Graham's crystalloids and colloids. Give examples. What is the significance of the term colloid as it is used now?
2. How are the colloidal systems classified? Give two examples of each system.
3. Write notes on Colloids and Crystalloids. (*Gauhati B.Sc., 1954*)
4. How will you separate a crystalloid from a colloid employing *dialysis* and *ultrafiltration*? Discuss the merits and demerits of the methods.
5. How is a colloidal solution different from a true solution? How would you prepare colloidal solutions of gold and ferric hydroxide? Describe the properties of colloids. (*Andhra B.Sc., 1953*)
6. What is a colloidal solution? Describe the preparation of a colloid and discuss its important properties. (*Calcutta B.Sc., 1954*)

7. What are the chief characteristics of colloids? How would you prepare a colloidal solution of (a) gold, (b) arsenious sulphide? What are reversible colloids?
(Agra B.Sc., 1952)
8. What is a colloidal solution? How do you distinguish between a homogeneous and a colloidal solution? How would you prepare a colloidal solution of gold?
(Nagpur B.Sc., 1953)
9. What are colloids? Explain various methods of preparing colloidal solutions and discuss their optical and electrical properties.
(Poona B.Sc., 1954)
10. What is meant by "colloidal state"? Give an account of the different methods employed to purify colloidal solutions.
(Baroda B.Sc., 1954)
11. Explain the use of (a) dialysis, (b) electrodialysis, and (c) ultrafiltration in the purification of colloidal solutions.
(Gujarat B.Sc., 1954)
12. Explain the main differences between the properties of hydrophobic and hydrophilic sols. Write notes on (a) dialysis, (b) Brownian movement, (c) Protective action.
(Mysore B.Sc., 1954)
13. Write a note on colloidal state, which throws light on (a) Tyndall phenomenon, (b) Brownian movement, (c) Charge on colloid, (d) Coagulation, (e) Peptization.
(Lucknow B.Sc., 1954)
14. Write short notes on any three of the following:—(a) Tyndall Effect, (b) Valency Rule pertaining to the coagulation of colloids, (c) Gold number, (d) Cataphoresis.
(Madras B.Sc., 1953)
15. Write concise notes on any four of the following:—(a) Brownian movement, (b) gold number, (c) Tyndall cone, (d) electrodialysis, (e) electrophoresis, (f) peptization.
(Ceylon Final, 1954)
16. Write a short note on coagulation of colloids.
(Andhra B.Sc., 1953)
17. How the charge on a lyophobic colloid is developed? What connection it has with coagulation?
(Karnatak B.Sc., 1953)
18. How may the sign of the charge on colloid particle be determined? How does the charge function in determining the stability of a colloid?
(Rajputana B.Sc., 1954)
19. Give an account of the factors which determine the stability of lyophobic and lyophilic colloids.
(Ceylon Final, 1953)
20. Write short notes on (a) emulsions, (b) Gel. Give two examples of each.
21. Explain the different methods for the preparation of colloidal solutions. Give the various applications of colloidal chemistry in everyday life, explaining the underlying principles.
(Annamalai B.Sc., 1954)
22. Give some important properties of the colloidal solutions of (a) arsenious sulphide, (b) gelatine, and (c) soap.
(Nagpur B.Sc., 1954)
23. What are colloids? How are colloidal solutions of metals prepared? Explain fully what happens when a colloidal solution of gold is treated as follows:
(a) A beam of light is passed through it. (b) An electrolyte is added. (c) It is brought under the influence of an electric field.
(Delhi B.Sc., 1954)
24. Explain the term 'colloidal solution'. Describe the different methods of preparing a 'colloidal solution'. In what respects do the physical properties of a colloidal solution differ from those of true solution?
(Banaras B.Sc., 1954)
25. (a) What do you understand by the term 'colloidal solution'? Describe the important methods employed for their preparation.
(b) Explain: (i) dialysis, (ii) cataphoresis, and (iii) coagulation by electrolytes.
(Allahabad B.Sc., 1954)
26. Define the colloidal state of matter in solid-liquid, liquid and liquid-gas systems. Give two examples of each and their special properties.
(Rajputana B.Sc., 1955)
27. Write a full account of the optical and electrical properties of colloidal solution.
(Karnatak B.Sc., 1955)

28. Give an account of the various methods available for the preparation of colloids. Discuss the phenomenon of coagulation of a colloid.

(Andhra B.Sc., 1955)

29. What are reversible colloids? Give the important methods for preparing colloidal solutions. What are their important properties?

(Banaras B.Sc., 1955)

30. What is a colloid? How would you prepare a colloidal solution of ferric hydroxide and purify it? Write its important properties.

(Osmania B.Sc., 1955)

31. What is a colloidal solution? How would you prepare a colloidal solution of ferric hydroxide? How can you determine the charge on colloidal particles?

(Nagpur B.Sc., 1955)

32. Describe some general methods of preparing colloidal solutions. What do you understand by cataphoresis, coagulation, Brownian movement and Tyndall effect?

(Agra B.Sc., 1955)

33. What are colloidal solutions? How will you differentiate a colloidal solution from a true solution? Explain the properties of a suspension.

(Rangoon B.Sc., 1956)

34. How are colloidal solutions of metals prepared? Write what you know about cataphoresis, Brownian movement and Tyndall phenomenon.

(Delhi B.Sc., 1956)

35. Write a brief note on the preparation, properties and applications of colloids.

(Punjab B.Sc., 1956)

36. Write an essay on: "Properties of colloids in relation to their practical applications."

(Madras B.Sc., 1955)

37. Compare hydrophobic solutions with hydrophilic ones. Discuss the stability of hydrophilic sols.

(Lucknow B.Sc., 1955)

38. How is a colloidal solution of arsenic sulphide prepared? In what respects does a colloidal solution, such as this, differ from a solloidal solution, such as that of starch? Give some important applications of colloids and indicate the particular property of the colloid made use of in each case.

(Mysore B.Sc., 1955)

39. Define the terms: disperse phase, dispersion medium, lyophilic sol., emulsion.

Describe the main methods employed for the preparation of colloidal solutions.

(Gujarat B.Sc., 1956)

40. What is a colloidal solution? How do you distinguish between homogeneous and heterogeneous solutions?

How do you prepare a colloidal solution of gold?

(Banaras B.Sc., 1956)

41. What are colloidal solutions and how are they prepared? Discuss their optical and electrical properties. Point out their applications.

(Poona B.Sc., 1956)

42. Write a brief account of the preparation and properties of colloidal solutions. In what respect do the properties of a colloidal solution of silicic acid differ from those of an aqueous solution of sodium chloride.

(Lahore B.Sc., 1956)

43. Explain the terms 'colloids' and 'crystalloids'. How would you separate one of them? Describe the important methods of preparation and properties of colloids.

(Nagpur B.Sc., 1956)

44. Write an essay on colloids.

(Allahabad B.Sc., 1957)

45. (a) What do you understand by the term 'colloidal solution'? In what respects do the physical properties of a colloidal solution differ from those of a true solution? (b) Explain, (i) dialysis, (ii) cataphoresis, (iii) coagulation by electrolytes.

(Nagpur B.Sc., 1957)

46. Give the general methods of preparing colloids by dispersion and condensation methods. Indicate their industrial applications.

(Travancore B.Sc., 1957)

47. What are the characteristic properties of colloidal solutions? Give their important applications.

(Aligarh B.Sc., 1957)

48. Classify the various types of colloidal solutions. Discuss the electrical properties of colloidal particles and explain the action of electrolytes on them.

(Jammu & Kashmir B.Sc., 1957)

49. Explain the following : (a) Charge on colloid, (b) coagulation, (c) Brownian movement, and (d) dialysis. (Allahabad B.Sc., 1958)

50. Distinguish between lyophobic and lyophilic colloids. Explain Schulze-Hardy law. (Aligarh B.Sc., 1958)

51. Write short essay on the colloidal state of matter. (Gauhati B.Sc., 1958)

52. Discuss the precipitation of colloids by electrolytes. What is the influence of the ions carrying the same charge as the colloid on its stability ? (Andhra B.Sc., 1958)

53. Describe any two important methods of preparing colloidal solutions. What do you understand by (i) Tyndall phenomenon, (ii) Brownian movement, and (iii) Gold Number ? (Poona B.Sc., 1958)

54. Describe one important method for the preparation of colloids. How is the sign of the charge on a colloidal particle determined ? What is meant by (a) Tyndall effect, and (b) Brownian movement ? (Punjab B.Sc., 1959)

55. Write an account of adsorption. (Rangoon B.Sc., 1958)

56. Give general methods of preparation and properties of colloids. (Aligarh B.Sc., 1959)

57. Explain and illustrate the following : (a) Schulze-Hardy law, (b) Cataphoresis, and (c) Gold Number. (Delhi B.Sc., 1959)

58. Describe various methods of preparing colloids. Discuss their stability. (Lucknow B.Sc., 1959)

59. What are colloids ? State their optical and electrical properties. their industrial applications. (Karnatak B.Sc., 1959)

60. What are colloids ? Give in brief the properties of colloidal solutions and their applications in industry ? (Marthwada B.Sc., 1959)

61. Explain why (a) A colloidal solution is not precipitated in the presence of gelatine. (b) A colloidal solution contains electrically charged particles. (c) Alum is used in town water supply. (d) A beam of light passes through a colloidal solution of gold. (Osmania B.Sc., 1959)

62. Write notes on the following :— (a) Brownian movement, (b) Peptization, and (c) Dialysis. (Vikram B.Sc., 1959)

CHAPTER VII

CLASSIFICATION OF ELEMENTS

HISTORICAL

One of the strongest instincts of mankind is to systematise. As soon as sufficiently large number of elements had been isolated and described, it was felt that there must be some order or regularity which controlled their properties. Right from the early days we find attempts being made to interpret elements into something regular and unified.

Unitary theory of Prout, or Prout's Hypothesis. Prout (1815) pointed out that atomic weights of all elements are simple multiples of the atomic weight of hydrogen and he suggested that *all elements are really built up of hydrogen atoms.* Further and more accurate atomic weight determinations made by Stas, however, showed that quite a large number of elements had fractional atomic weights, and Prout's theory fell into disrepute. There is no doubt, however, that Prout's theory for the first time indicated that all elements are related to one another through their atomic weights and that some interesting relationship between the properties and atomic weight might be discovered.

Dobereiner's Triads. Dobereiner (1829) pointed out that in certain groups of three elements with similar properties, which he called **triads**, the atomic weight of the middle element was approximately the arithmetic mean of the other two. For example,

Lithium	Sodium	Potassium	
7	23	39	$\frac{7 + 39}{2} = 23$
Phosphorus	Arsenic	Antimony	
31	75	120	$\frac{31 + 120}{2} = 75.5$

The study of the elements constituting triads made it certain that properties and atomic weights of elements are somehow inter-dependent. Dobereiner's Law was not, however, followed up because it was found to be true only in case of very few elements.

Dumas's Homologous Series. Dumas (1853) pointed out that in certain elements having similar properties there existed a relation similar to that of a homologous series so far as the atomic weights were concerned. Thus :

Nitrogen	14	=	14	a
Phosphorus	31	=	$14 + 17$	$a + b$
Arsenic	75	=	$14 + 17 + 44$	$a + b + c$
Antimony	119	=	$14 + 17 + 88$	$a + b + 2c$
Bismuth	207	=	$14 + 17 + 176$	$a + b + 4c$

where $a = 14$, $b = 17$ and $c = 44$.

Newlands' Law of Octaves. Newlands (1866) arranged the then known first 14 elements in the ascending order of atomic weights and discovered that any one element had properties similar to the eighth element after it.

H	[He]	Li	Be	B	C	N	O
F	[Ne]	Na	Mg	Al	Si	P	S
[sa]		re	ga	ma	pa	dha	ni]

He compared this relationship to an octave in music and enunciated his **law of octaves** as follows :—

"If the elements be arranged in the ascending order of their atomic weights the eighth element standing from a given one, is a kind of repetition of the first, like the eighth note in an octave of music."

Although Newlands was of the opinion that all the elements could be arranged in octaves, he met with an utter failure as he discovered that the law was not true for elements of higher atomic weights. The discovery of inert gases, which would also fall in the first two series shown above, strikes at the very root of the law of octaves as now the properties of the ninth element would be similar to those of the first. Newlands' law of octaves, however, contained the germ of a great idea which later on developed into the Periodic Law.

Lothar Meyer's Atomic Volume—Atomic Weight Curve.

Lothar Meyer (1869) stated the general **Periodic Law** that *the properties of elements are largely a periodic function of their atomic weights.* He concentrated his attention mainly on the physical properties, particularly the atomic volumes.*

Meyer plotted the atomic volumes of the elements against their atomic weights and drew attention to the well-marked periodic character of the curve. Similar elements occupy similar positions on the curve. With the exception of lithium the alkali metals are on the peaks of the curves and halogens are on the corresponding points of the ascending portions. In general the acid-forming elements lie on the ascending portions of the curves and the base-forming on the descending portions, whereas elements at or just before the troughs form oxides which are both acidic and basic in character.

Meyer showed clearly that atomic volumes are a periodic function of atomic weights and thus brought out the law of periodicity much more boldly and clearly than any attempt hitherto made.

Mendeleeff's system of classification—The Periodic Law. Mendeleeff in 1869 gave a full statement of **periodic law** which was in reality an extension of Newlands' Law of Octaves. It may be expressed as follows :—

The physical and chemical properties of elements are a periodic function of their atomic weights.

Mendeleeff improved and developed the Newlands' scheme of arranging elements. He arranged the elements in the form of a table, known as Mendeleeff's Periodic Table, the modern form of which is shown in this page. The inert gases and numerous other elements which were not known at the time of Mendeleeff have been included in the table. Thus the original table of Mendeleeff had no Group 0,

*Atomic volume = $\frac{\text{Atomic weight}}{\text{Density}}$

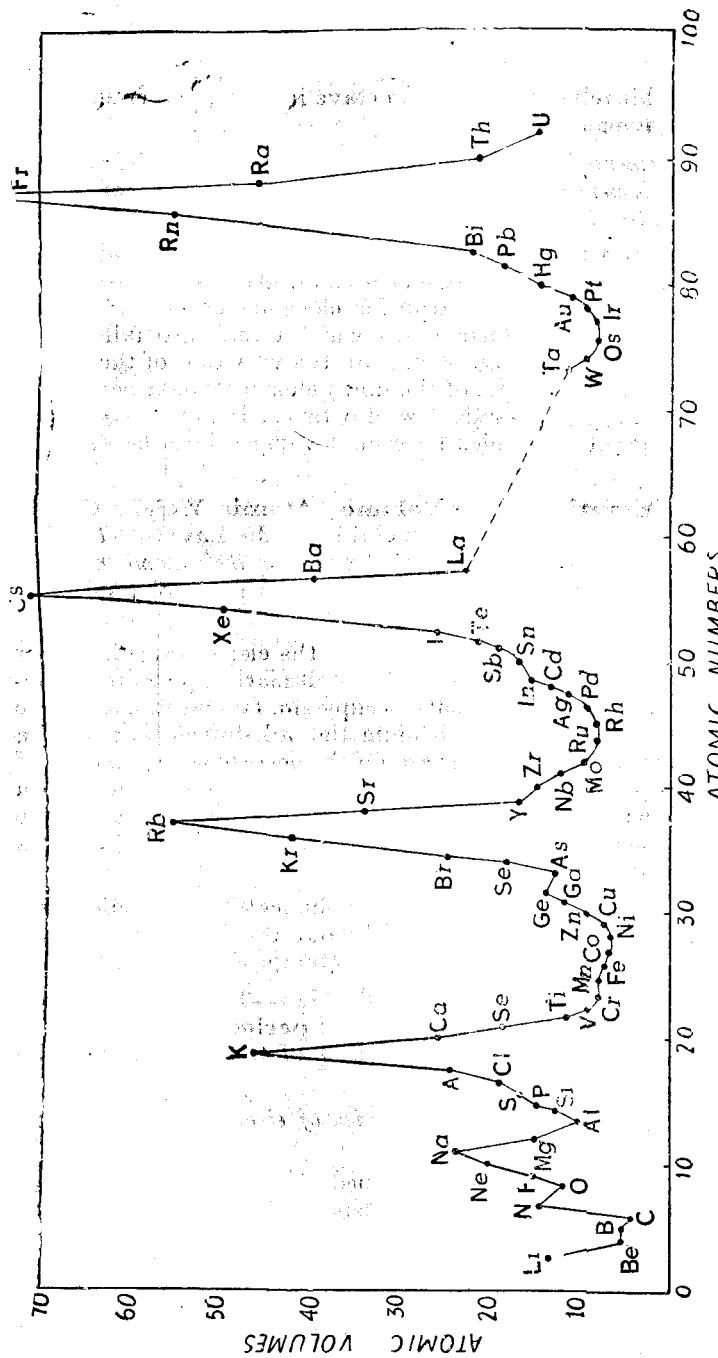


Fig. 104. Here atomic volumes are plotted against atomic numbers instead of atomic weight as done by Lothar Meyer.
This removes certain irregularities noted in the original curve of Lothar Meyer.

and its special feature was a number of vacant places, or *gaps* for the then undiscovered elements.

MODERN PLAN OF THE PERIODIC TABLE

With all the later additions of elements the plan of the table stands thus :

(a) **Periods (Horizontal Rows).**

1st of two elements.

2nd and 3rd of 8 elements each (**Short Periods**).

4th and 5th of 18 elements each (**Long Periods**).

6th of 32 elements (**Long Period**), including 14 Rare Earths.

7th of 6 naturally occurring elements and 6 elements recently discovered by nuclear reactions (**Incomplete Long Period**).

(b) **9 Groups (Vertical Columns).**

I to VII. Normal Groups,

VIII Group of 'transition elements.'

Zero-Group of inert gases.

(c) **Sub-Groups.** The vertical columns or Groups have been further divided into two *sub-groups* each. The elements placed to the left in the column form **Sub-Group A** and those placed to the right form **Sub-Group B**.

GENERAL CHARACTERISTICS OF THE PERIODS

1. Gradual change in Properties. *Elements in a period show a gradual change in properties.* Let us, for example, consider the second short period consisting of typical elements.

	Na	Mg	Al	Si	P	S	Cl
Nature of Oxide	Strongly basic	Basic	Amphoteric	Weakly acidic	Acidic	Strongly acidic	very strongly acidic

Sodium is strongly electro-positive metal while chlorine is strongly electro-negative. The intervening elements Mg to S show a gradual decrease in the electro-positive character, the element in the 4th group (Si) showing the least *electro-chemical character* and is practically neutral.

Again, we find that the *metallic character* is lost as we move towards chlorine which is a typical non-metal. The physical properties also show a similar transition as indicated by the *melting points* and the *boiling points* of the elements.

	Na	Mg	Al	Si	S	Cl
Melting point	97.9°	651°	658.7°	1420	112—118.9°	—109°
Boiling point	882.9°	1380°	1800°	2600°	444.4°	—34.5°

The variation in *atomic volume* has already been described and is depicted in Fig. 104.

2. Change of Valency. In each short Period, the valency with respect to oxygen increases from one to seven (Na_2O to Cl_2O_7) while that with respect to hydrogen rises from one to four (NaH to SiH_4) and then falls back to one (PH_3 to HCl).

3. Diagonal Relationship. Elements of period 2, i.e., *Typical elements*, show a diagonal relationship with elements of Period 3.

PERIODIC TABLE

Group	Period	II		III		IV		V		VI		VII		VIII		0			
		B	A	B	A	B	A	B	A	B	A	B	C	D	E	F	G		
H 1	1.008			B 5		C 6		N 7		O 8		F 9				He 2 4.003			
Li 3	6.940	Be 4			10.82		Al 13		P 15		S 16		Cl 17				Ne 10 20.183		
Na 11	23.00	Mg 12			24.32			28.06		31.02		32.06		35.46				A 18 39.944	
K 19	39.10	Ca 20		Sc 21		Ti 22		V 23		Cr 24		Mn 25		Fe 26		Co 27 58.69			
{ First Series	39.10	Ca 20	40.48	Sc 21	45.10	Ti 22	47.90	V 23	50.95	Cr 24	54.93	Mn 25	55.84	Fe 26	Co 27 58.69	Ni 28 68.69	Kr 36 83.7		
{ Second Series	63.57	Cu 29	65.38	Zn 30	65.72	Ga 31	65.72	Ge 32	72.69	As 33	74.91	Se 34	78.96	Br 35	79.92	Ru 44 101.7	Rh 45 102.91	Pd 46 106.7	Xe 54 131.3
{ First Series	85.48	Rb 37	87.63	Sr 38	88.92	Y 39	91.22	Zr 40	92.91	Nb 41	95.95	Mo 42	97.8	Ta 43	101.7	Ru 44 101.7	Rh 45 102.91	Pd 46 106.7	Xe 54 131.3
{ Second Series	107.88	Ag 47	112.4	Cd 48	114.76	In 49	114.76	Sn 50	118.70	Sb 51	121.76	Te 52	127.61	Re 75	126.92	Os 76 190.2	Ir 77 193.1	Pt 78 195.23	Rn 86 222
{ First Series	132.91	Cs 55	137.36	Ba 56	138.92	La 57*	138.92	Hf 72	138.92	La 73	140.88	W 74	185.92	Te 85	186.31	At 85	U 92 238.07	Gd 64 156.9	Lu 71 174.99
{ Second Series	197.2	Au 79	Hg 80	200.62	Tl 81	204.38	Pb 82	207.21	Bi 83	209.00	Po 84	210	U 92 238.07	Gd 64 156.9	Lu 71 174.99	Am 95 243	Bk 97 245	Cf 98 246	Rn 86 222
* Rare Earths (Lanthanides)	Ce 58		Pr 59		Nd 60		Pm 61		Sm 62		Eu 63		Gd 64						
	140.13		140.9		144.27		147		150.4		152		156.9						
	Th 65		Dy 66		Ho 67		Er 68		Tm 69		Yb 70		Lu 71						
	159.2		162.46		163.5		167.2		169.4		173.04		174.99						
	Th 90		Pa 91		U 92		Np 93		Pu 94		Am 95		Cm 96						
	232.12		231		238.07		231		242		243								
	, 7		Fr 87		Ra 88		Ac 89**		Th 90		Pa 91		U 92 238.07						

** ACTINIDES

CLASSIFICATION OF ELEMENTS

For example, there is undoubtedly resemblance between lithium and magnesium, between beryllium and aluminium, and between boron and silicon

Group (2nd Period)	I	II	III	IV
(3rd Period)	Li Na	Be Mg	B Al	C Si

The elements of the second period, since they form a connection or 'bridge' between their own group and the one that follows are sometimes called the *Bridge Elements*.

4. Typical Elements. Elements of the second short period are the best representative of their Groups and are commonly referred to as the *Typical Elements*.

5. Normal and Transition Elements. In the long periods, eight of the elements resemble the typical elements in the 2nd short period and are known as *Normal elements*, the rest being the *Transition elements*. For example, consider the first long period. This consists of 18 elements. The first two *viz.*, K and Ca are normal elements which resemble the typical elements Na and Mg and are separated from the rest of the normal elements (Ga, Ge, As, Se, Br and Kr) by a set of ten transition elements (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn).

GENERAL CHARACTERISTICS OF THE GROUPS

1. Resemblance of elements in a sub-group. The elements of a sub-group resemble one another but there is usually little resemblance between the elements of the two sub-groups of the same Group. Thus while lithium, sodium, potassium, rubidium, and caesium, all members of Group IA, resemble one another, they have but little resemblance to the elements of Groups IB, that is, to copper, silver and gold.

2. Gradual change of properties with rise of At. Wt. Elements in the same Group have similar physical and chemical properties which vary gradually with increase of atomic weight. For example, Group I contains the electro-positive alkali metals lithium, sodium, potassium and caesium. They all decompose cold water, and give rise to strongly basic hydroxides of the type NaOH. Their base-forming tendency increases with increase of atomic weight. Thus sodium is more reactive than lithium and less reactive than potassium.

OVERALL RELATIONSHIP OF THE PERIODIC TABLE

If the VIII group and Zero group are left out and a diagonal line is drawn across the table as shown in the chart on page 152, the following general relationships may be observed :—

(1) The elements falling below and to the left of the diagonal line have the properties of metals. For the elements in any given group, the metallic character is more marked the farther an element is removed from the diagonal line. Thus the most pronounced metallic elements like silver and gold occur in the lower left-hand region of the table.

(2) The elements falling above and to the right of the diagonal

line possess non-metallic character. The non-metallic character becomes more pronounced the farther an element lies from the diagonal line. Thus the most non-metallic elements (O, F, Cl, S, etc.) appear in the upper right-hand region of the table.

(3) The diagonal line while it divides the metals and non-metals in the table, represents a common boundary of the two regions and thus the elements lying on or near it possess the properties of both metals and non-metals. These elements (As, Sb, etc.) are known as *metalloids*.

(4) The position of an element in the Periodic Table also gives a fairly good idea about its chemical activity. The activity of metals in each group increases with the rise of atomic weight, but this tendency becomes less marked as we go towards the diagonal line in the table. In case of non-metals the chemical activity decreases with increase of atomic weight in a group and this trend is less marked as we move from Group VII towards the diagonal line. Accordingly the most active metals appear in the lower left-hand corner of the table, while the most active non-metals are to be found in the upper right-hand corner.

Some of the relationships described above are illustrated in Fig. 105.

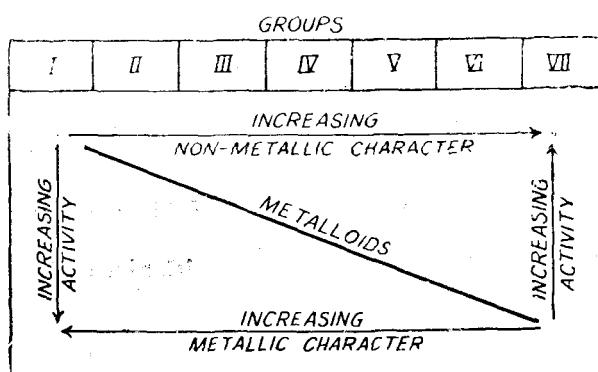


Fig. 105.

ADVANTAGES OF MENDELEEFF'S TABLE

1. Hastened in the Discovery of New Elements. The gaps in the original table of Mendeleeff showed the places of the elements which were then yet to be discovered. Mendeleeff predicted their At. Wts. and other physical and chemical properties which were the mean of the properties of the neighbouring elements. His predictions have frequently been fulfilled. Thus the three elements gallium, germanium and scandium were discovered many years after Mendeleeff had predicted their existence. Their properties were found to be closely related to the predicted properties and they occupied the positions reserved for them.

2. Helped in the Determination of Atomic Weights. We know that $\text{Atomic Weight} = \text{Valency} \times \text{Equivalent Weight}$. The

position of an element in the Mendeleeff's Table indicates its valency. Hence the atomic weight of an element can be calculated when its equivalent weight and its position in the table are known. This was done in the case of beryllium. The equivalent weight of this element was found to be approximately 4.5 and Mendeleeff placed it in the second Group. Thus the atomic weight of beryllium was determined to be $4.5 \times 2 = 9.0$. The correctness of this value has since been abundantly confirmed.

3. Helped in Correcting Doubtful Atomic Weights. Atomic weights of some elements as known at the time of Mendeleeff were wrong. Mendeleeff placed those elements in the appropriate positions in the Table according to their properties and pointed out that their atomic weights needed correction. For example, the elements, osmium, iridium and platinum were then believed to have the following atomic weights :—

$$\text{Os} = 198.8, \text{Ir} = 196.7 \text{ and Pt} = 196.7.$$

If they were to be arranged in order of atomic weights, the Group-VIII would read thus :

Fe	Co	Ni
Ru	Rh	Pd
Pt	Ir	Os

But such an arrangement is opposed to the general properties of these elements, platinum resembling nickel and palladium more closely than it does iron and ruthenium. Thus Mendeleeff in his table arranged the transition elements as :

Fe	Co	Ni
Ru	Rh	Pd
Os	Ir	Pt

The suspected atomic weights of Os, Ir, Pt were redetermined and following correct values were obtained : Os = 191, Ir = 193 and Pt = 195.2.

4. Helped in Guiding Research. Mendeleeff's table in its present form is the most complete and perfect summary of chemical knowledge that has ever been made. At a glance, one can form an idea how particular element is going to behave with respect to other elements. Thus it has proved extremely helpful in guiding research.

DEFECTS IN MENDELEEFF'S TABLE

Although Mendeleeff's Table was a great advance over all the previous attempts to arrange elements, it could not satisfactorily accommodate on the basis of atomic weights the post-Mendeleeff developments. In the Table itself also, certain anomalies were observed.

1. Position of Hydrogen. The position of hydrogen in the Table is undecided. It behaves both like alkali metals and halogens. Because of this it claims to be represented at the head of the Table in Group I and then again in Group VII along with the halogens.

2. Rare Earths. In the sixth period, there occur after lanthanum a series of 14 rare earth elements with atomic weights

differing by one, two or even four, which are all trivalent and claim position in the third Group. These *rare earths*, known as Lanthanides, make it impossible to proceed normally if they be arranged according to rising atomic weights.

3. Anomalous Pairs of Elements

(a) *Tellurium and Iodine*. From chemical considerations, tellurium properly belongs to Group VI and iodine to Group VII, but the atomic weight of the former element is found to be higher than that of iodine.

		Atomic weight	Group
Tellurium	...	127.61	VI
Iodine	...	126.92	VII

This implies that the position of these elements in the Table should be reversed.

(b) *Argon and Potassium*. Argon is an inert gas and must be in Group 0 whereas potassium is an alkali metal claiming its position in Group I, but the atomic weight of potassium is lower than that of argon.

		Atomic Weight	Group
Argon	...	39.94	0
Potassium	...	39.10	I

If arranged according to atomic weights, potassium would fall in zero group and argon in first group, which looks ridiculous.

(c) *Nickel and Cobalt*. The atomic weight of nickel is slightly less than that of cobalt although when arranged according to properties it occurs first in Group VIII.

Fe	Co	Ni
(55.84)	(58.94)	(58.69)
Ru	Rh	Pd

Os Ir Pt

Nickel resembles palladium and platinum more than it does rhodium and iridium. Obviously, when arranged in order of atomic weights it would fall in a wrong position.

4. **Isotopes.** If we arrange elements according to rising atomic weights, *isotopes* have no place in the table. If we attempt to continue normally with them, the periodic character of the table would be marred.

5. **Group VIII.** In Group VIII, we find nothing but discrepancies. These elements do not fit into the system at all and have, therefore, been placed by themselves as a separate Group. It is questionable whether we can call it Group VIII, since it is in no physical or chemical sense a true extension of the system one step beyond Group VII. For example, all elements from Group I to VII exhibit valency towards oxygen corresponding to the group number but of all the elements in the so-called Group VIII, there is only one, *viz.*, osmium which has a value of eight towards oxygen.

6. **Similar Elements Separated in the Table.** Certain elements which have similar properties are separated in the table. For example :

Copper and Mercury, Silver and Thallium, Barium and Lead
Group → I II I III II IV

7. Dis-similar Elements placed together in the same Group. Some elements have been allotted places in the same group of the table in opposition to their properties. For instance Cu, Ag and Au fall into one group with the alkali metals. The bivalence of copper and trivalence of gold appear to be uncomfortable with the valency of their companions. Manganese has been classified along with halogens with which it has little similarity.

THE MODERN PERIODIC TABLE

The existence of well-defined exceptions to Mendeleeff's system led chemists to the conclusion that the position of an element in the Table is not dependent upon the atomic weight, but rather on some other property of the atom to which the atomic weight bears some connection.

The credit for showing that *atomic number*, and not the atomic weight, is the fundamental property of the atom, goes to Mosley (1911). Today, **Mosley's periodic table**, based on atomic numbers completely displaces the periodic table of Mendeleeff. Thus the **Periodic Law** in its modern form may be stated as :

Properties of elements are a periodic function of their atomic number.

We shall presently see that when atomic number becomes the basis of classification some of the irregularities or anomalies in the Mendeleeff's Table disappear. It may not be out of place to mention here that Mendeleeff's classification depended on the happy accident that atomic weights generally increase with increase in atomic number and only rarely go astray.

Defects in Mendeleeff's Table removed by Mosley Classification. The elements which would fall in wrong places in the Table if arranged in order of atomic weights now occupy their natural places when arranged according to atomic numbers.

	At. Number	At. Weight
A	18	39.94
K	19	39.10
Co	27	58.94
Ni	28	58.69
Te	52	127.61
I	53	126.92

(2) The *isotopes* of an element, since they have same atomic number, are placed in one and the same place in the Table.

Defects in the Table which still persist

There is no doubt that the classification in order of atomic numbers is an improvement over Mendeleeff's system and perhaps a better classification is not possible, but it has not changed the position very much as regards defects in the Table. Flaws in the Table which still persist are :

(1) *Dual behaviour of hydrogen* remains unexplained. It may be placed in Group I or VII.

(2) The problem of the location of rare earth elements in the Table has not been solved. They have different atomic numbers

but their chemical behaviour claims a position in the third group along with lanthanum. These rare earths defy the arrangement according to atomic number.

(3) The *Group VIII*, which in fact is no normal group but a creation, still exists.

(4) Certain *similar elements* are *separated* in the Table while on the other hand there are such elements which have been allotted places in the same Group in opposition to their properties.

MODERN PERIODIC TABLE JUSTIFIED BY ATOMIC STRUCTURE *

Our present knowledge of the structure of the atom has shown that the Periodic Table as it stands is valid and that the defects which still persist cannot possibly be removed by any new scheme.

1. Periodic character of the Table. The arrangement of electrons in the first 15 elements may be written as

At. No.	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Element	H	He	Li	Be	B	C	N	O	F	Ne	Na	Mg	Al	Si	P
1st orbit	1	2	2	2	2	2	2	2	2	2	2	2	2	2	2
2nd orbit	—	0	1	2	3	4	5	6	7	8	8	8	8	8	8
3rd orbit	—	—	—	—	—	—	—	—	—	0	1	2	3	4	5

The elements with the same number of valency electrons have similar chemical properties and as is clear from above, the *properties of elements* will, therefore, be repeated after certain period.

2. Length of the periods. The length of the periods is fully borne out by the arrangement of electrons in different orbits. The completion of the last orbit marks the end of period.

3. Dual behaviour of hydrogen. The *dual behaviour of hydrogen* has been explained. Hydrogen atom has only one extra nuclear electron which can easily be lost forming positive hydrogen ion H^+ . Hydrogen on the other hand can also gain one electron and acquire stable helium configuration, thus yielding negative hydrogen ion H^- . In this way hydrogen can behave both like an alkali metal and like a halogen.

4. Position of Rare Earths. The electronic configuration of rare earth elements may be written as $2, 8, 18, (18 + x), 9, 2$ where $x = 0 \rightarrow 13$. This means that after lanthanum, no doubt the increase of one extra nuclear electron corresponds to an increase in atomic number by one unit, but this does not affect the valency electrons as the new electrons go to complete an inner namely, the $4f$ shell (*Cerium 4f¹ to lutecium 4f¹⁴*) Thus the chemical behaviour of rare earths which depends mostly on the valency electrons remains the same, although the atomic number increases.

A similar position is now found to exist in Period 7, which has been enlarged during the last few years as a result of researches on atomic energy. In this period, the $5f$ shell gains the electrons from *Thorium 5f¹ to Californium 5f³* the elements following californium being still undiscovered.

*This may be read by the student in his second reading of the book when he has studied the structure of the atom.

5. Existence of VIII Group. The existence of the transition elements of the VIII group is justified on their electronic configuration. All of them possess two valency electrons and are bivalent in general. Although their atomic No. changes, their chemical properties remain the same. Hence they cannot be fitted in the Table and must be placed in separate group outside the Table.

JULIUS THOMSEN'S TABLE

Out of the many attempts made to improve the Mendeleeff's Table, Julius Thomsen's Table may be mentioned. Bohr in his survey of atomic structures made use of Thomsen's classification which brought out some new features. This classification is given in Fig. 106.

			55 Cs — 87 —
		56 Ba	88 Ra
		57 La	89 Ac
		58 ↑	90 Th
		59	91 Pa
		60	92 U
		61	
		62	
		63	
	19 K - 31 Rb	64	
	20 Ca - 38 Sr	65	
	21 Sc	66	PARE EARTHS
	22 Ti	67	
	23 V	68	
	24 Cr	69	
	25 Mn	70	
	26 Fe	71	
	27 Co	72	H.F.
	28 Ni	73	Ta
1 H	29 Cu - 47 Ag	74	W
2 He	30 Zn - 48 Cd	75	Re
	31 Ga - 49 In	76	Os
	32 Ge - 50 Sn	77	Ir
	33 As - 51 Sb	78	Pt
	34 Se - 52 Te	79	Au
	35 Br - 53 I	80	Hg
	36 Kr - 54 Xe	81	Tl
		82	Pb
		83	Bi
		84	Po
		85	-
		86	Nelby

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Fig. 106. Julius Thomsen's Periodic Table.

In this scheme, each vertical column represents a horizontal series of the Mendeleeff's table. H and He are placed in a separate series. Li to Ne and Na to A are small series of 18 elements; K to Kr and Rb to Xe are two long series of 18 elements; and from Cs to Rb is the longest series of 32 elements. The outstanding features

of the scheme are : (i) the chemically allied elements are similarly placed in this scheme e.g., Li, Na, K, Rb and Cs ; Ne, Ar, Kr, Xe and Rn ; (ii) the position of transitional elements, and of the sub-group members is clearly seen (iii) the pairs are arranged according to valencies, the first pair Li-Na-K is monovalent, the second Be-Mg-Ca is bivalent, and so on.

GAPS IN THE TABLE RECENTLY FILLED UP

<i>Atomic Number</i>	<i>New Name</i>	<i>Discoverer</i>	<i>Old Name</i>
43	<i>Technetium</i>	Perrier and Segre	Masurium
61	<i>Promethium</i>	Marinsky and Glendenin	Illinium
85	<i>Astatine</i>	Corson and Segre	Alabamine
87	<i>Francium</i>	Mlle Perey	Virginium

QUESTIONS AND PROBLEMS

1. Give a critical survey of the development of the periodic classification. What is the present position of the Periodic Law ?
2. Describe the plan of the Mendeleeff's Table and point out the general relationships between the members of (i) a period, and (ii) a bridge element and (iii) transition elements ?
3. Give a historical development of the periodic classification of elements indicating its merits and demerits. Describe how recent investigations have contributed to solve the observed imperfections.
4. Write an essay on periodic classification of elements. Discuss the position of hydrogen and radio-active elements. (*Banaras B.Sc., 1952*)
5. Write an essay on periodic classification of elements with special reference to the position of rare gases and the transition elements.
6. Give a brief account of the Periodic classification of elements and its use in organising our knowledge of inorganic chemistry. How do modern developments alter the classical ideas on which the classification was based ?
7. Give a brief account of the essentials of Mendeleeff's Periodic classification of elements. What are the apparent difficulties with this classification ?
8. Give an account of the methods used for the classification of elements. What is the method adopted by Mendeleeff ? Describe its advantages and disadvantages. (*Osmania B.Sc., 1954*)
9. What is the basis of the arrangement of the elements in the Periodic Table ? How do the properties of the elements in (a) a period and (b) a group vary as the atomic weight increases ? What valencies are characteristic in the table ? (*Rajputana B.Sc., 1953*)
10. Discuss the periodic classification. Point out its defects, and state how these defects have been removed. What are isotopes ? How would you assign them position in the periodic table ? (*Andhra B.Sc., 1953*)
11. Outline briefly the attempts that have been made to classify the chemical elements. What shortcomings exist in periodic classification ? (*Ceylon Final, 1954*)
12. Discuss concisely the different kinds of relationship that the elements exhibit when arranged in the periodic table. (*Patna B.Sc., 1954*)
13. Mention the anomalies in the periodic classification of elements and point out how they have been explained. (*Madras B.Sc., 1950*)
14. Write an essay on the position of Rare gases in the classification of elements. (*Madras B.Sc., 1951*)

15. Discuss the position of any two of the following in the Periodic Table :—

- (a) Elements of the rare earths ;
- (b) Rare gases of the atmosphere ;
- (c) Transition elements.

(Bombay B.Sc., 1953)

16. Discuss the position of Rare Earths in the Periodic Table.

(Poona B.Sc., 1953)

17. What are the anomalies of Mendeleeff's system of classification of elements and how will you account for them ? (Annamalai B.Sc., 1954)

18. Mention the advantages and defects of Mendeleeff's Table. How far the Mosley classification according to atomic number is an improvement over Mendeleeff's system ?

19. What light has the atomic structure thrown on the validity of the Periodic Table as it stands today ?

20. Discuss and illustrate by taking the examples of the elements of the second period of the Periodic Table the correlation between the arrangements of electrons in their atoms and the Periodic Table. (Rajputana B.Sc., 1954)

21. Explain what do you understand by the following statement :

'The properties of the elements are a periodic function of their atomic weights. Discuss the role of atomic numbers in the periodic table.'

(Rajputana B.Sc., 1955)

22. Describe the chief features of periodic classification, and discuss the merits of such classification. (Rangoon B.Sc., 1955)

23. State Mendeleeff's periodic law and discuss the different kinds of relationships that the elements show when arranged in the Periodic Table. Illustrate, with suitable examples, the various advantages of the Periodic Table. (Patna B.Sc., 1953)

24. Illustrate with examples the statement that atomic number is a better basis than atomic weight for the classification of elements.

(Kerala B.Sc., 1957)

25. State Mendeleeff's Periodic Law. What is meant by (i) short period, (ii) long period, and (iii) atomic number ? (Bombay B.Sc., 1958)

26. Write a brief account of the periodic classification of elements and discuss the merits and demerits of such an arrangement. (Rangoon B.Sc., 1958)

27. Discuss the classification of elements.

(Lucknow B.Sc., 1959)

28. How has the Periodic classification accommodated (i) the Rare Earth elements ; and (ii) the Transition elements ? What were the misfits and how were they explained after Mendeleeff ? (Delhi B.Sc., 1959).

CHAPTER VIII

STRUCTURE OF THE ATOM

INTRODUCTORY

As far back as 1803 Dalton showed that matter is made up of extremely small particles called *atoms* (Greek, *a*-*tom* = *can't be cut*). For some time it was believed that atoms were the ultimate particles of matter but later work proved clearly that even atoms have a structure. J. J. Thomson's study (1904) of the discharge of electricity through rarefied gases led to the discovery of the electrons. Soon after, Rutherford's researches into the nature of radio-activity led him to conclude that an atom is made up of a massive small nucleus about which revolve the relatively light electrons. Our further knowledge of the number and arrangement of these electrons is derived from the concept of atomic number put forward by Mosley (1913) and the study of emission and absorption spectra.

The structure of the atomic nucleus is highly complex and till recently our knowledge of it was limited to the study of a few fundamental particles which are thrown out by unstable radio-active nuclei. Later research on *artificial disintegration* of stable nuclei have enhanced considerably our knowledge of the atomic nucleus.

In this chapter we shall study mainly the outer atom while the composition of the nucleus would be considered in detail at the end of the chapter on Radio-activity.

CATHODE RAYS—THE ELECTRONS

Sir J. J. Thomson (1897) showed that when an electric discharge from a high potential source is passed through a gas contained in a tube (discharge tube) at a very low pressure, 'rays' are shot out from the cathode (Fig. 107). These were named **Cathode Rays**.

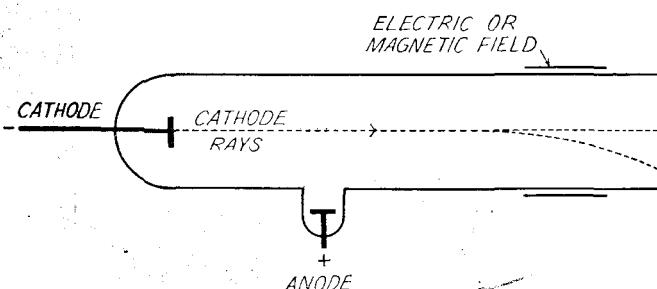


Fig. 107. Production of cathode rays and their deflection in electric or magnetic field.

Cathode rays were shown to have the following properties:—

- (i) They **travel in straight lines** normal to the cathode and cast shadows of opaque objects placed in their path.

(ii) They are deflected from their straight path by the electric and magnetic field in a way which indicates that they are **negatively charged**.

(iii) Their negative charge has also been demonstrated by allowing the rays to fall on an insulated metallic disc connected to an electroscope.

(iv) Cathode rays cause mechanical motion of small paddle wheel placed in their path and, therefore, must be consisting of **material particles**.

(v) From their behaviour in electric and magnetic fields it has been proved that cathode rays **consist of small particles called electrons** which carry one unit negative charge on a mass equal to some $\frac{1}{1837}$ th of that of the hydrogen atom.

The electrons constituting the cathode rays may have been formed by the disintegration of the atoms of the gas under high electric pressure or from the material of the cathode itself. The electrons have been shown to have the same properties no matter what gas is used in the tube or what material is used for the electrodes. This is a strong indication that *electrons are alike irrespective of their source*. Electrons are also obtained by the action of X-rays and ultra violet rays on metals, from heated metal filaments, and as β -particles from radio-active substances. The electrons obtained in all these ways have the same mass and the same charge and are quite identical. Hence the *electrons must be a common constituent of all atoms or that atom has a structure involving electrons*.

ANODE RAYS OR POSITIVE RAYS

The atom is electrically neutral. The gas atoms robbed of a few negative electrons in the discharge tube would naturally acquire a positive charge. These positive particles will move away from the anode and dash against the cathode. If a hole be cut through the

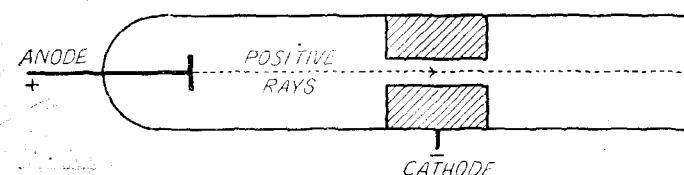


Fig. 108. Production of Positive Rays.

cathode (Fig. 108) these particles will pass through it and appear behind the cathode in streams or 'rays'. Originally discovered by Goldstein (1886) the properties of these rays were investigated in detail by Sir J. J. Thomson.

(i) They are deflected by electric and magnetic field just as cathode rays, but in the opposite direction showing that unlike cathode rays *they consist of positively charged particles*. For the same reason, Thomson named them **Positive Rays**.

(ii) The charge and mass of the particles constituting positive rays varies and depends on the nature of the gas contained in the discharge tube.

(iii) The mass of these positively charged particles is virtually the same as that of the atoms from which they are derived and is found to be equal to the at. wt. of the gas in the tube.

It has thus been concluded from the study of electrical phenomenon in gases, that atom consists of

- (a) electrons,
- (b) a positive residue with which the mass of the atom is associated.

RUTHERFORD'S NUCLEAR ATOM

The study of the positive rays and cathode rays obtained as a result of the breaking down of gas atoms in the discharge tube, shows clearly that atom is made up of negative electrons and a positive part. Rutherford carried us further by suggesting the **nuclear atom**.

As a result of his experiments on the bombardment of the atoms by high-speed alpha particles, Rutherford (1911) observed that most of the particles went very nearly straight through the atom indicating that *atom is extraordinarily empty*. A few of them, however, passed very close to the centre of the atom and were deflected from their rectilinear course as a result of which they were scattered in all directions. Since alpha-particles are helium atoms carrying two positive charges, they could be deflected or repelled only by something positively charged. Thus in order to account for the

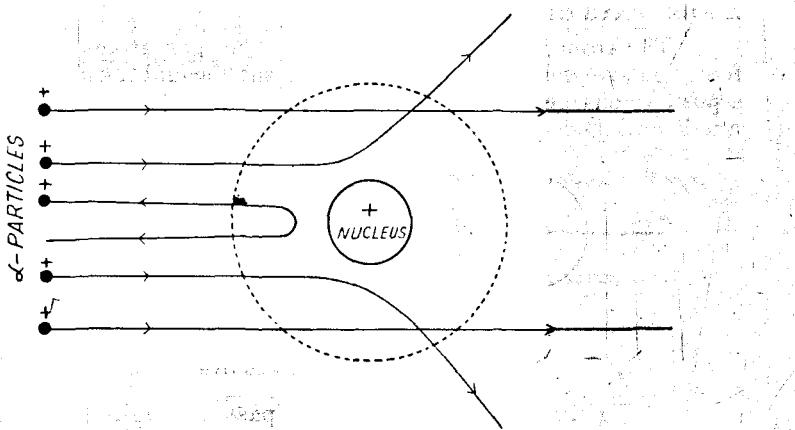


Fig. 109. Scattering of α -particles.

scattering of α -particles, Rutherford assumed that *an atom has a small positively charged central nucleus* and that the whole atomic mass is concentrated in it. Since the atom as a whole is electrically neutral the negative electrons must be distributed in space round the nucleus to balance its positive charge. These *extranuclear electrons* cannot be stationary. If it were so they would be gradually attracted by the nucleus till ultimately they fell into it. To have a stable atom, therefore, the surrounding electrons are supposed to be

moving about the nucleus in closed orbits, their motion balancing the force of attraction between them and the nucleus.

BOHR'S MODEL ATOM

Bohr pointed out that even Rutherford's picture of the atom is defective and does not ensure a stable atom. With the gradual loss of energy due to its motion, the orbit of the revolving electron will become smaller and smaller until it dropped into the nucleus. Bohr (1913) studied the motion of electrons in the light of the **Quantum Theory** according to which energy is absorbed or lost not gradually, but in 'bundles' or *quanta*. He assumed that electrons move only in certain 'fixed' or 'stationary' orbits, associated with a definite amount of energy. The energy of an electron moving in an orbit could change by a fixed quantity. Thus an electron can jump from one orbit to the other under suitable conditions but cannot lose energy regularly by smaller amounts than a quantum. In other words, under ordinary conditions the electrons move in the fixed orbits without any loss of energy.

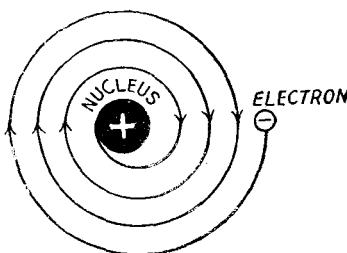


Fig. 110. Path indicating the fate of an electron due to the gradual loss of energy

Hence our final picture of the atom is that of the solar system, consisting of the sun with the planets revolving round it in fixed orbits. The electrons revolving round the nucleus are, from analogy called **Planetary electrons**. Instead of circular orbits, Sommerfeld has suggested elliptical orbits.

ATOMIC NUMBER

Our further knowledge of the atomic structure is largely derived from the concept of atomic number put forward by Mosley in 1913. He showed that there is a number, which he called the **atomic number**, characteristic of each element. When the elements are arranged according to their properties as in the Periodic Table and then numbered off 1, 2, 3, 4, etc., we get the atomic numbers of the elements.

Mosley arrived at the idea of atomic numbers in the following way. He bombarded one element after another with high-speed

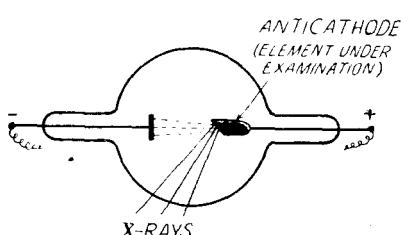


Fig. 111. X-ray Tube

electrons (cathode rays) when they emitted light waves of very short wavelength, X-rays. The frequency of these X-rays proved in each case to be characteristic of the element bombarded. It was independent of temperature, chemical combination and other external conditions, thus indicating that it depends only on the inner structure of the atom from which the X-rays emanate.

Mosely noticed that for each element a series of X-rays of different wave-lengths are obtained. He investigated only the rays of greatest frequency for a large number of elements and plotted square roots of their frequencies against the atomic numbers.

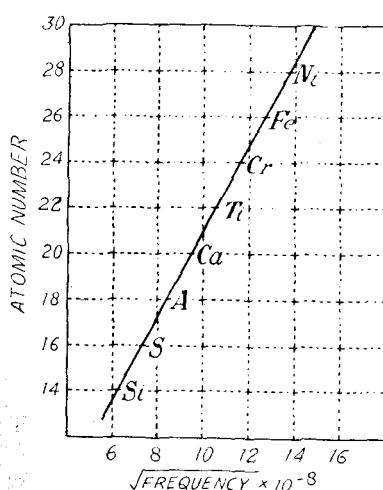


Fig. 112. Relationship between X-ray frequencies and Atomic numbers.

elements in order of atomic number has removed many irregularities previously noticed in the table.

The great significance of Mosley's work from the point of view of atomic structure lies in his suggestion that the **atomic number of an element is numerically equal to the free positive charges on the nucleus**. This has been verified by Chadwick's measurements of the deflection of α -particle taking place in the vicinity of the nucleus of a known atom. Mosley's suggestion leads to an important conclusion that to have an electrically neutral atom the *number of planetary electrons must be equal to the free positive charges on the nucleus and, therefore, to the atomic number*.

HYDROGEN ATOM—THE PROTON

Since the atomic number of hydrogen is one, there is one free positive charge on the nucleus and, therefore, only one planetary electron (Fig. 113). Since the electron has negligible weight the entire weight of the atom is due to the weight of the nucleus.

The nucleus of hydrogen—the first element—is called a **Proton** (Greek *proton* = the first). It has *one positive charge and unit weight*.

THE NEUTRON

Until the year 1933, it was believed that the nucleus consisted

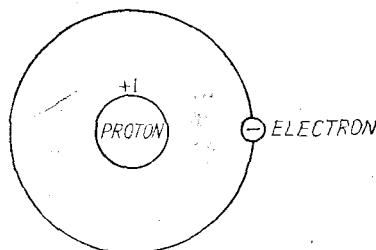


Fig. 113. Structure of Hydrogen Atom.

of *protons* and *electrons* only, the atomic weight of the atom being determined entirely by the number of protons present in it.

In 1933, however, Chadwick discovered a new fundamental particle by bombarding beryllium with fast α -particles. This particle was found to be *uncharged* and to possess a mass equal to that of a hydrogen atom. Because of its neutral character, it was named as **Neutron**.

With the discovery of the neutron, the prevalent idea that the nucleus consisted of protons and electrons was discarded and it was suggested that the nucleus is built up out of protons and neutrons. The number of protons present in the nucleus determine the net positive charge on it i.e., its *atomic number* while the *atomic weight* is equal to the sum of the protons and neutrons present therein.

ATOMIC STRUCTURE FROM AT. NO. & AT. WT.

If the atomic number of an element is N, it means that the number of planetary electrons in its atom is N. This also gives the number of protons in the nucleus of the atom. If W be the atomic weight, it will be accounted for by N protons and $(W-N)$ neutrons in the nucleus.

Proceeding on these lines the atomic structure of a few elements is given below :—

Element	Atomic Number (N)	Atomic Weight (W)	No. of Planetary Electrons =(N)	Nucleus	
				Protons =(N)	Neutrons (W-N)
Hydrogen	1	1.00728	1	1	0
Helium	2	4.00215	2	2	2
Lithium	3	6.94	3	3	4
Sodium	11	23.00	11	11	12

The atomic models given in Fig. 114 illustrate the atomic structure of some common elements.

ELECTRONIC ARRANGEMENT IN ORBITS

Having known that planetary electrons numerically equal to the atomic number are revolving about the atomic nucleus in closed orbits, the question arises as to how they are arranged in these orbits.

Langmuir Scheme. We are indebted to Langmuir for putting forward the first elaborate scheme of the arrangement of extra nuclear electrons in 1919. His fundamental conception is that the inert gases possess the *most stable electronic configuration and, therefore, contain complete electron orbits*. Since helium has two planetary electrons, the first orbit is considered fully saturated with 2 electrons. In the next inert gas neon, we have 10 planetary electrons and since 2 electrons would fully saturate the first orbit, the remaining 8 will form the next stable orbit. Argon with atomic number 18

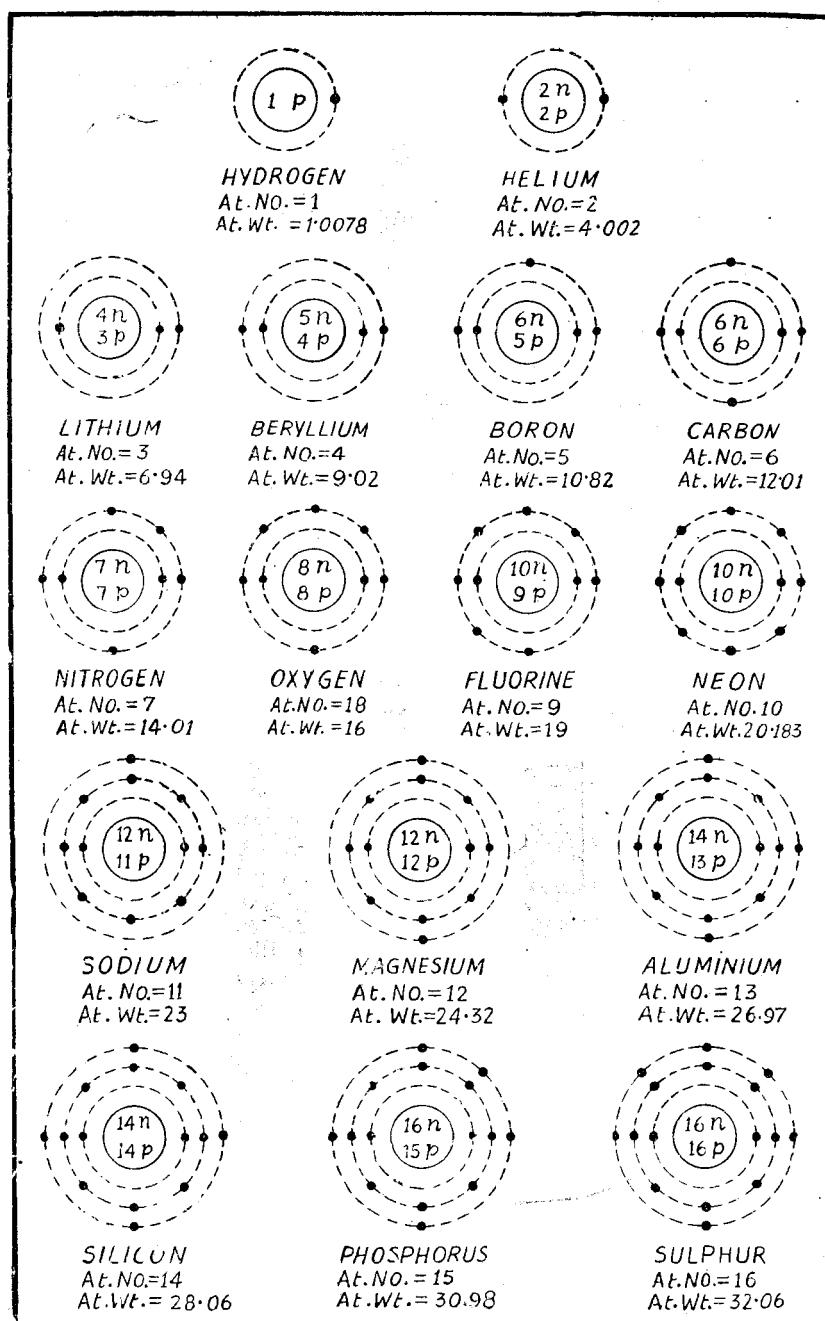


Fig. 114. Atomic Models.

will similarly have the same arrangement 2, 8, 8. Proceeding in this manner the successive orbits would contain 2, 8, 8, 18, 18, 32 electrons. Langmuir scheme although quite correct for the first few elements, failed to explain the behaviour of higher elements.

Bohr-Bury Scheme. In 1921 Bury put forward a modification of Langmuir scheme, which is in better agreement with the physical and chemical properties of certain elements. At about the same time as Bury developed his scheme on chemical grounds, Bohr (1921) published independently an almost identical scheme of the arrangement of extra-nuclear electrons. He based his conclusions on a study of the emission spectra of the elements. Bohr-Bury scheme as it may be called, can be summarised as follows :—

(i) *The maximum number of electrons which each orbit can contain is $2 \times n^2$, where n is the number of orbits.*

The first orbit can contain $2 \times 1^2 = 2$; second $2 \times 2^2 = 8$; third $2 \times 3^2 = 18$; fourth $2 \times 4^2 = 32$ and so on.

(ii) *The maximum number of electrons in the outermost orbit is 8 and in the next-to-the-outermost 18.*

(iii) *It is not necessary for an orbit to be completed before another commences to be formed. In fact a new orbit begins when the outermost orbit attains 8 electrons.*

(iv) *The outermost orbit cannot have more than 2 electrons and next-to-the-outermost cannot have more than nine so long as the next inner orbit, in each case, has not received the maximum electrons as required by rule (i).*

According to Bohr-Bury scheme the configuration of the inert gases is given in the table below :—

Inert Gas	Atomic Number	Electronic Orbit					
		1st (K)	2nd (L)	3rd (M)	4th (N)	5th (O)	6th (P)
Helium (He)	2	2
Neon (Ne)	10	2	8
Argon (Ar)	18	2	8	8
Krypton (Kr)	36	2	8	18	8
Xenon (Xe)	54	2	8	18	18	8	...
Radon (Rn)	86	2	8	8	32	81	8

A complete statement of the electronic configuration of elements elucidating the various postulates of Bohr-Bury scheme is given in the table on page 170 for ready reference.

Energy Levels. According to the Bohr theory the electrons are moving at very high velocity in different concentric orbits. There is a definite quantity of energy associated with an electron while it is revolving in an orbit, and hence the orbits are also called

ELECTRONIC CONFIGURATION OF ELEMENTS

(Atomic numbers are given after the symbols of the elements)

Energy Levels An electron can absorb light or heat energy and can thus move to a higher energy level. Since the position of the moving electrons at any moment is uncertain, the electronic orbits are commonly named as K, L, M, N, O, P, and Q energy levels. These have been illustrated in Fig. 114 (a).

SUB-SHELLS. The electrons in the several orbits or shells are divided into sub-shells, or orbitals. With the exception of the first or K-shell, all others have from two or four sub-shells. These are denoted as s, p, d, and f sub-shells or orbitals. The s sub-shell can have up to 2 electrons, the p sub-shell 6, the d sub-shell 10 and the f sub-shell upto 14 electrons. In writing the number of electrons present in an orbital, the shell number is prefixed to the symbol of the orbital and the number of electrons present in the orbital are placed at the top right hand corner of it. Thus 3s^2 stands for two electrons present in the first sub-shell of the third i.e., M shell and 2p^6 stand for 6 electrons of the 2nd sub-shell (p) of the 2nd i.e., L shell.

The distribution of electrons in the case of some common elements is given in the Table below :—

Element	At. No.	1st Orbit	2nd Orbit	3rd Orbit	4th Orbit	5th Orbit	6th Orbit
Boron		s. 2	p. 2,1	s.p.d. ...	s.p.d.
Carbon	6	2	2,2
Nitrogen	7	2	2,3
Oxygen	8	2	2,4
Fluorine	9	2	2,5
Neon	10	2	2,6
Sodium	11	2	2,6	1
Chlorine	17	2	2,6	2,5
Zinc	30		2,6	2,6,10	2
Gold	79	2	2,6	2,6,10,	2,6,10,14	2,6,10	...

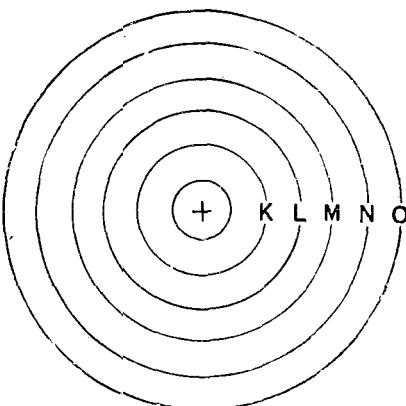


Fig. 114 (a). Energy Levels.

QUESTIONS AND PROBLEMS

1. "Matter is made of small indivisible particles called atoms." Comment on this statement.
2. Describe the Rutherford's nuclear atom. How has it been modified by Bohr?
3. Write an essay on development of the nuclear theory of the atom. (*Punjab B.Sc., 1954; Agra B.Sc., 1957*)
4. Describe the part played in elucidating the atomic structure by the following :—
 - (a) Positive rays, (b) Cathode rays, (c) X-rays.
5. What is meant by atomic number? How is it experimentally determined? Discuss its importance. (*Andhra B.Sc., 1953*)
6. Write a note on atomic numbers and their importance in the periodic classification of elements. (*Banaras B.Sc., 1952*)

7. Discuss the work of Mosley on the determination of atomic numbers. Indicate the importance of atomic numbers in Chemistry. (Bombay B.Sc., 1953)
8. What is meant by the atomic number of an element ? Discuss the statement that the atomic number of an element is more fundamental than its atomic weight. How is the atomic number of an element determined ?
9. What are electrons and protons ? Give the complete atomic structure of an element with atomic number 35 and atomic weight 80.
10. The atomic number of an element is 17.
- How are the 17 electrons arranged round the nucleus ?
 - How many electrons are there in the outermost orbit ?
 - What is the valency of the element ?
11. Give the scheme of the arrangement of planetary electrons. Show how the electronic configuration of elements explains the 'periodic law' ?
12. Describe the arrangement of electrons in atoms and point out how they are related to valency and atomic number. How has the atomic number been determined ? (Andhra B.Sc., 1952)
13. What is a proton ? Explain the difference between the proton, the positron and the electron.
- Show how the electronic structure of the atoms of elements explains the periodic law. (Rajputana, B.Sc., 1954)
14. Write an essay on the modern conception of atom. (Jammu & Kashmir B.Sc., 1953)
15. Trace the growth of our present knowledge of the extra-nuclear structure of an atom. (Baroda B.Sc., 1954)
16. Write an essay on Atomic Structure. (Punjab B.S.c., 1944 ; Agra 1952 ; Osmania 1954)
17. Write clearly an account of Structure of Atoms. (Aigarh B.Sc., 1954)
18. Give a short account of atomic structure and show how the arrangement of electrons explains the Variable Valency. (Nagpur B.Sc., 1954)
19. Write an account of the modern concept of the atom. (Madras B.Sc., 1955)
20. Write an account of the modern views about the structure of the atom. (Jammu & Kashmir B.Sc., 1957 ; Aligarh 1957)
21. What is the significance of the term 'atomic number' of an element. Describe with illustrations the structure of atoms in terms of their atomic number and mass number. (Gujarat B.Sc., 1956)
22. Write all you know about the atom. How has atomic structure helped in the development of the periodic table ? (Banaras B.Sc., 1956)
23. Write an account of the arrangement of electrons in elements. How are the chemical properties of elements dependent on their electronic structure ? (Mysore B.Sc., 1956)
24. Illustrate with examples the statement that atomic number is a better basis than atomic weight for the classification of elements. (Travancore B.Sc., 1957)
25. What is atomic number, and how it has been determined ? Discuss the importance of this number in Chemistry. (Aligarh B.Sc., 1958)
26. Write an essay on the structure of atom, giving in detail Bohr's atomic model and the modifications which resulted therefrom. (Karachi B.Sc., 1958)
27. Write an essay on the structure of the atom. (Lucknow B.Sc., 1959)
28. Describe the electronic structure of atoms and show how it has helped in understanding the chemical behaviour of elements. (Karnatak B.Sc., 1959)
29. What is atomic number ? Explain how the atomic number is a better index of the chemical properties of elements than their atomic weights. (Marthwada B.Sc., 1959)
30. Discuss briefly the modern theory of the structure of the atom. (Delhi B.Sc., 1959)

CHAPTER IX

ISOTOPES AND ISOBARS

ISOTOPES

From a study of radio-activity, Soddy recognised the presence of such elements which are virtually identical in every respect except mass and radio-active properties. They have *different atomic weights but same atomic number*, and, therefore, occupy the same place in the periodic table. They are called **Isotopes** (Greek *isos* = same, *topes* = place).

Ionium (At. Wt. 230) and thorium (At. Wt. 232) both have atomic number 90 and are said to be isotopes of one another. Though indistinguishable by any chemical means, they are easily recognised from the difference in their radio-active behaviour.

Lead was the first non-radio-active element which was shown to exhibit isotopy. The metal is the final product of disintegration of the radio-elements. The sample of lead derived from the disintegration of radium has atomic weight of 206, whereas that obtained from thorium has its atomic weight 208, and ordinary lead At. Wt. = 207.2 is merely a mixture of the two isotopes.

IDENTIFICATION OF ISOTOPES

The deflection of positive rays (which have already been shown to consist of nuclei of atoms) in an electric and magnetic field is proportional to e/m , the charge on the particle divided by its mass. The nuclei obtained from a mixture of isotopes will have the same positive charge, and, therefore, their *deflection will be inversely proportional to their masses*. Thus with a suitable application of electric and magnetic field we can identify the isotopes present in a given element.

(i) **Thomson's Parabola Method.** The apparatus devised by Thomson (1911) for the identification of isotopes is shown in

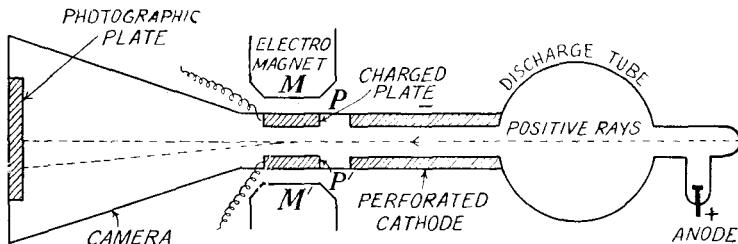


Fig. 115. Thomson's Parabola Method.

Fig. 115. The discharge tube is filled with the vapour of the element under examination and the positive rays produced from it emerge from the perforated cathode. The beam of positive rays then passes through the iron plates P and P' between which electric field can be applied. These plates P and P' are also the pole-pieces

of an electromagnet, so that electric and magnetic fields can be applied simultaneously. As the rays pass through these plates each kind of isotope suffers a different deflection depending on its mass, and records a separate parabolic impression on the photographic plates. By appropriate measurements of the parabolas thus formed, the mass of various isotopes constituting the element under examination can be determined.

(2) Aston's Mass Spectrograph Method. Aston (1919) improved upon Thomson's apparatus and devised an easier method for the identification of isotopes. By the successive application of electric and magnetic fields, he got a series of impressions on the photographic plate, each of which represented a different isotope. Thus he obtained in a way 'a mass spectrum' and hence his apparatus is often called the **Aston's Mass Spectrograph**.

Aston's Spectrograph is illustrated diagrammatically in Fig. 116. The discharge tube is filled with the gaseous element under examination and the positive rays as they emerge from the perforated

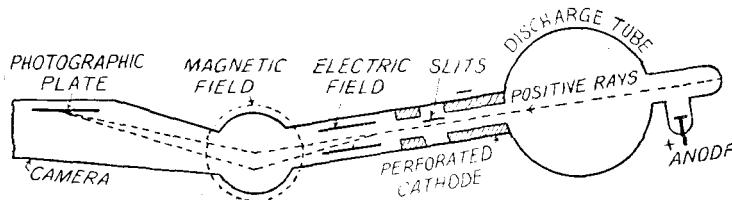


Fig. 116. Aston's Mass Spectrograph.

cathode pass through two slits. The narrow ribbon of positive rays so obtained is then subjected to electric and magnetic fields successively. By suitable adjustment of the two fields the particles having the same mass are focused at the same point on the photographic plate. Thus each point recorded on the photographic plate shows the existence of an isotope. By comparing these points on the plate with the standard marks on it we can determine the masses of the isotopes present in the given element.

List of Isotopes. With the help of his mass spectrograph Aston has shown that practically all the elements particularly those with the fractional atomic weights are composed of two or more isotopes. A list of isotopes of common elements is given in the table on page 177.

SEPARATION OF ISOTOPES

Since isotopes have exactly similar chemical properties, their separation by chemical means appears to be out of question. Their difference in those physical properties which depend on the mass of the atom has been utilised to effect their separation. The methods employed with varying degree of success are:

(1) Diffusion. Since the rate of diffusion of a gas is inversely proportional to the square root of the molecular weight, it is obvious

No.	Element	At. No.	At. Wt.	Isotopes (indicated by their atomic weights)*
1	Hydrogen	1	1.0081	1,2,3
2	Lithium	3	6.94	7,6
3	Boron	5	10.82	11,10
4	Carbon	6	12.00	12,13
5	Nitrogen	7	14.008	14,15
6	Oxygen	8	16.00	16,18,17
7	Neon	10	20.183	20,21,22
8	Magnesium	12	24.32	24,25,26
9	Silicon	14	28.06	28,29,30
10	Sulphur	16	32.06	32,33,34
11	Chlorine	17	35.457	35,37,39
12	Argon	18	39.944	40,36
13	Potassium	19	39.096	39,41
14	Chromium	24	52.01	52,53,50,54
15	Iron	26	55.84	56,54
16	Nickel	28	58.69	58,60
17	Copper	29	63.57	63,65
18	Zinc	30	65.38	64,66,68,67,70
19	Bromine	35	79.916	79,81
20	Krypton	36	83.7	84,86,82,83,80,78
21	Strontium	38	87.63	88,86,87
22	Silver	47	107.88	107,109
23	Cadmium	48	112.4	114,112,110,111,113,116
24	Tin	50	118.7	120,118,116,124,119 117,122,112,114,115
25	Antimony	51	121.76	121,123
26	Xenon	54	113.3	129,132,131,134,136 128,130,126,124
27	Barium	56	137.36	138,137,136,135
28	Tungsten	74	184.0	184,186,182,183
29	Mercury	80	200.6	202,200,199,198,201,204,196
30	Lead	82	207.22	205,203,210,209,207 206,208

that the separation of isotopes by this method is possible. The molecules of the light isotope will diffuse quicker leaving behind

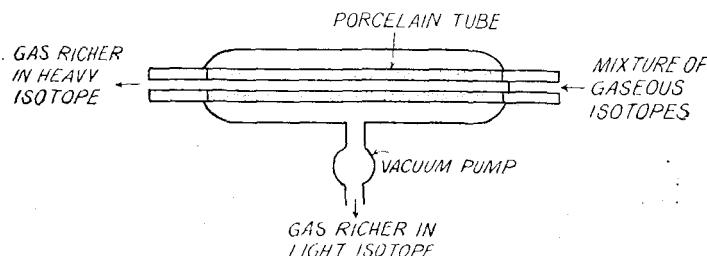


Fig. 117. A unit of the diffusion apparatus for the separation of gaseous isotopes.

those of the heavier one. This method has been successfully applied in the separation of ordinary oxygen into its constituent isotopes O¹⁶ and O¹⁸ and neon into Ne²⁰ and N²². (Fig. 117).

*Isotopes of an element are generally represented by the symbol of that element with atomic weight at the head. Thus Cl³⁷ and Cl³⁵ are the two isotopes of Chlorine.

(2) **Thermal Diffusion.** If a gaseous mixture of the isotopes be enclosed in a tube, the two ends of which are kept at different temperatures, there is a concentration of the heavier isotope at the cooler end.

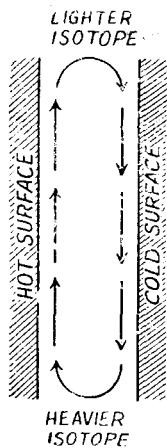


Fig. 118. Separation of isotopes by Thermal Diffusion.

Bronsted and Hevesy (1922) succeeded in affecting the partial separation of isotopes of mercury by distillation in vacuum. The apparatus used by them is shown in the diagram (Fig. 119). Mercury vapours condense on the lower surface of the inner jacket, which is chilled with liquid air. The sample obtained as condensed mercury is richer in light isotopes.

In 1935, Kessom, Van Dyk and Hantjes succeeded in separating partially the neon isotopes by this method.

(4) **Evaporation.** Light isotopes will evaporate in preference leaving the residue richer in the heavy isotope. Liquid neon was evaporated under low pressure when partial separation of its isotopes was effected.

(5) **Fractional Electrolysis.** Urey succeeded in 1933 in separating ordinary hydrogen into two isotopes H^1 and H^2 by the fractional electrolysis of heavy water. The ions of heavy hydrogen are comparatively sluggish and are liberated at the cathode later than the ions of light isotope.

(6) **Mass-Spectrograph.** Aston announced in 1928 that by placing cooled chambers instead of the photographic plate in his spectrograph it has been possible to obtain small quantities of isotopes.

Although the quantities obtained by this method are very minute, the separation is complete.

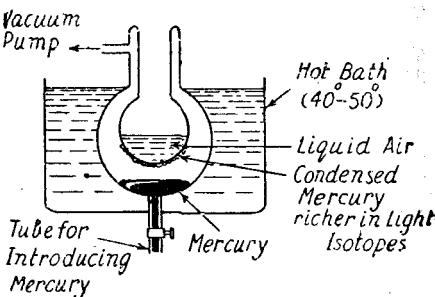


Fig. 119. Vacuum Distillation of Mercury.

STRUCTURE OF ISOTOPES

Since isotopes of an element have the same atomic number, the number and arrangement of extra-nuclear electrons must also be the same. Their nuclei, however, differ in composition. Since the number of protons in the nucleus is the same as the atomic number, the nuclei of different isotopes of an element will have an equal number of free protons and the difference in their atomic weights is naturally due to unequal number of neutrons present in each of them.

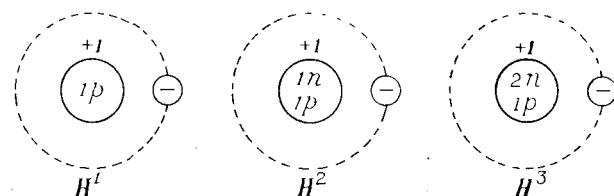


Fig. 120. Structure of the Isotopes of Hydrogen.

Similarly the structure of the isotopes of lithium, neon and chlorine will be

Isotopes	At. Wt.	At. No.	Extra-nuclear Electrons	NUCLEUS	
				Protons	Neutrons
L ⁶ Li ⁷	6 7	3 3	2, 1 2, 1	3 3	3 4
Ne ²⁰ Ne ²¹ Ne ²²	20 21 22	10 10 10	2, 8 2, 8 2, 8	10 10 10	10 11 12
Cl ³⁵ Cl ³⁷	35 37	17 17	2, 8, 7 2, 8, 7	17 17	18 20

CONCLUSIONS FROM ISOTOPY

(1) **Fractional atomic weights explained.** The general recognition of isotopes in various elements has *explained their fractional atomic weights*. An element consisting of two or more isotopes, with whole number atomic weights, in a fixed ratio gives a constant fractional atomic weight. In chlorine gas the two isotopes, Cl³⁵ and Cl³⁷ are always present in the ratio 3 : 1 and hence the average atomic weight is approximately $\frac{1}{4}(3 \times 35 + 37) = 35.5$.

(2) **Atomic number and not the atomic weight is the fundamental property of the atom.** The study of isotopes has shown that *the atomic number and not the atomic weight, is the fundamental property of an atom*. The different isotopes of an element have similar chemical properties although their atomic weight is different. They have same atomic number and similar chemical

character. Thus it is the atomic number which is related to chemical properties and not the atomic weight.

(3) **Prout's whole-number theory revived.** Prout (1815) pointed out that all atoms were ultimately made of hydrogen atoms and, therefore, atomic weights, in general should be whole numbers. With the discovery of fractional atomic weights in a large number of elements, Prout's whole-number theory fell into disrepute. The work on isotopes has now shown that most of the elements are really mixtures of isotopes, and each isotope has an atomic weight which is a whole-number. This has virtually revived Prout's whole-number theory.

(4) **Law of constant proportion is not universally valid.** The discovery of isotopes has shown that the law of constant proportions* is not of absolutely universal application.

Lead has two isotopes Pb^{206} and Pb^{208} and the molecular weights of lead chlorides obtained from these would be $(206 + 2 \times 35.5) = 277$ and $(208 + 2 \times 35.5 = 279)$ respectively. The combining ratios by weight, of lead and chlorine in the samples of the two lead chlorides would be different. This goes against the law of constant proportions. This law would, therefore, hold rigidly only in case of compounds obtained from the same isotope or a mixture of isotopes in the same definite proportions.

ISOBARS

The elements with the same atomic weight and different atomic numbers are called **Isobars** (Greek, *isso*=equal; *barys*=heavy). The

	At. Wt.	At. No.
Argon	40	18
Calcium	40	20

best known example is afforded by the most abundant isotopes of argon and calcium (Ar^{40} ; Ca^{40}).

Structure of Isobars

Since atomic weight for two isobaric elements is identical, the total sum of protons and neutrons in each case must be the same. The number and arrangement of planetary electrons will be different on account of different

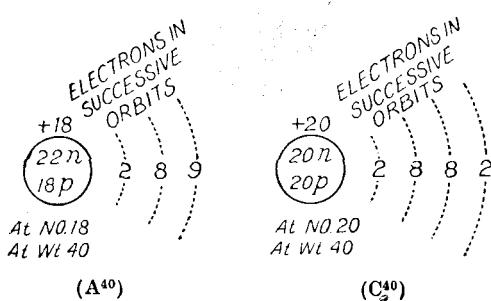


Fig. 121.

atomic numbers. The atomic structure of isobars A^{40} and Ca^{40} is given in Fig. 121.

QUESTIONS AND PROBLEMS

- What are isotopes? How are they identified?
- Write a note on the separation of isotopes.
- Show that the atomic structure of the different isotopes of the same element differs only in the composition of the nucleus.

***Law of constant proportions** states that a chemical compound always consists of the same elements combined together in the same fixed proportions by weight.

4. Use your knowledge of isotopes to
 - (i) explain fractional atomic weights,
 - (ii) show that atomic number and not the atomic weight is the fundamental property of the atom.
5. What are isobars ? How do they differ from isotopes ?
6. What are isotopes ? How are they identified ? How has the discovery of isotopes led to the further development of chemistry ?
(Punjab B.Sc., 1954)
7. Explain the term "isotope". How has the existence of isotopes in the elements been demonstrated ? How have isotopes been used in the determination of atomic weights ?
8. Give a brief account of Aston's work on positive ray analysis.
9. Write a short note on Isotopes.
10. Give an account of the theory and the principal parts of the apparatus employed by Thomson and Aston for the analysis of positive rays from various elements. Point out the significance of the results obtained from this study.
(Poona B.Sc., 1954)
11. What are isotopes ? Explain the methods employed for the separation of isotopes.
(Gujarat B.Sc., 1951)
12. Write an essay on isotopes.
(Baroda B.Sc., 1954)
13. Write a note on Isotopes and Isobars.
(Delhi B.Sc., 1953)
14. Describe Aston's Mass Spectrograph. What are its practical applications ?
(Bombay B.Sc., 1955)
15. (a) Define the following terms:—(i) Atomic number ; (ii) Isotopes ;
 (iii) Isobars.
(b) Describe the use of Aston's Mass Spectrograph.
(Punjab B.Sc., 1956)
16. What are isotopes ? Indicate two methods of separating the isotopes from a mixture containing two isotopes of an element.
(Mysore B.Sc., 1955)
17. What are positive rays ? How are these rays used to detect the isotopes of an element ? How do you account for the fact that the isotopes of an element have the same atomic number but different atomic weights ?
(Mysore B.Sc., 1956)
18. Describe Aston's Mass Spectrograph and indicate how it is used.
(Jammu & Kashmir B.Sc., 1957)
19. Give Prout's hypothesis and discuss it in the light of the discovery of isotopes.
(Andhra B.Sc., 1958)
20. What is an isotope ? Describe any two methods for the separation of isotopes.
(Osmania B.Sc., 1959)

CHAPTER X

RADIO-ACTIVITY

DISCOVERY OF RADIO-ACTIVITY

It was noticed by Prof. Henry Becquerel in 1895 that the element *uranium* and its compounds possessed certain peculiar properties uncommon to other elements. They affected a photographic plate in the dark as if they emitted invisible rays which were similar to X-rays. The rays obtained from them were able to penetrate solid matter, ionise gases, and produce luminosity in substances like zinc sulphide and barium platinocyanide. A substance which possessed the property of emitting such active rays was said to be **Radio-active** and the property itself was called **Radio-activity**.

Madame Curie and Schmidt (1898) working independently made a systematic search for other radio-active substances, and found

that the salts of the metal *thorium* also emitted radio-active rays. In 1902 Prof. Curie and his wife, Mme. Curie, discovered that a certain *uranium* mineral, pitchblende, was four times as radio-active as uranium itself. They concluded, therefore, that this mineral must contain some impurity which was more radio-active than uranium. After a troublesome process of working many tons of pitchblende, the Curies succeeded in isolating a new element *radium* which possessed intense radio-activity, several million times that of uranium. In subsequent years, a number of other radio-active elements or *radio-elements* as they are called in brief, were discovered until at the present time some forty are known. The study of these elements and the rays emitted by them has proved of considerable interest from the point of view of atomic structure.

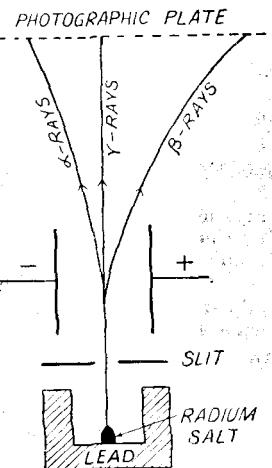


Fig. 122. Sorting out of radioactive rays by passing them between two oppositely charged plates.

RADIO-ACTIVE RAYS

Soon after the discovery of radium it was suspected that the rays given out by radium and other radio-active substances, were not all of one kind. Rutherford (1902) devised an ingenious method for separating these rays from each other by passing them between two oppositely charged plates. On so doing he found that there were three distinct kinds of radio-active rays. The rays bending towards the left in the diagram (Fig. 122) carry positive charges and are called *alpha* (α) rays. Those deflected to the right carry negative charge and are named *beta* (β) rays. The third type, *gamma* (γ) rays, go unaffected as they carry no charge at all.

Alpha Rays. To call them rays is misnomer. They are not rays at all. They consist of streams of small positively charged particles called α -particles. From their deflections in electric and magnetic fields, α -particles have been shown to be *doubly charged atoms which are 4 times as heavy as hydrogen atom*. Since the atomic weight of helium is 4 and its atom has only two outer electrons, α -particles must be **Helium Nuclei** or helium ions (He^{++}). This was confirmed by Rutherford who collected enough of α -particles in a vacuum tube and showed spectroscopically that they were ultimately converted into helium. The helium ion picks up two electrons and becomes helium atom.

Following are some of the important characteristics of α particles.

(i) α -particles are shot out from radio-active substances with *tremendous velocity* on the average about one-tenth of that of light. The actual velocity, however, depends on the nature of the substance from which the particles are ejected.

(ii) Being relatively large in size, α -particles cannot pass very easily through solid matter. They can penetrate *thin layer of solids such as mica, aluminium, or a few centimetres of air at atmospheric pressure*. They are stopped by a piece of aluminium foil that is 0.1 millimetre thick.

(iii) High speed α -particles, when they collide with gas molecules break off electrons from them and then produce *intense ionisation* of the gas through which they pass.

(iv) The power of α -particles to excite luminosity in zinc sulphide and their action on photographic plate is largely due to their *high kinetic energy*.

Beta Rays. Deflection experiments with magnetic and electric fields showed that β -rays consist of negatively charged particles. β -particles, which have the same e/m as the cathode rays. They are, therefore, **merely electrons**. Some of the characteristics of β -particles are given below :—

(i) The velocity of the β -particles is on the average about 10 times that of the α -particles.

(ii) Because of their minute size and enormous velocity, they are *far more penetrating than α -particles*. While a few centimetres of air will stop α -particles, β -particles will travel 100 times as far. They are stopped by a 1 centimetre thick sheet of aluminium.

(iii) Although the velocity of the β -particle is very high, its mass is so small that its *kinetic energy is much less than that of the α -particle*. Therefore, the ionisation it produces in a gas is *small as compared to the α -particle*.

(iv) Due to their very low kinetic energy β -particles have *very little effect on zinc sulphide plate*. Their photographic activity is, however, greater than that of the α -particles. This is perhaps due to the fact that just like cathode rays, β -particles on being stopped by matter produce X-rays which have great photographic activity.

Gamma rays. They are not deflected by the most intense magnetic or electric field and, therefore, carry no charge. **γ -rays** are known to be merely *light waves of very short wave-length* much shorter than even X-rays. Some of their important properties are :

(i) They travel with *extremely high velocity*, which is equal to that of light.

(ii) Owing to their high velocity coupled with the non-material nature, they are the *most penetrating of the three types of radio-active rays*.

(iii) They are *weak ionisers of gases*.

(iv) The power of these rays to affect a photographic plate and to produce luminosity in zinc sulphide is also small.

MEASUREMENT OF RADIO-ACTIVITY

The measurement of radio-activity of a substance *consists in the determination of the rate of emission of α , β and γ -rays by it*. The rate of emission of these rays can conveniently be known from the *ionisation produced by them in a gas*.

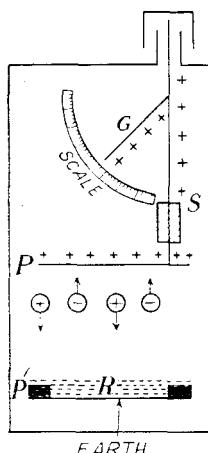


Fig. 123. Electroscope for measurement of radio-activity.

E. Electroscope box.

A. Ionisation Chamber.

P & P'. Metallic Plates.

R. Radio-active material.

S. Insulating sulphur block.

G. Gold leaf.

A common type of electroscope used for this purpose is shown in the diagram (Fig. 123). It has an ionisation chamber A and an electro-scope box E. The ionisation chamber, which is made of lead, consists of two metallic plates, P and P' separated by the gas which is to be exposed to the rays. The lower plate is connected with the wall of the chamber and earthed. The upper plate, which is insulated by a block of sulphur (S) and connected with the gold leaf system (G) is initially charged to a high potential. The radio active material is then placed in the cavity of the plate P'. The air between the two plates gets ionised and the charge leaks away between P and P'. The gold leaf falls and its rate of fall is proportional to the rate of leakage and thus to the intensity of the rays. The rate of leakage so found is compared with that of substance of known activity under exactly similar conditions and thus the total radio-activity of the substance under examination determined.

The β and γ rays are weak ionisers, the ionisation caused in a gas exposed to a radio-active substance is mainly due to α -rays. But if the substance, placed in the cavity of the lower plate, be covered with 0.1 mm. thick aluminium foil, all the α rays are cut off and the ionisation is largely due to β -rays. Similarly 3 mm. thick plate of lead absorbs both α and β -rays when the ionisation is simply due to γ -rays. Thus the apparatus can be employed to determine the rate of emission of α , β and γ -rays separately.

The electroscope, in the apparatus, has now been replaced by the more sensitive electrometer which can measure 'ionisation currents' conducted between the two plates directly.

THEORY OF RADIO-ACTIVITY

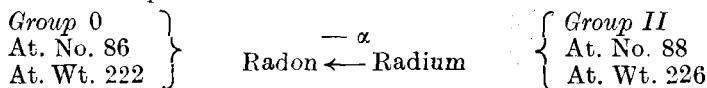
Soon after the nature of the rays given out by radio-active substance had been established, it was realised that **radio-activity is essentially a nuclear property**. Rutherford and Soddy (1903) gave an ingenious interpretation of the radio-active processes and the origin of the rays. This theory may be summarised as below :—

- (i) *The atoms of a radio-active element are unstable.*
- (ii) *These atoms are undergoing a process of disintegration forming new atoms, distinct in physical and chemical properties from the parent atom.*
- (iii) *The α and β -particles emitted by radio-atoms are parts of the nucleus.*
- (iv) *γ -rays are secondary effects of atomic disintegration. They may have been formed by β -particles in a manner similar to the production of X-rays by cathode particles.*

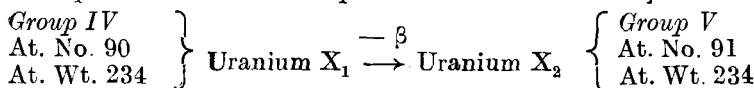
RADIO-ACTIVE CHANGES

Radio-active elements undergo two types of changes. The change brought about as a result of the ejection of an α -particle is called *α -ray change* and that caused by the expulsion of a β -particle is called a *β -ray change*. We shall see presently how these changes result in the formation of new elements.

α -Ray Change. When an α -particle (He^{++}) is shot out of the nucleus it takes away from it four units of weight and two units of positive charge. *The new atom will, therefore, have atomic weight less by 4 and atomic number less by 2 than the original atom.* The element so formed will lie two columns to the left of its parent in the periodic table. For example :



β -Ray Change. When an electron leaves the nucleus in the form of a β -particle, one positive charge will be set free on the nucleus and since an electron has negligible mass its emission results in practically no change in atomic weight. *The atomic number of the new element will, therefore, be greater by one and it will have the same atomic weight as the original element.* It will fall one column to the right of its parent element in the periodic table. For example :



The results of α and β -ray changes have been summed up in the form of **Group Displacement Law** of Fajans, Russel, and Soddy (1913). The law states that *in an α -ray change the new element obtained has an atomic weight less by four and it falls in a group of the periodic table two columns to the left of the original element, and in a*

β -ray change the element generated has the same atomic weight as its parent but lies one column to its right. The strict validity of the displacement law can be perceived from the consideration of the uranium-radium disintegration series shown in the following diagram (Fig. 124).

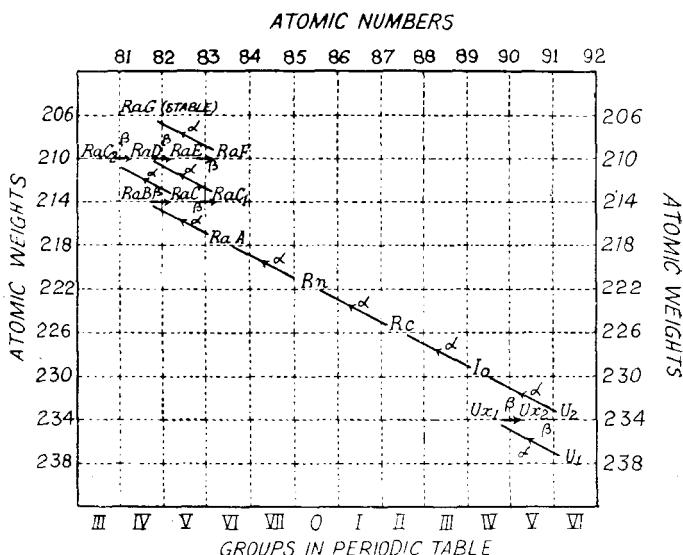
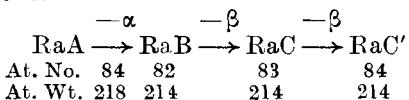


Fig. 124. Uranium Radium Disintegration Series
(Illustration of the Displacement Law)

Abbreviations. Ra = Radium; Rn = Radon; Io = Ionium; U = Uranium

It may also be noted from the following chart that a β -ray change results in the production of an isobar, whereas one α -ray change and two β -ray changes yield an isotope of the parent element.

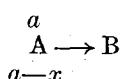


In this series RaB emits a β -particle and generates RaC which is isobaric with RaB. RaA expels one α -particle and two β -particles to form RaC' which is isotopic with RaA.

RATE OF RADIO-ACTIVE DISINTEGRATION

The rate of disintegration of a radio-active element is found to be independent of the temperature, pressure, or its state of chemical combination. Each element thus disintegrates at a characteristic rate independent of all external factors.

Since in a radio-active transformation an atom breaks down to give one or more new atoms, it may be regarded as a chemical reaction in which one molecule changes to yield one or more products (*unimolecular reaction*). Let us consider an atom A changing to B.



If to start with $t=0$, the number of atoms of A present is a . After t seconds x atoms will have decomposed leaving behind $(a-x)$ atoms. If then in a small time dt , dx is the number of atoms which change, the rate of disintegration $\left(\frac{dx}{dt}\right)$ can be expressed as

$$\frac{dx}{dt} = k(a-x) \quad \dots (1) \text{ [Law of Mass Action]}$$

where k is ordinarily called velocity constant, and here it may well be named as *disintegration constant or transformation constant*.

From the expression (1), it follows

$$\frac{dx}{a-x} = k \times dt \quad \dots (2)$$

If $dt = 1$ second, $k = \frac{dx}{a-x}$.

Thus the **Disintegration constant** k , may be defined as *the fraction of the total number of atoms $\frac{dx}{a-x}$ present at any time (t) which disintegrate per second*; k has a definite characteristic value for a particular radio-active element.

On integrating the expression (2)* and changing the base of the logarithm, we have the equation for a unimolecular reaction

$$k = \frac{2.303}{t} \log \frac{a}{a-x}.$$

Then say after time T , $x = \frac{a}{2}$, that is when half the atoms have disintegrated, the equation becomes

$$k = \frac{2.303}{T} \log 2 = \frac{0.693}{T}$$

$$\text{or } T = \frac{0.693}{k}.$$

It is clear from above that for a particular radio-active disintegration the value of T is independent of amount of the substance present and depends only on k . *The time (T) required for the disappearance of one half of the original amount of the radio-active substance is called its Half Life Period.* While denoting the rate of disintegration as k does, it has a rather more concrete significance. The statement that the half-life period of radium is 1580 years means that of any given quantity of radium one half will have disintegrated after 1580 years.

The reciprocal of the disintegration constant (k) gives the Average Life (λ) of the disintegrating atom, i.e.,

$$\lambda = \frac{1}{k} = 1.44T.$$

The average life is frequently used to express the rate of transfor-

* For details see Chapter XV.

mation of a radio-active substance. The average life of radium is 2,440 years.

Radio-active Equilibrium. Let there be a radio-active substance A which breaks down to give a second element B which in turn disintegrates to give a third one C.



B is said to be in **radio-active equilibrium** with A *when its decay is exactly compensated by its production from A*. When the equilibrium is reached, the amount of B remains constant because it is being formed and disintegrated at the same rate. If k_1 , k_2 represent the disintegration constants of A and B, N_1 and N_2 the number of atoms of each radio-element present, we have at equilibrium

$$k_1 N_1 = k_2 N_2$$

or

$$\frac{N_1}{N_2} = \frac{k_2}{k_1} = \frac{\lambda_1}{\lambda_2}.$$

Hence at equilibrium A and B are present in the ratio of their average life periods. This also implies that when radio-active elements are in equilibrium, the one with a higher average life is present in greater amount than the other with short average life.

Since the radio-active disintegrations are not influenced by any external means whatsoever, they cannot be reversed. The radio-active equilibrium thus differs from chemical equilibrium that the radio-active changes are not reversible.

RADIO-ELEMENTS AND THEIR FAMILIES

We have already seen how a radio-element disintegrates to give a new element which again disintegrates to give another element and so on. The process of disintegration and formation of elements continues till a non-radio-active end-product is reached. *The whole chain of such elements starting from the parent to the end product is called Radio-active Family or a Series.* The radio-elements are divided into three series—the *uranium series*, the *actinium series* and *thorium series* (See page 197).

Radium—The King of Radio-elements. Amongst the radio-elements radium occupies the first position both as regards its theoretical importance and practical utility. It is intensely radioactive, a million times more than uranium. Its life is sufficiently long and that makes it all the more useful. Thus radium may rightly be called as the king of radio-elements.

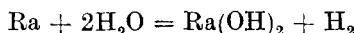
Isolation. Radium is isolated from pitch-blende in which it occurs in minute quantities along with uranium and barium salts. The ore is roasted with sodium carbonate when a mixture of the carbonates of radium, uranium and barium is obtained. On treatment of the mixture with dilute sulphuric acid, uranium dissolves while radium and barium sulphates are left behind. The insoluble sulphates are again converted into carbonates by boiling with sodium carbonate solution. When treated with hydrobromic acid, the carbonates yield a mixture of radium bromide and barium bromide. Due to the difference of solubility, the radium bromide is separated

from barium bromide by fractional crystallisation. The metallic radium can be prepared by electrolysing the radium bromide or the chloride.

The metallic radium is so very difficult to obtain that it is seldom used in the free state. Any salt of radium, say, radium bromide, serves the purpose equally well.

Properties and Uses. The atomic number of radium is 88 and it lies in the second group of the periodic table along with the alkaline earth metals. It closely resembles barium in its properties.

Radium is a white solid which melts at 960° . It has a silvery lustre and will tarnish when exposed to air forming a nitride. It reacts with water forming radium hydroxide and hydrogen.



Radium is highly radio-active and is continuously emanating alpha, beta and gamma rays. On disintegration it yields the heaviest inert gas *radon* (At. Wt. 222, At. No. 86).

Radium has the wonderful property of causing fluorescence in zinc sulphide when mixed up with it in small amounts. This *luminous paint*, as it is called, is largely used for making dials of watches and also for painting the danger points of machinery and electrical apparatus so that they can be seen in the dark.

The rays given out by radium and its salts have been found to be very effective as a *cure for cancer* and other malignant growths deep inside the body. All modern hospitals are equipped with small sealed tubes containing radium bromide for this purpose.

ARTIFICIAL DISINTEGRATION OF THE ATOMS

The radio-active changes are a result of the spontaneous disintegration of unstable nuclei. The first indication that the stable nuclei could also be broken down was afforded by the observation of Rutherford (1919) that nitrogen atoms on bombardment by fast-moving α -particles yielded protons which, of course, on picking up one electron became hydrogen atoms. *All elements from boron to nitrogen with the exception of carbon and oxygen underwent similar disintegration yielding protons in each case.*

In 1933 Chadwick identified a new particle obtained from the bombardment of beryllium by α -particles. It had a *unit mass and carried no charge*. It was named **Neutron**. Being a neutral particle, neutron can penetrate into the nuclei of even the heavier elements and has been usefully employed to produce artificial changes in the atoms. Accelerated protons and **Deutrons** (*nuclei of deuterium, i.e., heavy hydrogen*, ${}^1\text{H}^2$) have also been used as projectiles for the disruption of the stable nuclei. The nature of changes taking place in such collision processes may be summarised by equations, in which superscripts and subscripts indicate respectively the nuclear masses and charges of the various particles. It may be noted that the total positive charge and mass before and after the bombardment remains the same.

Some of the common examples of artificial disintegration are illustrated below :

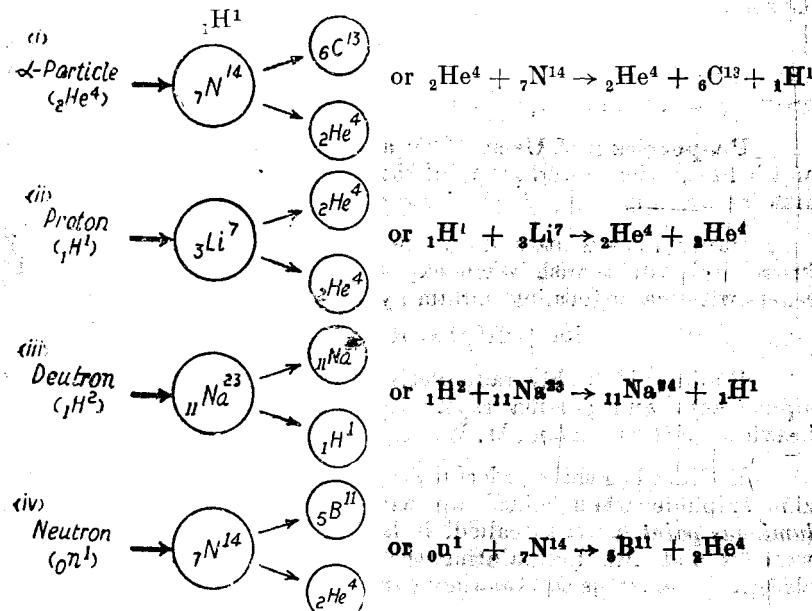


Fig. 125. Artificial disintegration of atoms. The thick arrow indicates the bombardment whereas the thin arrows indicate the products.

Artificial Radio-Activity. When a light element is bombarded by α -particles, protons are thrown out by the nucleus. This

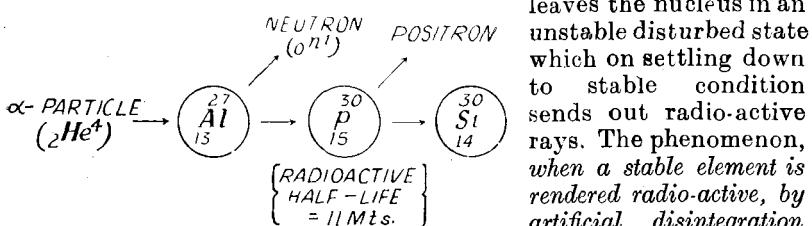


Fig. 126. Artificially radio-active Phosphorus.

1913 by Irene (daughter of Mme. Curie) in collaboration with her husband, Prof. Federic Joliot. Curiously enough the radio-active phosphorus produced by α -ray bombardment of aluminum, emits positive electrons.

A positive electron is associated with one positive charge and negligible weight. It has been named **Positron**. Positron is an addition to the already known ultimate particles of the nucleus. Unlike the electron, however, which is very stable, the positron is very short-lived. Ejected from the nucleus, it loses its kinetic energy in about 10^{-10} sec. and then combines with an electron, the process

of combination resulting in the destruction of both and the emission of energy in accordance with the Einstein relation $E=mc^2$, E being the energy, m its mass equivalent and c , the velocity of light :

Bombardment with neutrons and deuterons has also been employed to cause artificial radio-activity.

NUCLEAR FISSION

The neutrons possess considerable advantage over the other projectiles employed for the disintegration of atoms because of their neutral character owing to which they do not experience any repulsion when approaching the nucleus. They could not be used, however, on a large scale because of the difficulty in producing them.

In 1939, Hahn and Strassmann showed that when Uranium-235 is bombarded with fast or slow neutrons, it splits up into two

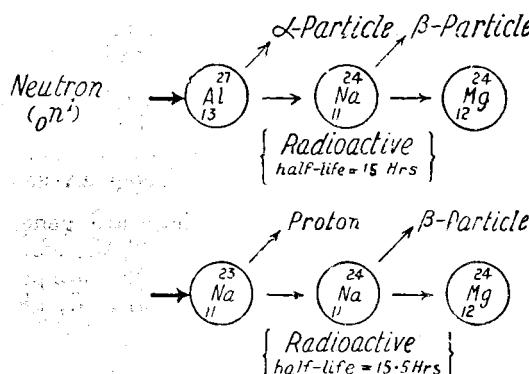
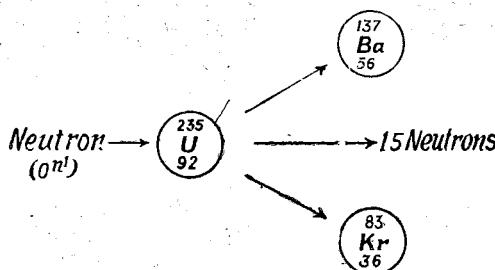


Fig. 126 (a). Artificially radioactive Sodium



- 1) Some neutrons explode more U-235 atoms
- 2) The remaining neutrons are converted into energy.

Fig. 127. Neutrons captured by U-235 yielding, Ba, Kr, and 15 neutrons.

large fragments and a number of neutrons are also emitted in this process called **nuclear fission**. The chief products of fission are barium (${}_{56}^{137}\text{Ba}$) and krypton (${}_{36}^{83}\text{Kr}$) which together account for a mass ($137+83$) or 220. The balance mass is in the form of neutrons, some of which explode more U-235 atoms and set up a *chain reaction* whilst most of them are converted into energy according to the Einstein formula $E=mc^2$. When thousands of uranium nuclei thus break up, an enormous amount of energy is set free which, if *uncontrolled*, causes havoc with life and property as in the *Atom Bomb*. It has been possible, however, to devise methods by which this chain reaction can be controlled and the liberated energy converted into useful channels for running atomic power plants.

NUCLEAR REACTOR

A nuclear reactor is a device for "burning" fissionable material

for useful purposes. In it the chain reaction is made to develop under control. The five essential parts of an atomic reactor are :—

(i) **Core.** It consists of aluminium plated uranium rods usually $1\frac{1}{2}$ " thick and 4" long placed in numbered holes.

(ii) **Moderator.** It is a huge block of specially purified graphite containing holes in which the uranium rods are inserted. In the "swimming pool" type reactor, the moderator is heavy water in a tankful of which the uranium rods are suspended.

(iii) **Control Rods.** These are generally made of cadmium steel and absorb the neutrons. If, therefore, the process of nuclear fission is to be slowed down, these rods are pushed in. As soon as these rods are raised, the neutrons begin to fly about and the splitting of U-235 grows in intensity.

(iv) **Coolant.** The heat generated in the reactor is taken out by circulating air or some suitable liquid like sodium potassium alloy which takes the heat to a boiler for raising steam to turn a turbine-generator to make electricity.

(v) **Protective Screen.** It serves to keep the heat, rays and neutrons etc. from escaping and is made of special concrete about eight feet thick.

On August 4, 1956 a "swimming pool" type reactor was installed in India at Trombay. It has 35 rods of enriched 50% U-235 hanging in a tank of heavy water $28' \times 10' \times 28'$ with a protective screen $8\frac{1}{2}$ feet thick.

NUCLEAR FUSION

Another way in which atomic energy may be liberated is by the thermal fusion of heavy hydrogen to form helium.

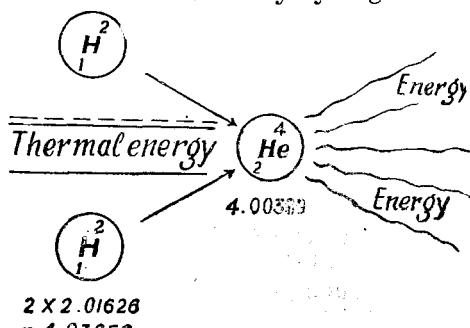


Fig. 128.

From two heavy hydrogen atoms with atomic weight $(2 \times 2.01626 = 4.03252$, one atom of helium is obtained with atomic weight 4.00389. The balance of mass 0.02863 is converted into energy according to the equation

$$E=mc^2$$

$$\text{or } E=0.02863 \times 9 \times 10^{20} \text{ erg.}$$

It is on this principle of nuclear fusion that *hydrogen bomb* is based. Unlike the fission of uranium, it has

not been possible so far to let this fusion proceed in a controlled manner.

COMPOSITION OF THE NUCLEUS

Having studied the radio-active processes we are now in a position to sum up our knowledge of the elementary particles of the nucleus.



PROF. HIDEKI YUKAWA, N.L.

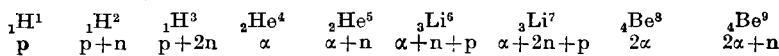
He is the first Japanese to win the Nobel Prize in Physics (1949) for his prediction of a new particle *meson* which holds the protons and neutrons of the atomic nucleus. Yukawa was born in Tokyo in 1907 and graduated from Kyoto University in 1929 where he was appointed a professor in 1939. In 1948 he joined the staff of the Institute for advanced study, Princeton, New Jersey (U.S.A.).

In 1950 he joined the Columbia University.

	SYMBOL	CHARGE	MASS
Proton	p	+1	1
Electron	e or	-1	Negligible ($\frac{1}{1845}$ of H atom)
Neutron	n	0	Approximately 1.
Positron	e ⁺	+1	Negligible ($\frac{1}{1845}$ of H atom)
Deutron	d	+1	2
α -particle	α	+2	4

Although electrons and positrons are given off when certain atomic nuclei disintegrate, they do not necessarily exist in the nuclei as separate entities.

Now that the neutron has been discovered, the older hypothesis that the nuclei consist of protons and electrons as such, no longer has any justification. It is suggestive that perhaps all nuclei can be built up from neutrons and protons. α -particles may be considered as the bigger unit of the nucleus and whenever two protons and two neutrons are contained in the same nucleus, the four units are believed to combine to give an α -particle. Thus the composition of the first few elements may be written as



It must, however, be borne in mind that it is rather impossible to draw an exact picture of the inside of the nucleus. The simple fact that the elementary particles are produced by the disintegration of nuclei is no proof that they exist as such in them. For example, smoke is given out of a pistol when it is fired, although gunpowder and not the smoke was originally present in it.

Heavy Electron or Meson. Yukawa, Bhabha, and others (1935) have claimed the existence of a new particle which has the charge of the electron either positive or negative, and a mass approximately 100 times that of the electron. This particle has been named **Heavy Electron** or **meson** and was first detected in cosmic rays.

CONTRIBUTIONS OF RADIO-ACTIVITY

The discovery of radio-activity and its subsequent study has made valuable contributions to modern Physics and Chemistry. The most important developments in atomic structure and the artificial disintegration of atoms are the direct outcome of our knowledge of radio-activity phenomenon. The study of radio-activity has led to the discovery of new elements, isotopes and isobars, and above all it has given the clue to the vast stores of energy in atomic nucleus which may, some day be harnessed as the chief power for running machines. All these achievements of radio-activity have already been discussed in detail and here we shall only make a brief mention of them by way of recapitulation.

(1) **Discovery of New Elements.** Till 1902 the only radio-elements known were uranium, thorium and radium. The study of these elements indicated that their atoms disintegrate to form new elements. In this way the study of the few radio-elements first

discovered revealed the existence of as many as 40 new isotopes which were hitherto unknown.

During the last fifteen years, a number of elements beyond uranium have also been established known as **Trans-Uranic Elements**. These have obtained considerable importance owing to their use in the liberation of atomic energy.

At. No.	Name	Symbol	Discoverer	
93	Neptunium	Np	McMillan	(1940)
94	Plutonium	Pu	Seaborg	(1941)
95	Americium	Am	"	(1944)
96	Curium	Cm	"	(1944)
97	Berkelium	Bk	"	(1945)
98	Californium	Cf	"	(1950)

(2) Knowledge of Atomic Structure. Our present knowledge of atomic structure has been largely derived from a study of radio-active phenomena.

(a) The scattering of alpha-particles by atoms proved clearly the presence of a heavy positively charged nucleus in its centre. The measurements of the extent of deflection of alpha particles by different atoms established the fact that *atomic number is numerically equal to the number of positive charges on the nucleus and, therefore, to the number of planetary electrons in the atom.*

(b) The emission of alpha and beta rays from radio-elements showed that atomic nucleus contains helium nuclei and electrons probably moving in closed orbits with high speed.

(c) The artificial disintegration of light atoms like that of beryllium and nitrogen by alpha particles disclosed the presence of protons and neutrons in the nuclei of these atoms.

(3) Discovery of Isotopes and Isobars. While studying radio-elements, Soddy discovered such elements which had the same atomic number but different atomic weights. These elements were named isotopes. The discovery of isotopes amongst radio-elements led to the search of isotopes in non-radio elements. The brilliant researches of Aston have established the existence of isotopes in almost all the known elements. The concept of isotopy has proved very valuable in explaining the fractional atomic weights of elements.

The study of radio-elements also revealed the existence of isobars. In fact a beta ray change always results in the formation of an isobar while two beta rays changes followed by an alpha ray change yield an isotope of the parent element.

(4) Artificial Disintegration of Atoms. Rutherford first conceived that the energy of a fast-moving alpha-particle could be utilised to break down atoms into simpler parts. Thus the disintegration of nitrogen atom yielded a proton and that of beryllium gave a neutron. Now we know that any atom can be broken by bombard-

ment with high speed protons, neutrons, deuterons and an alpha-particle, etc. Very often the bombarded atom becomes temporarily radio active. Thus induced radio-activity has proved of considerable interest in recent times.

THE RADIO-ACTIVE SERIES

URANIUM SERIES ACTINIUM SERIES THORIUM SERIES

At. wt. At. No.	Symbol	Half-life Period	At. wt. At. No.	Symbol	Half-life Period	At. Wt. At. No.	Symbol	Half-life Period
238.92	U I ↓ α	5×10^9 Y	231.90	U Y ↓ β	24.6h	232.90	Th ↓	2×10^{10} Y
234.90	U X ₁ ↓ β	24.5d	231.91	P a ↓ α	4.2×10^4 Y	228.88	M s Th ₁ ↓ β	6.4Y
234.91	U X ₂ ↓ β	.17m	227.89	A c ↓ β	20 Y	228.89	M s Th ₂ ↓ β	6.2h
234.92	U II ↓ α	2×10^5 Y	227.90	R d A ↓ α	1.2d	228.90	R d Th ↓ α	1.9Y
230.90	I o ↓ α	8×10^6 Y	227.90	R d A ↓ α	1.2d	228.90	R d Th ↓ α	1.9Y
226.88	R a ↓ α	1580Y	223.88	A c X ↓ α	11.2d	224.88	T h X ↓ α	0.64d
222.86	R a Em ↓ α	3.85d	219.86	A c Em ↓ α	3.92S	220.86	T h Em ↓ α	54.4S
218.84	R a A / ↓ α	3.05m	215.84	A c A ↓ β	5×10^{-3} S	216.84	T h A ↓ α	0.14S
214.82	R a B ↓ β	26.8m	211.82	A c B ↓ β	26.1m	212.82	T h B ↓ β	10.6h
214.83	R a C β ↓ α	19.5m	211.83	A c C β ↓ α	2.1m	212.83	T h C β ↓ α	60.8m
214.84	R a C' ↓ α R C'	10^{-6} S	211.84	A c C' ↓ α A c C'	5×10^{-2} S	212.84	T h C' ↓ α T h C'	3×10^{-2} S
210.81	↓ β	1.38m	207.81	↓ β	4.76m	208.81	↓ β	3.2m
210.82	R a D ↓ β	16Y	207.82	A c D ↓ β	Stable	208.82	T h D ↓ β	Stable
210.83	R a E ↓ β	4.85d	(Actinium lead)		(Thorium lead)			
210.84	R a F ↓ α	138d						
206.82	R a G (Radium lead)	Stable						

Abbreviations :— U=uranium ; Ra=radium ; Io=ionium ; Em=emanation ; Pa=proto-actinium ; Ac=actinium ; Rn=radon ; Th=thorium ; Ms=meso ; Y=years ; d=days ; h=hours ; m=minutes ; S=seconds.

(5) **Clue to Atomic Energy.** The emission of alpha, beta, and gamma rays from radio-elements gave a clue to vast stores of energy in atomic nucleus. This energy has been recently made available in the form of atomic reactors. Directed in the proper channels, atomic energy may some day become the chief source of power to run machinery.

(6) **Radio-active Tracers.** The radio-active isotopes of certain metals* have been used as tracers in various types of investigations.

*Th C is isotopic with Bi, and Ra B is isotopic with Pb.

The stable metal and a little of its radio-active isotope are mixed and converted to a compound under study. The stable and the radio-active isotope always go together in the same ratio through all physical and chemical changes. Thus at any stage the direction and estimation of the compound can be done by simply measuring the radio-activity of the active isotope. In this way the active isotope acts as indicator of the behaviour of the stable metal. This method has been applied to the precipitation phenomenon and to determine the solubility of highly insoluble substances. The radio-active indicators have been used to study the biochemical and physiological properties of certain compounds. For example, a compound prepared from the stable metal and its radio-active isotope is fed to an animal. The compound distributes itself to the various parts of the body where it can be detected and estimated by ashing the sample and determining the radio-activity. The radio-active indicators promise an important role in the field of research.

QUESTIONS

1. What is radio-activity and how was it discovered ? Explain clearly how would you determine if a certain mineral is radio-active.
2. How was the nature of radio-active rays established ? Discuss the properties of these rays.
3. Describe the Electroscope method of comparing the radio-activity of radio-elements.
4. Write a note on the *theory of radio-activity* or the *disintegration hypothesis*.
5. What do you understand by *alpha*-and *beta-ray* changes ? Give two examples of each type of change.
6. What is the Group Displacement Law in radio-activity ? How does it lead to the idea of radio-active isotopes ? Explain (a) half-life period, (b) average life of a radio active element, and show how they are related to each other.
(Punjab B.Sc., 1954)
7. Explain the terms (a) radio-active constant, (b) half-life period, (c) average life of a radio-active element. Show how they are related to one another.
- Radio-active sodium has a half-life period of 53300 seconds. How much time will be taken for the radio-activity to fall to one-tenth of its original value.
(Gujarat B.Sc., 1952)
8. A certain radio-element has a disintegration constant of 16.5×10^{-6} sec. $^{-1}$. Calculate its half-life period and average life. *(Ans. 4.85 days ; 7 days)*
9. Give an account of the nature of the radiations emitted by radio-active substances. Show how this information has been utilised in explaining the disintegration of radio elements.
(Poona B.Sc., 1954)
10. Explain the terms 'radio-active constant', 'half-life period' and 'average life' as applied to radio-active elements and show how they are related to one another.
(Baroda B.Sc., 1953)
11. Write an essay on radio-activity with particular reference to the following terms :—(a) isotopes, (b) artificial disintegration of elements.
(Banaras B.Sc., 1940)
12. Write notes on :—(i) Atomic number, (ii) Isotopes, (iii) artificial disintegration, (iv) Nuclear fission.
(Mysore B.Sc., 1954)
13. Give an account of the several agents which have been employed to cause the artificial disintegration of elements. Illustrate their action by suitable examples.

14. What is meant by artificial radio-activity ? What are the uses of radio-active isotopes to medicine and to physical chemistry ?
 (Karnatak B.Sc., 1953)
15. Discuss the principles involved in the preparation of the atomic bomb.
 (Lucknow B.Sc., 1953)
16. Trace the development of our knowledge of radio-activity and discuss its influence on chemical theory.
 (Madras B.Sc., 1952)
17. Write an essay on radio-activity.
 (Banaras B.Sc., 1950)
18. Write clearly an account of radio-activity.
 (Aligarh B.Sc., 1954)
19. Explain the half-life period and average life period of a radio-active element. How can you bring about the disintegration of atoms ? Discuss its importance.
 (Punjab B.Sc., 1955)
20. Write a short account of—
 (a) α -particles,
 (b) neutrons, and
 (c) accelerated protons.
- Give some instances of disintegration brought about by these particles.
 (Bombay B.Sc., 1955)
21. Write a short note on radio-activity and isotopes.
 (Rajputana B.Sc., 1956)
22. Write an account of the radio-active disintegration of elements.
 (Aligarh B.Sc., 1957)
23. Write an essay on radio-activity.
 (Delhi & Rajputan B.Sc., 1958)
24. Give a concise account of induced radio-activity. Discuss the use of isotopes as indicators.
 (Mysore B.Sc., 1958)
25. What is radio-activity ? Give preliminary ideas about artificial disintegration.
 (Aligarh B.Sc., 1959)
- | 26. Write a brief account of radio-activity. State and explain the group displacement law.
 (Lucknow B.Sc., 1959)
27. Write a note on the artificial disintegration of elements and explain the nature of the changes involved in the process.
 (Delhi B.Sc., Hons. 1959)

CHAPTER XI

ELECTRONIC THEORY OF VALENCY

THE CONCEPT OF VALENCY

Valency is a general term used to describe the power which atoms possess of combining with one another to form molecules. The **Valency** of an element may be defined in a simple way as *the number of hydrogen atoms or twice the number of oxygen atoms with which one atom of that element can combine*. Three hydrogen atoms combine with one atom of nitrogen to form ammonia (NH_3) and the valency of nitrogen is 3. In calcium oxide (CaO) one atom of oxygen is in combination with one atom of calcium indicating that the valency of calcium is 2. This definition of valency, however, has failed to represent certain facts. For example, carbon forms a series of compounds with hydrogen, C_2H_2 , C_2H_4 , C_2H_6 , CH_4 in which the apparent valency of carbon is 1, 2, 3 and 4 respectively. According to the previous definition, the valency of carbon in these compounds varies from 1 to 4 whereas actually carbon is known to be tetravalent in all such compounds. For such many more reasons the conception of valency as a mere number was gradually dropped and attempts were made to explain the 'combining capacity' of elements in the light of the modern atomic structure so as to discover the electronic mechanism by which atoms are held together in molecules. It is now recognised that there are at least three different ways in which an atom may establish links with other atoms. This has fully explained why it is not possible to assign to each element a number which expresses its valency. The term valency, however, still remains as vague as ever. All that we can say is that valency may be considered to represent the number of various types of chemical links an atom can form with other atoms.

ELECTRONIC THEORY OF VALENCY

Many theories were propounded from time to time to offer an explanation of the mechanism of valency. It was only after the elucidation of the electronic structure of the atom that Kossel and Lewis succeeded in putting forward independently in 1916 a comprehensive theory of valency. Since it was based on the electronic conception of the atom, it was named the **Electronic Theory of Valency**. The sphere of study of Kossel was limited to the valency bonds in inorganic salts and that of Lewis to organic compounds. According to them valency of an atom depends chiefly on the electrons in the outermost shell. They assumed that the number of electrons in the last orbits of the atoms of inert gases, (helium having 2 and the rest 8) formed a most stable grouping. Excepting the inert gases all other elements have atoms with unstable and incomplete outer shell. They tend to lose or gain electrons so as to acquire an electronic configuration identical with that of the nearest inert gas in the periodic table. *It is this tendency of atoms to complete*

and thus stabilise their outermost ring of electrons which causes them to combine chemically. Thus the molecules are formed by the redistribution of electrons in two or more atoms in such a way that the last electronic orbit of each atom possesses complete group of two electrons (*duplet*) or as is generally the case, eight electrons (*octet*). Leaving aside H, Li, and Be which tend to acquire a duplet, all other atoms tend to attain the octet and for this reason the theory of valency under discussion is sometimes referred to as the **Octet Theory**. We now proceed to study how this theory has been applied to explain the three common types of linkages which the chemical evidence shows to exist. They are

- (1) *Electrovalent linkage*,
- (2) *Covalent linkage*, and
- (3) *Co-ordinate linkage*.

Electrovalent Linkage

This type of linkage is established by the transference of electrons from one atom to the other. It is, therefore, essential that the two linked atoms should be dissimilar in character, one tending to lose and the other tending to gain electrons. Let us, for example, consider a general case when an atom A has one valency electron and another atom B has seven valency electrons. A possesses one electron in excess and B is short of one electron than the stable number. A loses one electron, B gains that electron and thus both acquire an inert gas configuration.

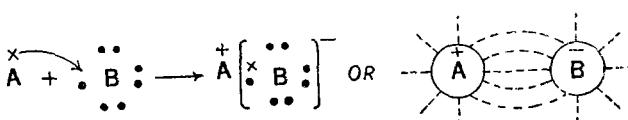
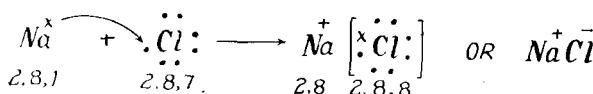


Fig. 129. Symbols represent atomic nuclei with their inner rings of electrons. Dots and crosses are used merely to differentiate as to which atom a particular electron originally belonged.

In this transaction A acquires one positive charge due to the loss of one electron whereas B gains one electron and thereby acquires one negative charge. In other words, the molecule A^+B^- , has acquired polarity and the linkage established between the atoms may be called *Polar linkage*. Since the two atoms are held together by electrostatic lines of force, the linkage is often termed **Electrovalent linkage** and the compound thus produced is called an **Electrovalent compound**.

This type of linkage is found to exist in ionisable compounds i.e., acids, bases and salts. *Sodium chloride molecule*, for example, is formed by the combination of sodium and chlorine atoms as shown below :



As already pointed out, the oppositely charged ions in sodium chloride are held together by the electrostatic lines of force. When,

however, it is dissolved in water the lines of force are mostly cut off, owing to the high dielectric constant of the solvent, and consequently ions separate.

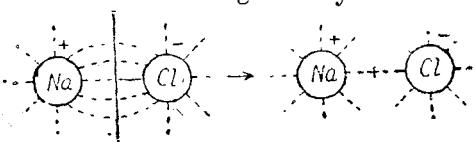
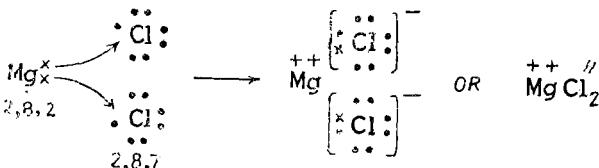


Fig. 130. Ionisation of sodium chloride.

The salts in which electrovalency exists contain linked ions even in the solid state which readily separate when dissolved in water. Hence an electrovalent linkage is also named as **Ionised** or **Ionisable linkage**.

Magnesium chloride molecule is formed by the combination of one atom of magnesium and two atoms of chlorine because magnesium has two electrons in the outermost orbit and two chlorine atoms take one each from it, magnesium acquiring the neon configuration with a double positive charge (*bi-electrovalent*).



Let us now consider a series of elements lying about an inert gas in the periodic table.

Electronic Arrangement	S	Cl	A	K	Ca
Ions formed	S"	Cl'	...	K ⁺	Ca ⁺⁺
Valency	-2	-1	0	+1	+2

We will thus have the formation of the salts of the type K₂S", Ca⁺⁺S", K⁺Cl', Ca⁺⁺Cl'₂, etc. It is clear from the above that the electrovalency of an element may be positive or negative according as its atom loses or gains electrons in forming an ion. Also it is evident that *the number of electrovalent bonds established is always equal to the number of electrons gained or lost by an atom in order to attain the nearest inert gas configuration.*

CHARACTERISTICS OF ELECTROVALENT COMPOUNDS

(1) The linkage between the two oppositely charged atoms is simply due to the electrostatic attraction between them and is, therefore, non-rigid and non-directional. *They are incapable of exhibiting any type of space isomerism.*

(2) When dissolved in water or in the molten state *electrovalent compounds dissociate and, therefore, conduct electricity.*

(3) As we have already seen, an electrovalent molecule (A—B) as a whole behaves just like a bar magnet. In the solid state these molecules cling together like small magnets with the result that electrovalent compounds neither vaporise nor dissolve in organic solvents.

Their boiling-points and melting points are high because considerable work has to be done in separating the molecules from each other.

(4) Electrovalent compounds are usually soluble in water but insoluble in organic solvents.

Covalent Linkage

Kossel's theory of electron-transference was quite satisfactory as an explanation of the ionised links present in the majority of inorganic compounds but it was entirely incapable of accounting for non-ionised links met with so commonly in organic substances and compounds of non-metals. Lewis put forth the solution in 1919. He assumed, like Kossel, that the cause of chemical combination lay in the tendency of the electrons to redistribute themselves among the atoms so as to form more stable arrangements such as occur in inert gases. He made an advance of fundamental importance by suggesting that it was possible for an electron to be shared between two atoms so that in some way it counts towards the stability of both. Let us consider two atoms A and B each with one valency electron. Both are short of one electron than the stable helium structure. If the two atoms share these electrons between them, by doing so both of them acquire helium structure as shown below :



This new form of linkage is expressed in formulae by a line (-). In this type of linkage the two atoms contribute one electron each and then the two electrons become a common property. Since the linkage is brought into existence by the joint contribution of the two atoms, it was named as **Covalent Linkage** (Co = mutual or joint). Unlike the electrovalent linkage, covalent linkage may connect two similar atoms when both are a few electrons short of a stable number. It may also be pointed out that in the establishment of a covalent linkage since electrons are not transferred from one atom to the other, the molecule does not acquire polarity and no ions are formed. A covalent linkage may, therefore, be called *non-polar* and *non-ionised*. The formation of this type of linkage may be illustrated by the following examples :—

Hydrogen molecule may be formed as :



How the two shared electrons can act towards the stability of both the atoms is easy to understand with a dynamic model of the atom. An electron may be held in common, spending part of its time on one, part on the other, and part in the region between. In doing so it helps to fill up the shells of both the atoms. Thus hydrogen molecule may be represented as shown in Fig. 131.

Chlorine atom has seven valency electrons

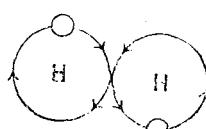
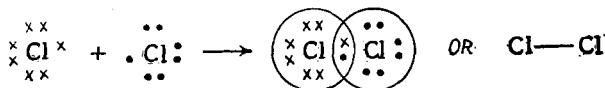


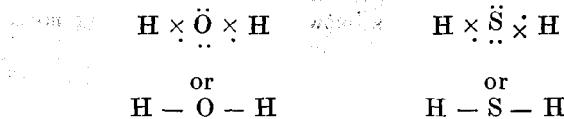
Fig. 131. Hydrogen molecule.

and *Chlorine molecule* is, therefore, formed by sharing a pair of electrons by two chlorine atoms.

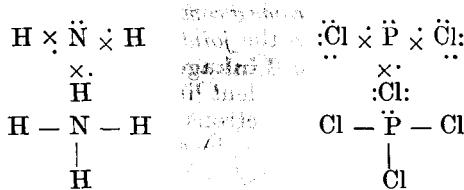


It may be noted that since for each electrovalency or covalency the atom of an electro-negative element gains one electron to make up the stable number, *the numerical value of its electrovalency and covalency must be the same*. Thus we can see why chlorine atom is univalent in sodium chloride, chlorine molecule and organic halides.

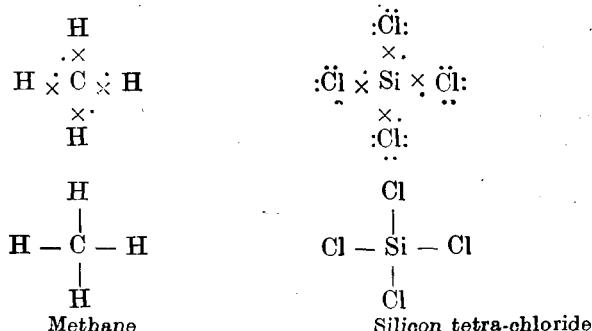
Elements whose atomic structures permit the sharing of two pairs of electrons are *bi-covalent*. Among these are oxygen and sulphur containing six electrons in the last orbit. They can complete their octets by forming two covalent bonds. This will be clear from the structures of molecules of water and hydrogen sulphide given below:



Elements allowing the sharing of three electrons are tricovalent, as for example, nitrogen in *ammonia* and phosphorus in *phosphorus trichloride*



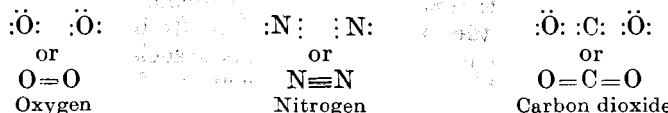
Carbon and silicon are tetra-covalent in *methane* and *silicon tetra-chloride* respectively.



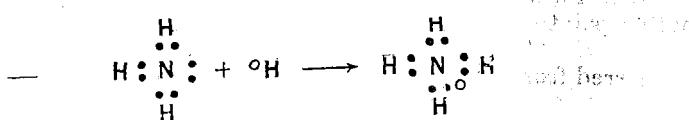
It is not essential always that one atom be linked to another by one covalent linkage only. Poly-covalent elements may form a

molecule in which two atoms are linked by 2 or more pairs of shared electrons.

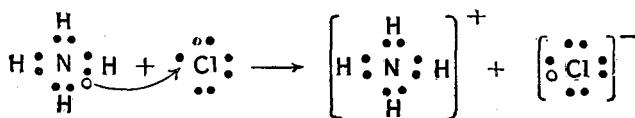
Examples.



Formation of Ammonium Chloride molecule. The nitrogen in ammonia molecule has a completed octet. If this nitrogen were to combine covalently with a hydrogen atom, it would increase the number of electrons in the valency orbit to 9.



The nitrogen atom would then have an electronic configuration 2, 8, 1 resembling that of sodium. Like sodium it can attain neon configuration (2,8) by transferring one electron to an electro-negative element chlorine. In doing so ammonium acquires a positive charge while chlorine gets a negative charge. The combination then occurs in the same way as shown in the case of sodium chloride.



CHARACTERISTICS OF COVALENT COMPOUNDS

(1) A covalent linkage is rigid and directional, the atoms being held together by the shared electrons and not by lines of force. It offers opportunity for different spatial arrangements and stereo-isomerism of molecules.

(2) Since the atoms in a covalent molecule are firmly held together by electrons, they cannot be separated without chemical decomposition. Thus when put in water or melted, covalent compounds do not dissociate or conduct electricity.

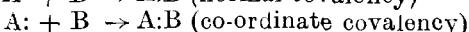
(3) A covalent molecule being non-polar has no external field of force. Covalent compounds are, therefore, volatile solids, liquids, or gases. They have low boiling-points and melting-points.

(4) Covalent compounds are usually insoluble in water and soluble in organic solvents.

Co-ordinate Linkage

This type of linkage unites apparently saturated compounds to electro-negative atoms. Since it affords an explanation of the 'Co-ordination compounds' of Werner, it was named **Co-ordinate Linkage** (Co-ordinate=to bring into relation). This is a special type of covalent linkage in which both of the shared electrons are contributed by

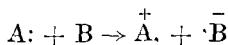
one atom only and not one by each atom as in a covalent linkage.



It will be noted that since the shared pair counts as one electron to each atom, out of the two electrons originally belonging to A we may consider that one electron now remains associated with it and the other with B. It means that the formation of this type of linkage is accompanied by a transfer of electron from A to B. Thus the

molecule AB will acquire polarity and can be represented as $A^+ - B^-$. This linkage is, therefore, often referred to as a **Semipolar linkage**.

The formation of the semi-polar bond can be examined from another point of view. It may be imagined that an electron is first transferred from A to B yielding A^+ and B^- .

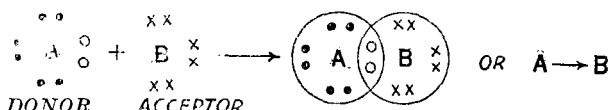


The resulting ions acquire greater stability by sharing one electron



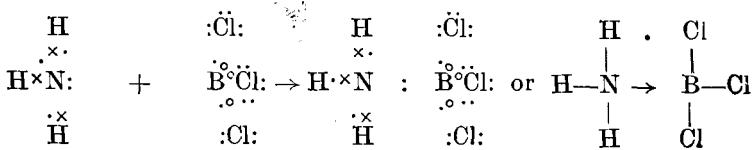
This type of bond thus implies a combination of one electro-valency and one covalency. Sugden has rightly named it "*Semi-polar double bond*."

A co-ordinate linkage is established between two atoms *one of which although it possesses a completed octet has a pair of free valency electrons and the other is short of two electrons*. While the first atom can donate the free pair of electrons, the second is ready to accept it in order to complete its octet. Showing all the necessary electrons with A and B we have,

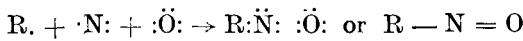


The co-ordinate linkage connecting A and B is denoted by an arrow (\rightarrow) pointing away from the A atom which has contributed the pair of electrons forming the link. The atom which donates the two electrons is called the **Donor** and B which accepts them is called the **Acceptor**. The pair of valency electrons possessed by the donor is called a **Lone pair**. Let us now consider some examples for illustration.

Combination of Ammonia and Boron trichloride :-

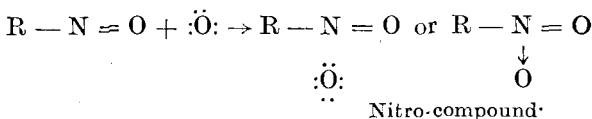


Nitro-compounds. In a nitro-compound we have one monovalent radical (R) and two oxygen atoms connected to a nitrogen atom.

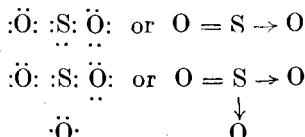


Nitroso compound

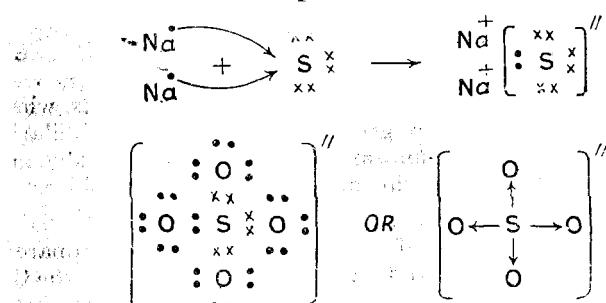
Although the nitrogen has completed its octet in the nitroso-compound, it has still a lone-pair of electrons which it is able to donate to another oxygen atom.



Sulphate dioxide (SO_2) and *Sulphur trioxide* (SO_3).

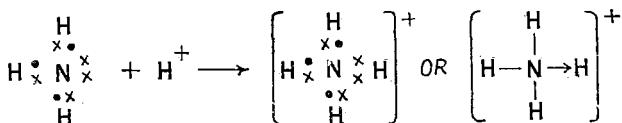


Sulphate Ion (SO_4^{2-}). The metallic atoms, say, of sodium first transfer their electron to sulphur atom.



Sulphur atom has completed its octet and can be linked to the four oxygen atoms by donating the four lone pairs it now has.

Ammonium Radical (NH_4^+) may be formed as follows:



CHARACTERISTICS OF CO-ORDINATE COMPOUNDS

(1) The co-ordinate linkage is rigid and directional. In this respect it is equivalent to a covalent link and offers opportunity for space-isomerism of molecules.

(2) Just like a covalent link, atoms in a co-ordinate compound are firmly held by electrons and they do [not dissociate when it is placed in water or melted].

(3) Since a co-ordinate linkage is a union of one electrovalent and one covalent linkage, in respect of volatility the co-ordinate compounds stand between the electrovalent and the covalent compounds. *Their boiling and melting points are relatively higher than those of the covalent compounds and lower than those of the electrovalent compounds.*

(4) The co-ordinate compounds are *insoluble in water but soluble in organic solvents.*

Exception to the Octet Rule

It has been assumed so far that the maximum number of electrons in the valency shell is 8. Sidgwick, however, believes that this number can be exceeded. For example, sulphur forms a hexafluoride, SF_6 , which is a stable compound. Since it is a gas, it must be a covalent compound. This means that all the six fluorine atoms are connected with the central sulphur atom by covalent links.

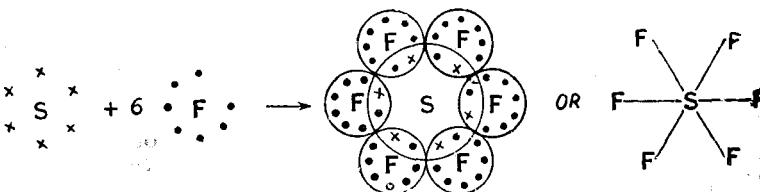


Fig. 132. Sulphur hexafluoride molecule.

All the fluorine atoms now possess completed octets whereas the sulphur atom has a valency group of 12 electrons. Similarly in osmium octafluoride, OsF_8 , osmium would have the valency group of 16 electrons and in PCl_5 , the phosphorus atom would be surrounded by 10 electrons.

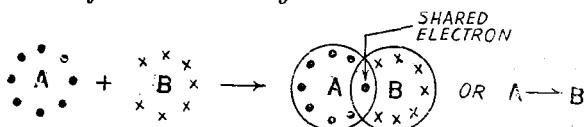
There are also examples of stable compounds which apparently possess an insufficient number of electrons than allowed by the Octet Rule. For example, in boro-ethane B_2H_6 , the two boron atoms each possessing three electrons can share these with six hydrogen atoms without leaving any electrons for the bond between the two boron atoms.

Singlet Linkage

Contrary to the views of Sidgwick, Sugden believes that the maximum number of electrons in the valency orbit cannot exceed eight. He accounts for the formation of a compound like phosphorus pentachloride and sulphur hexafluoride by assuming that some or all the halogen atoms are joined to the central atom by linkages, involving the sharing of a single electron. This type of union of two atoms by means of a single electron only, has been given the name Singlet Linkage or simply a Singlet.

A singlet is established between atoms one of which has a complete octet of electrons and can denote some of the electrons to other atoms each of which is short of one electron.

Thus a singlet could be visualised as a co-ordinate linkage formed by the donation of one electron only.



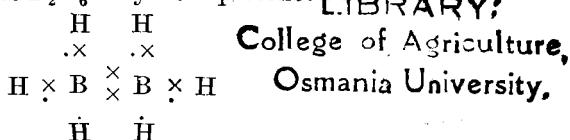
According to Sugden's theory the central atom in phosphorus pentachloride is not surrounded by 10 electrons, but three of the chlorine atoms are supposed to be attached to the phosphorus atom by ordinary covalent links, whereas the other two are joined to it by singlet linkages, thus making a total of 8 electrons round the central atom.

Sugden's view is supported by the fact that PCl_5 ($\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$), dissociates to give PCl_3 and Cl_2 which

indicates that two chlorine atoms in PCl_5 are differently connected than the other three.

In the case of sulphur hexafluoride, SF_6 , we may have a combination of two pairs and four singlets while in OsF_8 , we may have all the eight as singlet bonds.

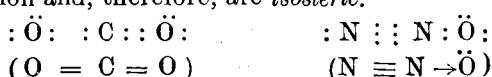
The structure of B_2H_6 may be represented as



The stability of compounds such as above is now explained in the light of the concept of **Resonance**. The singlet electrons instead of being fixed, oscillate between the bonds involving the singlets so that each singlet bond would possess an electron doublet for a part of the time of an oscillation.

ISOSTERES

It is very interesting to note that *compounds containing the same total number and arrangement of electrons have similar physical properties*. Such compounds are called **Isosteres**. Carbon dioxide and nitrous oxide each have the same number of electrons arranged in the same fashion and, therefore, are *isosteric*.



Most of their physical properties including critical temperature and critical pressure, viscosity, surface tension and dielectric constant are nearly identical.

Other examples of *isosteres* are

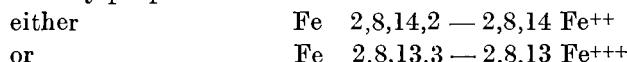


VARIABLE VALENCY

Certain elements display two or more than two valencies in chemical combination. For example, iron is bivalent or trivalent, cobalt is bivalent or trivalent, and so on. The variable valency in such cases can be explained from a study of the electronic configuration of these elements (See Chart on page 170). In the first two short periods the loss of valency electrons leaves a stable outer orbit of 8 electrons.



and the valency corresponds to the number of electrons lost in this manner. In the long periods, however, it is not always the case. In the long periods, the first two and the last six elements behave normally while the intervening elements, which have only two electrons in the valency orbit and an incomplete next inner orbit, behave differently. In the atoms of these elements, since the next inner orbit is unstable, one or more electrons can be drawn out from it for valency purposes. Thus in the case of iron we have,



In the case of cobalt it is more difficult to draw out the third electron against a stronger pull of the nucleus whose charge is one unit higher than that of Fe, and thus the trivalent cobaltic ion is formed with greater difficulty. In nickel the tendency to form a trivalent ion is altogether absent.

QUESTIONS AND PROBLEMS

1. Define the term valency and discuss its applicability in the light of modern views on the structure of the atom.
2. Write an essay on the historical development in our ideas of valency up to the present day, emphasising more on the modern views.
(Annamalai B.Sc., 1954)
3. Explain the terms (a) electrovalence, (b) Covalence, (c) Co-ordinate valence. In what respects do they resemble and differ from one another ? Assign electronic formulae to the following :
 $\text{H}_2\text{O}_2, \text{C}_2\text{H}_6, \text{C}_2\text{H}_2, \text{NH}_4\text{Cl}$.
4. Explain with suitable examples the full significance of the terms electro-valence, covalence, and co-ordinate valence.
(Bombay B.Sc., 1953)
5. Classify and discuss briefly the various types of bonds which occur in chemistry.
(Ceylon Final, 1953)
6. What are the different types of valency recognised in modern chemical theory ? Illustrate each type by a consideration of the examples of each type.
(Nagpur B.Sc., 1953)
7. Write down the electronic formulae of the following compounds and indicate what type of chemical combinations they represent :
 - (a) Sodium fluoride ; (b) Sodium hydride ; (c) Hydrochloric acid ;
 - (d) Sulphuric acid ; (e) Ammonium ion ; (f) Silico-fluoride ion.

8. Write the electronic formulae of the following and say what kind of linkage is found in each :

- (a) Sodium fluoride ; (b) Sodium hydride ; (c) Hydrogen chloride ;
- (d) Sulphuric acid ; (e) Ammonium ion ; (f) Sulphur dioxide ;
- (g) Sulphur mono-oxide. (Lucknow B.Sc., 1954)

9. Write a brief account of the electronic theory of valency. What are the main differences, between the electrovalent and covalent compounds ? (Agra B.Sc., 1958 ; Banaras B.Sc., 1952)

10. What do you understand by 'co-ordinate linkage'? Give examples of the compounds in which this type of linkage is found and show how its existence can be verified.

11. Give an account of the modern views regarding valency. (Andhra B.Sc., 1943)

12. State briefly the modern conception of valency. Why does an electrovalent compound ionize in water while a covalent one does not ?

13. Give an account of the electronic theory of valency.

14. How would you proceed to show that a given compound contains an electro-valent or covalent linkage? Also point out the differences between normal co-valency and co-ordinate covalency.

15. Explain the terms electrovalency and covalency, giving examples. What are the physical properties associated with these two kinds of valency ? (Allahabad B.Sc., 1950)

16. Give a description of the electronic theory of valency with examples to illustrate different types of valency. Give reasons for the variable valency of manganese. (Travancore B.Sc., 1953)

17. Give a brief description of the electronic theory of valency and point out its relation to the electronic arrangement in the atom. (Andhra B.Sc., 1954)

18. Comment on the statement : "The maximum number of electrons in the valency shell can exceed the octet."

19. Write an essay on valency. (Agra B.Sc., 1952)

20. Write a short note on isosteres.

21. Write a note on : Electronic theory of valency. (Delhi B.Sc., 1953)

22. Explain the various types of valency from the stand-point of electronic theory. Illustrate your answer by the electronic formulae of methane, ammonia and ammonium chloride. (Osmania B.Sc., 1955)

23. Trace the historical development of the conception of valency and give an account of the modern electronic theory. (Banaras B.Sc., 1955)

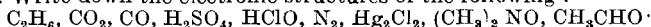
24. Write an essay on the electronic theory of valency. (Allahabad 1957 ; Aligarh 1955 ; Madras 1955)

25. Trace the development of the conception of valency and give an account of the modern electronic theory. (Nagpur B.Sc., 1956)

26. What types of valency are recognised in modern chemical theory? Give two examples of compounds illustrating each type of valency and write down their detailed electronic formulae. (Lahore B.Sc., 1956)

27. Give an account of the electronic theory of valency, illustrating your answer with examples of each type. (Patna B.Sc., 1958)

28. Write down the electronic structures of the following :—



(Venkateswara B.Sc., 1958)

29. Explain the electronic theory of valency. Give examples of various types of linkages. (Osmania B.Sc., 1959)

30. What types of valency are recognised in modern chemical theory? Illustrate your answer with suitable examples. (Karnatak B.Sc., 1959)

31. Explain the terms electrovalency and covalency, giving examples. Why does an electrovalent compound ionize in water while a covalent one does not ? (Marthwada B.Sc., 1959).

CHAPTER XII

SPECTRUM ANALYSIS

THE NATURE OF LIGHT

According to the wave theory, light comes to us from the sun in the form of transverse electromagnetic wave-motion in a hypothetical medium called *ether*. The origin of this radiation is traced to the violent disturbances taking place in the sun with its excessively high temperature. The atoms and the molecules of the substances present in it suffer vigorous collisions in all possible directions as the result of which many of their electrons are displaced from their normal positions. Such atoms are said to be *excited*, and within a fraction of a second the displaced electrons return to their less excited state. As this happens, a disturbance radiates from them, nature of which is analogous to one produced when a pebble falls into a pond of still water.

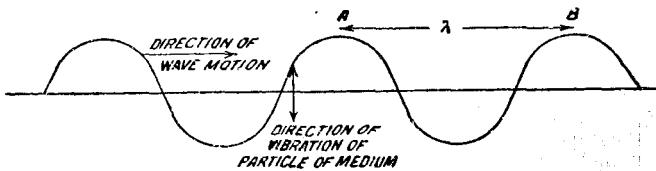


Fig. 133. Illustrating the propagation of a simple wave.

The propagation of a simple wave is shown in Fig. 133, the horizontal arrow showing the direction in which the disturbance called Wave Motion is travelling while the vertical double pointed arrow shows the direction of the vibration of the medium particles which move only up and down perpendicular to the path of the wave motion. The distance from wave crest to wave crest (AB in the figure) is called **Wave-Length** and is denoted by the Greek letter λ (Lambda). It is constant for light of any given colour and measured in Angstrom units, one **Angstrom unit** (A°) being equal to 1×10^{-8} cm.

The number of times a medium particle is shaken up and down per second or the *number of waves passing any given point per second* is denoted by v and is termed **Frequency**. The product of wave length and frequency gives the *velocity*,

$$C = \lambda \times v.$$

QUANTUM THEORY OF RADIATION

The transfer of energy from matter to radiation and *vice versa* is supposed to take place according to the **Quantum Theory** of radiation postulated by Max Planck in 1900 and extended by Einstein in 1905. According to this theory :

- (i) *When a body emits or absorbs energy in the form of radiation, it cannot do so in a continuous manner.*

(ii) The emission or absorption of energy occurs in integral multiples of a certain unit known as a **Quantum**.

(iii) The energy E associated with each quantum for a particular radiation of frequency ν is given by the relation :

$$E = h\nu$$

where h is a universal constant known as **Planck's Constant**. Its value has been found to be 6.624×10^{-27} erg-seconds.

It is evident that the energy associated with each quantum of a certain radiation is directly proportional to its frequency and inversely proportional to its wave-length and thus **varies in size**. It is comparatively very large for radiations like X-rays, γ -rays, cosmic rays etc., which possess small wave-lengths and is small for infra-red and wireless waves.

THE VISIBLE SPECTRUM

If a narrow beam of white light is allowed to pass through a prism suitably placed in a dark room and then received on a screen, we see instead of the beam of white light a band of seven colours the like of which we see in the rainbow. This separation of white light into the seven colours of which it is made of, is known as **Dispersion** and the band produced is called **Visible Spectrum**. The various colours in order are *Red, Orange, Yellow, Green, Blue, Indigo and Violet*.

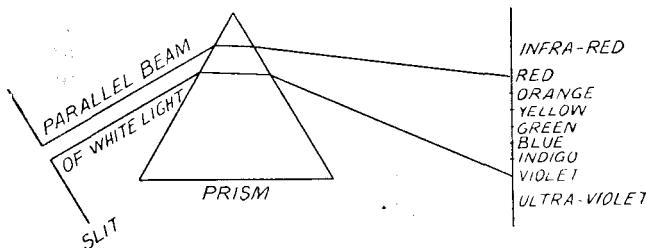


Fig. 134. The spectrum of white light.

Each of these colours has got a characteristic wave-length as shown in the Table below and on passing through the prism, radiations of different wave-lengths are deviated to a different extent and this causes their separation from each other.

TABLE—WAVE-LENGTHS OF THE VISIBLE SPECTRUM

Colour	Wave-length in Angstrom Units (\AA)
Red	6,300—7,500
Orange	6,000—6,300
Yellow	5,800—6,000
Green	5,100—5,800
Blue	4,600—5,100
Indigo	4,200—4,600
Violet	4,000—4,200

THE INVISIBLE SPECTRUM

The visible light constitutes only a small part of the total range of the electro-magnetic radiation. Only those radiations whose wave-lengths fall within this range can affect our eyes. There are, however, other radiations to which our eye is not sensitive. Beyond the red, we have the still longer *infra-red radiation* of wave-lengths $7,230\text{A}^\circ$ to $3 \times 10^6\text{A}^\circ$ and the wireless waves with wave-lengths from $4 \times 10^7\text{A}^\circ$ to 10^{14}A° . Beyond the violet, we have the invisible ultra-violet region, the ultra-violet waves having wave-lengths smaller than the violet *viz.*, $500-4,000^\circ$. The *X-rays*, λ -rays (wave-lengths $0.03-10\text{A}^\circ$) and the *Cosmic rays* are manifestations of the same phenomenon with wave-lengths which are extremely short. The **complete spectrum** may be defined as the *analysis of all types of radiations into wave-lengths*.

THE SPECTROSCOPE

A very useful instrument with the help of which the spectrum can be produced and studied was devised by Bunsen and Kirchoff in

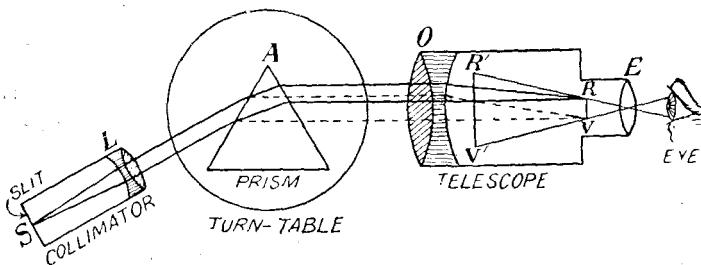


Fig. 135. The Spectroscope.

1859 and for chemical purposes the same is used even these days. It consists essentially of three parts: the *Collimator*, the *Turn-Table* and the *Telescope*. The collimator is a brass tube containing an adjustable slit which faces the Bunsen flame in which the substance to be examined is vaporised. A narrow beam thus comes towards the prism through this slit. It is made parallel by the compound lens present in the collimator and is focused on the prism which is placed on small iron table known as the *turn-table*.

The prism is made of flint glass for visible light. For experiments in the ultra-violet region, it is made of quartz but owing to the optical activity of the latter, a special prism known as the "Cornu Prism" is used. For infra-red work, a prism made of rock salt is used.

As the light passes through the prism, it is dispersed into different wave-lengths. The dispersed light passes through the objective lens O of the telescope and gives the spectrum RV. This spectrum when viewed through the eye-piece is seen in the magnified form R'V'. The telescope is so placed that it can be moved round to receive any part of the spectrum.

In many forms, the image of a glass scale fixed in another illuminated tube is also thrown by reflection from the prism face over-

the spectrum. By this arrangement it is possible to locate the position of the lines by comparison with the lines given by a known standard substance. Direct vision spectroscope and *spectrometers* with vernier attachments are also in use but their description is beyond the scope of this book.

DIFFERENT TYPES OF SPECTRA

Spectra are of two types :

(a) *Emission Spectrum.* (b) *Absorption Spectrum.*

Emission Spectrum. When a solid is heated to a high temperature or a discharge of electricity is passed through a gas there occurs an emission of light. The spectrum produced when this emitted light is examined through a spectroscope is known as **Emission Spectrum**. It can be divided into three characteristic classes :

(i) *Continuous Spectrum.* If the light emitted by an incandescent solid is examined through a prism, we get a spectrum similar to the one produced from sunlight. It shows all the colours from red to violet and it is not possible to say confidently where the one colour ends and the other begins. Such a spectrum is known as *Continuous Spectrum* and is given by all incandescent solids, e.g., electric light, limelight, arc light, etc.

(ii) *Line Spectrum.* The light emitted by hot vapours of elementary substances when examined through a spectroscope gives a spectrum which consists of bright lines separated from each other by dark spaces. This kind of spectrum which is characteristic of the atom is known as **Line Spectrum** or **Atomic Spectrum**. Sodium gives two yellow lines 5890A° and 5896A° in the yellow region and whenever sodium is present in a sample under examination these two lines are invariably there. Strontium gives three prominent lines, one in the red, the second in the orange and the third in the blue region.

(iii) *Band Spectrum.* It consists of groups of lines or flutings closely packed together giving the appearance of broad luminous bands sharply defined at one end gradually shading off at the other. This spectrum, known as the **Band Spectrum**, is characteristic of molecules.

Absorption Spectrum. Consider a spectroscope set up for obtaining a pure continuous spectrum of white light. If a sodium flame be interposed between the white light source and the collimator, the continuous spectrum of white light is crossed by two *dark lines* in the yellow region. If the white light source be now removed, the whole of the continuous spectrum disappears leaving behind only two bright yellow lines occupying the position of the two dark lines in the previous case.

These dark lines are known as *Absorption Line Spectrum* and their existence is explained by **Kirchoff's Law** according to which :

"The vapour of any element at a lower temperature selectively absorbs the wave-lengths which it will itself emit when at a higher temperature."

In the above case the two dark lines correspond to the two yellow-D-lines (5890A°) (and 5896A°) of sodium which are selectively absorbed from white light (containing wave-lengths $4,000$ — $7,500\text{A}^\circ$) because the Bunsen flame is at a lower temperature than the arc light.

Absorption spectrum is also produced when white light is passed through transparent solids, liquids or solutions of salts. Thus ruby glass will cut off all wave-lengths excepting the red portion ; a solution of copper sulphate will remove all the spectrum except the blue, and a dilute solution of potassium permanganate produces five dark lines in the green region.

Another example of absorption spectrum is the **Solar spectrum** which is crossed by a large number of dark lines known as the *Fraunhofer Lines*. These are due to the vapours of the different elements present in the chromosphere of the sun which selectively absorbs different wave-lengths from the white light emitted from the photosphere which is comparatively at a very high temperature.

SPECTRUM ANALYSIS

It has been already pointed out that line spectrum is characteristic of the atoms of an element and since atoms of different elements differ in all respects, *no two elements give lines which occupy the same position in the spectrum*. For example, take the case of sodium. If in a sample under examination, sodium is present, the two yellow D-lines are invariably there. If sodium is absent, these two lines are also absent, no other element being able to produce these two lines. Sodium can, therefore, be identified by an examination of its line spectrum and this method of qualitative analysis first introduced by Bunsen and Kirchoff in 1859 is known as **Spectrum Analysis**. The emission spectra of all known elements have been carefully mapped out. *By examining the spectra of the given substance and comparing it with the maps, the nature of the elements present in it can easily be determined.*

The method is so very sensitive that 0.0000005 mg. of an element in a sample can be detected and it has been instrumental in the discovery of new elements like Helium, Rubidium, Caesium, Indium, etc. It has also given an insight in the composition of the sun, stars and other heavenly bodies.

The absorption likewise has been useful in the identification of a number of substances because every substance has its own characteristic absorption spectrum. It has been successfully employed to the study of dyes, oils, drugs, etc.

Spectrum analysis has proved very valuable in determining chemical constitution and the elucidation of molecular structure.

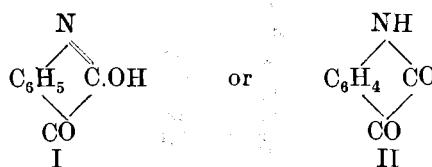
ABSORPTION SPECTRA AND CHEMICAL CONSTITUTION

The absorption spectra of the visible and the ultraviolet regions are generally studied with the help of Hilger's Spectrophotometer. It was shown by Hartley that "*Substances of similar constitution have similar absorption spectra*". This rule, known as **Hartley's**

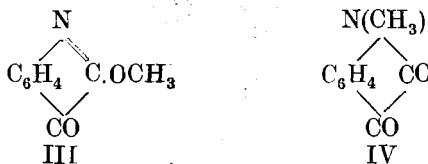
Rule, has been verified in a number of cases and has proved to be of great use in elucidating molecular structure.

All permanganates produce similar absorption bands. Other similarly constituted compounds are also found to give similar absorption bands. Now if two unknown substances give similar absorption spectra, we can safely conclude that their structures are identical. The following two examples will make the point clear :—

The absorption spectrum of isatin was found to be identical with the spectrum of its N-methyl derivative which shows that the two have identical structure. Isatin may have either of the two structures I or II shown below :

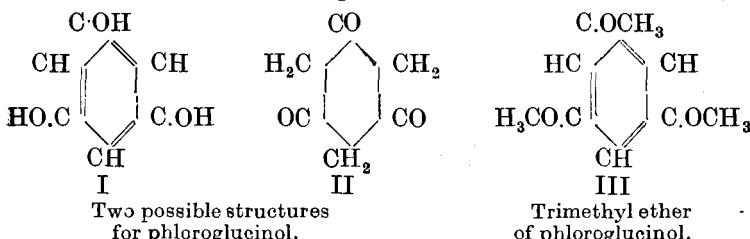


Isatin gives two isomeric methyl derivatives having the structures



The absorption spectrum of IV is identical with that of isatin and from this we conclude that the formula of isatin is represented by II.

Similarly it has been shown that phloroglucinol (I or II) gives an absorption spectrum identical with its trimethyl ether (III) indicating that it possesses a true phenolic structure represented by I.



ORIGIN OF ATOMIC SPECTRA

It was pointed out in Chapter VIII on *Structure of the Atom* that Maxwell's electro-magnetic theory could not explain the discontinuous or line spectra of atoms and in order to account for the same, Bohr suggested in 1913 that the nucleus of an atom is surrounded by a limited number of **Stationary States** or **Energy Levels** which the electrons can occupy. So long as the electrons rotate in a particular energy level, there, is no emission or absorption of radiation. When, however, an electron moves from one energy level to another,

the difference in the energy of the atom thus caused gives rise to a spectral line with a definite frequency.

Let E_1 be the energy of the level from which the electron starts and E_2 the energy of the level to which it is displaced. The difference in energy is $(E_1 - E_2)$. According to the Quantum Theory;

$$E_1 - E_2 = h \nu;$$

So, the frequency of the spectral line produced will be

$$\nu = \frac{E_1 - E_2}{h}.$$

If E_1 , is greater than E_2 , i.e., the electron moves from a higher to a lower energy level, this line will appear in the **Emission spectrum**. If, however, E_1 is less than E_2 , i.e., the electron jumps from a lower to a higher energy level, the line will form a part of the **Absorption spectrum**.

It also follows that the greater the energy difference $(E_1 - E_2)$, the greater is the frequency of the radiation emitted or absorbed and the shorter is its wave-length.

Quantum Number and Electronic Transition. Each energy level is characterised by a quantum number n which determines the energy E of the electron rotating in it. The two are related by the expression,

$$E = -\frac{R\hbar}{n^2}$$

where \hbar is Planck's constant and R is Rydberg's constant whose value on the basis of quantum mechanics is $\frac{2\pi^2 me^4}{h^3}$, m being the mass of the electron and e the charge on it. So, when we have transition from one energy level whose quantum number is n_2 to one of quantum number n_1 , ($n_2 > n_1$), the energy quantum set free is

$$E_2 - E_1 = h\nu = \frac{2\pi^2 me^4}{h^3} \times h \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

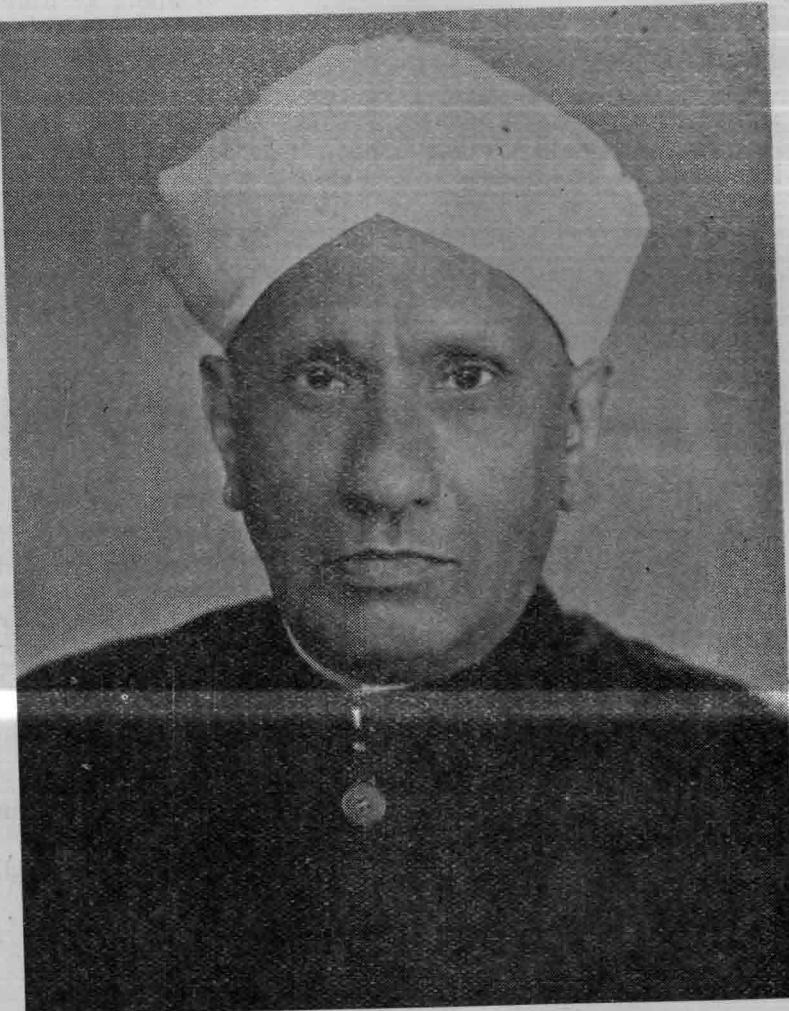
and the frequency of the spectral line produced in the emission spectrum will be

$$\nu = \frac{2\pi^2 me^4}{h^3} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right).$$

By making use of this equation, it has been possible to calculate the frequencies of the spectral lines which agree fairly well with the observed values.

The Hydrogen Spectrum. The simplest atom is that of hydrogen with only one electron and offers a case for study free from complexities. Its spectrum consists of four series of lines, the **Lyman series** in the ultra-violet region, the **Balmer series** in the visible region, the **Paschen series** in the infra-red region and the **Brackett series** in the far infra-red region. An explanation of their origin is readily forthcoming in the light of the Bohr Theory outlined above.

Under normal conditions, the electron in the hydrogen atom occupies the ground energy level near the nucleus with quantum



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number $n = 1$ and least energy. When energy is imparted to hydrogen gas in the Geissler tube, the electrons move to higher energy levels with n equal to 2, 3, 4, 5, 6, etc. From these high levels, the electrons return by jumps to one or the other lower energy levels and in this process emit energy quanta which give rise to the spectrum.

The Lyman series is produced by the electrons which return to the orbit with $n_1 = 1$. (See Fig. 136).

$$\nu = \frac{2\pi^2 me^4}{h^3} \left(\frac{1}{1^2} - \frac{1}{n_2^2} \right),$$

where n_2 is 2, 3, 4, 5, 6, etc.

Those returning to the level with quantum number $n_1 = 2$ give rise to the Balmer series.

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

The Paschen series is produced when they come up to the level with $n_1 = 3$ and the Brackett series when the level reached is one with $n_1 = 4$.

Thus :

In Lyman series, $n_1 = 1$ and $n_2 = 2, 3, 4, 5, 6$ etc.

„ Balmer series, $n_1 = 2$ and $n_2 = 3, 4, 5, 6$, etc.

„ Paschen series, $n_1 = 3$ and $n_2 = 4, 5, 6, 7$, etc.

„ Brackett series, $n_1 = 4$ and $n_2 = 5, 6, 7$, etc.

RAMAN SPECTRA

Sir C. V. Raman (1928) noticed that when a beam of strong light is passed into a transparent substance (solid, liquid, or a gas)

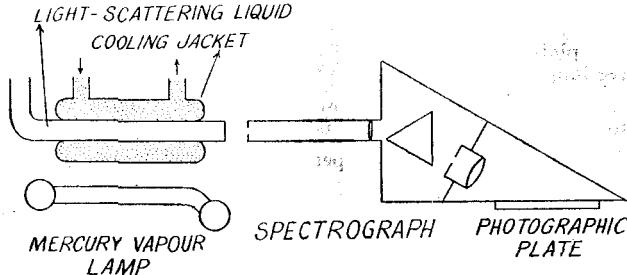


Fig. 137. The method of obtaining Raman Spectrum.

the scattered light has a slightly different frequency from that of the incident light. Since the amount of the scattered light is usually

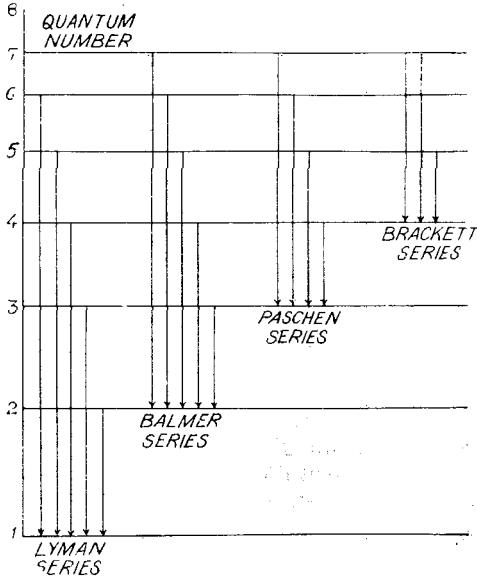


Fig. 136. Energy levels and origin of hydrogen series.

very small, he employed a special device to examine its spectrum which falls in the infra-red region.

A liquid contained in water-cooled tube is placed in front of the spectrograph and illuminated with a mercury-vapour lamp. A long exposure (up to 100 hours) gives the **Raman Spectrum** on the photographic plate.

The incident light is associated with energy $h\nu_1$ a part of which is used up for displacement of the atoms within the molecule, so that the scattered light has a lower energy content $h\nu_2$ and thus a new line appears in the spectrum. *The phenomenon due to which the scattered light has a slightly different frequency from that of the incident light and there is a change in the atomic oscillations within the molecule,* is called **Raman Effect**. The frequency difference $\nu_1 - \nu_2$ is characteristic of the scattering molecules and is known as **Raman Frequency** (ν_r).

$$\nu_1 - \nu_2 = \nu_r$$

Raman spectra have been measured for a great many organic and inorganic compounds by several workers in India and abroad, and much useful data collected regarding the molecular structure of different substances. For illustration we mention here some simple cases.

(i) Concentrated nitric acid has the same Raman frequency as shown by solutions of nitrites whereas that of the dilute acid corresponds with the one given by solutions of nitrates. Thus it has been inferred that the concentrated and the dilute nitric acid have the following structures :—



(ii) Similarly, the Raman frequency of 25% sulphuric acid corresponds with that given by KHSO_4 , but on dilution the Raman frequency corresponds with that of K_2SO_4 . Thus the existence of the intermediate HSO_4^- ions is indicated.

(iii) Raman spectrum of carbon monoxide suggests that it has the structure $\begin{array}{c} \text{C}=\text{O} \\ \swarrow \end{array}$.

QUESTIONS AND PROBLEMS

1. Explain the propagation of a simple wave. What do you understand by (a) Wave-length, (b) Frequency, (c) Quanta.
2. What is a spectrum and how is it obtained ? Describe the construction of a spectroscope and explain its uses.
3. What are the different types of spectra ? Explain the principle of spectrum analysis.
4. Describe a solar spectrum and give a general explanation of Fraunhofer lines in the spectrum.
5. Write a short note on Absorption spectra and chemical constitution.
6. What is Raman Effect ? What role has it played in the advancement of chemical knowledge ?
7. Give an account of the applications of the Raman Effect to the elucidation of the molecular structure.

8. Describe the important parts of a spectroscope. Explain carefully the principles on which spectrum analysis is based. What important elements were discovered by the aid of the spectroscope ?

9. Give an account of the experimental arrangement used for the study of emission spectra of elements and absorption spectra of solutions. Indicate fully the useful results obtained from such studies. (Madras B.Sc., 1947)

10. How do you study the line spectrum of elements? Describe the general principle of the method in a simple manner. (Rajputana B.Sc., 1955)

11. Discuss the relation between the absorption spectrum of a substance and its chemical constitution. (Rajputana B.Sc., 1958)

12. Show how the structure of simple molecules can be investigated by the study of absorption spectra. Point out precisely the difference between this kind of spectra and emission spectra. (Bombay B.Sc., Subs., 1958)

13. What do you understand by :

(a) Line spectra and

(b) Band Spectra ?

How are they excited? Discuss the applications of Band Spectra.

(Karnatak B.Sc., 1958)

CHAPTER XIII

PHOTOCHEMISTRY

GENERAL

A great many chemical reactions proceed only under the influence of light which supplies the energy needed to set the reaction going. Combination of hydrogen and chlorine on exposure to light, and the action of light on silver halides on which the process of photography is based are too well-known. Such chemical reactions which are produced directly or indirectly by means of light are called **Photochemical Reactions** and the study of these reactions is known as **Photochemistry**.

Sources of Photochemical Radiations

In general, visible and ultraviolet light are photochemically active while infra-red light has practically no effect on chemical reactions. According to the modern views, the two former kinds of light have the effect of raising the molecule to a higher electronic energy level and the molecule 'excited' in this manner is more ready to react.

For a study of photochemical reaction we need a steady source of ultraviolet radiations.

1. *The Sunlight.* The sunlight is rich in ultraviolet radiations. Since the intensity of these radiations varies with place, season and time, they are not very useful for a quantitative study of photochemical reactions.

2. *The Arc Light.* The establishment of an arc between electrodes of iron, and carbon, is a good source of ultraviolet light. With such an arc, however, a constant intensity of radiations cannot be maintained.

3. *Mercury Vapour Lamp.* The fact that a brilliant light is emitted when mercury is vaporised in an electric arc has been utilized in the construction of a mercury vapour lamp. A mercury vapour lamp is the best source of ultraviolet radiations.

Measurement of Intensity of Radiations—Radiometry.

The intensity of radiations available for photochemical reaction can be measured by the following methods :—

1. **Radio Micrometer.** This is a very sensitive apparatus for the measurement of the intensity of radiations. It consists of a 'couple' of unlike metals, say Bi and Ag, connected in a circuit that is suspended between the poles of an electromagnet. When the couple is heated at the junction by exposing to radiations, a current is produced in circuit. As the current is sent round the coil, the latter is deflected in the magnetic field. The deflection can be measured by a lamp and scale arrangement. Obviously, the deflection is proportional to the intensity of radiations.

2. Photo-Electric Cell. Ultraviolet radiations as they fall on metals like Li, Na, K cause them to emit electrons. Thus the residual metallic atoms gradually become positive. The rate of emission of electrons which is determined by the intensity of radiations, can be measured by noting the divergence of gold leaves connected to the exposed metal. In the modern apparatus, the gold leaf system has been replaced by an electrometer.

3. The Chemical Actinometers. The photochemical activity of light can be measured by the amount of photochemical reaction produced in an instrument called **Actinometer**. Bunsen and Roscoe (1857) devised an apparatus shown in Fig. 140 which may be described for illustration. The glass tube is filled with a mixture of equal parts of hydrogen and chlorine. The lower portions of the bulbs B and D contain water saturated with the reacting gases. The bulb B is now exposed to light when some of the gases react to form hydro-

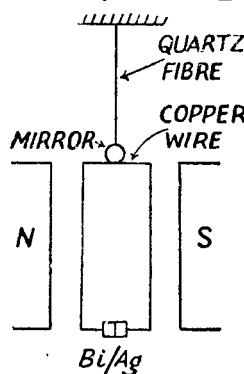


Fig. 138. Radio micrometer.

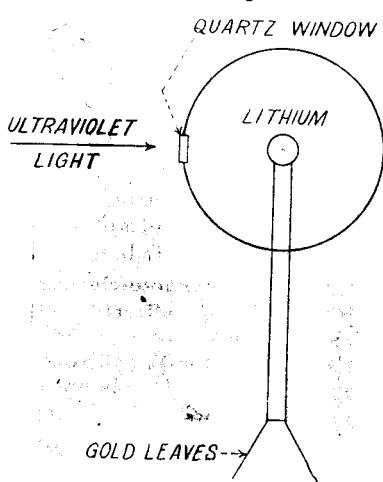


Fig. 139. Photo electric cell.
connected to a galvanometer.

chloric acid. The latter is absorbed in water in B and the thread of water in C moves towards the right. The motion of the water thread would be proportional to the amount of hydrochloric acid formed and also to the intensity of the light employed.

The *Uranayl Oxalate* Actinometer which was studied with great accuracy by Leighton and Forbes (1930) is the best for most purposes.

In modern experimental procedure, the intensity of light available for photochemical reactions is measured most accurately with the help of a **Thermopile** consisting of a series of junctions of unlike metals, say bismuth and silver, alternate junctions of the thermo-

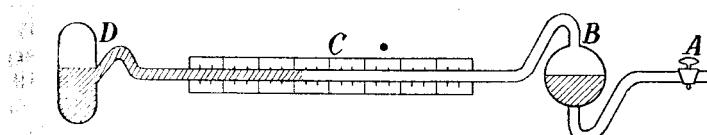


Fig. 140. Bunsen and Roscoe's Actinometer.

pile are heated by exposure to light when the galvanometer deflections correspond to the intensity of light employed.

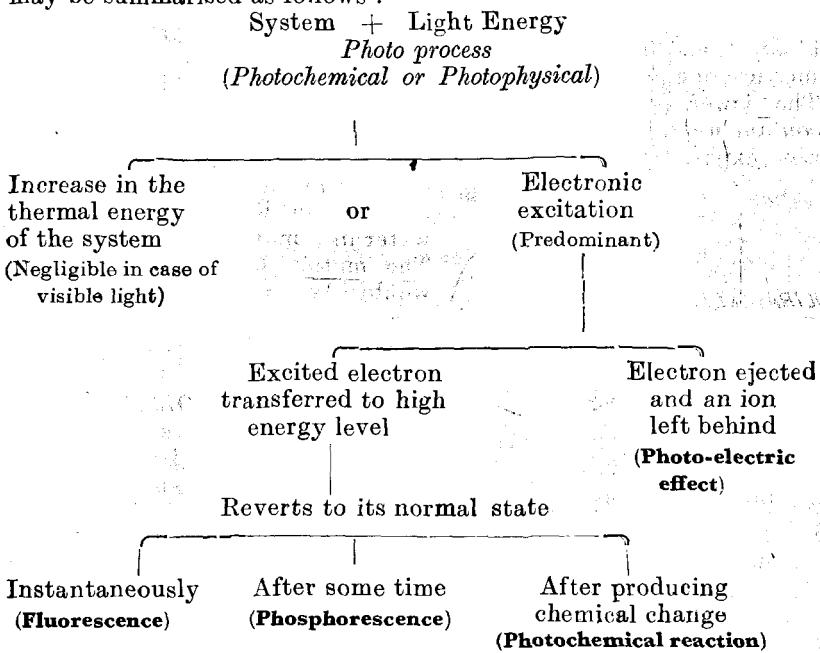
LAWS OF PHOTOCHEMISTRY

There are two important laws governing all photochemical reactions.

1. Grotthus Draper Law. The first law of photochemistry enunciated by Grotthus (1818) and revived by Draper in 1839 states :—

Only those rays of light which are absorbed can produce chemical action.

This, however, does not mean that chemical action must necessarily follow the absorption of light. When conditions are not favourable for the molecules to react, the absorbed light energy may be given out as heat energy or as light of a different wavelength. The various possible **consequences of the absorption of light** may be summarised as follows :—



Grotthus Draper Law which is also simple and obvious is purely qualitative in nature. It gives no idea of the relation between the amount of light absorbed and the number of molecules which have reacted.

2. Law of Photochemical Equivalence. According to the Quantum Theory of Light, energy is absorbed or emitted only in small packets or *quanta* of magnitude $E = h\nu$, where E is the energy, ν is the frequency of light, and h is Planck's constant. In 1913, Einstein applied Quantum Theory to photochemical reactions and deduced the **Law of Photochemical Equivalence** which may be stated as :

When a substance undergoes a photochemical reaction each quantum of energy absorbed results in the decomposition of one molecule only; e.g., $AB + h\nu = A + B$.

The Law of Photochemical Equivalence made Photochemistry a quantitative science and in fact it has now become the guiding principle in the theoretical interpretation of photochemical reactions.

Deviations from Equivalence Law. Einstein's Law of Photochemical equivalence is very general and theoretically sound but in practice the deviations from the law are many. Numerous reactions are known in which the quantum yield* differs considerably from unity.

In many reactions one quantum of energy decomposes more than one molecule of the reactants. There is, no doubt, that one quantum of energy activates or decomposes only one molecule of the reactants but the extra energy possessed by the reacting molecule is often transferred to the molecules of the products. These activated molecules of the products are capable of starting secondary reactions which result in a higher quantum yield.

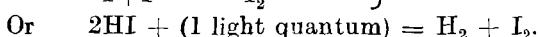
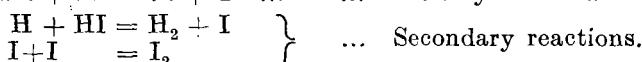
The usual reasons for low quantum yield are :—

- (i) Some process involving the deactivation of the excited molecules before they get the opportunity to react.
- (ii) Some of the excited molecules may not receive energy sufficient enough to enable them to react.
- (iii) Dissociation fragments resulting from the excitation may recombine so as to give low apparent yield.

PHOTOCHEMICAL REACTION

Photochemical reactions are studied with a view to discover the mechanism of the chemical changes which take place when a system is exposed to light. Generally these reactions are complex in nature and a distinction must be made between the main reaction which is produced directly by the absorption of light (**Primary Reaction**) and the possible secondary reactions of the substances produced which follow as secondary effects of light absorption (**Secondary Reactions**). As we have already remarked, the primary reaction strictly obeys the equivalence law whereas secondary reactions which are more complex, account for the abnormal quantum yield. We will now illustrate the above by taking examples of some simple cases.

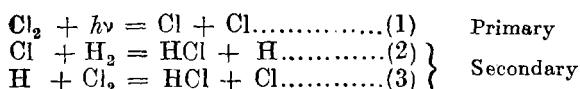
Photochemical Decomposition of Hydrogen Iodide. In the decomposition of hydrogen iodide it is found that the absorption of one quantum of light leads to the decomposition of two molecules. This may be explained as follows :



Combination of Hydrogen and Chlorine—Chain Reactions. The combination of hydrogen and chlorine is a classical

***Quantum Yield.** This term denotes 'yield per quantum' i.e., the number of molecules decomposed per quantum of light absorbed.

example of a photochemical reaction which was first observed by Gay Lussac and Thenard in 1809. The *hydrogen-chlorine* actinometer which we have already described is based upon this reaction. It was found that the quantum yield in this case is extraordinarily large, approximately 10^5 . Nernst (1918) gave a simple satisfactory explanation of the high quantum yield by suggesting that chlorine first dissociates into atoms and then these atoms further enter into 'chains of reactions':



The reactions (2) and (3) repeat alternately many times and the cycle continues, so that by a long chain of these reactions the combination of millions of molecules takes place. The chain reaction does not stop until the entire reactants are consumed. In many cases, however, the chain may be broken when molecules or atoms in the chain collide with the wall of the containing vessel or some inert molecule.

Similarly, hydrogen-bromine combination has been explained by 'chain theory' of Nernst. Such photochemical reactions, in which 'chains of reactions' are set up and thus millions of molecules react for each quantum of light absorbed, are generally called **Chain Reactions**.

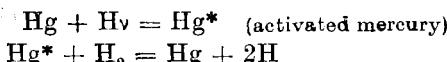
Ordinary thermal reactions sometimes prove to be chain reactions. Christiansen suggested that all reactions which can be retarded by traces of foreign materials, **Inhibitors**, are chain reactions. What the foreign material does is to break the reaction chains at the very outset and thus lower the rate of reaction considerably. For example, the explosion of petrol is a chain reaction and a small quantity of lead tetra-ethyl, $Pb(C_2H_5)_4$ is added to it in order to retard the explosion in internal combustion engines.

PHOTOSENSITISATION

Certain reactions which are not sensitive to light, are made so in the presence of a small quantity of a foreign substance which can absorb light and stimulate the reaction without apparently taking part in it. Such a substance which can absorb light and thus induce a photochemical change without itself taking part in the reaction is called a **Sensitiser** and the phenomenon is termed **Photosensitisation**. The function of a sensitiser is to absorb light energy and, in some way, to pass over this energy to reactants which are thus enabled to enter into reaction. They are carriers of energy.

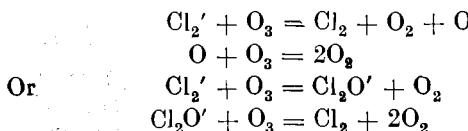
At first though we might be tempted to suggest that photosensitisation is akin to *catalysis* but on closer examination we, however, find that it is quite different in nature from ordinary catalysis. Photosensitised reactions are spontaneous and also involve an increase in the free energy of the system.

Examples. (1) The dissociation of hydrogen into atoms by excited mercury vapour has been decisively demonstrated by Senftleben (1925).



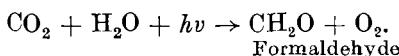
Mercury acts as a photosensitiser and the hydrogen atoms obtained readily reduce metallic oxides, ethylene, etc.

(2) Decomposition of Ozone into Oxygen is photosensitised by Chlorine : Bonhoeffer suggested the following reaction mechanism :—



Photography. A photographic plate coated with a simple gelatin-silver bromide emulsion is sensitive only to the blue or blue-violet part of the spectrum because it cannot absorb energy from the incident light if it happens to be of wave-lengths longer than blue or blue-violet and thus associated with smaller energy. The modern *Orthochromatic* and *Panchromatic* plates are made on the principle of photosensitisation. It was noticed by Vogel in 1873 that a plate dyed yellow with an aniline dye becomes sensitive to the green rays of light. Tailfer and Clayton (1882) noticed that a plate dyed with *eosin* could be made sensitive to the green, yellow and orange parts of the spectrum as well (**Orthochromatic Plates**). Cyanin, erythrosin, pinachrome, and orthochrome T are also used for this purpose. Pinacyanol sensitises the plate even to the red part of the spectrum (**Panchromatic Plates**). In 1930 Babcock found that Neocyanin will sensitise the photographic plate even to the infra-red part of the spectrum. The infra-red photography is of special interest as it can be used to see many things not visible to the naked eye.

Photosynthesis in Plants. The photochemical reaction between carbon dioxide and water taking place in plants is photosensitised by chlorophyll. This important reaction involved in the growth of the plants may be depicted as



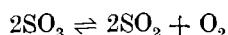
The primary product formaldehyde is immediately converted into cellulose and other carbohydrates.

Short ultraviolet light ($2,300\text{\AA}$) can provide necessary energy for photosynthesis in plants but there are no radiations of this wave length in sun's radiation that reaches the earth. Chlorophyll, however, absorbs red and blue light, and makes it available for photosynthesis in plants.

PHOTOCHEMICAL EQUILIBRIUM

If a reversible reaction is sensitive to light in one or both directions, then under constant illumination it will be characterised by 'equilibrium state' which is different from the equilibrium state in dark. This equilibrium caused by the illumination of a reversible reaction is termed **Photochemical Equilibrium**. An example

of such an equilibrium is afforded by the dissociation of sulphur trioxide.



In the dark this reaction proceeds very slowly and the equilibrium corresponds to practically speaking undissociated sulphur trioxide. Under illumination by ultraviolet light an equilibrium is set up in which the dissociation of sulphur trioxide predominates.

LUMINESCENCE

When a bulb is switched on, the current heats up the metal filament which then begins to emit light, the heat energy being converted into light energy. Light can also be produced by agencies other than heat and the phenomenon is called **Luminescence**. The production of light in all cases is attributed to the fact that electrons which are imparted extra energy from some source are displaced from their original orbits and when they return to their normal position the extra energy is emitted as light.

(i) **Chemiluminescence.** It is interesting to note that certain chemical reactions are accompanied by the emission of light.

The phenomenon of the conversion of chemical energy into light energy is called **CHEMILUMINESCENCE**.

Examples. (a) Oxidation of phosphorus is attended by bluish light.

(b) Ethereal solution of magnesium *p*-bromophenyl bromide gives rise to marked chemiluminescence (Evans and Dufford, 1923).

(ii) **Fluorescence.** It has already been remarked that it is not always necessary that chemical action may follow the absorption of light energy. When conditions are not favourable for the molecules to react, the absorbed light energy is given out as heat energy or light of a different wave length. When an illuminated medium emits light of a wave-length different from that of the incident light the phenomenon is termed **FLUORESCENCE**. When the source of light is cut off the fluorescence also ceases.

Examples. (a) Solutions of dyestuffs of eosin, fluorescein, and quinine sulphate, etc.

(b) Barium platino-cyanide when exposed to X-rays exhibits fluorescence.

(iii) **Phosphorescence.** It differs from fluorescence in the fact that the emission of light is continued even after the incident light is cut off. *When a substance absorbs light energy and then emits it as light of a different wave-length even though the incident radiation is cut off, the phenomenon is called PHOSPHORESCENCE.* The sulphides of calcium, barium and strontium are phosphorescent substances.

QUESTIONS AND PROBLEMS

- What do you understand by a photochemical reaction?
How can the rate of such a reaction be studied?
- State Einstein's Law of Photochemical Equivalence. How do you account for the deviations from this law? What is the importance of this law in photochemistry?

3. What are *chain reactions*? Discuss the theory of such reactions.
4. Define the term *photosensitisation* and give examples of this phenomenon. How does it differ from Catalysis?
5. Write notes on :—
 - (i) Luminescence, (ii) Chemiluminescence, (iii) Fluorescence, and (iv) Phosphorescence.
6. State Einstein's law of photochemical equivalence and give examples of its application to photochemical reactions. How do you explain that photochemical yield in the reaction between hydrogen and chlorine is very high?
7. State and explain Einstein's law of photochemical equivalence, explaining the various terms involved. Discuss the mechanism of photosynthesis of hydrochloric acid explaining clearly the steps involved.

(Bombay B.Sc., 1951)

8. State the law of photochemical equivalence. Distinguish between the primary and secondary processes in a photochemical reaction. How does the distinction permit of explanation of reactions with very high quantum yield?

(Baroda B.Sc., 1953)

9. State Einstein's law of photochemical equivalence and show how it can be used to explain the mechanism of photochemical reactions (i) with low quantum efficiency and (ii) with high quantum efficiency.

(Karnatak B.Sc., 1954)

10. State Einstein's law of photochemical equivalence and explain the terms involved. Describe the experimental arrangement employed for the determination of the quantum efficiency of a photochemical reaction. How are the results explained if the observed value of the quantum efficiency is high or low?

(Poona B.Sc., 1954)

11. State the law of photochemical equivalence. How is the law verified experimentally? Discuss the results obtained and state briefly your reasons why the law is considered valid in all cases.

(Gujarat B.Sc., 1954)

12. Write a short note on Einstein's law of photochemical equivalence.

(Andhra B.Sc., 1954)

13. (a) Describe the different types of chemical changes brought about by the action of light, giving suitable examples.

- (b) State what is meant by the quantum efficiency of a photochemical reaction. Discuss the view put forward to account for the deviations of actual values of quantum efficiency from Einstein's law.

(Andhra B.Sc., 1955)

14. Write a note on the Law of photochemical equivalence.

(Punjab B.Sc., 1956)

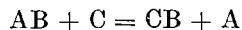
CHAPTER XIV

CHEMICAL EQUILIBRIUM

HISTORICAL INTRODUCTION

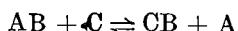
Earlier Views. The earlier theories of chemical change explained all reactions on the basis of **chemical affinity** which was defined as *the force that brings about chemical reaction*. The nature of this force remained a subject of speculation for some time. The Greeks attributed chemical union to 'love' and decomposition to 'hate' between the atoms. According to mechanical conception of chemical combination the atoms were thought to be provided with hooks which interlocked and formed chemical compounds. Newton's discovery of *the law of gravitation* led him to believe that the attraction between atoms and the attraction between large masses follow the same law. Modern researches have, however, shown that chemical affinity is purely electric in nature.

Geoffory and Bergmann's Affinity Tables. The earlier chemists were not satisfied by simply discussing the nature of chemical affinity, but proceeded further to explain chemical reactions on the basis of the relative affinities of substances. It was stated in general, that if the affinity of an element B is greater for C than for A, C will decompose AB with the formation of CB and the liberation of A.



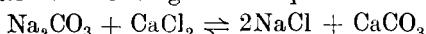
Such considerations led Geoffory and Stahl (1718) and Bergmann (1777) to compile '*Tables of affinity*' in which substances were arranged in the order of their affinity. It was found, however, that even with the help of these tables, it was not possible to explain a very large number of chemical changes especially those which were *reversible* in nature. Consider, for instance, the action between steam and iron. If steam be passed over heated iron, iron oxide is formed with the liberation of hydrogen ($3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$) showing thereby that the affinity of oxygen for iron is greater than its affinity for hydrogen. On the other hand, if hydrogen be passed over heated iron oxide, water is formed along with the reduction of iron oxide to iron ($Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$). According to this change the affinity of oxygen for hydrogen is greater than its affinity for iron; an inference which is in disagreement with the one obtained above.

Berthollet points out the Effect of Mass. Bergmann's theory was first of all contested by Berthollet who pointed out in 1799 that the reaction $AB + C \rightarrow CB + A$ does not always proceed to completion and may proceed in the opposite direction under another set of conditions or even under the same circumstances *i.e.*, $CB + A \rightarrow AB + C$. The complete reaction in such a case may be represented by the equation :



and is known as a **Reversible Reaction**. The extent to which the reverse action $CB + A \rightarrow AB + C$ may proceed will depend upon the affinity of A and C for B and upon their relative mass. A large mass may compensate the poor effect of a weak affinity because the progress of a chemical change is influenced by the product ; $Mass \times \text{affinity}$, and not by affinity alone as was held previously by Bergmann.

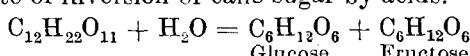
On this basis he explained the existence of sodium carbonate deposits on the shores of certain saline lakes in Egypt. Ordinarily sodium carbonate reacts with calcium chloride to give a precipitate of calcium carbonate according to the equation :



But in the case of these lakes, the great mass of sodium chloride or calcium carbonate causes the reaction to proceed in the reverse direction thus compensating for the weak affinity which the carbonate radical has for sodium.

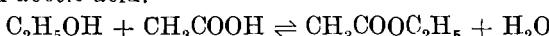
Berthollet's ideas did not receive immediate support because he maintained at the same time that a large mass could alter as well the ratio in which the substances react with each other, a fact against the Law of Constant Composition which was universally accepted.*

Wilhelmy's Law of Reaction Velocity. In 1850, Wilhelmy studied the rate of inversion of cane sugar by acids.



He varied the temperature, the amount of sugar, and used different acids. In each case he found that the rate of inversion is proportional to the quantity of unchanged sugar. He gave a general law that in a chemical reaction, *the amounts transformed in given time are proportional to the amounts present at that time*.

Work of Berthollet and St. Gilles. Berthollet and St. Gilles (1863) made an extensive study of the reaction between ethyl alcohol and acetic acid.



They noticed that (i) if one gm. mol. each of both $\text{C}_2\text{H}_5\text{OH}$ and CH_3COOH is taken, the forward reaction apparently stops when $\frac{2}{3}$ rd of the reactants have been converted into the ester.

(ii) If 1 gm. mol. of ethyl acetate and water are brought together, the back reaction proceeds until $\frac{1}{3}$ rd of the original substances have been converted into acid and alcohol.

From these facts it is clear that the reaction between alcohol and acid is reversible and a **state of equilibrium** is reached when the rate of the forward reaction is exactly equal to the rate of the back reaction. Now *at this point as much of the alcohol and acid is being changed into ester and water as is reformed from ester and water*

*Berthollet—"Researches into the Law of Affinity"—Cairo 1799. Berthollet was scientific adviser to Napoleon on his Egyptian expedition and the above treatise resulted from his observations in Egypt.

and the conditions do not alter with lapse of time. If, however, a fixed amount of acid is taken and the quantity of alcohol is varied a continuous displacement of the equilibrium follows, and the whole of the acid can thus be converted into ester. Some of the results obtained by Berthollet and St. Gilles are tabulated below :

TABLE : Equilibrium reaction between ethyl alcohol and 1 gm. mol. of acetic acid.

Mols. of Alcohol	Per cent Ester formed	Mols. of Alcohol	Per cent Ester formed
0·2	19·3	2·0	82·8
0·5	42·0	4·4	88·2
1·0	66·9	12·4	93·2
1·5	77·9	50·0	100·0

An examination of the results in the above table clearly shows the effect of increasing the concentration of alcohol on the course of reaction. Similar results are obtained when 1 gm. mol. of the alcohol is allowed to react with varying amounts of acetic acid.

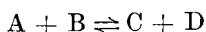
THE LAW OF MASS ACTION

The first generalisation based on quantitative observations and involving the influence of mass on reversible reactions in equilibrium, was put forward in 1807 by two Scandinavian investigators, Guldberg and Waage, and is known as the **Law of Mass Action**. It states that :

"The rate at which a substance reacts is proportional to its ACTIVE MASS and the rate of a chemical reaction is proportional to the product of the active masses of the reacting substances."

By the term '**Active Mass**' we mean molecular concentration i.e., the number of gram molecules of substance per unit volume. It is expressed by enclosing the symbol or the formula of the substance in square brackets.* Thus a gas mixture containing 1 gm. hydrogen and 12·7 gm. iodine per litre has $[H_2] = 0\cdot5$, and $[I_2] = 0\cdot05$. $[HCl] = 1$ means 36·5 gm. of HCl per litre.

Consider a general reaction



and let $[A]$, $[B]$, $[C]$ and $[D]$ represent the molecular concentrations of A, B, C and D respectively at the equilibrium point.

Rate of combination of A and B $\propto [A] \times [B]$

$$\text{(Direct velocity)} = k_1 [A] \times [B]$$

k_1 is called the **Velocity Constant** and would be the rate of reaction when $[A]$ and $[B]$ are both equal to one.

Similarly, the rate of formation of A and B $\propto [C] \times [D]$

$$\text{(Reverse velocity)} = k_2 [C] \times [D]$$

*It is also denoted by the symbol C at the base of which the symbol or the formula of substances is placed e.g., C_H , C_{HCl} .

At the equilibrium point :

Direct velocity = Reverse velocity

$$\therefore k_1 [A] \times [B] = k_2 [C] \times [D]$$

or $\frac{[C] \times [D]}{[A] \times [B]} = \frac{k_1}{k_2} = K_c \quad \dots(1)$

K_c is called the **Equilibrium Constant**. It is independent of the concentration of the reactants and products but depends upon the temperature and the nature of the reaction.

It is clear that this relation could also be expressed as

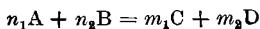
$$\frac{[A] [B]}{[C] [D]} = \frac{k_2}{k_1} = K_c'$$

If this be done, the value of the new equilibrium constant for the reverse reaction $K_c' = \frac{1}{K_c}$. Certain conventions are, therefore, observed in the use of equilibrium constants to avoid confusion. The equation for the reaction is written down and the **products of concentration of substances at the right of the equality sign i.e., products are placed in the numerator and concentrations of the reactants in the denominator while applying the law of mass action.**

The reaction $2A + B \rightleftharpoons 2C + D$ may be written as $A + A + B \rightleftharpoons C + C + D$ and the Mass Law equation at equilibrium would be

$$\frac{[C]^2 [D]}{[A]^2 [B]} = \frac{k_1}{k_2} = K_c \quad \dots(2)$$

In general, for the reaction



we have

$$\frac{[C]^{m_1} \times [D]^{m_2}}{[A]^{n_1} \times [B]^{n_2}} = K_c \quad \dots(3)$$

For gaseous equilibria the use of partial pressures instead of concentrations is often more convenient and since at any fixed temperature, the partial pressure of a substance is proportional to its concentration in the gas phase, the general Mass Law equation can now be written as

$$\frac{\frac{P_C^{m_1} \times P_D^{m_2}}{P_A^{n_1} \times P_B^{n_2}}}{\frac{P_A^{n_1} \times P_B^{n_2}}{P_C^{m_1} \times P_D^{m_2}}} = K_p \quad \dots(4)$$

where K_p is the equilibrium constant expressed in terms of partial pressures P_A , P_B , P_C , and P_D .

The relation between the two constants is given by the expression

$$K_p = K_c [RT]^{(m_1+m_2)-(n_1+n_2)}$$

When a reaction occurs with an increase in volume i.e., $(m_1+m_2) > (n_1+n_2)$, K_p is numerically greater than K_c . In cases where a decrease in volume occurs, K_p is less than K_c .

The value K_p is equal to K_c in those reactions in which there is no change in volume on reaction as for example in $2HI \rightleftharpoons H_2 + I_2$.

In deriving the above expression, use is made of the ideal gas equation $PV = nRT$

$$P = (n/V) RT = CRT$$

Substituting in equation (4), we have :

$$\frac{(C_C RT)^{m_1} \times (C_D RT)^{m_2}}{(C_A RT)^{n_1} \times (C_B RT)^{n_2}} = K_p$$

$$\frac{C_C^{m_1} \times C_D^{m_2}}{C_A^{n_1} \times C_B^{n_2}} \times \frac{(RT)^{m_1 + m_2}}{(RT)^{n_1 + n_2}} = K_p$$

or $K_c [RT]^{(m_1 + m_2) - (n_1 + n_2)} = K_p$

or $K_c [RT]^{\Delta n} = K_p$

where Δn is the change in the number of molecules.

KINETIC DERIVATION OF THE LAW OF MASS ACTION

According to kinetic considerations, a chemical reaction results from the collisions of the molecules of the reacting substances. Although some of these collisions are ineffective, the chemical change produced is proportional to the number of collisions actually taking place, for the effective collisions are a definite fraction of the total, and is determined at a fixed temperature by the number of molecules present per unit volume.

Consider a homogeneous gaseous reaction in which A and B react to form AB (Fig. 141). In the first case, unit volume contains one molecule of A and B and the possibilities of collision at any instant is $1 \times 1 = 1$. In the second case, the number of molecules of A and B are two each and the possibilities of collisions at any instant are $2 \times 2 = 4$. In the third case, there are two molecules of A and three of B and the possibilities of their colliding are increased

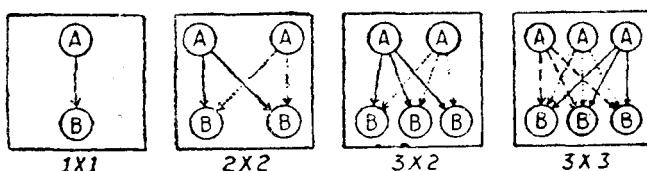


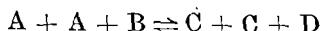
Fig. 141.

to $3 \times 2 = 6$. In the fourth case, we have three molecules of each and the number of possibilities of collisions between A and B is increased to $3 \times 3 = 9$. We find, therefore, that the possibilities are equal to the product of the number of molecules present per unit volume and since the chemical change is determined by the molecular impacts we have, Rate of reaction \propto Product of the Molecules of A and B per unit volume.

$$\propto [A] \times [B] = k [A] [B]$$

In a reaction $A + B + C$ the number of collisions depends on the concentration of each reactant and hence the rate of reaction $\propto [A][B][C] = k[A][B][C]$.

For a reaction of the type $2A + B \rightleftharpoons 2C + D$ to proceed, it is essential that two molecules of A should simultaneously collide with one molecule of B. Hence we have to consider the reaction in the form and

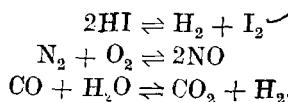


the rate of the forward reaction will be proportional to $[A] \times [A] \times [B]$.

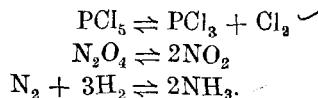
Verification of the Law of Mass Action and its Application to Homogeneous Gaseous Equilibria

Homogeneous Gaseous reactions are of two types :

(a) *First Type of Gaseous Reactions* in which there is no alteration in the total number of molecules as a result of the chemical changes, e.g.,



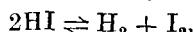
(b) *Second Type of Gaseous Reactions* in which the total number of molecules alters as a result of the chemical change e.g.,



We shall now consider some of the more important reactions.

(1) Dissociation of Hydrogen Iodide

Hydrogen iodide dissociates according to the equation



This reaction was selected by Bodenstein for the experimental verification of the law of mass action since it proceeds very slowly at ordinary temperatures, while at the temperature of the boiling sulphur (444°) equilibrium is established quite rapidly. He heated sealed glass bulbs containing varying mixtures of hydrogen and iodine in the vapour of boiling sulphur for a time sufficient to attain equilibrium. The bulbs were then suddenly cooled to the room temperature to "freeze" or "fix" the equilibrium. The bulbs were

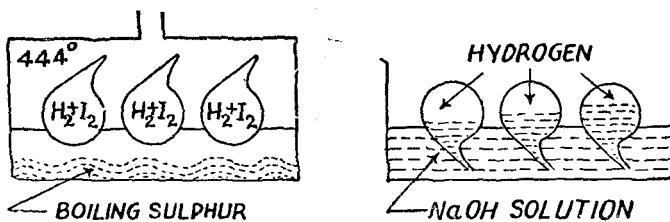


Fig. 143.

then opened under alkali solution which absorbed HI and I_2 leaving hydrogen behind, the amount of which was measured in each case.

Suppose we start with a gm. mols. of H_2 and b gm. mols. of I_2 and the amount of H_2 left in the bulb at equilibrium is $(a-x)$ gm. mols. Since in the formation of hydrogen iodide : 1 molecule of hydrogen combines with 1 molecule of iodine to give 2 molecules of hydrogen iodide, x mols. of H_2 must have reacted with x mols. of iodine to yield $2x$ mols. of HI. The amount of iodine at equilibrium will then be $(b-x)$ and that of HI = $2x$ gm. mols. If V be the total volume at equilibrium, we have :

$$[H_2] = \frac{a-x}{V}; [I_2] = \frac{b-x}{V}; [HI] = \frac{2x}{V}.$$

Applying the Law of Mass Action to the dissociation of hydrogen iodide, $2HI = H_2 + I_2$

$$\frac{[H_2][I_2]}{[HI]^2} = K \quad \dots(1)$$

$$\text{or} \quad \frac{\frac{a-x}{V} \times \frac{b-x}{V}}{\left[\frac{x^2}{V}\right]^2} = \frac{(a-x)(b-x)}{4x^2} = K \quad \dots(2)$$

The two unknown factors in the above equation are K and x and two ways of verifying the Mass Law are open to us.

(a) To find the value of x by analysis and substitute it in the above equation (2). If the value of K is always the same with different initial concentrations of H_2 and I_2 , the validity of the law of mass action is proved. The following results are due to Bodenstein :—

TABLE—Dissociation of HI at 356°C

Initial concentration		Equilibrium concentration			Equilibrium constant
$H_2 (a)$	$I_2 (b)$	$H_2 (a-x)$	$I_2 (b-x)$	$HI (2x)$	K
6.63	2.59	4.12	0.08	5.02	0.013
6.22	5.71	1.42	0.90	9.60	0.014
6.41	10.40	0.57	4.56	11.68	0.019
6.51	22.29	0.17	15.95	12.68	0.017

(b) To use in the above equation (2) a value of K calculated from accurate observations and to compare the theoretical value of x thus obtained with the experimental value,

$$\frac{(a-x)(b-x)}{4x^2} = K$$

or

$$ab - ax - bx + x^2 = 4Kx^2$$

or

$$x^2(1-4K) - x(a+b) + ab = 0$$

or

$$x = \frac{(a+b) \pm \sqrt{(a+b)^2 - 4(1-4K)ab}}{2(1-4K)}$$

Bodenstein obtained the following results at 448°C with varying amounts of a and b .

TABLE.—*Dissociation of Hydrogen Iodide*
 $K = 0.0194$ Temp. = 448°C

a	b	$2x \text{ observed}$	$2x \text{ calculated}$
2.94	8.10	5.64	5.66
5.30	7.94	9.49	9.52
9.27	8.07	13.47	13.34
14.44	8.12	14.93	14.82

A comparison of the observed and calculated values shows excellent agreement.

Effect of Pressure on the Equilibrium $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2^*$. It should be clear from a study of the equation (2),

$$\frac{(a-x)(b-x)}{4x^2} = K$$

that K is independent of the volume and hence *the change of pressure will not alter the final state of equilibrium*.

Alternatively, on making use of partial pressures instead of concentrations

$$\frac{P_{\text{H}_2} \times P_{\text{I}_2}}{P_{\text{HI}}^2} = K_p$$

Let the total pressure on the system be increased to n times its original value and since all the partial pressures will be increased in the same proportion

$$\frac{n P_{\text{H}_2} \times n P_{\text{I}_2}}{n^2 P_{\text{HI}}^2} = \frac{P_{\text{H}_2} \times P_{\text{I}_2}}{P_{\text{HI}}^2} = K_p$$

This is the same as the original expression showing thereby that the equilibrium is independent of the pressure.

Effect of adding substances to the equilibrium

$2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$. We have already shown that $\frac{P_{\text{H}_2} \times P_{\text{I}_2}}{P_{\text{HI}}^2} = K_p$.

On the addition of hydrogen, the partial pressure of hydrogen in the reaction vessel will increase momentarily from P_{H_2} to say, P'_{H_2} .

and

$$\frac{P'_{\text{H}_2} \times P_{\text{I}_2}}{P_{\text{HI}}^2} = K_p$$

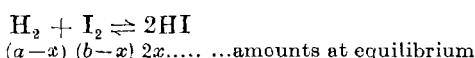
To maintain the value of the equilibrium constant K_p , P_{I_2} must decrease and P_{HI} must increase i.e., more of iodine and H_2 will react

*Effect of Pressure on the equilibrium also follows from *Louis Chatelier's Principle* discussed at the end of this chapter.

to give HI. Thus the degree of dissociation of HI will be suppressed by the addition of H₂. A similar result would follow on the addition of iodine at equilibrium.

If an inactive gas be added to the reaction vessel at equilibrium, the total pressure increases but the partial pressures of the original gases do not change, since they are independent of each other. Hence the addition of an inert gas has no effect on the state of equilibrium.

Example 1. 13.5 c.cs. of HI are produced from the interaction of 8.1 c.cs. hydrogen and 9.3 c.cs. of iodine vapour at 444°C. Calculate the equilibrium constant at this temperature of the reaction $H_2 + I_2 \rightleftharpoons 2HI$.



Since the number of molecules in a gas under the same conditions of temperature and pressure are proportional to volumes (Avogadro), c.cs. of gases may be used instead of molar concentrations.*

$$\text{Here } 2x = 13.5 \quad \text{or} \quad = 6.75 \text{ c.cs.}$$

$$\text{Volume of } H_2 \text{ at equilibrium} = (8.1 - 6.75) = 1.35 \text{ c.cs.}$$

$$\text{Volume of } I_2 \text{ at equilibrium} = (9.3 - 6.75) = 2.55 \text{ c.cs.}$$

$$\therefore K = \frac{[HI]^2}{[H_2][I_2]} = \frac{(13.5)^2}{1.35 \times 2.55} = 53.$$

Example 2. 6.35 c.cs. of hydrogen iodide were produced from the interaction of 5.29 c.cs. of hydrogen (at N.T.P.) and 0.0401 gm. iodine at 444°C. Calculate the equilibrium constant at this temperature for the reaction $2HI \rightleftharpoons H_2 + I_2$.

$$2 \times 127 \text{ gms. iodine occupy at N.T.P., Volume} = 22,400 \text{ c.cs.}$$

$$\therefore \text{Volume corresponding to } 0.0401 \text{ gm. } I_2 = \frac{22400 \times 0.0401}{2 \times 127}$$

$$= 3.53 \text{ c.cs.}$$

$$\begin{aligned} \text{Volume of } HI \text{ at equilibrium} &= 2x = 6.35, \\ \therefore x &= 3.175 \end{aligned}$$

$$\text{Hence Vol. of } H_2 \text{ at equilibrium} = 5.29 - 3.175 = 2.115$$

$$\text{, , } I_2 \text{, , } = 3.53 - 3.175 = 0.345$$

Using c.cs. of gases instead of molecular concentrations (see Example 1.)

$$K = \frac{[H_2][I_2]}{[HI]^2} = \frac{2.115 \times 0.345}{6.35 \times 6.35} = 0.01862.$$

Example 3. A mixture of 7.9 c.cs. hydrogen and 33.1 c.cs. iodine vapour was heated at 444°C until equilibrium was reached. If the equilibrium constant for the reaction $H_2 + I_2 \rightleftharpoons 2HI$ is 36.68, calculate the number of c.cs. of hydrogen present when equilibrium is obtained.

Let x c.cs. of hydrogen and iodine be changed to HI.

Then : Volume of H₂ remaining at equilibrium = $(7.9 - x)$ c.cs.

Volume of I₂ remaining at equilibrium = $(33.1 - x)$ c.cs.

Volume of HI formed at equilibrium = $2x$.

For the reaction $H_2 + I_2 \rightleftharpoons 2HI$

$$\frac{[HI]^2}{[H_2] \times [I_2]} = K.$$

*This is true only for First Type of Gas reactions.

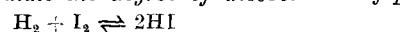
Since the number of molecules in a gas are proportional to the volumes (Avogadro), volumes can be used instead of molar concentrations.

$$\begin{aligned} \frac{(2x)^2}{(7.9-x)(33.1-x)} &= 36.68 \\ 4x^2 &= 36.68(7.9-x)(33.1-x) \\ 0.109x^2 &= (7.9-x)(33.1-x) \\ &= 261.49 - 41x + x^2 \\ 891x^2 - 41x + 261.49 &= 0^* \\ \text{Whence } x &= 7.8 \quad \text{or} \quad 38.2 \end{aligned}$$

38.2 cannot be the solution of the problem ; $\therefore x = 7.8$.

Hence number of c.c.s. of H_2 present at equilibrium = $(7.9 - 7.8) = 0.1$ c.c.

Example 4. 25 c.c.s. of H_2 and 18 c.c.s. of I_2 vapour were heated in a sealed glass bulb at $465^\circ C$ when at the equilibrium 30.8 c.c.s. of HI was formed. Calculate the degree of dissociation of pure HI at $465^\circ C$.



$a - x \quad b - x \dots \dots \dots 2x$ c.c.s. at equilibrium.

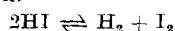
$$\begin{aligned} \text{Here } 2x &= 30.8 \text{ or } x = 15.4, \text{ therefore, } (a - x) = 25 - 15.4 = 9.6 \\ \text{and } (b - x) &= 18 - 15.4 = 2.6 \end{aligned}$$

Applying the Law of Mass Action

$$\frac{[HI]^2}{[H_2][I_2]} = K \text{ or } \frac{30.8 \times 30.8}{9.6 \times 2.6} = 38$$

$$\therefore K = 38 \text{ (at } 465^\circ \text{)}$$

Now if we start with 1 gm. mol. of pure HI and vaporise it in a sealed bulb heated to $465^\circ C$, x gm. mols. which decompose at the equilibrium, represents the degree of dissociation.



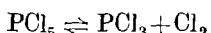
$$I - x \quad \frac{x}{2} \quad \frac{x}{2}$$

$$\frac{[HI]^2}{[H_2][I_2]} = \frac{(1-x)^2}{\frac{x}{2} \times \frac{x}{2}} = \frac{4(1-x)^2}{x^2} = K \text{ or } \frac{4(1-x)^2}{x^2} = 38$$

$$\text{Whence } x = 0.245$$

(2) Dissociation of Phosphorus Pentachloride

A typical example of the Second Type reactions is the dissociation of phosphorus pentachloride which takes place according to the equation



Suppose we heat a gm. molecules of PCl_5 in a closed vessel having a volume V . Let x gm. mols. of it dissociate by the time a state of equilibrium is attained.

Since one molecule of PCl_5 dissociates to give one molecule of PCl_3 and one molecule of Cl_2 , x gm. molecules will decompose to yield x gm. molecules of PCl_3 and x gm. molecules of Cl_2 . Thus at equilibrium, we have :

$$[PCl_5] = \frac{a - x}{V}; [PCl_3] = \frac{x}{V} \text{ and } [Cl_2] = \frac{x}{V}$$

Applying the Law of Mass Action,

$$\frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\frac{x}{V} \times \frac{x}{V}}{\frac{a-x}{V}} = \frac{x^2}{(a-x)V} = K.$$

*The roots of a quadratic equation are given by the relation

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Effect of Pressure on the Equilibrium $\text{PCl}_5 \rightleftharpoons \text{PCl}_3 + \text{Cl}_2$

In this case V occurs in the denominator of the Mass Law equation. Since K must remain constant, increase of V would cause x also to increase. In other words, the dissociation of PCl_5 is favoured by reducing the pressure. An increase of pressure would decrease V and to maintain the constant value of K , x must decrease. Thus the increase of pressure would suppress the dissociation of PCl_5 .

Alternatively, the effect of pressure may be directly deduced as follows :

At the equilibrium, total number of mols. is

$$(a - x) + x + x = a + x,$$

when the number of mols. of $\text{PCl}_5 = a - x$ and that of PCl_3 and Cl_2 is x each.

If P is the total pressure, the partial pressures are

$$\text{P}_{\text{PCl}_5} = \frac{a - x}{a + x} P; \quad \text{P}_{\text{PCl}_3} = \frac{x}{a + x} P; \quad \text{and} \quad \text{P}_{\text{Cl}_2} = \frac{x}{a + x} P$$

$$\text{Hence } \frac{\text{P}_{\text{PCl}_3} \times \text{P}_{\text{Cl}_2}}{\text{P}_{\text{PCl}_5}} = \frac{\frac{x}{a + x} P \times \frac{x}{a + x} P}{\frac{a - x}{a + x} P} = \frac{x^2 P}{(a - x)(a + x)} = K,$$

It easily follows from the above equation that if P is increased, x or the dissociation of PCl_5 must correspondingly decrease in order that K_p may remain constant.

Effect of adding substances to the Equilibrium



Let chlorine be added to the equilibrium mixture in closed vessel. The partial pressure of Cl_2 will increase momentarily to, say, P'_{Cl_2} . Applying the Law of Mass Action, now

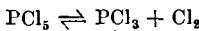
$$\frac{\text{P}'_{\text{Cl}_2} \times \text{P}_{\text{PCl}_3}}{\text{P}_{\text{PCl}_5}} = K$$

Since K must maintain its value, P_{PCl_3} will decrease and P_{PCl_5} will increase. In other words more of PCl_3 would react to give PCl_5 i.e., the degree of dissociation will be suppressed. Similar effect would be produced by adding PCl_3 .

As in the case of the dissociation of HI , by the addition of an inert gas the total pressure is increased but individual partial pressures of the gases constituting the equilibrium mixture remain unchanged as they are independent of each other and hence there is no effect on the state of equilibrium.

Example 1. 2 gram molecules of phosphorus pentachloride are heated in a closed two litre vessel. When equilibrium is attained the pentachloride is 40% dissociated into PCl_3 and Cl_2 . Calculate the equilibrium constant.

Here



At equilibrium, the amount of PCl_5 is $\left[2 - \frac{2 \times 40}{100} \right]$ or $(2 - 0.8)$ mols. while that of PCl_3 and Cl_2 is 0.8 gm. mols. each.

*Here we shall consider only the effect of additions at constant volume; for additions at constant pressure the student should refer to some advanced Physical Chemistry.

Since the total volume is 2 litres,

$$[\text{PCl}_5] = \frac{2 - 0.8}{2} = \frac{1.2}{2} = 0.6$$

$$[\text{PCl}_3] = \frac{0.8}{2} = 0.4$$

$$[\text{Cl}_2] = \frac{0.8}{2} = 0.4$$

We know that

$$\frac{[\text{PCl}_3] \times [\text{Cl}_2]}{[\text{PCl}_5]} = K$$

$$\frac{0.4 \times 0.4}{0.6} = K = 0.267.$$

Example 2. 0.1 mol. PCl_5 is vaporised in a litre vessel at 250° . What will be the concentration of chlorine at equilibrium? The equilibrium constant for the dissociation of PCl_5 is 0.0414.

Let x gm. mol. be the amount of Cl_2 at equilibrium. Then the concentration of PCl_5 = $(0.1 - x)$ gm. mol. and that of PCl_3 is x gm. mol. Since the total volume is one litre, the amounts represent the active mass.

Now $\frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = K$

or $\frac{x \times x}{(0.1 - x)} = 0.0414$

or $\frac{x^2}{(0.1 - x)} = 0.0414$

Whence $x = 0.0469$ gm. mol. per litre.

(3) Dissociation of Nitrogen Peroxide, $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$

Suppose we start with 1 gm. mol. of N_2O_4 and let x of it decompose at the equilibrium. If V be the total volume at equilibrium

$$[\text{N}_2\text{O}_4] = \frac{1-x}{V} \text{ and } [\text{NO}_2] = \frac{2x}{V}$$

Applying the Law of Mass Action,

$$\frac{[\text{NO}_2] \times [\text{NO}_2]}{[\text{N}_2\text{O}_4]} = \frac{\frac{2x}{V} \times \frac{2x}{V}}{\frac{1-x}{V}} = \frac{4x^2}{(1-x)V} = K$$

The partial pressures of N_2O_4 and NO_2 at the equilibrium, when the total pressure is P , are

$$P_{\text{N}_2\text{O}_4} = \frac{1-x}{1+x} P$$

$$P_{\text{NO}_2} = \frac{2x}{1+x} P$$

According to the Law of Mass Action,

$$\frac{P_{\text{NO}_2} \times P_{\text{NO}_2}}{P_{\text{N}_2\text{O}_4}} = \frac{\left[\frac{2x}{1+x} P \right]^2}{\frac{1-x}{1+x} P} = \frac{4 \times x^2 P}{(1+x)(1-x)} = K_p$$

Example. The equilibrium constant of the reaction $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ at 497°C is found to be 636. If the pressure of the gas mixture is 182 mm., calculate the percentage dissociation of N_2O_4 . At what pressure will it be half dissociated?

We have already shown $\frac{4x^2 P}{(1+x)(1-x)} = K_p$.

where x = degree of dissociation, P = Pressure and K_p = equilibrium constant in terms of partial pressures.

In the present case $P = 182$ mm. and $K_p = 636$. Substituting in the above equation, we have

$$\frac{4x^2 \times 182}{(1+x)(1-x)} = 636 \text{ or } 1.873x^2 = 0.8736$$

Whence $x = 0.6829$

\therefore Percentage dissociation of $N_2O_4 = 68.29$.

When the gas will be half dissociated, $x = 0.5$ gm. mols. when initially we have 1 gm. mol. of N_2O_4 . Substituting the value of x and K_p in the equation

$$\frac{4x^2 P}{(1+x)(1-x)} = K_p, \text{ we have}$$

$$\frac{4 \times 0.5 \times 0.5 P}{1.5 \times .5} = 636, \quad \therefore P = 477.$$

Thus at 477 mm. pressure the gas will be half dissociated.

The conditions of equilibrium, in this case also, are the same as in the case of the dissociation of PCl_5 since both reactions are of the second type.

Calculation of the Degree of Dissociation from density measurements.

This method is of use in Second Type gaseous reactions only as they proceed with a change in density. Consider the two reactions :



Let d be the observed vapour density at a particular temperature when the degree of dissociation is x and let D be the theoretical vapour density if no dissociation were to occur.

If the total number of gm. mols. when there is no dissociation = 1

No. of gm. mols. when degree of dissociation is $x = (1-x) + 2x = (1+x)$

because $(1-x)$ undissociated molecules are left and since in both the above cases 1 molecule dissociates to give 2 molecules, x molecules on dissociation will give rise to $2x$ molecules of the products.

Assuming that under the temperature and pressure of the experiment 1 gm. mol. occupies V litres, the volume after dissociation = $(1+x)V$.

Since density is inversely proportional to volume,

$$D \propto \frac{1}{V} \quad \dots (1)$$

$$d \propto \frac{1}{(1+x)V} \quad \dots (2)$$

Dividing (1) by (2) we have

$$\frac{D}{d} = \frac{(1+x)V}{V} = 1+x; \quad x = \frac{D}{d} - 1.$$

or $x = \frac{D - d^*}{d}$.

*If a molecule dissociates into n simpler molecules, we shall have $(1-x+nx)$ gm. mols. after dissociation and the general relation $x = \frac{D-d}{d(n-1)}$.

Example 1. When PCl_5 is heated it gasifies and dissociates into PCl_3 and Cl_2 . The density of the gas mixture at $200^\circ C$ and $250^\circ C$ is 70.2 and 57.9 respectively. Find the degree of dissociation of PCl_5 at $200^\circ C$ and $250^\circ C$.

If no dissociation were to occur, the vapour density (D) of PCl_5 would be

$$\frac{\text{M. Wt.}}{2} = \frac{31 + 177.5}{2} = 104.25$$

At $200^\circ C$ $D = 104.25$

(observed density) $d = 70.2$

$$\text{Degree of dissociation } x = \frac{D - d}{d} = \frac{104.25 - 70.2}{70.2} = \frac{34.05}{70.2} = 0.485$$

At $250^\circ C$ $D = 104.25$

$d = 57.9$

$$\therefore x = \frac{D - d}{d} = \frac{104.25 - 57.9}{57.9} = \frac{46.35}{57.9} = 0.800.$$

Example 2. At $90^\circ C$ the vapour density of nitrogen peroxide (N_2O_4) is 24.8. Calculate the percentage dissociation into NO_2 molecules at this temperature.

If no dissociation were to occur, the vapour-density of N_2O_4 would be

$$\frac{\text{M. Wt.}}{2} = \frac{28 + 64}{2} = \frac{92}{2} = 46$$

Here then $D = 46$ and $d = 24.8$

$$\text{Degree of dissociation, } x = \frac{D - d}{d} = \frac{46 - 24.8}{24.8} = 0.8547.$$

∴ Percentage dissociation = 85.47.

(4) The Combination of Nitrogen and Hydrogen.

The combination of nitrogen and hydrogen to form ammonia according to the reversible reaction



is a reaction of great industrial importance and has been studied in detail by Haber and co-workers and more recently by Larson and Dodge.

A mixture of nitrogen and hydrogen in the ratio of 1 : 3 is passed through an iron coil lined inside with finely divided iron and maintained at a constant temperature. The issuing gases are analysed for nitrogen, hydrogen and ammonia to find out the composition of the equilibrium mixture. K_p is then calculated by applying the Dalton's law of partial pressure as in the case of PCl_5 .

Suppose x is the molar fraction of ammonia in the equilibrium mixture at a certain temperature and the total pressure P. The partial pressure of ammonia, therefore, is xP .

The pressure of nitrogen plus hydrogen mixture will be $(1-x)P$ and as these gases are present in the ratio 1 : 3;

$$p_{N_2} = \frac{1}{4}(1-x)P \text{ and } p_{NH_3} = \frac{3}{4}(1-x)P$$

The equilibrium constant K_p will, therefore, be given by the expression

$$K_p = \frac{P_{NH_3}}{p_{N_2}^{\frac{1}{2}} \times p_{H_2}^{\frac{3}{2}}} = \frac{xP}{[\frac{1}{4}(1-x)P]^{\frac{1}{2}} \times [\frac{3}{4}(1-x)P]^{\frac{3}{2}}}$$

Example. The ammonia in equilibrium with a nitrogen-hydrogen mixture in the ratio 1 : 3 at 400°C and 100 atmosphere pressure is 24·91 mole per cent. Calculate the equilibrium constant.

Partial pressure of ammonia = $0 \cdot 2491 \times 100 = 24 \cdot 91$ atm.

The pressure of hydrogen plus nitrogen, therefore, is $(100 - 24 \cdot 91) = 75 \cdot 09$ atm.

Since N₂ and H₂ are present in the ratio 1 : 3;

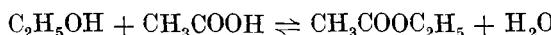
$$P_{H_2} = \frac{3}{4} \times 75 \cdot 09 = 56 \cdot 32 \text{ atm.}$$

$$\text{and } P_{N_2} = \frac{1}{4} \times 75 \cdot 09 = 18 \cdot 77 \text{ atm.}$$

$$\therefore K_p = \frac{P_{NH_3}}{P_{N_2}^{\frac{1}{2}} \times P_{H_2}^{\frac{3}{2}}} = \frac{24 \cdot 91}{(18 \cdot 77)^{\frac{1}{2}} \times (56 \cdot 32)^{\frac{3}{2}}} = 0 \cdot 0136$$

Equilibrium in Liquid Systems. Formation of Ethyl Acetate.

An important example of homogeneous equilibrium in liquid system is the reaction between alcohol and acid to form ester and water.



Suppose we start with a gm. mols. of alcohol and b gm. mols. of acid and at the equilibrium point, x gm. mols. of the ester and water are present. If V is the total volume, then

$$[C_2H_5OH] = \frac{a - x}{V}$$

$$[CH_3COOH] = \frac{b - x}{V}$$

$$[CH_3COOC_2H_5] = \frac{x}{V}$$

$$(H_2O) = \frac{x}{V}$$

Applying the Law of Mass Action,

$$\frac{\frac{x}{V} \times \frac{x}{V}}{\frac{a - x}{V} \times \frac{b - x}{V}} = K \text{ or } \frac{x^2}{(a - x)(b - x)} = K$$

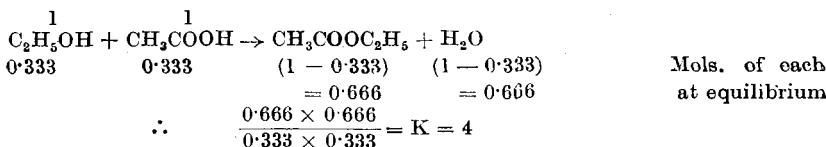
As already mentioned, Berthelot and St. Gilles made an exhaustive study of this reaction and obtained constant values of K from varying amounts of initial concentrations. They also tried the second method and noted a remarkable agreement between the observed and calculated values of x .

It may be noted that in the above equation the volume terms V cancel out, and just like First Type gas reactions the equilibrium constant is not affected by changing the volume. In liquid systems when there is a change in the number of molecules, however, it is necessary to consider the volume of the solution while calculating the equilibrium constant.

Example 1. In an experiment one gm. mol. of acetic acid was allowed to react with 1 gm. mol. of ethyl alcohol until equilibrium was established. The equilibrium mixture was found to contain 0·333 gm. mol. of unused acid. Calculate the equilibrium constant of the reaction.

$$\frac{[\text{ester}] \times [\text{water}]}{[\text{alcohol} \times [\text{acid}]]} = K.$$

Since the volume terms in this case cancel out the gm. mol. may here be taken instead of concentration. Thus



Example 2. A mixture of 3 gm. mols. of ethyl alcohol and 1 gm. mol. of acetic acid are allowed to come to equilibrium. If the equilibrium constant for the reaction is 4, how much ethyl acetate is present at the equilibrium? (Punjab 1937; Delhi B.Sc., 1936)

We have already shown that

$$\frac{x^2}{(a-x)(b-x)} = K$$

where a and b are initial concentrations of alcohol and acetic acid and x is the amount of ester formed at the equilibrium,—

In the present case $a=3$, $b=1$, and $K=4$.

Substituting these values in the above equation; we have

$$\frac{x^2}{(3-x)(1-x)} = 4$$

or

$$3x^2 - 16x + 12 = 0^*$$

whence

$$x = 0.91 \text{ or } 4.5$$

Since the value 4.5 is not permissible, $x=0.91$. Thus 0.91 gm. mols. of the ester are present at the equilibrium.

LE CHATELIER'S PRINCIPLE

A general principle with the help of which we can predict qualitatively the influence of change in temperature, pressure or concentration on systems in equilibrium was first enunciated by Le Chatelier and Braun in 1884. According to this principle:

If a system in equilibrium is subjected to a constraint, the equilibrium reacts in a way as to annul the effect of the constraint.

This principle is a general one and not restricted to chemical equilibria. Before applying it to chemical reactions we shall try to make the principle clear with reference to certain physical equilibria.

APPLICATION TO PHYSICAL EQUILIBRIA

1. Effect of pressure on solubility.—Consider the solution of a gas in equilibrium with the gas itself. If pressure on this system is increased, say by placing the solution in a cylinder and compressing it with a piston, constraint has been applied to the system which reduces the volume without affecting the pressure and some of the gas dissolves in the solvent. *The effect of the increased pressure, therefore, is an increase in the solubility of the gas.*

Similarly these solids which dissolve in a solvent with a decrease in volume will have their solubility increased at higher pressure while increasing pressures will lower the solubility of those solids which dissolve with an increase in volume.

*The roots of a quadratic equation are given by the relation

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

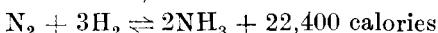
2. Effect of temperature on solubility.—Now consider a saturated solution of potassium nitrate in equilibrium with solid potassium nitrate. This salt, like many others, dissolves in water with the absorption of heat. If the temperature of the system is raised by heating the solution, a change will occur in the system which absorbs heat so that the effect of the increased temperature is annulled. This change is the dissolution of more potassium nitrate. It means that *the solubility of all such substances which dissolve with the absorption of heat will increase with the temperature while substances like calcium acetate and calcium hydroxide which dissolve with the evolution of heat have their solubility lowered at higher temperatures.*

3. Effect of pressure on the melting point of ice.—Imagine a mixture of ice and water at 0°C and under atmospheric pressure. Let this mixture be placed in a cylinder provided with an airtight piston and the pressure on it increased. What will happen? The system has been subjected to a constraint which will have the effect of reducing the volume. According to Le Chatelier's Principle, a change should occur within the system which reduces the volume without change of pressure. Now water occupies less volume than ice at the same temperature so that some of the ice melts. In other words, the melting point of ice is lowered as a result of increased pressure.

APPLICATION TO CHEMICAL EQUILIBRIA

A constraint is applied to a chemical reaction in equilibrium when we alter the temperature, pressure, or concentration. Let us see how we can predict the effect of these changes by the application of Le Chatelier's Principle in some more important reactions.

i. Combination of nitrogen and hydrogen to form ammonia (*Haber's Process*).



(a) **Effect of temperature.** If the temperature be lowered when the equilibrium is attained, the equilibrium will react by proceeding in a direction in which heat is evolved. Since the production of ammonia is an exothermic change, a low temperature will favour its formation. If we were to raise the temperature, the reaction would proceed in the opposite direction because in this way heat is absorbed.

The above conclusions are borne out by the percentage of ammonia determined by Larson and Dodge (1923) at 50 atmosphere pressure.

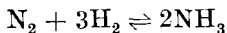
Temperature	350°	400°	450°	500°
Percentage of ammonia	2.511	10.11	9.17	5.58

(b) **Effect of Pressure.*** 1 volume of nitrogen and 3 volumes of hydrogen react to form 2 volumes of ammonia i.e., during the formation of ammonia decrease in volume occurs.

***Effect of pressure** may also be explained as follows :

According to *Kinetic theory* the pressure of a gas is proportional to the number of molecules and since the formation of ammonia is accompanied by a decrease of molecules from 4 to 2, the pressure of the system will correspondingly decrease. Hence increase of pressure will favour the formation of ammonia.

Now if pressure be increased on the equilibrium



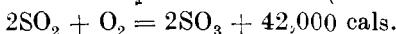
the system will be displaced in a direction in which volume is lowered. Hence the formation of ammonia since it is accompanied by a decrease of volume, will be favoured by a high pressure.

The effect of pressure on the synthesis of ammonia is illustrated by the following data due to Larson and Dogde :

Pressure in atmospheres	50	100	300	600
Percentage of ammonia at 500°C	5.58	10.2	26.2	42.1

(a) **Effect of concentration.** According to Le Chatelier's principle the increase of concentration will shift the equilibrium in such a way as to favour the reaction which proceeds with a decrease in the number of molecules. Thus the addition of nitrogen or hydrogen will result in a greater yield of ammonia.

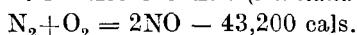
2. Formation of Sulphur Trioxide (*Contact Process*)



The above reaction resembles the synthesis of ammonia because it is exothermic and takes place with a decrease in volume. Following the same reasoning we conclude that the formation of sulphur trioxide will be favoured by

- (i) a low temperature,
- (ii) a high pressure, and
- (iii) excess of oxygen or sulphur dioxide.

3. Formation of Nitric Oxide (*Birkland-Eyde Process*).



In the formation of nitric oxide, no change in volume occurs because one volume of nitrogen reacts with one volume of oxygen to give two volumes of nitric oxide. Consequently, there will be no effect of any change in pressure.

The reaction, however, is endothermic and if we raise the temperature, the equilibrium will shift in that direction in which heat is absorbed. The yield of nitric oxide will, therefore, be higher with increasing temperature. The following results due to Nernst confirm the above conclusions :—

Temperature	2033°	2195°	3000°	3200°
Percentage of NO at equilibrium	0.64	0.997	4.5	5.0

The formation of nitric oxide will be favoured by an excess of nitrogen or oxygen.

QUESTIONS AND PROBLEMS

A. Law of Mass Action

1. What do you understand by a reversible reaction ?
Give examples of such reactions.
2. Give briefly the history of the Law of Mass Action and discuss fully its importance. (*Agra B.Sc., 1941 ; Delhi B.Sc., 1939*)
3. Deduce the Law of Mass Action from kinetic considerations. What efforts have been made to verify it ? (*Andhra B.Sc., 1952*)
4. State the Law of Mass Action. Explain the terms "Chemical equilibrium" and "Equilibrium constant". Apply the above principles to the study of one homogeneous and one heterogeneous reaction. (*Mysore B.Sc., 1954*)

5. Deduce the Law of Mass Action from kinetic considerations and apply it to the equilibrium $N_2 + 3H_2 \rightleftharpoons 2NH_3$. How is this equilibrium affected by temperature and pressure? (Punjab B.Sc., 1941; Nagpur 1953)

6. Deduce the Law of Mass Action on the considerations of the kinetic theory and apply it to equilibria of the reactions underlying the following process:—

(a) Haber Process for the synthesis of ammonia.

(b) Deacon's process for the manufacture of chlorine.

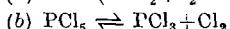
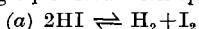
(Banaras B.Sc., 1952)

7. Enunciate Guldberg and Waage's law. Discuss the effect of temperature and pressure on the reaction $H_2 + I_2 \rightleftharpoons 2HI$.

2×20.57 gms. of H_2 were added to $2 \times 127 \times 5.22$ gms. of I_2 vapours at $445^\circ C$. Hydrogen iodide formed was 10.22×128 gms. Calculate the equilibrium constant of the above reaction. ($H = 1, I = 127$). (Agra B.Sc., 1954)

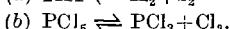
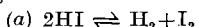
8. When 2.94 mols. of iodine and 8.10 mols. of hydrogen are heated at constant volume at 444° until equilibrium is established, 5.64 mols. of hydriodic acid are formed. If we start with 5.30 mols. of iodine and 7.94 mols. of hydrogen, how much hydriodic acid is present at equilibrium at the same temperature?

9. State the Law of Mass Action. Illustrate its application to the following equilibria with special reference to the effect of pressure.



(Aligarh B.Sc. 1953)

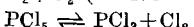
10. Give an account of the Law of Mass Action. On the basis of this law, discuss the effect of variation of pressure on the equilibrium positions in the following reactions:—



(Osmania B.Sc., 1954)

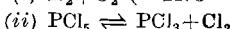
11. How much PCl_5 must be added to litre vessel at 250° in order to obtain a concentration of 0.1 gm. mol. of chlorine? Equilibrium constant for the dissociation of PCl_5 at 250° is 0.0414 .

12. State the Law of Mass Action, and illustrate its application to the following equilibria with special reference to the effect of temperature and pressure.



(Calcutta B.Sc., 1954)

13. State the Law of Mass Action and illustrate its application to the following equilibria with special reference to the effect of temperature and pressure.



(Banaras B.Sc., 1940)

14. 7.8 gms. of ethyl alcohol and 10 gms. of acetic acid were kept at a constant temperature and equilibrium was established when 2.7 gms. of acetic acid remained in the mixture. Calculate the equilibrium constant of the reaction.

15. The equilibrium constant for the reaction between acetic acid and alcohol forming ethyl acetate and water is 4 at $25^\circ C$. If 5 gm. mols. of acetic acid react with 1 gm. mol. of alcohol at $25^\circ C$, what will be the composition of the equilibrium mixture?

16. The equilibrium constant for the reaction $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$ is 4 . What will be the composition of the equilibrium mixture if one mol. of acetic acid is taken along with 8 mols. of ethyl alcohol?

(Osmania B.Sc., 1959)

17. State and explain the Law of Mass Action. If one gram-molecular weight of ethyl alcohol and one of acetic acid are heated together until equilibrium is reached, 0.67 of a gram-molecular weight of ethyl acetate is formed. Calculate the equilibrium constant of the reaction, and show how you would obtain the maximum yield of the ester from a given quantity of acetic acid.

18. Explain and illustrate the Law of Mass Action. When ethyl alcohol and acetic acid are mixed in equivalent proportions, equilibrium is attained when two-third of the acid and alcohol are consumed. How much ester will be present in the equilibrium mixture if we start with 120 gms. acetic acid and 92 gms. of ethyl alcohol ?

19. When alcohol and acetic acid are mixed together in equimolecular proportions, 66·5% are converted into ester. Calculate how much ester will be produced, if one mol. of acetic acid is treated respectively with 0·5, 4 and 8 mols. of alcohol. (Osmania B.Sc., 1953)

20. State Guldberg and Waage's Law of Mass Action. What is meant by the active mass of a substance ?

The equilibrium constant in the reaction between ethyl alcohol and acetic acid to form water and ethyl acetate is 4 at 25°. What weight of ethyl acetate will be obtained from 50 gms. of alcohol and 50 gms. of acetic acid the reaction being carried out at 25° in a closed vessel. (Punjab B.Sc., 1953)

21. Explain how the degree of dissociation of a gas can be calculated from observation on its vapour density. At 250° PCl_5 dissociates to an extent of 78·4%. Calculate the value which would be found for the vapour density of the compound at this temperature.

22. The vapour density of phosphorus pentachloride at 200°C and 250°C are respectively 70·2 and 57·9 at one atmosphere pressure. Calculate the values of its dissociation constant at these temperatures.

23. Discuss with reference to suitable examples the applications of the Law of Mass Action to homogeneous reactions.

4·5 gms. of PCl_5 (M. Wt. 208·5) were completely vaporised at 250° and the vapour occupied 1·7 litres at one atmosphere pressure. Calculate the degree of dissociation and the equilibrium constant of PCl_5 at this temperature.

24. Discuss the effect of pressure on the chemical equilibrium of a gaseous reaction. 5 grms. of phosphorus pentachloride (molecular weight 208·5) was completely vaporized at 250° and occupied 1·9 litres at 760 mm. pressure. Calculate the degree of dissociation and equilibrium constant of phosphorus pentachloride at this temperature. (Allahabad B.Sc., 1954)

25. Show how the degree of dissociation of a gas can be calculated from observations of its vapour density.

What is the vapour density of PCl_5 at 250°C when it has dissociated to the extent of 80 per cent. (Nagpur B.Sc., 1953)

26. Explain the Law of Mass Action with reference to the dissociation of phosphorus pentachloride vapour and discuss the effect of an excess of one of the products of dissociation at constant volume.

One gram of phosphorus pentachloride sealed in an evacuated bulb of 100 cc. capacity was heated at 227°C. The pressure developed was found to be 2·75 atmospheres. Calculate the degree of dissociation under the conditions of the experiment. (Annamalai B.Sc., 1954)

27. The molecular weight of phosphorus pentachloride is 208·30. At 200° the partially dissociated vapour is 62 times as heavy as hydrogen. Calculate the degree of dissociation of the vapour. (Gauhati B.Sc., 1954)

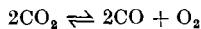
28. What is meant by chemical equilibrium ? Discuss the effect of changes of (a) temperature, (b) pressure, (c) Concentration of H_2 on the equilibrium.



29. Enunciate the Law of Mass Action. How does the equilibrium constant of a reaction depend upon temperature and pressure ? Discuss the hydrogen iodine reaction and nitrogen ammonia reaction in this connection.

30. The dissociation of hydrogen iodide is a reversible reaction. Bodenstein showed that at equilibrium 1308·16 gms. hydrogen iodide, 30·92 gms. hydrogen and 2·794 gms. iodine were present in a reaction mixture at 440°C. Calculate the equilibrium constant. (Agra B.Sc., 1958)

31. The following chemical reaction



represents the gaseous dissociation of carbon dioxide. Obtain the dissociation constant K_p of this reaction in terms of the total pressure of the system and degree of dissociation of carbon dioxide. (Lucknow B.Sc., 1954)

32. State (i) the Law of Mass Action, and (ii) Le Chatelier's principle. Discuss the application of the latter to predict the effect of pressure and temperature on the synthesis of ammonia and of nitric oxide from the elements. What, therefore, would be the appropriate conditions for the maximum yield in each case? (Delhi B.Sc., 1953)

33. State and explain the Law of Mass Action. Describe an experiment to test the validity of the law. (Travancore B.Sc., 1954)

34. Derive an expression for calculating the degree of dissociation in a system from vapour density measurements.

The vapour density of nitrogen peroxide is 25.67 at 100°C and 760 mm. Calculate the percentage of NO_2 molecules in the gas at this temperature. (Patna B.Sc., 1954)

35. In the thermal dissociation of iodine molecules into atoms at 1000°C and at a pressure of 1 atmosphere, the iodine molecules dissociate to the extent of 40 per cent by volume. Find out the total pressure on the gas in equilibrium so that the dissociation is reduced to 20 per cent, temperature remaining the same. (Punjab B.Sc., 1954)

37. Explain with examples what do you understand by reversible and irreversible reactions, and chemical equilibrium. In what way the concept of affinity has been modified by the study of reversible reactions? (Rajputana B.Sc., 1955)

37. What do you understand by equilibrium constant? When 1 gm. mol. of ethyl alcohol reacts with 1 gm. mol. of acetic acid until equilibrium is reached, then there is present in solution 0.333 gm. mol. each of alcohol and acetic acid and 0.666 gm. mol. each of ester and water. Determine the amount of ester present at equilibrium when 3 gm. mols. of alcohol react with one gm. molecule of acetic acid. (Osmania B.Sc., 1955)

38. State the Law of Mass Action. When alcohol and acetic acid are mixed together in equimolecular proportion, 66.5 per cent are converted into ester. Calculate how much ester will be formed if 1 mol. of acetic acid is treated with 0.5 mol. of alcohol.

39. Enunciate the Law of Mass Action and apply it to discuss the esterification of an acid by an alcohol.

When 1 mol. of ethyl alcohol reacts with 1 mol. of acetic acid, $2/3$ mol. of ethyl acetate is formed. Determine the amount of ester present at equilibrium when

(a) 3 mols. of alcohol react with 1 mol. of acid;

(b) 1 mol. of alcohol reacts with 1 mol. of acid in the presence of 1 mol. of water. (Agra B.Sc., 1955)

40. Discuss the dissociation of phosphorus pentachloride from the viewpoint of the Law of Mass Action. Explain how variations of pressure and addition of chlorine to the system would effect the degree of dissociation. (Nagpur B.Sc., 1955)

41. Deduce the Law of Mass Action from kinetic considerations and apply it to cases of homogeneous reactions.

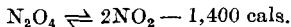
The vapour density of PCl_5 is 104.16; but when heated to 230°, its density is reduced to 62.0. Calculate the degree of dissociation at 230°. (Banaras B.Sc., 1955)

42. Explain the thermal dissociation of nitrogen tetroxide.

At one atmosphere pressure 0.92 gm. of nitrogen tetroxide occupies a volume of 0.295 litre at 27°C. Calculate the degree of dissociation of nitrogen tetroxide into nitrogen peroxide at the above temperature. ($N = 14$, $O = 16$; 1 gm. mol. of any gas at N.T.P. occupies a volume of 22.4 litres). (Rangoon B.Sc., 1955)

43. Discuss the Law of Mass Action and show its application in (a) Haber's synthesis of ammonia and (b) manufacture of lime. (Allahabad B.Sc., 1955)

44. State the Law of Mass Action and apply it to the following equilibrium :



The vapour density of the gas at 60°C is 30·6. Calculate the percentage dissociation. Discuss the effect of increase of pressure and temperature on the above dissociation. (Delhi, B.Sc., 1955)

45. What is meant by 'chemical equilibrium'? Give an account of the typical experimental methods of determining the equilibrium constant. (Indian Administrative Services 1953)

46. Explain the application of the Law of Mass Action to homogeneous equilibria in solution.

3 gm. molecules of ethyl alcohol are mixed with 4 gm. molecules of acetic acid and kept at constant temperature until equilibrium is attained. If K for the above reaction be 4, find the amount of ethyl acetate formed. (Rangoon B.Sc., 1956)

47. Enunciate the Law of Mass Action. Describe some of its applications.

When 2·94 mols. of iodine and 8·1 mols. of hydrogen are heated at constant volume at 444° , until the equilibrium is established, 5·61 mols. of hydriodic acid are formed. Find out the equilibrium constant. (Agra B.Sc., 1956)

48. Deduce the Law of Mass Action from kinetic considerations and apply it to the equilibrium $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$. How is this equilibrium affected by temperature and pressure? (Aligarh B.Sc., 1959)

49. Deduce the Law of Mass Action from kinetic considerations and apply it to the equilibrium $\text{Ca CO}_3 \rightleftharpoons \text{Ca O} + \text{CO}_2$. How is the equilibrium affected by pressure? (Allahabad B.Sc., 1957)

50. State the Law of Mass Action and discuss its application to

(a) Thermal dissociation of PCl_5 and

(b) Precipitation of substances from aqueous solutions. (Karnatak B.Sc., 1956)

51. State and discuss the Law of Mass Action. Show how the law has been applied to the case of electrolytic dissociation. (Bombay B.Sc., Subs., 1956)

52. Explain the meaning of the term 'Equilibrium Constant' of a reversible reaction.

(a) The equilibrium constant for the reaction at 450°C is found to be 64. If 6 gm. mols. of hydrogen are mixed with 3 gm. mols. of iodine in a litre-vessel at this temperature, what will be the concentration of each of the three components when equilibrium is attained?

(b) If the volume of the reaction vessel is reduced to half a litre, will any effect occur on the equilibrium? (Gauhati B.Sc., 1956)

53. Distinguish between decomposition and dissociation, giving examples of each. The vapour density of PCl_5 was determined at 520°C and was found to be 57·92. Calculate the degree of dissociation. ($P = 31$, $\text{Cl} = 35·5$). (Patna B.Sc., 1956)

54. Describe in brief the Law of Mass Action.

The dissociation pressure of solid ammonium hydrosulphide at 27° is 60 cms. What will be the total pressure when it dissociates at the same temperature in the presence of ammonia at a pressure of 45 cms.? Assume that ammonium hydrosulphide dissociates completely into ammonia and hydrogen sulphide. (Lucknow B.Sc., 1956)

55. Trace the development of the Law of Mass Action. Discuss its application to the following heterogeneous systems:

(a) $\text{NH}_4\text{HS} \rightleftharpoons \text{NH}_3 + \text{H}_2\text{S}$

(b) $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$

(Nagpur B.Sc., 1957)

56. Explain the terms (a) homogeneous equilibrium, (b) heterogeneous equilibrium and (c) equilibrium constant of a reaction.

The vapour density of phosphorus pentachloride at 250°C is found to be 57·9. Calculate its percentage dissociation at that temperature. (Allahabad B.Sc., 1957)

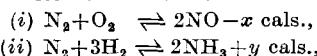
57. In each of the following three experiments one gram-molecule of acetic acid was allowed to react with different quantities (x gram-molecules) of ethyl alcohol, until equilibrium was established. It was found that the following amounts of ethyl acetate (y gram-molecules) were produced :—

Experiment	(i)	(ii)	(iii)
x	0.5	1.0	2.0
y	0.42	0.66	0.83

Show that these results are in accord with the Law of Mass Action.
(Aligarh B.Sc., 1957)

58. State the Law of Mass Action and discuss its application to the dissociation of hydrogen iodide.
(Mysore B.Sc., 1958)

59. Discuss the reactions—



from the point of view of the Law of Mass Action. How are the above reactions affected by temperature ?
(Allahabad B.Sc., 1958)

60. State the Law of Mass Action and explain the term "active mass". Indicate its importance in Haber's process for the manufacture of ammonia.

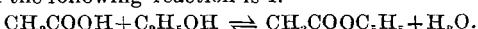
What weight of ethyl acetate will be formed if 240 gms. of acetic acid react with 138 gms. of ethyl alcohol at 25°C (H = 1, C = 12, O = 16). The equilibrium constant (K_e) for the reaction at 25°C is equal to 4.
(Karachi B.Sc., 1958)

61. Explain the thermal dissociation of nitrogen tetroxide in the light of the Law of Mass Action.

The vapour density of nitrogen tetroxide at 60°C is 36. Calculate the degree of thermal dissociation of nitrogen tetroxide into peroxide. (N = 14, O = 16).
(Rangoon B.Sc., 1958)

62. State the Law of Mass Action and obtain an expression for the equilibrium constant.

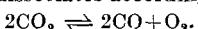
What will be the composition of the equilibrium mixture when one mole of acetic acid is taken with 8 mols. of ethyl alcohol ? The equilibrium constant of the following reaction is 4.



(Lucknow B.Sc., 1959)

63. State the Law of Mass Action.

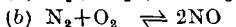
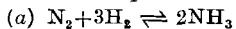
Carbon dioxide dissociates according to the reaction



Calculate the dissociation constant of the reaction assuming that 40.0 per cent of the carbon dioxide has dissociated under a pressure of 1.0 atmosphere.
(Rajasthan B.Sc., 1959)

B. Le Chatelier Principle

1. State Le Chatelier's Theorem. Discuss the influence of temperature and pressure on the equilibrium of the following reactions :—



(Banaras B.Sc., 1953)

2. State Le Chatelier's Theorem. Illustrate its use by a discussion of three types of reactions.
(Madras B.Sc., 1951)

3. Explain clearly what you understand by Le Chatelier principle. Illustrate your answer by two suitable examples. In what way is the equilibrium constant of a reaction influenced by a change in temperature ?
(Jammu & Kashmir B.Sc., 1954)

4. Explain the effect of pressure and temperature on the following reaction :

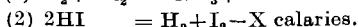
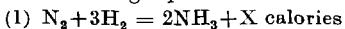


(Rangoon B.Sc., 1955)

5. State Le Chatelier's Theorem. Illustrate its application by suitable examples.
(Madras B.Sc., 1955)

6. State Le Chatelier principle. Discuss its application in the synthesis of (a) ammonia and (b) sulphur trioxide.
(Mysore B.Sc., 1955)

7. State and explain the principle of Le Chatelier and discuss its application to the following equilibria :—



(Poona B.Sc., 1957)

8. Write a note on Le Chatelier's Theorem with special reference to the effect of temperature and pressure on chemical equilibria.

(Allahabad B.Sc., 1958)

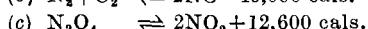
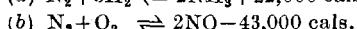
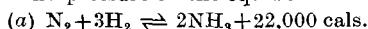
9. What is Le Chatelier's Theorem ? Illustrate by examples.

(Aligarh B.Sc., 1958)

10. State Le Chatelier's Theorem. Discuss the application of the theorem to chemical equilibria.

(Venkateswara B.Sc., 1959)

11. State and explain Le Chatelier's Theorem. Discuss the influence of temperature and pressure on the equilibrium of the following reactions :—



(Marathwada B.Sc., 1959)

ANSWERS

A. LAW OF MASS ACTION

7. 61.42

8. 9.474 mols.

11. 0.3415 gm. mols.

14. 6.868.

15. 0.945 mols. ethyl acetate and water; 4.055 mols. acetic acid and 0.055 mol. alcohol.

16. 0.967 mols. ethyl acetate and water; 0.033 mol. acetic acid and 7.033 mols. alcohol.

17. 4.122.

18. 1.333 gm. mols.

19. 0.423 mol.; 0.930 mol.; 0.967 mol. or 117.33 gms.

20. 0.00162.

21. 58.44.

22. $K_p = 0.307$ and 1.77.

23. 0.835; $K_p = 2.302$.

24. 0.846; $K_p = 2.518$.

26. 0.397.

25. 57.91.

30. 0.01082.

27. 0.680

35. 4.57 atmos.

34. 79.2%.

38. 0.423 gm. mol.

37. 0.9 gm. mol.

41. .68.

39. (a) 0.9 mol.

44. 50.32%.

(b) 0.543 mol.

46. 2.25.

47. 50.2.

52. $\text{HI} = 5.68$ mols.; $\text{H}_2 = 3.16$ mols. $\text{I}_2 = 0.16$ mol.

54. 65 cms.

53. 79.9%.

60. 2.25 gm. mol.

55. 80.05%.

62. 0.967 mol. ethyl acetate and water;

61. 27.78%.

0.33 mol. acetic acid;

63. 0.074.

7.033 mol. ethyl alcohol.

CHAPTER XV

KINETICS OF CHEMICAL REACTIONS

VELOCITY OF A REACTION

The definition of **Reaction Velocity** is very similar to that of velocity of motion in kinetics and the term denotes *the quantity of a given substance which undergoes change in unit time*. The matter, however, is not so simple as that because the rate of a reaction is never uniform and falls off with time as the reactants are used up. The variation of reaction velocity with time is shown in Fig. 144 and it is clear that we cannot get the velocity of a reaction by dividing the amount of substance transformed by the time taken for such a transformation. If, however, we take an infinitely small interval of time dt , an interval so small that it may be assumed that the velocity is constant throughout the interval, then if dx is the amount of substance transformed in this interval, the velocity of the reaction at that instant is $\frac{dx}{dt}$.

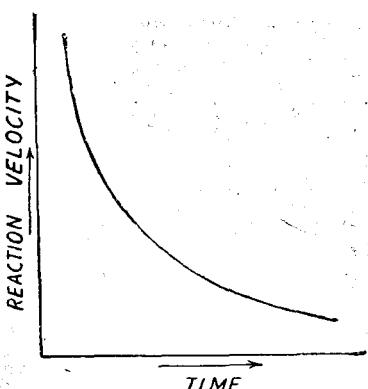


Fig. 144. Change of reaction velocity with time.

VELOCITY CONSTANT

The reaction velocity at any instant is influenced by the concentration of the reactants. It is proportional, according to the Law of Mass Action to the molecular concentration and when more than one substance is involved, to the product of their molecular concentrations. Consider a simple transformation :



If C be the molecular concentration of A at any instant, then

$$\frac{dx}{dt} \propto C \quad \text{or} \quad \frac{dx}{dt} = k C$$

k , here, is a proportionality factor known as the **Velocity Constant** or **Specific Reaction Rate**. At a fixed temperature, it is equal to the reaction velocity when the molecular concentration is unity.

IONIC AND MOLECULAR REACTIONS

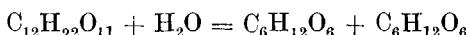
The reaction velocity of all chemical reactions cannot be measured. For example, if we add a solution of silver nitrate to an excess of an aqueous solution of sodium chloride, the chemical reaction is instantaneous and is complete in the twinkling of an eye, all the silver being precipitated as silver chloride. Likewise, it is

very difficult to measure the rate of reaction in the neutralization of an aqueous solution of an acid with an aqueous alkali solution. These are examples of reactions between ions and are called **Ionic Reactions.**

The reactions which take place between non-ionised molecules are called **Molecular Reactions.** These take a fairly long time to complete and in such cases we measure the reaction velocity. The total number of molecules involved in the chemical change is sometimes termed the **Molecularity** and reactions are classified as *unimolecular*, *bimolecular* or *termolecular* according as the number of molecules taking part in the change is one, two or three respectively.

ORDER OF A REACTION

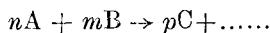
As a result of quantitative measurements on reaction velocity, it has been found that all the molecules represented in the chemical equation of a reaction do not determine its value but only those molecules whose concentration undergoes a measurable change during the reaction. For example, in the inversion of cane sugar



the molecularity of the reaction is two but only one molecule *viz.*, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ determines the reaction velocity, water being in such a large excess that its concentration does not measurably alter during the change.

The number of reacting molecules whose concentration alters as a result of chemical change is termed the Order of the reaction.

Consider a general reaction



where the concentration of both A and B alters during the reaction.

At any instant, the velocity $\frac{dx}{dt}$ is given according to the Law of Mass Action by the expression

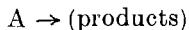
$$\frac{dx}{dt} = k[\text{A}]^n [\text{B}]^m$$

The sum $(n+m)$ represents the order of the reaction.

In the study of chemical kinetics, reactions are classified as those of *first*, *second* or *third order* according as the order is one, two or three respectively and this classification gives us valuable information about the mechanism of a chemical change.

REACTIONS OF THE FIRST ORDER

In a reaction of the *first order*, only one molecule is necessary for the reaction to proceed and the change may be represented in a general way as :



Let a be the initial concentration of A in gm. mols. per litre and suppose that after an interval of time t , the concentration is $(a-x)$ gm. mols. per litre. According to the Law of Mass Action the reaction velocity at any time t will be given by the expression :

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

In order to get the value of k , the velocity co-efficient, we integrate this expression

$$\int \frac{dx}{a-x} = \int k \cdot dt$$

or $-\log(a-x) = kt + c$ (constant of integration)

When $t=0; x=0$

Substituting these values in the above equation, we have

$$-\log a = c$$

$$\therefore -\log(a-x) = kt - \log a$$

or $\log a - \log(a-x) = kt$

or $\log_e \frac{a}{a-x} = kt$

or $k = \frac{1}{t} \log_e \frac{a}{a-x}$

$$= \frac{1}{t} \log_{10} \frac{a}{a-x} \times \log 10$$

$$= \frac{1}{t} \log_{10} \frac{a}{a-x} \times 2.303$$

or $k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$

This is known as the **equation for a unimolecular reaction**. When the experimental values of t , a , and x are inserted in this equation the value of k always comes out to be constant if the reaction under examination is unimolecular one.

For simplifying calculations, the unimolecular equation may be written as

$$\frac{k}{2.303} = \frac{1}{t} \log_{10} \frac{a}{a-x}$$

or $0.4343 k = \frac{1}{t} \log_{10} \frac{a}{a-x}$

$$\therefore \frac{1}{t} \log_{10} \frac{a}{a-x} = k' \text{ (a new constant)}$$

From a study of the above equation, we draw two important conclusions :

(i) *The time taken for the completion of the same fraction of change is independent of initial concentration.*

At half change for instance, $x=0.5a$

$$\therefore k = \frac{1}{t} \log \frac{a}{0.5a} = \frac{1}{t} \log 2$$

or $t = \frac{1}{k} \log 2$

$\therefore t$ is independent of a .

* The equation for First order reaction can also be written as

$$K = \frac{2.303}{t_2 - t_1} \log_{10} \frac{(a - x_1)}{(a - x_2)}$$

where x_1 and x_2 are amounts decomposed at time t_1 and t_2 respectively from the start.

(ii) A change in concentration units will not alter the velocity coefficient.

For let the new unit be n times the first. Then we have

$$k = \frac{1}{t} \log \frac{ma}{m(a-x)}$$

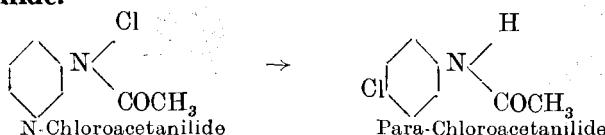
$$t = \frac{1}{k} \log \frac{a}{a-x}$$

This expression is the same as the original unimolecular reaction equation.

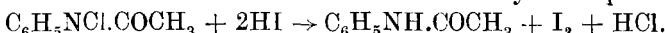
EXAMPLES OF FIRST ORDER REACTIONS

Very few examples of truly unimolecular reactions are known. Some cases are mentioned below and these include **pseudo-unimolecular reactions** i.e., the reactions which are not truly unimolecular but conform to the first order equation for certain reasons.

1. Conversion of N-Chloroacetanilide into Para-Chloroacetanilide.



This reaction takes place in the presence of HCl which probably acts as a catalyst, for its concentration does not alter at the end of the reaction. The progress of the change can be examined from time to time by adding excess of KI solution to a known volume of reaction mixture. Iodine is liberated as shown by the equation.



Para-Chloroacetanilide has no action on the iodine. The iodine liberated in each operation is titrated with a standard solution of sodium thiosulphate. The amount of sodium thiosulphate required corresponds to the concentration of unchanged N-Chloroacetanilide.

EXPERIMENT. Dissolve about 20 gms. N. Chloroacetanilide in 100 c.c. of 20 per cent acetic acid and place the flask in a thermostat. In a similar flask take 100 c.c. N-HCl and place it alongside the first flask. When the flasks have attained the temperature of the thermostat, mix the two solutions and immediately withdraw 5 c.c. of the mixture and run it into excess of KI solution. Titrate the iodine liberated against sodium thiosulphate solution. Now withdraw 5 c.c. at intervals of an hour each and repeat the above process. Substitute the value in the unimolecular reaction equation and see if k comes out to be constant.

Example. From the following results due to Blanksma, show that the conversion of N-Chloroacetanilide into Para-Chloroacetanilide is a unimolecular reaction.

Time in Hours	0	1	2	3
N	49.3	35.6	25.75	18.5

where N is the number of c.cs. of $\text{Na}_2\text{S}_2\text{O}_3$ solution required for a definite volume of the reaction mixture.

We have already shown for a monomolecular reaction.

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

* Such reactions as are not strictly unimolecular but which under the given conditions, behave as if they were unimolecular, are called **Pseudo-unimolecular reactions**.

where a = initial concentration and $(a-x)$ = the amount which is left after time t .

In the present case a in terms of c.c.s. of thiosulphate = 49.3 and the volume of $(a-x)$ at different times are 35.6, 25.75 and 18.5.

Substituting these values in the above equation we have

$$k = \frac{2.303}{1} \log_{10} \frac{49.3}{35.6} = 0.32214$$

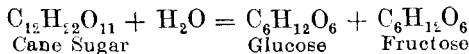
$$k = \frac{2.303}{2} \log_{10} \frac{49.3}{25.75} = 0.32357$$

$$k = \frac{2.303}{3} \log_{10} \frac{49.3}{18.5} = 0.32610$$

Since the values of k are fairly constant, the reaction is unimolecular.

2. Inversion of Cane Sugar

The inversion of cane sugar according to the equation



gives a unimolecular constant because the active mass of water does not alter appreciably in dilute solutions. The change can be very easily followed by noting the rotation of the plane of polarisation of light in a polarimeter because *change in rotation is proportional to the amount of sugar decomposed*.

Let the final reading be r_∞ , the initial reading r_0 while the reading at any time is r_t . Since $(r_0 - r_\infty)$ is proportional to a while $(r_t - r_\infty)$ is proportional to $(a-x)$.

$$k = \frac{2.303}{t} \log_{10} \frac{r_0 - r_\infty}{r_t - r_\infty}$$

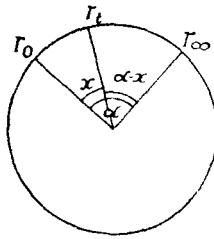


Fig. 145.

EXPERIMENT. Dissolve 20 gms. pure sugar in 100 c.c. water. Add to it a drop of thymol in order to preserve it. Also prepare N. HCl solution. Transfer 50 c.c.s. of sugar solution in a flask and place it in a thermostat. In another flask transfer 50 c.c.s. of N.HCl and place it alongside the first flask. When the solutions have acquired the temperature of the thermostat, mix them and pour the mixture in a polarimeter tube. Note the rotation at regular intervals. The final reading may be taken the next day after the expiry of about 24 hours or more.

Example. The optical rotation of sucrose in 0.9 N. HCl at various times is given in the following table:

Time (minutes)	0	7 18	18	27.05	∞
Rotation (degrees)	+24.09	+21.4	+17.7	+15	-10.74

Show that the reaction is of the First Order.

If this reaction is of the first order the value of velocity co-efficient k will be given by the relation.

$$k = \frac{2.303}{t} \log_{10} \frac{r_0 - r_\infty}{r_t - r_\infty}$$

$$0.4342 k = \frac{1}{t} \log_{10} \frac{r_0 - r_\infty}{r_t - r_\infty}$$

Thus if the expression $\frac{1}{t} \log_{10} \frac{r_0 - r_\infty}{r_t - r_\infty}$ comes out to be constant (k') the reaction is a unimolecular one

$$r_0 = +24.09 \text{ while } r_\infty = -10.74$$

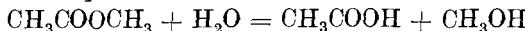
$$\therefore r_0 - r_\infty = 24.09 + 10.74 = 34.83$$

Time	$r_t - r_\infty$	$\frac{1}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$
7.18	32.14	$\frac{1}{7.08} \log \frac{34.83}{32.14} = 0.0047$
18	28.44	$\frac{1}{18} \log \frac{34.83}{28.44} = 0.0048$
27.05	25.74	$\frac{1}{27.05} \log \frac{34.83}{25.74} = 0.0048$

A glance at the value k' shows that the reaction is of the First Order.

3. Hydrolysis of methyl acetate

The hydrolysis of an ester e.g., methyl acetate, takes place according to the equation



This reaction is also an example of a pseudo-unimolecular reaction for although two molecules take part in the change, the active mass of water does not appreciably alter because of its being present in a large excess.

As the hydrolysis of an ester by pure water is very slow, mineral acids are added to the reaction mixture to catalyse the reaction. Since free acetic acid is produced in the change, the reaction can be followed by titrating known volumes of the reaction mixture with standard alkali at regular intervals, the final reading being taken after the expiry of 24 hours or more. The amount of the alkali consumed at any time corresponds to the quantity of ester decomposed up to that time. The velocity co-efficient may then be calculated from the expression

$$\frac{2.303}{t} \log_{10} \frac{T_\infty - T_0}{T_\infty - T_t} = k$$

where T_0 is the initial titration, T_t is the titration at any time t , and T_∞ is the final titration.

Example. 1 c.c. of methyl acetate was added to a flask containing 20 c.cs. of N/20 HCl maintained at a temperature of 25°C. 2 c.cs. of the reaction mixture were withdrawn at different intervals and titrated with a standard alkali.

Time (minutes)	0	75	119	183	∞
c.c. of alkali used	19.24	24.20	26.60	29.32	42.03

From the above data show that the hydrolysis of methyl acetate is a unimolecular reaction.

The alkali consumed for the total change is $(T_\infty - T_0)$ which is proportional to a . $(T_\infty - T_t)$ is proportional to $(a - x)$. Thus the unimolecular reaction becomes

$$\frac{2.303}{t} \log_{10} \frac{a}{a - x} = \frac{2.303}{t} \log_{10} \frac{T_\infty - T_0}{T_\infty - T_t} = k$$

Substituting the given values in this question we shall see if a constant value of k is obtained

	$T_\infty - T_0 = 42.03 - 19.24 = 22.79$	
Time	$T_\infty - T_t$	$\frac{2.303}{t} \log_{10} \frac{T_\infty - T_0}{T_\infty - T_t} = k$
75	$42.03 - 24.20 = 17.83$	$\frac{2.303}{75} \log_{10} \frac{22.79}{17.83} = 0.003195$
119	$42.03 - 26.60 = 15.43$	$\frac{2.303}{119} \log_{10} \frac{22.79}{15.43} = 0.00321$
183	$42.03 - 29.32 = 12.71$	$\frac{2.303}{183} \log_{10} \frac{22.79}{12.71} = 0.003160$

A glance at the value of k shows that the reaction is a unimolecular one.

4. Decomposition of Hydrogen Peroxide

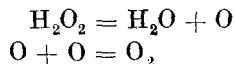
Hydrogen peroxide (H_2O_2) decomposes in solution in the presence of finely divided platinum and the reaction is represented by the equation



The progress of the reaction can be followed in two ways: (a) By collecting the oxygen gas evolved during the decomposition and measuring its volume at definite intervals, (b) Equal portions of hydrogen peroxide are titrated against standard $KMnO_4$ solution at regular intervals as the decomposition is in progress.

The second method is evidently convenient and is commonly employed. The reaction gives a unimolecular constant.

It should be clearly understood that if the decomposition were to take place according to the equation $2H_2O_2 = 2H_2O + O_2$, then the reaction would be of the second order. Since experiment shows that it is a unimolecular reaction the total reaction must be taking place in two steps



As the combination of oxygen atoms is extremely rapid the observed rate of reaction corresponds to the reaction taking place in the first step which proceeds more slowly.

Example. Following data was obtained in a determination of the rate of decomposition of hydrogen peroxide when equal volumes of the decomposing mixture were titrated against standard $KMnO_4$ solution at regular intervals :—

Time (in minutes)	0	10	20	30
Volume of $KMnO_4$ used (in c.cs.)	25	16	10.5	7.08

Show that it is a unimolecular reaction.

For a unimolecular reaction

$$\begin{aligned} k &= \frac{2.303}{t} \log_{10} \frac{a}{a-x} \\ k' &= \frac{1}{t} \log_{10} \frac{a}{a-x} \end{aligned}$$

Here the volume of $KMnO_4$ solution used at any time corresponds to undecomposed hydrogen peroxide i.e., $(a-x)$ at that time. The initial reading corresponds to a . Inserting these values in the above equation

$$(i) k' = \frac{1}{10} \log \frac{25}{16} = 0.0194$$

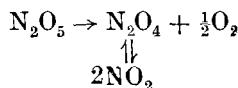
$$(ii) k' = \frac{1}{20} \log \frac{25}{10.5} = 0.0188$$

$$(iii) k' = \frac{1}{30} \log \frac{25}{7.8} = 0.0183$$

The constancy of k' indicates that the decomposition of hydrogen peroxide is a unimolecular reaction.

5. Decomposition of Nitrogen Pentoxide

Nitrogen pentoxide is a volatile crystalline solid which decomposes in the gaseous state or when dissolved in some organic solvent like carbon tetrachloride. The total reaction is represented by the equation :



When the reaction is carried in carbon tetrachloride, N_2O_4 and NO_2 remain in solution and thus the progress of the reaction can be noted by collecting the oxygen evolved and measuring its volume from time to time. If V_t be the volume at any time t and V_∞ the final volume of oxygen when the reaction is completed, then V_∞ is a measure of the original concentration (a) of N_2O_5 and $(V_\infty - V_t)$ is a measure of undecomposed nitrogen pentoxide ($a-x$) still remaining at time t . Thus

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x} = \frac{2.303}{t} \log_{10} \frac{V_\infty}{V_\infty - V_t}$$

Example. From the following data for the decomposition of N_2O_5 in carbon tetrachloride solution at 48° , show that the reaction is of the First Order.

Time (Minutes)	10	15	20	25	∞
Volume of Oxygen	6.30	8.95	11.40	13.50	34.75

If it is a unimolecular reaction

$$\frac{1}{t} \log_{10} \frac{V_\infty}{V_\infty - V_t} = k'$$

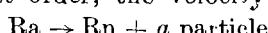
In this case, $V_\infty = 34.75$

Time	$V_\infty - V_t$	$\frac{1}{t} \log_{10} \frac{V_\infty}{V_\infty - V_t} = k'$
10	$34.75 - 6.30 = 28.45$	$\frac{1}{10} \log_{10} \frac{34.75}{28.45} = 0.00868$
15	$34.75 - 8.95 = 25.80$	$\frac{1}{15} \log_{10} \frac{34.75}{25.80} = 0.00862$
20	$34.75 - 11.40 = 23.35$	$\frac{1}{20} \log_{10} \frac{34.75}{23.35} = 0.00863$
25	$34.75 - 13.50 = 21.25$	$\frac{1}{25} \log_{10} \frac{34.75}{21.25} = 0.00854$

Since the value of k' is constant, it is a reaction of the First Order.

Other Examples of First Order Reactions

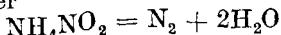
6. Radio-active disintegration. The disintegration of a radio-element is of the first order, the velocity of the transformation



can be followed by noting the radio-activity of Ra as the gaseous products can easily be removed. If R_0 and R_t be the radio-activity at the start and at time t respectively.

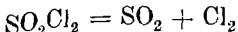
$$k = \frac{2.303}{t} \log \frac{R_0}{R_t}$$

7. Decomposition of ammonium nitrite in aqueous solution into nitrogen and water



The change can be followed by measuring the volume of nitrogen evolved.

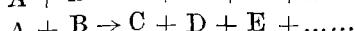
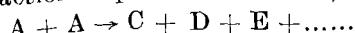
8. Decomposition of sulphuryl chloride into sulphur dioxide and chlorine,



The progress of this reaction can also be noted by measuring the volume of the gases evolved.

REACTIONS OF THE SECOND ORDER

In a *second order* reaction, the minimum number of molecules required for the reaction to proceed is two i.e.,



Let a be concentration of each of the reactants to start with and $(a-x)$ their concentration after any time t . Then we have :

$$\begin{aligned} \frac{dx}{dt} &= k(a-x)(a-x) \\ &= k(a-x)^2 \dots \text{Law of Mass Action.} \end{aligned}$$

or $\frac{dx}{(a-x)^2} = k \cdot dt.$

In order to get the value of k , we integrate this expression

or $\int \frac{dx}{(a-x)^2} = \int k \cdot dt.$

or $\frac{1}{a-x} = kt + C \text{ (constant of integration)}$

When $t = 0 ; x = 0$

Substituting these values in the above equation, we get $C = \frac{1}{a}$

$$\therefore \frac{1}{a-x} = kt + \frac{1}{a} \quad \text{or} \quad \frac{1}{a-x} - \frac{1}{a} = kt$$

or $\frac{a-a+x}{a(a-x)} = kt \quad \text{or} \quad \frac{x}{a(a-x)} = kt \quad \text{or} \quad \frac{1}{t} \times \frac{x}{a(a-x)} = k$

This is known as the **equation for a Second Order reaction**.

When the experimental value of t , a and x are inserted in the equation the value of k always comes out to be constant if the reaction under examination is a bimolecular one.

If we start with different amounts a and b of the reactants; then according to the Law of Mass Action

$$\frac{dx}{dt} = k(a-x)(b-x)$$

and by integration this expression, the equation obtained for a bimolecular reaction is

$$k = \frac{1}{t(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

Here again we draw some important conclusions :

(i) *The time taken for the completion of the same fraction of change is inversely proportional to concentration.*

At half change, for instance, $x = 0.5a$

Substituting this value in the equation $\frac{1}{t} \times \frac{x}{a(a-x)} = k$;

$$k = \frac{1}{t} \times \frac{0.5a}{a \times 0.5a} = \frac{1}{at}$$

or $t = \frac{1}{ka}$ or $t \propto \frac{1}{a}$

(ii) *The velocity co-efficient is not independent of the unit in which the concentration is expressed.*

For, let the new unit be $\frac{1}{m}$ times the first one ; we have

$$k = \frac{1}{t} \times \frac{mx}{ma \times m(a-x)} = \frac{1}{t} \times \frac{x}{a(a-x)} \times \frac{1}{m}$$

The new value of k is $\frac{1}{m}$ the original value.

(iii) *Bimolecular reaction conforms to the First Order when one of the reactants is present in large excess.*

For different initial quantities of the reactants

$$k = \frac{1}{(a-b)} \log \frac{b(a-x)}{a(b-x)}$$

When one of the reactants is present in very large excess we can neglect x and b as compared to the concentration a . The above equation is then reduced to

$$k = \frac{1}{ta} \log \frac{ba}{a(b-x)} = \frac{1}{ta} \log \frac{b}{b-x}$$

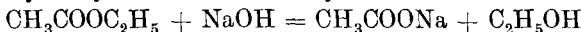
Since a remains nearly constant throughout the change

$$k = \frac{1}{t} \log \frac{b}{b-x}$$

This equation is identical with the First Order reaction equation.

EXAMPLES OF REACTIONS OF SECOND ORDER

(1) *Hydrolysis of an Ester by an Alkali*



To follow the progress of this reaction, a dilute solution of ethyl acetate in distilled water is mixed with an equivalent quantity of NaOH solution and the reaction mixture kept at constant temperature throughout the experiment, since the reaction velocity is influenced by temperature. Measured volumes of liquid are withdrawn at regular intervals and quickly titrated against a standard acid. The volume of acid in each case corresponds to the amount of unchanged caustic soda or ethyl acetate, i.e., $(a-x)$ at that time. The volume of acid required initially, of course, corresponds to the original concentration a . Inserting these values in the equation :

$$k = \frac{1}{t} \times \frac{x}{a(a-x)}$$

we find that the value of k comes out to be constant.

Example. In the hydrolysis of ethyl acetate by NaOH using equivalent concentrations, the progress of the reaction was examined by titrating 25 c.cs. of the reaction mixture at regular intervals against standard acid. The following figures give the volume of the acid used by the unchanged alkali.

(mins.)	0	5	15	25	35
c.cs. of acid ($a - x$)	16	10.24	6.13	4.32	3.41

Show that the reaction is of the Second Order.

The bimolecular reaction equation is

$$k = \frac{1}{at} \times \frac{x}{(a-x)}$$

$$\text{Here } a = 16$$

Time	$a - x$	x	$\frac{1}{at} \times \frac{x}{a-x} = k$
5	10.24	5.76	$\frac{1}{16 \times 5} \times \frac{5.76}{10.24} = 0.0070$
15	6.13	9.87	$\frac{1}{16 \times 15} \times \frac{9.87}{6.13} = 0.0067$
25	4.32	11.68	$\frac{1}{16 \times 25} \times \frac{11.68}{4.32} = 0.0069$
35	3.41	12.59	$\frac{1}{16 \times 35} \times \frac{12.59}{3.41} = 0.0066$

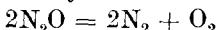
The value of k is fairly constant which shows that the reaction is bimolecular.

Other Examples of Second Order Reactions

(2) Decomposition of Ozone into oxygen.



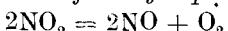
(3) Thermal decomposition of nitrous oxide.



(4) Conversion of Benzaldehyde into Benzoin.

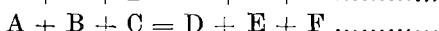
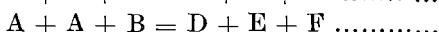


(5) Thermal decomposition of nitrogen peroxide



REACTIONS OF THE THIRD ORDER

In a termolecular reaction, the minimum number of molecules required for the reaction to proceed is three and the change may belong to any of three types :



We shall here consider the simplest case in which the initial concentration of all the three reacting molecules is the same and is represented by a . Let the concentration at the time t be $(a-x)$. Then,

$$\frac{dx}{dt} = k(a-x)^3 \dots \dots \dots \text{Law of Mass Action.}$$

Integrating to get the value of k :

$$\int \frac{dx}{(a-x)^3} = \int k \cdot dt.$$

or $\frac{1}{2(a-x)^2} = kt + C$ (constant of integration)

When $t = 0$; $x = 0$. Substituting these values in the above, we find $C = \frac{1}{2a^2}$

$$\therefore \frac{1}{2(a-x)^2} = kt + \frac{1}{2a^2}$$

or $kt = \frac{1}{2(a-x)^2} - \frac{1}{2a^2}$

or $k = \frac{1}{2t} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right]$
 $= \frac{1}{t} \times \frac{x(2a-x)}{2a^2(a-x)^2}$

In this case we find that :

(i) The time required for the completion of the same fraction of the change is inversely proportional to the square of the initial concentration.

At half change for instance; $x = 0.5a$

Substituting this value in the equation $k = \frac{1}{t} \times \frac{x(2a-x)}{2a^2(a-x)^2}$

$$k = \frac{0.5a \times 1.5a}{2a^2 \times 0.5a \times 0.5a} \times \frac{1}{t} = \frac{1.5}{a^2} \times \frac{1}{t}$$

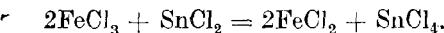
or $t = \frac{1}{k} \times \frac{1.5}{a^2} = \frac{1.5}{k} \times \frac{1}{a^2}$

or $t \propto \frac{1}{a^2}$.

(ii) The velocity co-efficient is not independent of the units in which the concentration is expressed.

EXAMPLES OF THIRD ORDER REACTIONS

(i) Reaction of ferric chloride by stannous chloride. This reaction can be written as



This reaction was studied by Noyes who found that it was of the third order. The progress of the reaction can be followed by mixing equivalent solutions of ferric chloride and stannous chloride and keeping the mixture in a constant temperature bath. Equal portions of the mixture are withdrawn at definite intervals as the reaction proceeds. These are run into mercuric chloride solution to remove the excess of stannous chloride and then the ferrous ions can be estimated by titration against standard potassium dichromate.

Example. In an experiment in the reduction of ferric chloride with stannous chloride, the following results were obtained by Noyes :—

Initial concentration $a = 0.0625$

x	0.01434	0.02664	0.03612	0.04102
t (min.)	1	3	7	11

Show that the reaction is termolecular.

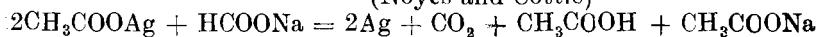
$$a = 0.625$$

t	x	$(a - x)$	$\frac{1}{2t} \times \frac{x(2a - x)}{a^2(a - x)^2} = k$
1	0.01434	0.04816	$\frac{0.01434 \times 0.11066}{2 \times (0.0625)^2 \times (0.04816)^2} = 87.58$
3	0.02664	0.03586	$\frac{0.02664 \times 0.09836}{6 \times (0.0625)^2 \times (0.03586)^2} = 86.96$
7	0.03612	0.02638	$\frac{0.03612 \times 0.08888}{14 \times (0.0625)^2 \times (0.02638)^2} = 84.33$
11	0.04102	0.02148	$\frac{0.04102 \times 0.08498}{22 \times (0.0625)^2 \times (0.02148)^2} = 87.92$

The value of velocity co-efficient k , is fairly constant showing thereby that the reaction is termolecular.

Other examples of Third Order reactions are :

(2) Action of sodium formate on silver acetate,
(Noyes and Cottle)



(3) Formation of nitrogen peroxide,
(Bodenstein and Lindner 1922)



(4) Conversion of cyanic acid into cyamelide
 $3\text{HCNO} \rightleftharpoons \text{H}_3\text{C}_3\text{N}_3\text{O}_3$

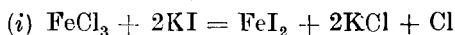
REACTIONS OF HIGHER ORDER—KINETIC EXPLANATION OF THEIR RARITY

While we have a few examples of termolecular reactions, reactions of higher order are very rare. The rarity of such reactions can be explained on the basis of the kinetic molecular theory according to which *the rate of a chemical reaction is proportional to the number of collisions taking place between the reacting molecules*. The chances of simultaneous collision of the reacting molecules will go on decreasing with the number of molecules i.e., the order of the reaction. For instance for a reaction of the fourth order to proceed it is necessary that all the four reacting molecules should come into contact with each other at the same time and the possibility of their doing so is comparatively much less than in the case of a bimolecular reaction where the simultaneous collision of only two molecules is to occur.

How are then we to explain the various complicated changes represented by chemical equations containing seven, eight or more reacting molecules? In such reactions it is believed that the entire change is composed of a series of simple reactions taking place side by side or one after the other. Some of these reactions are instantaneous whilst others are slow. The experimental measurement of the velocity in such a complicated reaction would give us the value for that composite reaction which is the slowest for it is the slow reaction that decides the velocity of the chemical change as a whole. An example of this type is reaction between ferric chloride and potassium iodide given by the equation



The reaction has been found to be termolecular and is supposed to take place in two steps:



Of these, the latter is very much faster than the former. The former reaction thus determines the order of the total change.

DETERMINATION OF THE ORDER OF A REACTION

It has already been pointed out that a chemical equation in all cases does not give a correct picture of a reaction and in order to understand the mechanism of a reaction it is essential to determine its order. There are at least four different methods to ascertain the order of a reaction.

(I) Integration Method. (*Substitution in Equations*).

This method consists in actually carrying out the change with known quantities of the reactants and noting the progress of the reaction by analysing the reaction mixture from time to time. These values are substituted in the velocity co-efficient equations of the first, second and the third order reactions. The order of the reaction is determined by that equation which gives a satisfactory constant value of k . This is a method of trial and failure but was the first to be employed and is still extensively used for simpler reactions.

Example. In the conversion of ammonium cyanate into urea, the following results were obtained by Walker and Hambly in 1895 :—

time (mts.)	0	72	157	312	600
($a-x$) in gm. mols.	0.0916	0.0656	0.0512	0.0348	0.0228

Find out the order of the reaction.

In order to find out the order of the reaction by the above method, we substitute this data in the unimolecular equation first and if this does not give a constant value k , we insert the same data in the bimolecular equation, and so on. In the present case

Time	$a-x$	x	$a = 0.0916$	$k = \frac{1}{t} \times \frac{x}{a(a-x)}$
			$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$	
72	0.0656	0.0260	0.00462	0.0601
157	0.0512	0.0404	0.00370	0.0548
312	0.0348	0.0568	0.00308	0.0551
600	0.0228	0.0688	0.00231	0.0549

Since the unimolecular equation does not give a constant value of k while the bimolecular equation yields a fairly constant value, the reaction is of the Second Order.

(2) Method of Equifractional parts. (*Half Change Method*).

We have already seen that the time required for the completion of the same fraction of change is independent of the initial concentration in a first order reaction, is inversely proportional to the initial concentration in a second order change and is inversely proportional to the square of the initial concentration in a third order reaction. In general, the time required for the completion of the same fraction of change is inversely proportional to the initial concentration raised to the power which is one less than the order of the reaction. If t_1 and t_2 be the times for the completion of the same fraction of change

with different initial concentrations, a_1 and a_2 and if n is the order of the reaction $t_1 \propto \frac{1}{a_1^{n-1}}$ and $t_2 \propto \frac{1}{a_2^{n-1}}$

$$\frac{t_2}{t_1} = \left(\frac{a_1}{a_2} \right)^{n-1} \text{ or } \frac{t_2}{t_1} = \left[\frac{a_1}{a_2} \right]^{n-1}$$

To determine the order of the reaction by this method, we start with two different concentrations of the reactants and note the time for the completion of say half change in each case. By substituting these values in the above expression, the value of n can be calculated.

Example 1. In the reduction of nitric oxide by hydrogen, Hinshelwood found that equimolecular mixture of the gases at 340.5 m.m. initial pressure was half changed in 102 seconds whilst in another experiment with an initial pressure of 288 m.m. the change was half completed in 140 seconds. Find the order of the reaction.

Since the pressure of a gas is determined by its concentration we may take $a_1 = 340.5$ and $a_2 = 288$.

Accordingly, $t_1 = 102$ and $t_2 = 140$. Substituting these values in the equation,

$$\frac{t_2}{t_1} = \left(\frac{a_1}{a_2} \right)^{n-1} : \left(\frac{340.5}{288} \right)^{n-1} = \frac{140}{102}$$

$$\text{or } (n-1) \log \frac{340.5}{288} = \log \frac{140}{102}$$

$$\text{or } (n-1) \times 0.0727 = 0.1375 \\ n = 2.89$$

Hence the reaction is of the third order.

Example 2. The time for half change (t) of a gaseous substance undergoing thermal decomposition was determined for various initial pressures (p) with the following results :

p (m.m.)	750	500	250
t (min.)	105	235	950

Find the order of the reaction.

Since the pressure of a gas is determined by its concentration we have $a_1 = 750$ and $a_2 = 500$ when $t_1 = 105$ and $t_2 = 235$.

$$\text{Now } \left(\frac{a_1}{a_2} \right)^{n-1} = \frac{t_2}{t_1}$$

$$\text{or } \left(\frac{750}{500} \right)^{n-1} = \frac{235}{105}$$

$$\text{or } (n-1) \log 1.5 = \log \frac{235}{105}$$

$$\text{or } 0.1761 (n-1) = 0.3499$$

$$\text{Whence } n = 2.9$$

With the second pair, $a_1 = 500$ and $a_2 = 250$

When $t_1 = 235$ and $t_2 = 950$

$$\therefore \left(\frac{500}{250} \right)^{n-1} = \frac{950}{235}$$

$$\text{or } (n-1) \log 2 = \log 950 - \log 235$$

$$\text{or } 0.3010 (n-1) = 0.6066. \therefore n = 3.0$$

From the two values of n obtained above we can conclude that the order of the reaction is 3.

An alternative method which is specially suitable in simpler cases is as follows :

If t is the time for the same fraction of change and a is the initial concentration :

In a unimolecular reaction ; t is independent of a , i.e., constant

In a bimolecular reaction ; $t \propto \frac{1}{a}$ i.e., $t \times a = \text{constant}$

In a termolecular reaction ; $t \propto \frac{1}{a^2}$ i.e., $t \times a^2 = \text{constant}$

The following examples illustrate the method :

Example 1. The study of the decomposition of phosphine gave the following data :—

Initial Pressure (m.m.)	707	79	37·5
Half life (seconds)	84	84	83

What is the order of the reaction ?

Since the Half-life or the time required for the half change with different initial pressures is constant, the reaction is of the First Order.

Example 2. The time for half change (t) of a gaseous substance undergoing thermal decomposition was determined for various initial pressures (p) with the following results :

p (m.m.)	205	300	350	400	450
t (mins.)	136	112·5	97	85	75·5

State the order of the reaction.

Since the pressure of a gas is proportional to its concentration, we can use p instead of a , the initial concentration.

As t is not constant in the above data, the reaction is clearly not of the first order. Let us now see if $p \times t = \text{constant}$.

p	250	300	350	400	450
t	136	112·5	97	85	75·5
$p \times t$	34000	33750	33950	34000	33975

Since the product $p \times t$ is fairly constant, the reaction is of the Second Order.

(3) Graphical Method. In this case the values of x (amount decomposed) are plotted against t (time) and $\frac{dx}{dt}$ at any time determined from the graph (Fig. 146) by measuring the angle θ , since $\frac{dx}{dt} = \tan \theta$.

The various values of $\frac{dx}{dt}$ are plotted against the corresponding concentrations ($a-x$) as shown in Fig. 147. If we get a straight

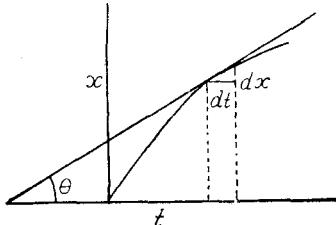


Fig. 146.

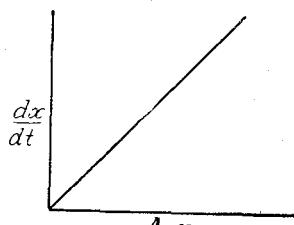


Fig. 147.

line, the reaction is monomolecular. If a straight line is obtained

by plotting $(a-x)^2$ or $(a-x)^3$ in place of $(a-x)$, it is a bimolecular or a termolecular reaction respectively.

(4) vant Hoff's Differential Method. If proceeding as in method (3), the variation of concentration be plotted against time, it should be possible to measure $\frac{dc}{dt}$ for any concentration.

For concentration c_1 we have $\frac{dc_1}{dt} = kC_1^n$ and for concentration c_2 we have $\frac{dc_2}{dt} = kC_2^n$ where n is the order of the reaction

$$\text{or } \frac{dc_1}{dt} / \frac{dc_2}{dt} = \left[\frac{c_1}{c_2} \right]^n$$

Taking Logarithms, we have :

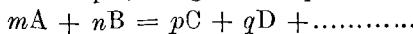
$$\log \frac{dc_1}{dt} - \log \frac{dc_2}{dt} = n [\log c_1 - \log c_2]$$

$$\text{or } n = \frac{\log (dc_1/dt) - \log (dc_2/dt)}{\log c_1 - \log c_2}$$

(5) Ostwald's Isolation Method. (*Addition of excess of Reactants*).

This method is employed in determining the order of complicated reactions by 'isolating' one of the reactants so far as its influence on the rate of reaction is concerned. This is achieved by taking all but one of the reactants in turn in a very large excess so that their active masses remain constant throughout the change and the concentration changes with respect to the isolated reactant only. A variation of this one reactant permits a direct determination of the order of the reaction with respect to it. The total order of the reaction will be the sum of the individual orders obtained for each of the reactants.

Consider for example, the general equation



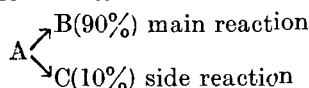
By taking A in large excess, the determination of the order of reaction from the concentration change of B will give the value n . Similarly, we may isolate A by taking B in large excess and get the order of reaction with respect to A (i.e., m). The total order of reaction will then be the sum ($m + n$).

DISTURBING FACTORS IN THE DETERMINATION OF ORDER

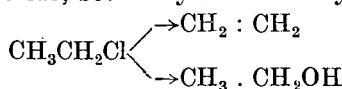
The reaction which follows a single course with no interfering reactions is the exception and not the rule. Many reactions are complicated so that the interpretation of their velocity data becomes difficult. Thus, it is found that a number of reactions do not give a constant value of velocity co-efficient with any one of the equations derived earlier while others, though apparently of a higher order, give a constant value of k with an equation of lower order. The smooth progress of a chemical change is marked in such cases by certain disturbing factors. Some of these factors are described below :—

(i) **Side Reactions.** Sometimes the reactants undergo two or more independent reactions at the same time, each reaction giving

rise to its own set of products. The reaction which utilizes the major portion of the reactants is called the **main reaction**, the others being termed as the **side reactions**.

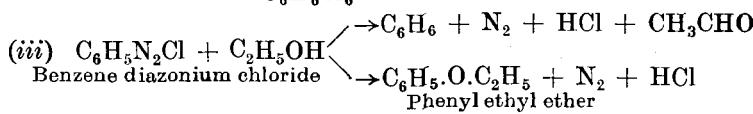
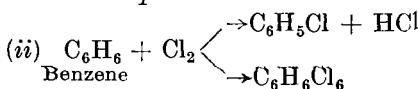


By adjusting the conditions it is possible to reduce considerably the velocity of a side reaction so as to make it negligible; at the same time a side reaction may become the main reaction under another set of circumstances. For instance, when caustic potash reacts with ethyl chloride, both ethylene and ethyl alcohol are produced.

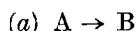


An alcoholic solution of KOH will, however, give mainly ethylene while an aqueous solution will give ethyl alcohol.

Other Examples :



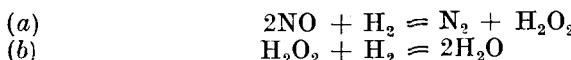
(2) Consecutive Reactions: We have already seen that reactions of higher orders are very rare and most of the complicated reactions take place in stages, the velocity co-efficient being determined by that reaction which is the slowest. Such reactions which take place in stages are called **consecutive or successive reactions** and are very common. If a substance A is transformed into C through an intermediate substance B, then these are the two reactions :



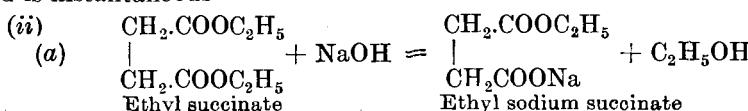
If the reaction (a) has very much greater velocity than reaction (b), then the velocity of the total change from A to C is practically the same as that of the slowest reaction (b).

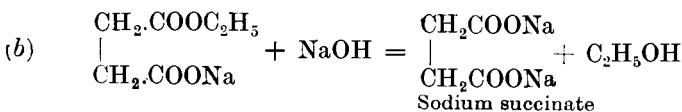
Examples :

(i) The reduction of nitric oxide by hydrogen according to the equation $2\text{NO} + 2\text{H}_2 = \text{N}_2 + 2\text{H}_2\text{O}$ should be a quadri-molecular reaction but Hinshelwood found it to be termolecular. Evidently the reaction must be proceeding in stages and the suggested mechanism includes two reactions :-

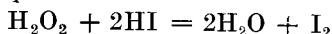


The first one is slow and determines the order of the reaction. The second is instantaneous.

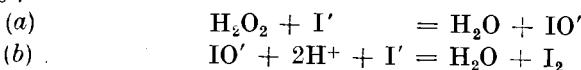




(iii) The oxidation of hydriodic acid by hydrogen peroxide is bimolecular although the equation



shows it to be termolecular. It takes place in the following two stages :

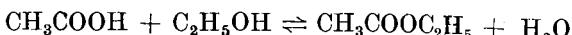


Of these, the first proceeds with measurable slowness and determines the order of the reaction. The second though quadrimolecular is instantaneous.

It must be noted that where the difference in the velocities of the consecutive reactions is not considerable, it becomes very difficult to determine the order of the reaction.

(3) Counter or Reversible Reactions. In this case the products of a chemical change react together to regenerate the original reacting substances. The reverse change takes place under the same set of conditions as the direct change and this causes a serious disturbance in the measurement of reaction velocity.

Consider the formation of ethyl acetate from ethyl alcohol and acetic acid.

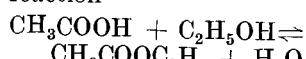


The forward reaction velocity represented in Fig. 148 by the curve AB gradually falls while the reverse velocity represented by the

dotted curve DC continuously increases. The two curves meet at the point E and here the forward velocity = the reverse velocity.

A state of equilibrium is thus established, as much of the ester being formed at any time as is decomposed back into alcohol and acid.

The rate of the reaction



at any time will be the rate in the forward direction minus the rate in the backward direction. Thus if a and b be the initial amounts of acid and alcohol respectively and at the time t if x of

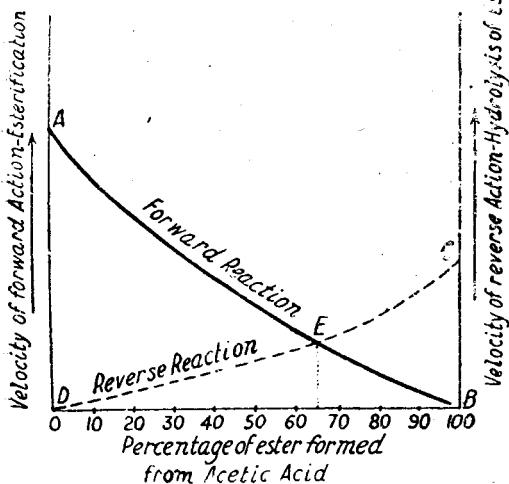


Fig. 148. State of equilibrium.

amounts of acid and alcohol respectively and at the time t if x of

acid be changed into ester, then :

$$\frac{dx}{dt} = k_1(a-x)(b-x) = k_2x^2$$

where k_1 and k_2 are the velocity coefficients of the forward and the reverse reactions. Here again, it is possible to suppress the forward or reverse reaction by adjusting the conditions and to determine the order of the reaction under these changed conditions.

(4) **Temperature Coefficient of a Chemical Reaction.** The temperature coefficient of a chemical reaction is defined as the ratio of the velocity constants of a reaction at two temperatures separated by 10°C , usually 25° and 35°C . Its value is generally between two and three though in a number of reactions, very high values are observed.

If the logarithm of reaction velocity be plotted against the reciprocal of absolute temperature, the various points obtained fall on a straight line for most of the chemical reactions. This variation may, therefore, be represented by the equation

$$\log k = a - \frac{b}{T}$$

where a and b are constants.

The exponential form of the equation known as **Arrhenius Equation** is

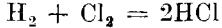
$$k = Ae^{-E/RT}$$

where A and E are related to a and b respectively. E is known as the **Energy of Activation** and represents the minimum energy required for the collision between molecules to be effective and determines the influence of temperature on reaction velocity.

(5) **Zero Order Reactions.** There are certain reactions including the photochemical reactions, whose reaction velocity does not depend on the concentration of the reactants. They proceed at the same rate regardless of the concentration. Their velocity expression may be written as

$$k = (\text{a constant})$$

Since no concentration factor is involved, such a reaction is said to be of the Zero Order. A reaction may be of the zero order when it is influenced by some outside source of energy. For example, the velocity of the reaction



is constant and does not at all depend on the concentration of the reactants. When a mixture of H_2 and Cl_2 is exposed to ultraviolet light, chains of reactions are set up and the reaction proceeds irrespective of the concentration of the reactants. Hence the reaction is of the zero order.

QUESTIONS AND PROBLEMS

1. Define the term "Velocity Constant of a reaction" and "order of a reaction." How would you determine experimentally the order of the reaction of the inversion of cane sugar in presence of an acid? (*Travancore B.Sc., 1954*)
2. Clearly explain the term 'order of a reaction' and detail the methods used for its determination. (*Nagpur B.Sc., 1954*)

3. Discuss the meaning of the velocity constant for a monomolecular reaction and show by what means it can be determined experimentally in any one case. (Ceylon Final, 1954)

4. What do you understand by the Order of a reaction and how can you determine it? How is the velocity constant of the inversion of cane sugar determined? (Annamalai B.Sc., 1953)

5. Write an essay on the Order of reaction and its determination. (Agra B.Sc., 1952)

6. Give a brief account of methods available for determining the order of a reaction. Explain under what circumstances a bimolecular reaction becomes monomolecular. (Gujarat B.Sc., 1954)

7. Give an account of the various methods for determining the order of a reaction. Deduce the relation between concentration and time for a given fractional change. What are zero order reactions? (Madras B.Sc., 1948)

8. Give various methods of determining the order of a reaction and discuss the method "time of half change". What is the influence of temperature on the velocity? (Andhra B.Sc., 1953)

9. What do you understand by the term "Order of reaction"? By what methods is the order of a reaction determined?

10. What is meant by zero order reaction? In presence of an acid, acetochloranilide changes slowly into *p*-chloro-acetanilide. The former substance liberates iodine from KI and not the latter; and so the progress of the reaction can be measured by periodic titration with sodium thiosulphate known as hypo. In an experiment the following results were obtained:

Time (hours)	0	1	2	4	6	8
(<i>a</i> - <i>x</i>) c.c. of hypo	45	32	22.5	11.3	5.7	2.9

Show from the above results that the reaction is monomolecular and find out the fraction of acetochloranilide decomposed after three hours.

(Panjab B.Sc., 1954)

11. The optical rotation of sucrose in 0.9 N.HCl at various times is given in the following table.

Time (mts.)	0	10	20	30	40	∞
Rotation (degrees)	+32.4	+28.8	+25.5	+22.4	+19.6	-14.1

Find the order of reaction.

12. The following data were obtained for the inversion of cane sugar:

<i>t</i> (mts.)	0	10	20	48	80	180	300	∞
Rotation	6.6	6.17	5.79	5.00	3.71	1.4	-0.24	-1.98

Find the order of the reaction.

13. What is meant by 'order of a chemical reaction'? In the inversion of cane sugar in presence of an acid the following polarimetric readings were obtained:

Time in mts.	0	30	90	330	∞
Readings	+46.75	+41.00	+30.75	+2.75	-18.75

Find the order of the reaction and the value of the velocity constant.

(Banaras B.Sc., 1953)

14. Hydrogen peroxide in solution decomposes to give water and oxygen gas. Describe in detail as to how you will proceed to find the order of this reaction.

15. From the following data show that the decomposition of H_2O_2 in aqueous solution is a first order reaction.

Time in minute	0	15	30
N	25.4	9.83	3.81

where N is number of c.c. of potassium permanganate required to decompose a definite volume of hydrogen peroxide solution. (Nagpur B.Sc., 1957)

16. Give in outline two methods for determining the order of a reaction. From the following data show that the spontaneous decomposition of an aqueous solution of hydrogen peroxide is unimolecular:

Time in minutes	0	10	20
N	22.8	13.8	8.28 c.c.

where N is the volume of potassium permanganate solution required to decompose a definite volume of the peroxide solution. (Delhi B.Sc., 1954)

17. Explain and illustrate what is meant by a monomolecular reaction. Derive an equation for determining the specific reaction rate of a monomolecular reaction. (Andhra B.Sc., 1953)

18. How is the order of a reaction usually determined? The data for the conversion of a compound A into its isomeride B are as follows:—

Time in hours	0	1	2	3	4	8
%age of A	49.3	35.6	25.8	18.5	13.8	4.8

Show that this is a first order reaction. (Nagpur B.Sc., 1953)

19. Describe what is meant by order of a chemical reaction and "velocity constant" of a reaction. Describe suitable methods by which the order of reaction can be determined. (Punjab B.Sc., 1943)

20. Outline any two methods for the determination of the order of a given reaction. The reaction $\text{AsH}_3(\text{g}) = \text{As}(\text{s}) + 3/2 \text{H}_2(\text{g})$ was followed at constant volume at 310°C by measuring the gas pressure of intervals.

Time in Hrs.	0	5	7.5	10
Total Pressure (in m.m.)	758	827	856	882

Find the order of the reaction.

21. The following data have been obtained from the thermal decomposition of malonic acid, $\text{CH}_2(\text{COOH})_2 \rightarrow \text{CH}_3\text{COOH} + \text{CO}_2$.

Time (Min.)	10	20	35	56	∞
Pressure (m.m.)	37	67	108	155	303

Find the order of the reaction.

22. In a certain first order reaction, half of the material is decomposed in 1,000 seconds. How long will it be until only one-tenth is left? (Andhra B.Sc., 1953)

23. In the decomposition of gaseous acetaldehyde at 518°C , the time taken to decompose half the material was found to be 410 secs., when the initial pressure was 363 mm., and 880 secs. for an initial pressure of 169 mm. What is the apparent order of the reaction? Calculate the time required to decompose half the reactant when the initial pressure is 1 atm. (Osmania B.Sc., 1954)

24. At a certain temperature the half-life periods for the decomposition of ammonia in contact with tungsten were as follows:—

Press. in m.m. of Hg	50	100	200
Relative half-life period	3.52	1.82	0.93

Find the order of the reaction. (Poona B.Sc., 1954)

25. Describe the expression for the velocity coefficient of a bimolecular reaction. How would you distinguish between a unimolecular and a bimolecular reaction?

26. What do you understand by the order of a reaction? Deduce the equation for the velocity constant of a reaction of the second order, and indicate fully, taking suitable examples, how you would proceed to determine the order of any given reaction.

27. Derive an expression for the velocity constant of a second order reaction involving different concentrations of the reactants. (Karnatak B.Sc., 1954)

28. What do you understand by the order of a reaction? How would you study (a) the rate of Hydrolysis of an ester and (b) the rate of Inversion of cane sugar. (Jammu & Kashmir B.Sc., 1954)

29. Derive an equation for the rate constant of a second order bimolecular reaction when the initial reactions of the reactants are the same. Show that time for half-decomposition in a second order reaction is proportional to the reciprocal of the initial concentration. (Sydney University, 1953)

30. If a reaction is proved to be of the second or third order, explain in simple language what this tells you about the reaction. What experimental observations would you make to determine the order of a reaction, say, the oxidation of acetaldehyde.

31. The following results were obtained for the saponification of ethyl acetate using equal concentrations of ester and alkali :—

t (minutes)	0	4·89	10·37	28·18	∞
c.e.s. of acid used	47·65	38·92	32·62	22·58	11·48

Show that the reaction is bimolecular.

32. In determining the rate of a reaction between KOH and C_2H_5Br , equal quantities of N/10 solution of the reactants were used. 20 c.c. of the reacting mixture were withdrawn at regular intervals and titrated against N/20 acid. The following data was obtained :—

t (mts.)	0	21	46	97	146
Vol. of acid required c.cs.	20·00	14·71	11·14	7·42	2·92

Find the order of the reaction.

33. Discuss consecutive and concurrent reactions. (*Andhra B.Sc., 1954*)

34. Explain the term 'Order of a reaction'. Discuss the various methods for determining the order of reaction. (*Andhra B.Sc., 1955*)

35. What is meant by 'Order of a reaction'? How is it determined?

At a certain temperature the half-life period for the decomposition of ammonia (catalytically) were as follows :—

Pressure in mm. of Hg	50	100	200
Half-life period in Hrs.	3·52	1·92	1·00

Find the order of the reaction. (*Nagpur B.Sc., 1955*)

36. Enumerate the methods employed in determining the "Order of a reaction." Discuss one method in detail.

Explain what is meant by "Consecutive reaction" and "Reverse reactions". (*Karnatak B.Sc., 1955*)

37. Define the term 'Order of a reaction' and describe one experimental method to determine it.

The decomposition of diazobenzene chloride was followed at constant temperature by measuring the volume of nitrogen evolved at suitable intervals. The readings thus obtained are given below :—

Time from start :	0	20	50	70	∞ minutes
Vol. of N_2 :	0	10	25	33	162 c.cs.

Calculate the order of reaction. (*Osmania B.Sc., 1955*)

38. How can you determine an order of a reaction?

A solution of hydrogen peroxide was decomposed by colloidal platinum at $0^\circ C$. Equal volumes of the mixture were taken out at times t and titrated with N/10 permanganate solution.

t in mins.	124	127	130	133
x in c.cs.	10·6	9·4	8·33	7·38

Show that the above decomposition is unimolecular reaction.

(*Rangoon B.Sc., 1956*)

39. Distinguish between the terms molecularity and 'order of a chemical reaction'. Derive an equation for determining the specific reaction rate of a monomolecular reaction. Give its characteristics. (*Baroda B.Sc., Subs., 1956*)

40. What is meant by the order of a reaction? What are unimolecular and pseudo unimolecular reactions? What are their characteristic features?

The decomposition of AsH_3 into solid arsenic and hydrogen may be followed by measuring the pressure at constant volume from time to time. In an experiment at 310° the pressures p in mm. of Hg were obtained after the time t hours. Show from these figures that the reaction is of the first order.

t	0	5·5	6·5	8	hours
p	733·32	805·78	813·11	835·34 m.m.	

(*Poona B.Sc., 1956*)

41. Mention various methods of determining the order of a reaction and describe in detail the half-time method.

At a certain temperature the half-value periods in the thermal decomposition of nitrous oxide were as follows :—

Pressure (mm. of Hg.)	296	139	52·2
Half-value periods (sec.)	255	470	860

Calculate the order of the reaction. (Lucknow B.Sc., 1955)

42. Enumerate the different methods employed in the determination of the "order of a reaction". Give one method in detail. Explain what is meant by "Consecutive reaction" and "Reverse reaction". (Karnatak B.Sc., 1956)

43. Define the velocity coefficient of a chemical reaction. How do you determine the velocity co-efficient for the decomposition of aqueous hydrogen peroxide ? (Madras B.Sc., Subs., 1956)

44. Describe one experimental method to determine the 'order of a reaction.'

Give two examples of first order reactions involving more than one reactant and explain their behaviour. (Osmania B.Sc., 1956)

45. What is meant by (a) the velocity constant and (b) the order of a reaction? How do you account for the fact that the inversion of cane sugar in a dilute aqueous solution is a reaction of the first order? How is the velocity of this reaction experimentally followed ? (Mysore B.Sc., 1956)

46. Derive the characteristic equation for a first order reaction. Show that the time taken to complete a definite fraction of a monomolecular reaction is independent of the initial concentration. (Gujrat B.Sc., 1956)

47. What is a unimolecular reaction? Give examples of this type of reaction. What explanation of them has been given ? (Punjab B.Sc., 1958)

48. Discuss the influence of temperature on the velocity of reaction.

A gram-mol. of ethyl acetate was hydrolysed with a gm. mol. of sodium hydroxide. The concentration of the alkali fell according to the following data :—

t (min.)	0	4	6	10	15	20
$a-x$	8·04	5·30	4·58	3·50	2·74	2·22

Show that the reaction is bimolecular and calculate the value of k from any three set of readings ; and from these obtain the average value. (Andhra B.Sc., 1958)

49. In the reaction $2\text{NO} + 2\text{H}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ an equimolecular mixture of gases at 336 mm. initial pressure was half changed in 108 seconds, whilst in another experiment with an initial pressure 288 mm. the change was half completed in 147 seconds. Determine the order of the reaction. (Bombay B.Sc., 1958)

50. Derive the expression for the velocity constant of a bimolecular reaction. Show under which condition such a reaction behaves kinetically as a first order reaction. (Lahore B.Sc., 1958)

51. Deduce an expression for a first order reaction. The following figures were found for the decomposition of nitrous acid in solution at a certain temperature.

Time in mins.	0	90	135	180
Gms. of nitrous acid in 140 c.cs.	·2936	·2564	·2396	·2240

Show that the reaction is of the first order and calculate the velocity constant of the reaction. (Rangoon B.Sc., 1958)

52. Derive the equation for the velocity co-efficient of a bimolecular reaction. How would you find whether the given reaction is unimolecular or bimolecular. (Osmania B.Sc., 1959)

53. Describe three methods for determining the order of a chemical reaction. Indicate how the order of a reaction gives an insight into the mechanism of a reaction, illustrating with suitable examples.

(Venkateswara B.Sc., 1959)

54. The following values were obtained for the decomposition of nitrous oxide at 900°C in contact with gold surface.

Time in mts.	15	30	53	65	80	100
% decomposed	16.5	32	50	57	65	73

Find the order of the above reaction. (Marthwada B.Sc., 1959)

55. Distinguish between equilibrium constant and velocity constant.

The decomposition of H_2O_2 was studied by titrating it at different intervals with $KMnO_4$. Calculate the velocity constant from the following data assuming it to be monomolecular.

t (secs.)	0	600	1200
$KMnO_4$ (c.c.)	22.8	13.8	8.2

(Lucknow B.Sc., 1959)

ANSWERS

- | | |
|--------------------|----------------------------------|
| 10. 0.646. | 11. First Order. |
| 12. First Order. | 13. First Order. |
| 20. First Order. | 21. First Order. |
| 22. 3,322 seconds. | 23. Second Order; 195.8 seconds. |
| 24. Second Order. | 32. Second Order. |
| 35. Second Order. | 37. First Order. |
| 40. First Order. | 41. Second Order. |
| 49. Third Order. | 51. 0.001441. |
| 54. First Order. | 55. 0.000845. |

CHAPTER XVI

CATALYSIS

The term *Catalysis* was first introduced by Berzelius (1835) to describe the phenomenon when the mere presence of a small quantity of a foreign material, the catalyst, in reaction mixture makes the reaction go faster. There is no doubt that usually a catalyst accelerates a reaction [**Positive catalysis**] as was originally thought by Berzelius, but a number of cases are now known where the catalyst definitely retards the rate of the reaction [**Negative catalysis**]. Thus **Catalyst** may be defined as *any substance which alters (accelerates or retards) the rate of a chemical reaction.*

TYPES AND EXAMPLES OF CATALYTIC REACTIONS

Catalytic reactions are divided into two classes :

- (a) Homogeneous catalytic reactions [*Homogeneous catalysis*].
- (b) Heterogeneous catalytic reactions [*Heterogeneous or contact catalysis*].

Homogeneous Catalytic Reactions. In such reactions the catalyst is in the same phase as the reactants and the reacting system is homogeneous throughout.

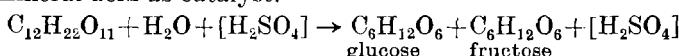
Examples :

(i) Combination of sulphur dioxide, steam, and atmospheric oxygen in the presence of nitric oxide as catalyst [*Chamber process for sulphuric acid*].



In this case the catalyst and the reactants are in the gaseous state.

(ii) *Hydrolysis of cane sugar* in aqueous solution in the presence of a mineral acid as catalyst.

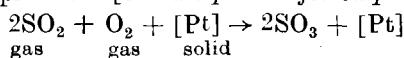


Here the catalyst as well as the reactants are in the liquid phase.

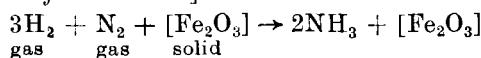
Heterogeneous Catalytic Reactions. In these reactions the catalyst is in a different phase than that of the reactants. The system is homogeneous so far as the reactants are concerned but is made heterogeneous by the introduction of the solid catalyst.

Examples :

(i) Combination of sulphur dioxide and oxygen in the presence of finely divided platinum [*Contact process for sulphuric acid*].

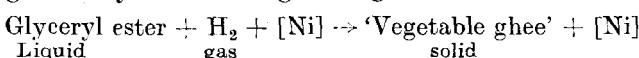


Combination of nitrogen and hydrogen in the presence of ferric oxide [*Haber process for ammonia*].



(ii) *Hydrogenation of Vegetable oils* in the presence of finely divided nickel as catalyst. These oils contain a high proportion of

esters of higher unsaturated organic acids and glycerine, which on hydrogenation yield solid 'vegetable ghee'.

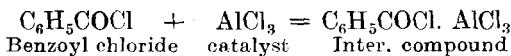


CHARACTERISTICS OF CATALYTIC REACTIONS

(i) **Unchangeableness of the Catalyst.** The catalyst remains unchanged at the end of the reaction both as regards *quantity* and *chemical composition* although it may not remain in the same physical state. For example, crystalline manganese dioxide added to heated potassium chlorate to accelerate the evolution of oxygen, is found to be changed to a fine powder at the end of the reaction.

(ii) **Small quantity of the Catalyst.** A small quantity of the catalyst is sufficient to effect huge quantities of reactants *provided* of course, *the activity of the catalyst remains unimpaired*. This is due to the fact that the catalyst itself is not used up in the reaction. One milligram of the fine platinum powder, for example, is enough to cause the union of 2·5 litres of a mixture of hydrogen and oxygen to form water.

There is no doubt that in *contact catalysis* when the reaction takes place by simple contact of the reactants on catalyst surface, a small quantity of the catalyst can cause the union of large amounts of the reactants. But this is not true of *homogeneous catalysis*. In homogeneous catalysis, the catalyst forms an intermediate compound with the reactants and obviously a large quantity is required for that. For example, in Friedal and Craft's reaction, the catalyst first reacts



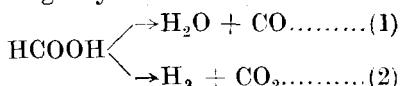
with the halide forming an intermediate compound and for that the two substances should be present in molecular ratio. Moreover, in homogeneous catalysis the catalyst is often disabled during the reaction and it has got to be replaced when it has catalysed the amounts of the reactants shown by the chemical equation.

(iii) **Equilibrium Point unaffected although reached sooner.** In a system of two opposing reactions the catalyst accelerates the reverse-reaction to the same extent as the forward reaction so that the ratio of their velocities, the equilibrium constant, remains unchanged. Thus *a catalyst does not alter the state of equilibrium but simply accelerates the velocity with which equilibrium point is approached*. This must be true as the equilibrium point cannot be shifted without the supply of energy to the system and a catalyst, unchanged in quantity and composition at the end of the reaction, cannot supply the required energy.

(iv) **Catalyst can start a reaction.** Ostwald believed that a catalyst never initiates a reaction but only accelerates a reaction already in progress though perhaps so very slowly as to appear at rest. The view is not universally accepted. It is now widely believed that *a catalyst can actually cause a reaction to start*. The catalyst, in some way makes such molecules to react which ordinarily do not possess enough energy to do so. For instance, it was shown

by Baker that a large number of gaseous reactions do not proceed if the reactants are *completely dried* by prolonged treatment with dehydrating agents (*intensive drying*). Addition of a trace of moisture causes the reaction to proceed smoothly. As examples we have the combination of hydrogen and chlorine to form hydrogen chloride and the combination of nitric oxide and oxygen to form nitrogen peroxide.

(v) **Specificity of catalysts.** The phenomenon of catalysis is universal. There is no chemical reaction which cannot be catalysed and there is no substance which cannot act as a catalyst. But the reaction of catalyst is specific, i.e., a substance which acts as a catalyst for one reaction may fail to catalyse another. Let us consider the decomposition of formic acid which at ordinary temperature may proceed, though extremely slowly, according to either of the following ways :



It is found that metallic copper can catalyse only (2) whereas alumina catalyses only the reaction (1); hence by a suitable choice of the catalyst either set of products can be obtained.

(vi) **Effect of temperature on catalysed reactions.** The effect of temperature on catalysed reactions is similar to that in homogeneous reactions as we have already studied under Le Chatelier Principle. Some catalysts, however, are physically altered by rise in temperature, and hence their catalytic power may be decreased. This is particularly true with colloidal catalysts like platinum sol, since a rise in temperature may cause their coagulation. In such a case there are two opposing effects : (a) increase of reaction velocity with increase of temperature, (b) decrease of reaction velocity due to partial destruction of the catalyst at higher temperatures. Thus *there must be an optimum temperature at which the efficiency of the catalysts is maximum.*

(vii) **Catalytic Poisoning.** Heterogeneous catalysts are very sensitive to the presence of traces of foreign substances which render them ineffective. Any substance which reduces or even completely destroys the activity of the catalyst to promote a reaction is termed **poison** and the phenomenon is known as **catalytic poisoning**. The poisoning of a catalyst may be *temporary* or *permanent*. In **temporary poisoning**, the poison is adsorbed on the catalyst surface in preference to the reactants. The diminution in activity of the catalyst is thus determined by the extent to which the surface of the catalyst and its active centres are covered up by the poison. As soon as the poison molecules leave the surface the activity is restored.

In **permanent poisoning**, the poison reacts chemically with the catalyst forming a new surface which is catalytically inert. In such cases, the catalyst can resume its activity only after the catalyst is regenerated in its original form by some chemical treatment. The compounds of sulphur and arsenic behave in this way as poisons to many metallic catalysts.

Examples :

(a) In Contact process for sulphuric acid, traces of *arsenic* present in the reacting gases render the platinum catalytically inert.

(b) In the Haber process for ammonia, *carbon monoxide* present as impurity in hydrogen gas, if not removed, poisons the catalyst.

(c) Colloidal platinum which catalyses the decomposition of hydrogen peroxide, is rendered ineffective by traces of *hydrogen cyanide*.

It is interesting to note that molecules of all poisons possess residual free valencies which play an important part in the preferential adsorption of these molecules on the catalyst surface.

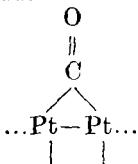


Fig. 149. Poisoning of platinum catalyst by carbon monoxide.

These free valencies of poison molecules and the unsatisfied valencies on the catalyst surface are mutually satisfied and a sort of 'loose chemical combination' results. It now becomes clear how even a minute quantity of the poison, just enough to form unimolecular layer on the catalyst

surface can render the catalyst altogether ineffective.

Curiously enough it has been noted that most effective catalytic poisons namely carbon monoxide, hydrogen cyanide, and arsenious oxide, are also deadly poisonous to living things.

(viii) **Activation of a Catalyst.** The efficiency of some catalysts is considerably enhanced by the presence of small amounts of foreign materials which may themselves be catalytically inert. Such a substance which promotes the activity of the catalyst, to which it is added, in relatively small amounts, is called a **Promoter** or **Activator** and the process is known as **Activation**. A promoter may be spoken of as '*catalyst for a catalyst*'. This action is very commonly found in the case of solid catalysts.

Examples :

(a) In the synthesis of ammonia, the addition of small amounts of some high melting and difficultly fusible oxides, e.g., aluminium oxide, chromium oxide, rare earths etc., to iron which acts as true catalyst results in a marked increase in the activity of the latter. Thus the catalyst widely used for the purpose is not iron alone, but a mixture of iron with aluminium oxide and potassium oxide.

(b) *Copper and tellurium* when added to nickel increase its catalyst activity in the hydrogenation of oils.

The mechanism of promoter action is not clearly understood. The increased catalytic activity may be due to increased adsorption of the reactants at the interfaces produced between the promoter and the catalyst. Also the reacting molecules are subjected, to a constraint by unequal forces pulling them on either side at these interfaces. This makes them very reactive.

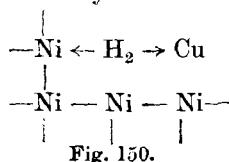


Fig. 150.

AUTOCATALYSIS

So far the catalyst has been regarded as a foreign substance added to the reacting system. It is, however, sometimes observed that *one of the substances formed during the reaction acts as a catalyst for that reaction.* This is known as **Autocatalysis**.

Examples :

(a) When nitric acid is poured on copper, the reaction is very slow in the beginning, gradually gains speed, and finally becomes very brisk. This is attributed to the formation of *nitrous acid* during the reaction which accelerates the process.

(b) The hydrolysis of ethyl acetate ($\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$) is catalysed by *acetic acid*, which is one of the products of reaction.

(c) The reaction between potassium permanganate and oxalic acid in the presence of dil. sulphuric acid, is catalysed by Mn^{++} ions formed during the reaction.

Also, if MnSO_4 be added to the solution in the very start, it accelerates the reaction.

NEGATIVE CATALYSIS

It is not always that a catalyst increases the rate of reaction. There are cases known where the *presence of a foreign substance retards the rate of reaction.* Such a substance is referred to as a **Negative catalyst** and the phenomenon is named as **Negative catalysis** or Inhibition. Negative catalysts act in two ways :

(i) In most cases a negative catalyst acts by poisoning or merely *destroying some catalyst* which already happens to be present in the reaction mixture. An important example of this action is furnished by the addition of certain acids to hydrogen peroxide solution. The traces of alkali dissolved from the glass container catalyse the decomposition of hydrogen peroxide but the addition of an acid would destroy the alkali catalyst and thus prevent the decomposition.

(ii) The negative catalyst *dislocates the mechanism* by which the reaction would ordinarily proceed. Lead tetraethyl is often introduced into petrol because it prevents the combination of petrol vapour and oxygen on compression and thus saves it from preignition.

THEORIES OF THE MECHANISM OF CATALYSIS

Catalytic reactions are of such varied nature that it is not possible to give a uniform explanation of the mechanism of the phenomenon. Only the more important theories will be discussed.

1. The Intermediate Compound Formation Theory

According to this theory the function of the catalyst consists in bringing about the desired reaction between molecules which do not possess enough energy to enter into chemical combination ordinarily. The high energy requirement is avoided by some low level by-bath. Usually it is achieved by forming an intermediate compound between the catalyst and one of the reactants. This compound is formed with less energy consumption than needed for

the actual reaction. It is unstable and decomposes to regenerate the catalyst with the simultaneous formation of the desired product of the reaction. *Thus the catalyst functioning through the alternate formation and decomposition of an unstable intermediate compound is used over and over again.*

Let there be two substances X and Y which combine in the presence of a catalyst C, X combines with the catalyst and an unstable compound XC results which then reacts with Y regenerating the catalyst C.

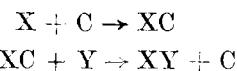
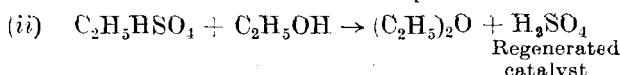
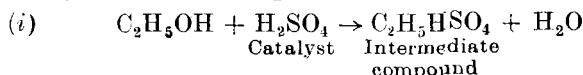
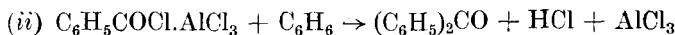
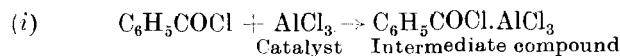


Illustration :

(a) The mechanism of the reaction between alcohol and sulphuric acid giving ether, is explained as follows :—

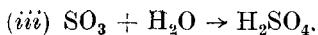


(b) Anhydrous aluminium chloride is used as a catalyst in the well-known Friedel-Craft's reaction. The formation of benzophenone (C_6H_5CO , C_6H_5) from benzene and benzoyl chloride takes place in the following steps :—



This mechanism is supported by experiment as the compound $C_6H_5COCl.AlCl_3$ has been isolated and found to react with benzene to give benzophenone.

(c) The catalytic action of nitric oxide in the Chamber process for sulphuric acid may be represented in the following manner :



The theory of intermediate compound formation gives an adequate explanation of the changes brought about in the physical state of the catalyst in the course of a reaction but fails to explain the action of catalytic poisons and activators. In fact the scope of the theory is limited as intermediate compound formation appears to be possible only in the case of homogeneous systems when the catalyst and the reactants are in one phase. In heterogeneous catalytic reactions when the catalyst is solid and the reactants are gases, no intermediate compound formation could be expected.

2. The Adsorption Theory

According to a former view, the reactants concentrate on the catalyst surface due to *simple physical adsorption* and thus the rate of reaction is promoted [Law of Mass Action]. This view has been modified.

3. The Modern Theory of Contact Catalysis

It is a compromise between the two previous theories. In fact, the two views of intermediate compound formation and simple physical adsorption have been completely fused.

According to this theory, the action of the catalyst is essentially two-fold :

(i) The catalyst concentrates the reactants on its surface and thus pushes forward the reaction (*Law of Mass Action*).

(ii) Due to the 'free valencies' on the catalyst surface, the reactant molecules enter into a sort of 'loose-chemical-combination' with the catalyst, and the molecules thus adsorbed are distorted from their original form. These distorted molecules which are now under strain, become more reactive.

Free valencies and Catalyst Action. Inside the mass of a metal every atom is linked to the surrounding atoms and all its valencies are satisfied. On the other hand, an atom situated in the surface of the catalyst possesses a free valency turned outward.

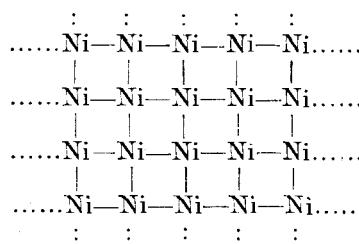


Fig. 151. Unsatisfied or free valencies on the surface of nickel.

The catalyst surface thus becomes a seat of 'chemical force of that action' which is akin to surface tension in liquids. When a gas comes in contact with such a surface its molecules are held up there due to 'loose-chemical-combination.' If different molecules are adsorbed side by side they may react and the new molecules so formed may evaporate leaving the way clear for the fresh molecules of the reactants to be adsorbed.

If the free valencies are responsible for the catalyst action as considered above, it follows that with the increase in the number of these valencies on the catalyst surface, its action would be enhanced. This increase of free valencies can be obtained in two ways :

- (i) By subdivision of the catalyst.
- (ii) By the rough surface of the catalyst.

Subdivision of the catalyst. Finely powdered or colloidal catalyst particles being very rich in free valencies, according to this

theory, should be more efficient than the solid catalyst.

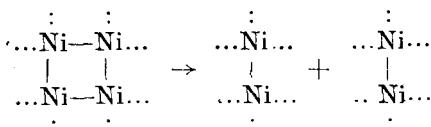


Fig. 152. Increase of free valencies on subdivision.

In actual practice, finely divided nickel and colloidal platinum are known to be most efficient catalysts. This supports the above theory very strongly.

PEAK

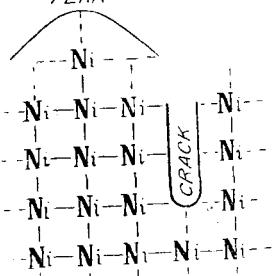


Fig. 153. Active centres on the surface of nickel.

Rough surface of the catalysts—Active centres.

It should be clear by now that the rough catalyst surface having greater number of free valencies crowding here and there, would be much more effective than a smooth one. The edges, corners, cracks, and peaks on the rough surface are the **active centres** and the efficiency of the catalyst is mainly due to them.

It may further be noted that an apparently smooth metallic surface consists of minute crystals at the corner of which the free valencies are 'over-crowded'. The presence of these crystals in the catalyst surface adds to the efficiency of the catalyst.

The Modern Theory of Catalysis has explained :

(i) *The efficiency of finely divided or colloidal catalysts* which has already been discussed.

(ii) *The Action of Poisons.* The poison molecules are preferentially adsorbed by the catalyst surface due to the residual valencies possessed by them. A very small number of molecules of the poison absorbed at the 'active centres' of the catalyst can bring down its activity almost to zero.

(iii) *The Action of Promoters.* The action of promoters may be explained by the increased adsorption of reactants taking place at the interfaces of the promoter and the catalyst where the free valencies are perhaps overcrowded.

(iv) *The Specific Action of catalysts.* Specific action of catalysts also becomes evident as it is, after all, the chemical affinity of the catalyst for the reactants which is responsible for their adsorption and subsequent reaction.

4. Lowry-Bronsted Theory of Acid-Base catalysis

The theory explains all those reactions where an acid or a base catalyses a reaction in aqueous solution.

According to this theory, *the reaction is catalysed by the transfer of a proton from the catalyst to the reactant X, to form an intermediate*

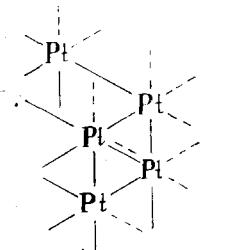
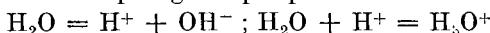


Fig. 154. Corner of a platinum crystal.

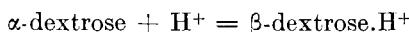
compound XH , which thereupon reacts, giving up the proton to another substance capable of accepting it.

Water can take up or give up a proton as desired. Thus :



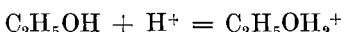
If a strong acid or a strong base is added to the water-solution, proton-giving or proton-accepting capacity of water is enhanced.

Example 1. α -dextrose on standing in aqueous solution is converted to β -dextrose and this is accompanied by a change in the rotatory power of the solution (*Mutarotation*). This may be explained as follows :



(taken by water)

Example 2. Formation of the ester from alcohol and acetic acid is catalysed by sulphuric acid. The probable mechanism of the reaction is



(taken by water)

ENZYMES AS CATALYSTS

Enzymes are complex organic compounds which are produced by living plants and animals. They form colloidal solution in water and are very effective catalysts. Many chemical reactions occurring within plants and animals are catalysed by them. Thus, before the process of digestion commences, starch is partly changed into sugar in the mouth. This transformation is accelerated by an enzyme called *ptyalin* present in saliva. Fermentation of sugar and acetic acid are also the result of the catalytic action of enzymes.

Characteristics of Enzyme Catalysis. In most respects enzymes are similar to inorganic heterogeneous catalysts. They, however, sharply differ from the latter in being highly specific and very susceptible to change of temperature. The following points may be noted about enzyme catalysis :

(i) *Enzymes, like inorganic catalysts, do not disturb the final state of equilibrium of a reversible reaction.*

(ii) *Generally the rate of the reaction is approximately proportional to the enzyme concentration.*

(iii) *Catalytic action of enzymes is highly specific* and in this respect they surpass even the inorganic catalysts. As a rule each enzyme acts catalytically on just one reaction. For example, the enzyme *diastase* will catalyse the hydrolysis of starch to maltose but a different enzyme *maltose* is needed to effect the further hydrolysis of maltose to glucose.

(iv) At increased temperature they are coagulated and lose their activity. *There is thus in general an optimum temperature at which their catalytic efficiency is maximum.* This usually lies between 35° and 40°C . At higher temperature than this the catalyst is injured and all enzymes are 'killed' at a temperature of 100°C .

(v) They can be poisoned and activated like ordinary catalysts. Hydrogen cyanide, hydrogen sulphide, and carbon disulphide are the usual poisons. The activation of one enzyme by another enzyme is very common and in fact it is believed that with every enzyme there is present a **co-enzyme** and the catalytic activity of the former is paralysed as soon as the two are separated.

(vi) Being colloidal in nature enzymes are coagulated by addition of small quantities of electrolytes, resulting in the loss of their catalytic activity.

(vii) Ultraviolet rays tend to destroy enzymes.

QUESTIONS AND PROBLEMS

- What do you understand by the term 'positive' and 'negative' catalysis ? Give examples.
- Differentiate between 'homogeneous' and 'heterogeneous' catalysis. Illustrate your answer with examples.
- What is a catalyst ? Describe four reactions of industrial importance in which the presence of a catalyst is needed.
- Describe briefly one example of each of the following substances as catalyst in chemical reactions :
 - platinum, (ii) nickel, (iii) ferric oxide, (iv) manganese dioxide and (v) hydrogen ions.
- What criteria will you apply before you regard a certain reaction as catalysed reaction ? Discuss their applicability.
[**Criteria of catalytic behaviour :** (i) unchangeableness of the catalyst, (ii) small quantity of catalyst used, (iii) equilibrium point unaffected)]
- Write notes on :
 - selective action of catalysts,
 - effect of temperature on catalytic reactions.
 - catalytic poisoning,
 - activation of a catalyst.
- What is 'autocatalysis' ? Give examples and probable explanation of the phenomenon.
- Give a clear account of the theory of catalysis. (*Agra B.Sc., 1954*)
- What is 'contact catalysis' ? What mechanism can be ascribed to this type of catalysis ?
- Discuss enzyme catalysis. How does it differ from heterogeneous catalysis ?
- Describe some reactions of industrial importance in which the presence of a catalyst is required. In what ways has the action of catalysts been explained ? (*Punjab B.Sc., 1939*)
- What is meant by the term 'catalysis' ? What criteria have been laid down for catalyst behaviour ? Discuss the applications of catalysis in industry. (*Banaras B.Sc., 1950*)
- What is 'heterogeneous catalysis' ? What are the criteria of a catalyst ? Discuss the application of catalysis to the synthesis of ammonia and the hydrogenation of vegetable oils. (*Annamalai B.Sc., 1954*)
- Write a note on catalysis and discuss the different views expressed about the nature of the phenomenon. (*Nagpur B.Sc., 1953*)
- Write an essay on heterogeneous catalysis. (*Madras B.Sc., 1953*)
- Give the industrial application of catalysis. (*Jammu & Kashmir B.Sc., 1954*)
- Write an essay on catalysis. (*Osmania B.Sc., 1954 ; Punjab B.Sc., 1953*)
- What are the characteristics of catalytic action ? Give examples of catalytic action of technical importance. (*Delhi B.Sc., 1953*)

19. Write an essay on catalysis and its industrial applications.
(*Banaras B.Sc., 1954*)
20. Write an essay on catalysis.
(*Delhi B.Sc., 1955*)
21. What do you understand by the term 'Catalysis' ? Name three substances used as catalysts and state reactions in which they are used.
Describe one example of a catalytic process as carried out (i) in the laboratory, (ii) on a manufacturing scale.
(*Utkal B.Sc., 1954*)
22. Write an account of catalysis.
(*Rangoon B.Sc., 1956*)
23. What criteria would you apply to show that a particular substance taking part in a reaction is not a reactant but is a catalyst ? What theories have been advanced to explain the phenomenon of catalysis ?
(*Agra B.Sc., 1956*)
24. Write an essay on : "Catalysis and its industrial importance."
(*Madras B.Sc., 1955*)
25. What is a catalyst ? What are the criteria of a catalyst ? Discuss the applications of catalysis in industry.
(*Nagpur B.Sc., 1956*)
26. What is a catalyst ? What are the conditions a substance must satisfy in order to be considered a catalyst ? Describe two industrially important catalytic processes.
(*Kerala B.Sc., 1957 ; Travancore B.Sc., 1957*)
27. What is catalysis ? Give examples of different types of catalysis
Discuss the theories of catalysis.
(*Vikram B.Sc., 1958*)
28. What are the characteristics of a catalyst ? On the basis of the theory of contact catalysis, explain.
(a) the action of catalytic poisons ;
(b) the specific nature of a catalyst ;
(c) the activity of finely divided catalysts.
(*Agra B.Sc., 1959*)

CHAPTER XVII

DISTRIBUTION LAW

So far we have restricted our study to **homogeneous systems** which are both physically and chemically uniform. We may now pass on to the study of **heterogeneous systems**, which consist of two or more homogeneous parts or 'phases' that are physically distinct. While the equilibria in homogeneous systems (*homogeneous equilibria*) can be studied satisfactorily by means of the *Law of Mass Action*, equilibria in heterogeneous systems (*heterogeneous equilibria*) are usually examined with the help of two important generalisations namely,

- (a) Phase Rule.
- (b) Distribution Law.

DISTRIBUTION LAW

The Distribution Law expresses the relation between the concentrations of a given substance in two different phases in equilibrium with each other.

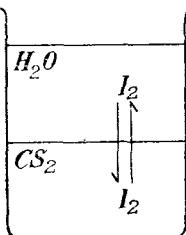


Fig. 155. Distribution of iodine in H_2O and CS_2 .

Consider a heterogeneous system formed by mixing carbon disulphide and water. On adding a small quantity of iodine to this mixture, it is noticed that the iodine added is shared by the two solvents and an equilibrium is set up. Let C_1 be the concentration of iodine in carbon disulphide and C_2 that in water. It is found that at a constant temperature the ratio $\frac{C_1}{C_2}$ is constant over a considerable range of concentrations, i.e., if more iodine be added to the above system in equilibrium it distributes itself between the two solvents in the same fixed ratio.

This behaviour has been found to be a general one and has been experimentally verified by a number of workers in the gas-liquid, solid-liquid, liquid-liquid and other such systems and is known as **Distribution Law** or **Partition Law**. It may be stated as follows :—

"A mathematically constant ratio exists between the concentrations of a given molecular species in any two phases in contact with each other at a constant temperature."

Thus if C_A and C_B represent the concentrations of a given molecular species in the two phases A and B respectively, we have :

$$\frac{C_A}{C_B} = K, \text{ at a constant temperature.}$$

The constant K is termed the **Distribution Co-efficient** or **Partition Co-efficient**.

Distribution in the System Liquid-Liquid

The distribution of a solid or a liquid between two immiscible solvents was thoroughly studied by Berthelot and Jungflesch in 1872 and they obtained fairly constant value of the distribution co-efficient in a number of cases e.g., iodine between water and carbon disulphide, bromine between water and carbon disulphide and oxalic acid between ether and water. Some of their results are tabulated below :

Oxalic acid between ether and water at 11°C			Iodine between carbon disulphide and water at 18°C		
Gms. Acid per 10 c.c. H_2O-C_1	Gms. Acid per 10 c.c. ether- C_2	$K = \frac{C_1}{C_2}$	Gms. Iodine per 10 c.c. H_2O	Gms. Iodine per 10 c.c. CS_2	$K = \frac{C_1}{C_2}$
0.473	0.053	9.2	0.0041	1.74	420
0.436	0.046	9.5	0.0032	1.29	400
0.304	0.031	9.8	0.0016	0.66	410
6.203	0.0205	9.9	0.0010	0.41	410

Similar results were obtained by Calvert in case of hydrogen peroxide between water and various organic solvents, by Abbeg, Fox and Herz in the case of boric acid between water and amyl alcohol and by Jakowkin in the case of bromine between water and bromoform ; iodine between water and chloroform and iodine between water and ethylene glycol.

Deviations from Distributive Law. In many cases, however, the value $\frac{C_1}{C_2}$ is either found to fluctuate or steadily decrease. The deviation from Distribution Law in such cases has been attributed to two causes :

(i) *Alteration in the mutual solubility of two liquids as a result of increasing concentration.*

(ii) *Change in the molecular state of the solute in the two solvents.*

(i) **Effect of change in solubility of the two solvents.** The Distribution Law can be successfully applied only if the solutions formed are very dilute. With increasing amounts of the dissolved substance the mutual solubility of the two liquids undergoes an alteration and three cases may accordingly arise :

(a) *The distributed substance may lower the mutual solubility.*

Successive additions of the solute will, in such a case, reduce the mutual solubility to zero so that the limiting distribution ratio would be that of the solubilities in the pure solvents.

(b) *The solubility of one liquid in the second may increase while that of the second in the first may decrease.* In such a case,

the distribution co-efficient will show fluctuations.

(c) *The distributed substance may increase mutual solubility.* Increased additions of the solute will, in such a case, cause the two liquid phases to become identical and dissolve in each other in all proportions. The distribution co-efficient will accordingly tend to alter and become unity. Klobbie pointed out in 1907 a case of this type in the distribution of malonic acid between water and ether.

When the amount of the solute added is small, its effect on mutual solubilities is of negligible dimensions and it is quite understandable why the law holds good in dilute solutions.

(ii) **Effect of the change in molecular state.** It was pointed out by Nernst (1891) that no distribution can occur between simple molecules of the solute in one phase and dissociated or associated molecules in the other. The ratio $\frac{C_1}{C_2}$ will be constant only if there is neither association nor dissociation of the solute molecules in both the phases.

Several complications may arise, which would influence the constancy of the partition co-efficient and thus necessitate a correction in the simple partition law equation.

(a) **Association in one of the phases.** The solute may have its normal molecular weight in phase I while it may be associated in phase II. This state of affairs is shown diagrammatically in Fig. 156. Let C_1 be the concentration of the simple molecules in phase I, and C_3 , the concentration of simple molecules in phase II and C_2 the concentration of the associated molecules in phase II.

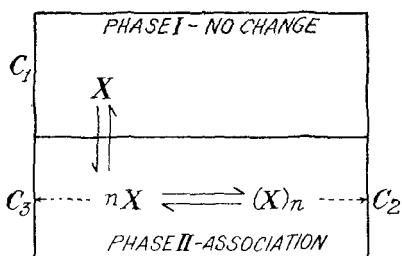


Fig. 156. Distribution diagram for an associated solute.

In such a case we can apply the Distribution Law to the distributed equilibrium and the Mass Law to the change in the second phase. Thus we have :

$$\frac{C_1}{C_3} = K \text{ (Distribution Law)} \quad \dots (i)$$

and
$$\frac{C_2}{(C_3)^n} = K' \text{ (Mass law)} \quad \dots (ii)$$

Taking n th root of equation (ii)

$$\frac{\sqrt[n]{C}}{C_3} = \sqrt[n]{K'} \quad \dots (iii)$$

Dividing equation (i) by (iii) we have

$$\frac{C_1}{\sqrt[n]{C_2}} = \text{a constant}$$

and this equation, if applied, will give a constant partition co-efficient value. The table given on next page illustrates the point.

TABLE—Distribution of Benzoic Acid between water and benzene.

Acid per 10 c.c. water C_1	Acid per 10 c.c. benzene C_2	$K = \frac{C_1}{C^2}$	$K = \frac{C_1}{\sqrt{C_2}}$
0.150	0.242	0.062	0.096
0.190	0.412	0.048	0.096
0.289	0.970	0.030	0.093

Since the value $\frac{C_1}{C_2}$ is not constant, the molecular state of benzoic acid in water and benzene is not the same. A constant value with $\frac{C_1}{\sqrt{C_2}}$ proves that benzoic acid exists in benzene as double molecules i.e., $(C_6H_5COOH)_2$.

(b) **Dissociation in one of the phases.** Suppose the substance dissociates in the second phase and x is the degree of dissociation. Let C_1 be the concentration in phase I and C_2 the concentration in phase II. (Fig. 157.) The distribution law can be applied to undissociated molecules only, of which the concentration in phase II is $C_2(1-x)$.

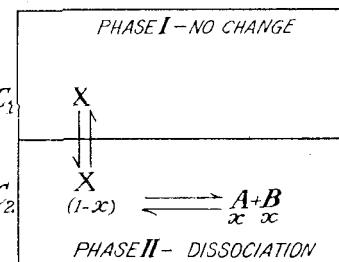


Fig. 157. Distribution when Dissociation occurs.

Therefore we shall modify the simple Distribution Law equation

to $\frac{C_1}{C_2(1-x)} = K$ in such a case.*

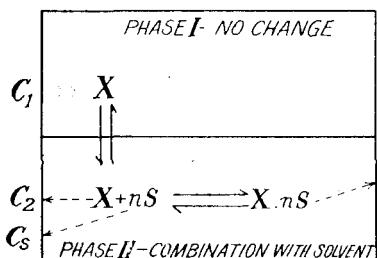


Fig. 158. Combination with one of the solvents.

(c) **Combination with one of the solvents.** This complication causes only a change in the numerical value of the constant.

As represented in Fig. 158, let n molecules of the solvent combine with the distributed molecules in the second phase to form compound molecules $X.nS$.

If C_1 = concentration of the distributed molecules in phase I,

C_2 = concentration of the distributed molecules in phase II,

C_s = concentration of the solvent molecules,

and C_c = concentration of the compound molecules,

then $\frac{C_1}{C_2} = K$ (Distribution Law) ... (i)

and $\frac{C_c}{C_2 \times (C_s)^n} = K_1$ (Law of Mass Action) ... (ii)

*The degree of ionisation can be determined by applying Ostwald's Dilution Law: See Chapter XXII.

The concentration of the solvent molecules C_s is very large and does not vary appreciably in dilute solution : $(C_s)^n$ may, therefore, be taken as constant and the above expression then becomes

$$\frac{C_c}{C_2} = K_1 \times (C_s)^n = K_2 \quad \text{or} \quad 1 + \frac{C_c}{C_2} = 1 + K_2$$

$$\frac{C_s + C_c}{C_2} = 1 + K_2 \quad \dots (iii)$$

Dividing (i) by (iii), we have

$$\frac{C_1}{C_2} \times \frac{C_2}{C_2 + C_c} = \frac{K}{1 + K_2} \quad \text{or} \quad \frac{C_1}{C_2 + C_c} = K_3$$

$(C_2 + C_c)$ is the total concentration of the solute in phase II as determined by analysis. The combination with solvent, therefore, has no influence except that it changes the numerical value of the constant.

NUMERICAL ILLUSTRATION OF DISTRIBUTION LAW

(1) Calculation of Partition Co-efficient :

Example. Succinic acid has the same molecular weight in water and ether. When varying amounts of the acid were shaken with ether-water mixture, the following results were obtained :

Concentration in water layer (C_w) 25·4 33·2 42·6

Concentration in ethereal layer (C_e) 4·2 5·5 7·1

Calculate the partition co-efficient and show that these figures illustrate the Distribution Law.

C_w	C_e	$\frac{C_w}{C_e}$
25·4	4·2	$\frac{25·4}{4·2} = 6·05$
33·2	5·5	$\frac{33·2}{5·5} = 6·04$
42·6	7·1	$\frac{42·6}{7·1} = 6·00$

The constant values of the partition co-efficient illustrate the Distribution Law.

Mean value of the partition co-efficient $\frac{C_w}{C_e} = 6·03$

(2) Calculation of Concentration Equilibrium :

Example 1. In the distribution of succinic acid between ether and water at 15°C, 20 c.cs. of the ethereal layer contain 0·092 gm. of the acid. Find out the weight of the acid present in 50 c.cs. of the aqueous solution in equilibrium with it if the distribution co-efficient for succinic acid between water and ether is 5·2.

Let the weight of succinic acid in aqueous layer be x gms.

Concentration in aqueous layer $= \frac{x}{50}$ gm./c.c.

Concentration in ethereal layer $= \frac{0·092}{20}$ gm./c.c.

$\frac{C_{\text{water}}}{C_{\text{ether}}} = 5·2 = \frac{x}{50} / \frac{0·092}{20}$ or $\frac{20x}{50 \times 0·092} = 5·2$

Whence $x = 1·196$ gms.

Example 2. An aqueous solution of succinic acid at 15°C , containing 0.07 gm. in 10 c.c. is in equilibrium with an ethereal solution which has 0.013 gm. in 10 c.c. The acid has its normal molecular weight in both the solvents. What is the concentration of the ethereal solution which is in equilibrium with an aqueous solution containing 0.024 gm. in 10 c.c.? (Punjab B.Sc., 1935, 42)

$$\text{Concentration in aqueous solution } C_w = \frac{0.07}{10} \text{ gm. per c.c.}$$

$$\text{Concentration in ethereal solution } C_E = \frac{0.013}{10} \text{ gm. per c.c.}$$

$$\text{Partition co-efficient } \frac{C_w}{C_E} = \frac{0.07}{0.013}$$

Concentration in aqueous solution in the second case

$$= \frac{0.024}{10} \text{ gm. per c.c.}$$

Let concentration in ethereal solution in the second case be
 $= x$ gm. per c.c.

$$\therefore \frac{0.024}{10x} = \frac{C_w}{C_E} = \frac{0.07}{0.013}$$

$$0.024 \times 0.013 = 0.7x$$

$$\therefore x = 0.00044 \text{ gm. per c.c.}$$

(3) Calculation of Solubility :

Example 3. At 25° an aqueous solution of iodine containing 0.0516 gram per litre is in equilibrium with a CCl_4 solution containing 4.412 gram per litre. The solubility of iodine in water at 25° is 0.34° gram per litre. Find the solubility in CCl_4 .

$$C_{\text{water}} = 0.0516 \text{ gm./litre}$$

$$C_{\text{CCl}_4} = 4.412 \text{ gm./litre}$$

$$k = \frac{C_{\text{CCl}_4}}{C_{\text{water}}} = \frac{4.412}{0.0516} = 85.5.$$

Applying Partition Law,

$$\frac{\text{Solubility of Iodine in } \text{CCl}_4}{\text{Solubility in water}} =$$

$$\therefore \frac{\text{Solubility of Iodine in } \text{CCl}_4}{0.340} = 85.5$$

$$\text{Hence solubility in } \text{CCl}_4 = 85.5 \times 0.34 = 29.07 \text{ gms. per litre.}$$

(4) Complexity of molecules in one of the solvents :

Example 4. Acetic acid was shaken with water and CCl_4 and following concentrations in gm. mols. per litre were found in the two layers :—

Aqueous layer	5.02	7.98	10.70
CCl_4 layer	0.292	0.725	1.41

Assuming that acetic acid has single molecules in water, show that it has double molecules in CCl_4 solution. (Delhi B.Sc., 1937)

Concentration in aqueous layer	(C_{H_2O})	5.02	7.98	10.70
Concentration in CCl_4 layer	(C_{CCl_4})	0.292	0.725	1.41
	$\frac{C_{H_2O}}{\sqrt{C_{CCl_4}}}$	$\frac{5.02}{\sqrt{0.292}}$	$\frac{7.98}{\sqrt{0.725}}$	$\frac{10.70}{\sqrt{1.41}}$
		$= \frac{5.02}{0.54}$	$= \frac{7.98}{0.85}$	$= \frac{10.70}{1.19}$
		= 9.3	= 9.3	= 9.4

Since $\frac{C_{H_2O}}{\sqrt{C_{CCl_4}}}$ comes out to be a nearly constant quantity, acetic acid

is present in CCl_4 as double molecule.

Distribution in the system Gas-Liquid—Henry's Law.

The distribution law can also be applied to the equilibrium existing between a gas and its solution in a liquid. If C_A is the concentration of the gas in the liquid phase and C_B is the concentration in the gaseous phase, then according to the Distribution Law :

$$\frac{C_A}{C_B} = K$$

But C_A denotes the solubility of the gas and C_B its density which in turn is proportional to the pressure. It follows, therefore, that the solubility of a gas in a liquid is proportional to the pressure of the gas at a certain given temperature.

The above generalisation which we have derived by the application of the Distribution Law was independently enunciated as early as 1805 by William Henry from a study of the solubility of a gas in a liquid and is known as **Henry's Law**.

As in the case of the system Liquid-Liquid, account must be taken of association and dissociation of the gas in the liquid phase and suitable corrections applied in order to get a constant value of the partition co-efficient which in this case is called the *Co-efficient of solubility*. Like all gas laws, Henry's Law shows marked deviations at low temperature and high pressures and is strictly valid only for ideal gases.

Derivation of Distribution Law from kinetic considerations

Consider the distribution of a solute between two immiscible solvents A and B. When a state of equilibrium has been reached, let C_A and C_B be concentrations in the two solvents respectively. At a certain fixed temperature and for the same quantity of the solute, C_A and C_B have the same constant value. It would seem, therefore, that the system is at rest, but it is not so. The molecules of the solute are in constant motion and they are leaving the solvent A and entering B as fast as they are leaving B and entering A. The rate at which the molecules leave a particular solvent is proportional to their concentration in that solvent.

Rate at which the molecules leave A $\propto C_A = k_1 C_A$

Rate at which the molecules leave B $\propto C_B = k_2 C_B$

At equilibrium, the two rates are equal :

$$k_1 C_A = k_2 C_B$$

or

$$\frac{C_A}{C_B} = \frac{k_2}{k_1} = K$$

Conditions under which Distribution Law holds correctly :

Having studied the various aspects of the Distribution Law, we are now in a position to summarise the conditions under which the law is strictly valid.

- (1) The temperature must remain constant throughout the experimental determination.
- (2) The molecular state of the distributed substance must remain the same in both the solvents. If the solute undergoes association or dissociation, the law will apply to that portion of the solute only which is in the same molecular state in both the solvents.
- (3) The two solvents must be mutually immiscible or at any rate their mutual solubility be not altered to an appreciable extent by the addition of the solute.
- (4) The concentration of the solute in the two solvents must be kept as low as possible.

APPLICATIONS OF THE DISTRIBUTION LAW

(1) Determination of molecular weights in different solvents. If the molecular weight of the solute is known in one of the solvents it is possible to determine its molecular weight in another solvent from a study of its distribution ratio between the two. For example benzoic acid forms double molecules in benzene and has single molecules in water since partition co-efficient comes

out to be constant if the equation $\frac{C_{\text{water}}}{\sqrt{C_{\text{benzene}}}} = K$ is employed.

See Table on p. 295.

(2) Distribution Indicators. The distribution ratio of iodine between CS_2 and water is approximately 400 so that if an extremely dilute aqueous solution of iodine is shaken with a drop of CS_2 the concentration of iodine in the latter becomes great enough to produce a violet colour. In this way iodine can be easily detected in solutions too dilute to produce a visible blue colour with starch.

(3) Process of Extraction. In the process of extraction, a substance is removed from solution by shaking it with another immiscible solvent in which it is more soluble. When the aqueous solution of an organic substance is shaken with ether, the distribution ratio of the organic substance being in favour of ether, most of the dissolved substance passes into the ethereal layer and by repeating this process it is possible to extract most of the dissolved organic substance from the aqueous solution. The distribution ratio of organic substances, is, as a rule, in favour of organic solvents which are generally employed for extracting the organic substances from

their aqueous solutions or separating them from inorganic impurities, the distribution ratio of which is almost wholly in favour of water.

The efficiency of the process of extraction depends upon :

(a) **The Distribution Ratio.** For the greater it is in favour of the organic solvent, the greater will be the amount extracted in any one operation.

(b) **The Number of Extractions.** The given quantity of the solvent will extract more of the substance if used in a number of instalments than all at once. Suppose we have 1000 c.cs. of the aqueous solution containing A grams of an organic substance which we want to extract with the help of ether in which it is twice as soluble as in water i.e., its distribution ratio is twice in favour of ether.

Suppose that the total quantity of ether at our disposal is one litre and we use the whole of it in one instalment and w is the amount of the substance extracted.

$$\text{Now } \frac{C_{\text{water}}}{C_{\text{ether}}} = \frac{1}{2}$$

$$\frac{A-w/1000}{w/1000} = \frac{1}{2}$$

$$\text{or } 2A - 2w = w$$

$$\text{or } 3w = 2A$$

$$\text{or } w = \frac{2}{3}A$$

$\therefore 66\cdot6\% \text{ of the solute is removed.}$

Now, let us employ one litre in two instalments of 500 c.c. each and w_1 be the amount extracted in the first instalment. Then :

$$\frac{A-w_1/1000}{w_1/500} = \frac{1}{2}$$

$$\text{or } 2A - 2w_1 = 2w_1$$

$$\text{or } 4w_1 = 2A$$

$$\text{or } w_1 = \frac{1}{2}A$$

... (i)

The amount left in solution now is $0.5A$ and we add the 2nd instalment of 500 c.c. ether which removes w_2 gms. of the substance.

Thus :

$$\frac{0.5A-w_2/1000}{w_2/500} = \frac{1}{2}$$

$$\text{or } A - 2w_2 = 2w_2$$

$$\text{or } A = 4w_2 \text{ or } w_2 = \frac{1}{4}A$$

$$\text{Total substance extracted } = w_1 + w_2 = \frac{1}{2}A + \frac{1}{4}A = \frac{3}{4}A$$

$\therefore 75\cdot0\% \text{ of the solute is removed.}$

Similarly it can be shown that by using four instalments of 250 c.c. of ether it is possible to extract 80.2% of substance. Five instalments of 200 c.c. each would remove 83.8%.

It is clear from the above that it is more advantageous to use a given quantity of the solvent in as many instalments as conveniently possible. It must be understood, however, that it is not possible to remove the whole of the dissolved substance, however, large the number of extractions may be. Every time, the substance distributes itself between the two solvents and a quantity, however small, must always be left behind.

In the **Washing of Precipitates**, we have the distribution of the impurity between water and the precipitate, and for the reason given above, it would be more effective to use small quantities of water and repeat the process a number of times.

In the **Parke's Process** for the desilverisation of lead, we employ zinc for extracting silver from argentiferous lead. Molten zinc and molten lead are immiscible with each other and silver is more soluble in zinc than in lead, the distribution ratio being 300 : 1 in favour of zinc at 800°C. When, therefore, argentiferous lead is heated to 800°C and treated with zinc, silver passes from the lower lead layer to the upper zinc layer and by repeating this process with fresh quantities of zinc most of the silver present in lead can be extracted.

(4) Distribution Law is also helpful in the study of *complexions*, *hydrolysis of salts* and in determining *association, dissociation etc.*

Example 1. 12 gms. of an organic substance A are present in 100 c.cs. of its aqueous solution. How much of it would be left behind after extracting the solution with two successive applications of 50 c.c. ether. The distribution co-efficient of A between water and ether is 2 in favour of ether.

Suppose x gms. of solute are extracted by the first application of 50 c.c. Then,

$$\text{Concentration in ether } \left(C_{\text{ether}} \right) = \frac{x}{50}$$

$$\text{Concentration in water } \left(C_{\text{water}} \right) = \frac{12-x}{100}$$

$$\text{But } \frac{C_{\text{ether}}}{C_{\text{water}}} = 2$$

Substituting the above values,

$$\frac{\frac{x}{50}}{\frac{12-x}{100}} = 2 \quad \therefore \quad \frac{x}{50} \times \frac{100}{12-x} = 2$$

$$\text{i.e.,} \quad x = 6$$

The amount left in aqueous solution after the first application is $(12-6)$ $\equiv 6$ gms.

If x' be the quantity extracted in the second operation, then in this case,

$$\frac{\frac{x'}{50}}{\frac{6-x'}{100}} = 2; \quad \frac{x'}{50} \times \frac{100}{6-x'} \approx 2 \quad \text{or} \quad x' = 3$$

The amount left behind after two extractions $= 12 - (6+3) = 3$ gms.

Example 2. An aqueous solution contains 10 gms. of solute per litre. When 1 litre of the solution is treated with 100 c.cs. of ether, 6 gms. of the solute are extracted. How much more of the solute would be extracted from the aqueous solution by a further 100 c.c. ether? (Assume that the molecular state of the solute is the same in the ether and water).

In the first case, concentration in ether $\left(C_{\text{ether}} \right) = \frac{6}{100}$

" " water $\left(C_{\text{water}} \right) = \frac{10-6}{1000} = \frac{4}{1000}$

$$\frac{C_{\text{ether}}}{C_{\text{water}}} = \frac{6}{100} \times \frac{1000}{4} \approx 15.$$

Suppose x is the amount of the substance extracted with the further 100 c.c. ether. In this case,

$$\begin{aligned} \frac{x}{100} &= 15 \\ \frac{4-x}{100} &= 15 \\ 10x &= 15(4-x) \\ &= 60 - 15x \\ 25x &= 60 \\ x &= 2.4 \end{aligned}$$

QUESTIONS AND PROBLEMS

1. Explain clearly the difference between homogeneous and heterogeneous equilibria. Give examples of each type.

2. Explain concisely what you understand by (a) Henry's Law and (b) law of partition co-efficient. Indicate the conditions under which they correctly represent the observed facts.

An aqueous solution of succinic acid at 15°C containing 0.07 gm. in 10 c.c. is in equilibrium with an ethereal solution containing 0.013 gm. in 10 c.c. Succinic acid has its normal molecular weight in both solvents. What is the concentration of an ethereal solution which is in equilibrium with an aqueous solution containing 0.024 gm. in 10 c.c.?

3. Explain what is meant by the distribution law for a substance between two immiscible solvents. Show how the distribution of a solute may be used to investigate molecular complexity.

The solubility of a substance is twice as great in ether as in water. Compare the quantities extracted from 100 c.c. of aqueous solution by (a) 100 c.c. of ether in a single operation, (b) successive applications of 50 c.c. ether.

4. The distribution co-efficient of H_2O_2 between amyl alcohol and water is 1 : 7. A solution of H_2O_2 in amyl alcohol contained 10 gm. of peroxide in 100 c.c. Calculate the amount of H_2O_2 extracted from 100 c.c. of the solution by 200 c.c. of water: (a) when used in one quantity (b) when used in two quantities of 100 c.c. each.

5. Derive the Distribution Law from kinetic considerations. What are its important applications?

6. From the physico-chemical standpoint, discuss the desilverisation of lead by Parke's Process.

7. Explain the theory of the extraction of solids and liquids from their solution with special reference to the assumptions made therein. Also explain the term "Partition co-efficient".

If the volume of an aqueous solution of benzoic acid of known strength be one litre and that of the ether added each time be 200 c.c., find the quantity of the acid which will be left in the water at the end of the third extraction. The partition co-efficient of benzoic acid between water and ether is 1/80.

8. Experiments on the ratio of distribution of phenol between water and chloroform gave the following results:

Aq. solution	0.074	0.163	0.274	0.436
CHCl_3	"	0.254	0.761	0.185

What conclusions can be drawn from these results concerning the molecular condition of phenol in CHCl_3 solution?

9. Discuss in detail the conditions under which the Distribution Law holds correct.

10. State Nernst's law of partition. Describe with all experimental details how you would determine the partition co-efficient of a solute between two immiscible solvents. What light do such measurements throw on the molecular state of the solute?

11. At 25° an aqueous solution of iodine containing 0.0516 gm. per litre is in equilibrium with a CCl_4 solution containing 4.412 gm. iodine per litre. If

the solubility of iodine in water at 25° is 0.340 gm. per litre, what is the solubility in CCl_4 ?

12. The following data show the concentrations of solutions of iodine in water and carbon disulphide in equilibrium at 18° :

Grams iodine per 10 c.c.	CS_2	1.74	1.29	0.63	0.41
" "	H_2O	0.0041	0.0032	0.0016	0.0010

Show that these results are in agreement with the Distribution Law.

13. A certain organic substance is to be extracted with ether from aqueous solution it being four times more soluble in ether. Compare the loss involved by extracting with an equal volume of ether with the loss when extracted three times with one-third its volume of ether.

Would this calculation be correct if this substance existed in double molecules in ether but in single molecules in water?

14. A solution of 10 gm. of A in 100 gm. water is shaken (a) with 100 gm. ether, (b) with five successive quantities of 20 gm. ether. Calculate the total amount of A removed from the aqueous solution in the two cases. The distribution ratio of ether : water of A is 5.

15. In the distribution of succinic acid between water and ether the concentrations of the acid in the two layers are :

C_{ether}	0.121	0.070	0.024	gram in 10 c.c.
C_{water}	0.022	0.013	0.0046	" " " "

In the partition of the same substance between water and benzene the concentrations of the acid are :

C_{water}	0.0150	0.0195	0.0289	gram in 10 c.c.
C_{benzene}	0.242	0.412	0.970	" " " "

Succinic acid has its normal molecular weight in water. What is its molecular weight (a) in ether, (b) in benzene?

16. Describe the law relating to the distribution of a substance between two liquid phases and discuss its practical applications.

17. Explain what is meant by the Distribution Law for a substance between two immiscible solvents. Show its relation to Henry's Law regarding the solubility of gases in liquids.

Calculate how much succinic acid would be extracted from 100 c.c. of water containing 5 gms. of the acid if extracted with 50 c.c. of ether. The partition co-efficient of succinic acid between water and ether is 5.5.

18. State the law which governs the distribution of a common solute between two immiscible solvents. Show how a study of the distribution of iodine (i) between carbon disulphide and water and (ii) between carbon disulphide and an aqueous solution of potassium iodide, can be used to determine the equilibrium constant of the action $\text{KI}_3 \rightleftharpoons \text{KI} + \text{I}_2$. (Travancore B.Sc., 1953)

19. What is meant by the term "partition co-efficient"? Describe the determination of the partition co-efficient of acetic acid between ether and water. Explain how the molecular complexity of benzoic acid in benzene can be determined. (Rangoon B.Sc., 1955)

20. State (a) the Distribution Law. Discuss the limitations and practical applications of one of these laws. (Mysore B.Sc., 1956)

21. State the Distribution Law. How is it modified when the solute undergoes association or dissociation in one of the solvents?

In the distribution of a solute between water (C_1) and chloroform (C_2), the following results were obtained :—

	C_1	C_2
	0.0160	0.338
	0.0237	0.753

What information do you gather regarding the molecular state of the solute in chloroform.
(Jammu & Kashmir B.Sc., 1957)

22. What is meant by partition co-efficient of a substance between two solvents?

A solution of hydrogen peroxide in amyl alcohol containing 20 gms. of hydrogen peroxide in 200 c.c. is to be extracted with 200 c.c. of water (a) in one time (b) when used in two quantities of 100 c.c. each. Calculate the amount of hydrogen peroxide extracted in each case. The partition co-efficient of hydrogen peroxide between amyl alcohol and water is 1.7. (Rangoon B.Sc., 1958)

23. State the law governing the distribution of a substance between two non-miscible solvents.

Succinic acid has its normal molecular weight in water. In this distribution of the acid between water and benzene, the concentrations in the aqueous and the benzene layers were found to be C_1 and C_2 respectively.

C_1	0.150	0.195	0.289	gm. per 100 c.c.
C_2	2.420	4.120	9.700	" " "

Calculate the molecular weight of succinic acid in benzene.

(Osmania B.Sc., 1959)

24. Explain Distribution Law. Succinic acid was shaken in a mixture of water and ether. The concentrations of the acid in the two layers are as follows (per 10 c.c. of the solution). Find out the partition co-efficient.

In water layer	0.0244	0.071	0.121
In ether layer	0.0046	0.013	0.022

If succinic acid (CH_2COOH) has normal molecular weight, i.e., 118 in water, find its molecular weight in ether. (Lucknow B.Sc., 1959)

ANSWERS

- | | |
|------------------------------------|------------------------------|
| 2. 0.44 gm./litre. | 3. 66.66% and 75.0% |
| 4. 9.33 : 9.843 | 7. 0.0002 gm. |
| 8. It exists as double molecules. | 13. 20% : 7.9%. |
| 11. 29.07 gm. per litre. | 14. (a) 8.3 gm., (b) 9.7 gm. |
| 15. (a) 118, (b) 236. | 17. 0.417 gm. |
| 21. It exists as double molecules. | 22. 17.5 gm. ; 19 gm. |
| 23. 236. | 24. 543 ; 118. |

CHAPTER XVIII

THE PHASE RULE

THE STATEMENT

The Phase Rule is an important generalisation dealing with the behaviour of heterogeneous systems.* In general it may be said that with the application of *phase rule* it is possible to predict qualitatively, by means of a diagram, the effect of changing pressure, temperature and concentration on a heterogeneous system in equilibrium. This relationship governing all heterogeneous equilibria was first discovered as early as 1874 by an American Physicist, Willard Gibbs. Gibbs' Phase Rule is free from flaws and limitations which are a common feature of all other generalizations of Physical Chemistry based on hypothetical assumptions as to the nature of the constitution of matter. It may be stated mathematically as follows:

$$F = C - P + 2\ddagger$$

where F is the number of *degrees of freedom*, C is the number of *components* and P is the number of *phases* of the system. The terms 'phase', 'component,' and 'degree of freedom' involved in the statement of the Phase Rule have a special significance and a clear understanding of these terms is essential before we proceed further with the subject.

1. Phases. A heterogeneous system is made up of two or more different parts each of which is homogeneous in itself and is separated from others by bounding surfaces. *These homogeneous, physically distinct, and mechanically separable portions of a heterogeneous system in equilibrium* are termed **Phases**. Thus with freezing water we have three phases, *viz.*, ice, water and vapour in equilibrium.

Mixtures of two or more gases are homogeneous and constitute one phase only. Two immiscible liquids in contact, form two different phases. A heterogeneous mixture of solid substances consists of as many phases as there are substances present. Thus calcium carbonate decomposes by heat giving calcium oxide and carbon dioxide. $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$ and at the equilibrium we have two solid phases, *viz.*, calcium carbonate and oxide and one gas phase, carbon dioxide.

2. Components. By the term *components* of a system we do not mean the number of the *constituents i.e.*, chemical individuals present in the system. As employed in the statement of the Phase

***Homogeneous system** is one which is uniform throughout in physical and chemical properties, *e.g.*, solution of sodium chloride in water; the system $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$. **Heterogeneous system** on the other hand, is one which consists of parts which have different physical properties, *e.g.*, Ice-water vapour system, in which the three portions are physically distinct and can be mechanically separated from one another.

†Phase rule equation is sometimes also written as $F = n - r + 2$ where n is the number of components and r the number of phases.

Rule the **Components** are defined as the MINIMUM NUMBER of independently variable constituents by means of which the composition of each phase can be expressed in the form of an equation. Zero and negative quantities of the components are permissible when expressing the composition of a phase in terms of the components.

Let us make the definition clear by applying it to some simple cases.

(i) With FREEZING WATER we have three phases, ice, water and vapour in equilibrium. These three phases are different physical forms of the same chemical substance H_2O which is, therefore, the only constituent present. Although hydrogen and oxygen enter into the constitution of water they cannot be regarded as components, firstly because they are combined in definite proportions (2 : 1) to form water and their amounts *cannot be* independently varied and secondly, because they do not take part in the equilibrium. The system ice-water-vapour is, therefore, a *one-component* system.

(ii) In the DECOMPOSITION OF CALCIUM CARBONATE ($\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$), as already pointed out, we have three phases, namely, solid calcium carbonate, solid calcium oxide and carbon dioxide gas. There are in all three constituents CaCO_3 , CaO , CO_2 taking part in the system. None of these constituents can be used to express the composition of all the phases. Now taking any two of the constituents as components and making the quantity of one of them zero or negative according to need, we can express the composition of all the phases by the following equations :—

(a) When CaO and CO_2 are selected as components :

Phase	Components
CaCO_3	$\text{CaO} + \text{CO}_2$
CaO	$\text{CaO} + \text{CO}_2$
CO_2	$\text{CaO} + \text{CO}_2$

(b) When CaCO_3 and CO_2 are taken as components :

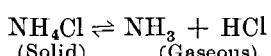
Phase	Components
CaCO_3	$\text{CaCO}_3 + 0 \text{ CO}_2$
CaO	$\text{CaCO}_3 - \text{CO}_2$
CO_2	$0 \text{ CaCO}_3 + \text{CO}_2$

(c) When CaCO_3 and CaO are chosen as components :

Phase	Components
CaCO_3	$\text{CaCO}_3 + 0 \text{ CaO}$
CaO	$0 \text{ CaCO}_3 + \text{CaO}$
CO_2	$\text{CaCO}_3 - \text{CaO}$

Since at least two of the three constituents are needed to represent the composition of all the phases, the system $\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$ is a *two-component system*.

(iii) The case of the dissociation of ammonium chloride is a bit different. When slowly heated, it changes into vapour and the vapour consists of a *homogeneous mixture* of ammonia and hydrogen chloride.



There are two phases present *viz.*, solid NH_4Cl and the gaseous homogeneous mixture which consists of the constituents of ammonium chloride present in the same proportion in which they are

present in the solid state. The Phase Rule does not make a distinction between a chemical compound and its constituents present in the same proportion so long as that mixture is homogeneous.

The composition of both the phases can, therefore, be represented by the same chemical individual NH_4Cl and the system will be a one-component system.

It will become a two-component system the moment NH_3 and HCl are not present in equivalent proportions.

3. Degree of Freedom or Variance of the system. A system in equilibrium is influenced by such factors as pressure, temperature and composition of the phases. *The minimum number of the variable factors, pressure, temperature, and composition of the phases which must be arbitrarily fixed in order that the condition of the system may be completely defined, is termed the Degree of Freedom or Variance of the system.* The following will make the definition clear :—

(i) A gaseous system consisting of two or more gases is completely defined when its composition, temperature and pressure are given. Thus a mixture containing 50% each of CO_2 and N_2 at 30°C and 780 mm. pressure is perfectly defined and any other sample of a mixture of the two gases made up according to the same conditions will be identical with the first one in all respects. The mixture of gases mentioned above is obviously a system with three degrees of freedom.

(ii) For the given sample of any one gas $PV = RT$, and if pressure and temperature be fixed, the volume can have only one definite value. Thus in this case only two factors have got to be fixed up in order to describe the system with two degrees of freedom.

(iii) The system consisting of saturated sodium chloride solution in contact with solid salt and vapour is completely defined if we mention only temperature, since the solubility of sodium chloride (hence the composition of solution) and vapour pressure have a definite value at a certain temperature. Hence it is a system with one degree of freedom. Similarly for the system water in equilibrium with its vapour, the fixing of temperature alone is enough and hence it has one degree of freedom.

(iv) For the system ice-water-vapour no further statement of conditions is necessary. The three phases can be in equilibrium only at one definite temperature and pressure. The system will have no degree of freedom.

We may also describe the system as being *non-variant, univariant bivariant and trivariant* according as the number of degrees of freedom is zero, one, two or three respectively.

ONE COMPONENT SYSTEMS

The conditions of equilibrium in a system can very well be studied by means of the phase rule equation $F = C - P + 2$. For a clear understanding of Phase Rule and its applications, the graphic representation has, however, proved more useful. For a one-component system the maximum degrees of freedom are 2 and all such systems can be completely described by stating pressure and

temperature variables only, concentration being out of question as there is only one constituent present in all the phases. The equilibrium conditions in a one-component system can conveniently be represented with the help of diagrams taking pressure and temperature as the two axes. Such diagrams are commonly called pressure temperature ($p-t$) diagrams. In these diagrams, areas will represent bivariant systems as the fixing up of both pressure and temperature is essential to define the system completely at any point in the area. A line will represent a monovariant system since at any point on the line the equilibrium could be defined by simply fixing up either the pressure or temperature, the other variable being fixed up by itself. A point on the diagram with three phases in contact will represent an invariant system as the system here is defined completely by itself and no further statement of either temperature or pressure is necessary.

THE WATER SYSTEM

This is a **one-component** system, H_2O being the only chemical individual involved. The **three phases** taking part in the system

are ice, water and vapour. The number of these phases which can exist in equilibrium at any time depends on the conditions of temperature and pressure. These conditions have been determined by direct experimental measurements and are summarised in the pressure-temperature diagram. (Fig. 159).

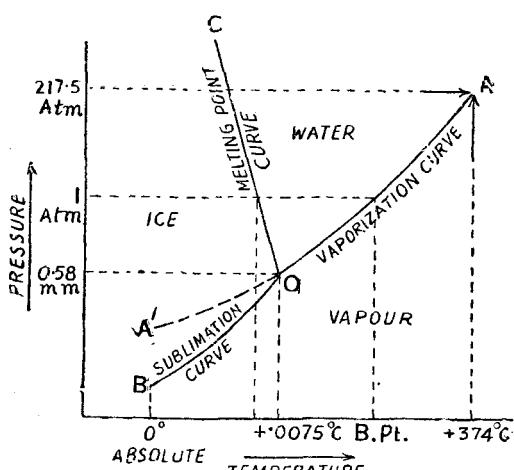


Fig. 159. The Water System
(not drawn to scale).

The equilibrium diagram consists of three curves OA, OB and OC all meeting at the point O. These curves divide the diagram into areas AOC, AOB and BOC.

When we examine the diagram with the help of the Phase Rule, we see that the following systems are possible :—

Areas (Bivariant Systems) :

The areas give the conditions of temperature and pressure under which single phases—ice, water and vapour are capable of stable existence. To define the system completely at any point in the area it is necessary to specify both the pressure and temperature. This follows from the fact that the location of a point in an area requires the fixing up of abscissa as well as the ordinate. Thus the system *vapour, water or ice* represented by the areas have 2 degrees of freedom. By the application of the phase rule equation also, we arrive at the same conclusion, $F = C - P + 2 = 1 - 1 + 2 = 2$.

Curves (Univariant Systems) :

(i) *Curve OA, the Vaporisation Curve or the Vapour Pressure Curve.* This curve shows a series of pressures and temperatures at which water and its vapour are in equilibrium, in a closed vessel from which all the air has been removed. To describe the system at any time, it is necessary to state either temperature or pressure. For example, at atmospheric pressure, water and vapour can be in equilibrium at one temperature only *i.e.*, the boiling point of water. In other words, pressure being fixed, the statement of temperature is unnecessary and is not required to define the system completely. The system water-vapour is, therefore, a univariant system. This also follows from the phase rule equation, $F=C-P+2=1-2+2=1$.

The upper end of the vaporisation curve is marked by the critical point A, since above this temperature the liquid and vapour phases merge into each other and one homogeneous phase results. At the lower end, the curve would normally terminate at the point O, where water freezes to ice. But by carefully eliminating solid particles, which induce crystallisation, water may be cooled far below its freezing point without the separation of ice, and thus by preventing water from freezing at the point O it is possible to follow the vapour pressure curve to even below the normal freezing point. The dotted curve OA' indicates the vapour pressure curve of 'supercooled' water. It represents a metastable equilibrium and is placed above the curve OB in the diagram as the *vapour pressure of the metastable phase at any point is greater than that of the stable phase*. If super-cooled water and solid ice are imagined to be separated from actual contact except by means of the vapour (Fig. 160) it is easy to understand why the unstable phase super-cooled water, will at once change into solid ice even at the slightest disturbance.

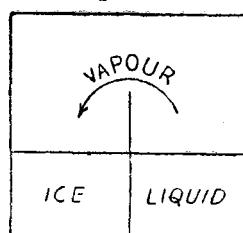


Fig. 160.

(ii) *Curve OB, the Sublimation Curve.* It is observed that snow disappears in frosty weather when the atmospheric temperature is not high enough to melt it. This fact proves that ice has vapour pressure, though very small. This vapour pressure is described as the *sublimation pressure* of ice and the curve OB representing the conditions when ice and vapour are in equilibrium is named as the **Sublimation Curve**. It may be noted from the diagram that this curve is not a prolongation of the curve OA but falls off more steeply. All that has been said in regard to the system liquid \rightleftharpoons vapour, also applies to the system ice \rightleftharpoons vapour. At any temperature arbitrarily fixed, the vapour pressure can have only one value and *vice versa*. The curve OB thus represents a univariant system.

The two curves OA and OB meet at the point O. This point lies on the curve OA where water and vapour are in equilibrium and also it lies on the curve OB where ice and vapour are in equilibrium, and hence all the three phases ice, water and vapour are in equilibrium at the point O which is called the **Triple point**. This point represents the freezing point of water when the solid ice and

water are in equilibrium under a pressure of 4.58 mm. equal to their vapour pressure. It should be noted clearly that the triple point is not identical with the melting point of ice, 0°C as ordinarily determined in an open vessel under atmospheric pressure. Since a decrease in the pressure equal to one atmosphere raises the melting point of ice by about 0.008°, it follows that melting point of ice at the vapour pressure of the triple point will be 0.0075° approximately.

At the lower limit the curve OB is assumed to terminate at absolute zero (-273°) where no vapour can be present and only ice is left.

(iii) *Curve OC, the Freezing Point Curve, the Fusion Curve or the Melting Point Curve.* This curve shows the effect of pressure on the melting point of ice. The line OC is somewhat inclined towards the pressure axis indicating that the melting point of ice is slightly lowered by increase of pressure.*

Along the curve OC there are two phases : ice and water in equilibrium and hence one degree of freedom.

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

The upper limit of the Curve OC as shown by Tamman and Bridgeman (1910) is marked by the appearance of four other crystalline forms of ordinary ice at high pressure. The different forms of ice are named ice I (ordinary ice), ice II, ice III, ice V and ice VI. The various systems formed as a result of the appearance of these phases are described in a separate diagram (Fig. 161) for a detailed study of

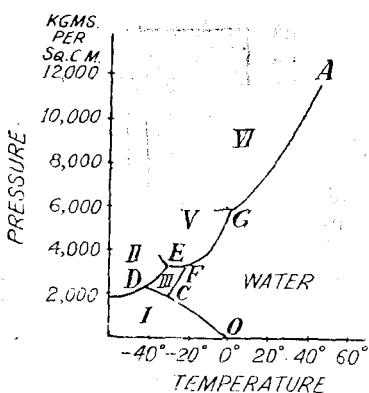


Fig. 161. Phase Rule Diagram for Ice.

which a higher book on Physical Chemistry can be consulted.

The Triple Point

The point O has a special importance. It expresses the only temperature and pressure at which solid, liquid and vapour can exist in equilibrium. If we vary either the pressure or the temperature from the values for this point, one of the three phases will vanish. Thus if the pressure is raised without altering the temperature we shall pass into the water area and the solid and vapour will both change into liquid. Conversely, if the pressure be lowered, both ice and water will change to vapour, since we shall have passed into the area which belongs exclusively to the vapour. It is possible, however, by varying pressure and temperature together to move along one of the curves OA, OB, OC, thus preserving two out of the three states of aggregation.

*This can be predicted from Le Chatelier's Principle according to which an increase in pressure will cause the equilibrium water—ice to shift in such a direction that there is a decrease in volume and since a volume decrease will take place when some ice melts into water taking latent heat of ice from within the system, the melting point of ice will be lowered by an increase of pressure.

It is clear from above that none of the two variables, pressure or temperature, can be varied without one of the phases disappearing from the system and hence the system at the point O has no degree of freedom. This inference also follows from the phase rule equation, $F = C - P + f = 1 - 3 + 2 = 0$.

The main features of the phase rule diagram of the water system are summarised in the table below :

TABLE : THE WATER SYSTEM : COMPONENT = 1

Name of the system as represented in the diagram	Phases in equilibrium	Degree of freedom (variance) ($F = C - P + f$)
<i>AREAS</i>		
(i) AOC, labelled 'WATER'	Water	Two (<i>Bivariant</i>) $F = 1 - 1 + 2 = 1$
(ii) AOB, labelled 'VAPOUR'	Vapour	"
(iii) BOC, labelled 'ICE'	Ice	"
<i>CURVES</i>		
(i) OA, the 'Vapourisation Curve'	Water and Vapour	One (<i>Univariant</i>) $F = 1 - 2 + 2 = 1$
(ii) OB, the 'Sublimation Curve'	Ice and Vapour	"
(iii) OC, the 'Melting Point Curve'	Ice and Water	"
<i>POINT</i> O, the 'Triple Point'		
O, the 'Triple Point'	Ice, Water and Vapour	Zero (<i>Invariant</i>) $F = 1 - 3 + 2 = 0$

THE SULPHUR SYSTEM

It is also a *one component system* as the only chemical individual representing the various phases is sulphur itself.

Sulphur can exist in the following *four phases* :—

- (i) Rhombic Sulphur ... (S_R)—Octahedral crystals.
- (ii) Monoclinic Sulphur ... (S_M)—Prismatic crystals.
- (iii) Sulphur vapour ... (S_V)
- (iv) Liquid Sulphur ... (S_L)

At 95.6° , the two crystalline forms, rhombic and monoclinic sulphur are in equilibrium with each other i.e., $S_R \rightleftharpoons S_M$. This is known as the **Transition Temperature** or *Transition Point*. At this temperature both S_R and S_M are stable. Below this temperature S_R is stable and S_M gradually passes into S_R .

Characteristics of the Transition Point. A transition point is as definite as a melting point and many of them have been determined correct to one-thousandth of a degree. Just like the melting point, the transition point is affected by pressure and this effect

can be qualitatively ascertained by the application of Le Chatelier's Principle. (See discussion of Transition Curve). But the transition from one crystalline form to another naturally takes place much more slowly than melting which is sharp and well-defined.

If enough time for the transition $S_R \rightarrow S_M$ is not allowed i.e., S_R is heated rapidly, it is possible to heat it to a temperature well above its transition point without getting S_M . Thus it is made possible to study the properties of metastable S_R right up to 115° , its melting point. With a melting point, superheating is not possible, for the moment that point is reached the whole of the solid changes into liquid state. The complete equilibrium diagram of

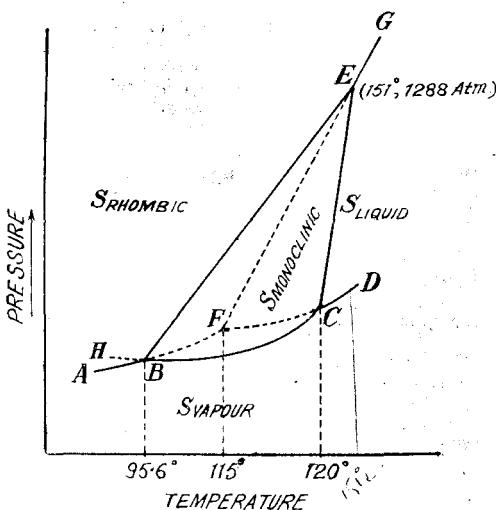


Fig. 162. Pressure-temperature diagram of sulphur (not drawn to scale).

the sulphur system is given in Fig. 162.

An examination of the diagram with the help of phase rule shows that the following systems are possible :—

Areas (Bivariant Systems) :

Just as in the case of water system, the areas represent the conditions for the stable existence of single phases. Monoclinic sulphur (S_M) is of particular interest, as it can exist in stable form only within certain narrow limits, its area being bound by curves BE, BC and CE on all sides. At any point outside this area, monoclinic sulphur can exist only in a metastable condition.

Curves (Univariant Systems) :

(1) **The Curve AB (BF).** **Vapour pressure curve of rhombic sulphur.** Along this curve S_R and S_V are in equilibrium and the degree of freedom is one. Although the vapour pressure of solid sulphur is comparatively small, direct measurements have been made down to about 50°C . Thus the point A corresponds to the lower limit up to which the vapour pressure of rhombic sulphur is measurable.

Point B (95.6°) is the transition point. Allowed sufficient time, about this point S_R changes to S_M and then this point becomes the upper limit of the vapour pressure of stable S_R . If heating is rapid the transition from one crystalline form to another is not possible and we have the vapour pressure curve of S_R extending even beyond B till we reach the point F (115°), the melting point of S_R . As already pointed out, S_R is metastable above the transition point,

the dotted curve BF is the metastable curve of S_R and point F is the melting point of metastable S_R .

(2) **The curve BC, vapour pressure curve of monoclinic sulphur.** S_M and S_v exist in equilibrium along this curve and the degree of freedom is one. This curve meets the vapour pressure curve of S_R at B. Point B being common to both the curves here S_R and S_M can co-exist with their vapour. It is a triple point and is non-variant.

The other end of the vapour-pressure curve of S_M is marked by the point C (120°), the melting point of S_M .

The dotted curve BH is a prolongation of the curve CB and represents the metastable vapour pressure curve of S_M . Here again, it should be noted that *the metastable phase has the higher vapour pressure than the stable phase at the same temperature*.

(3) **The curve CD, (CF), vapour pressure curve of liquid sulphur.** We have S_L and S_v in equilibrium along this curve and the degree of freedom is one.

The curve CD which is the vapour pressure curve of S_L meets the curve BC at C. At C we have S_M , S_L and S_v in equilibrium. This is a triple point with no degree of freedom. At the other end, the curve CD would terminate at the critical point beyond which only one phase S_v could exist.

The dotted curve CF is a continuation of CD and represents the metastable vapourisation curve of S_L . It corresponds with the metastable curve of supercooled water. The metastable curves CF and BF meet at the point F, which is the melting point of metastable S_R . Here metastable S_R , metastable S_L , and vapour co-exist. This is metastable triple point.

(4) **The curve BE, the transition curve.** It represents the effect of pressure on the transition point B. This curve is inclined away from the pressure axis showing thereby that the transition point is raised by the application of pressure, which may be explained as follows :—

The change from rhombic sulphur to monoclinic sulphur is accompanied by an absorption of heat and by an increase of volume (Density of S_R = 2.04 gm./c.c. and S_M = 1.9 gm./c.c.), i.e., $S_R + Q$ (heat energy) $\rightleftharpoons S_M$.

According to Le Chatelier's Principle the increase of pressure will shift the equilibrium in a direction in which decrease of volume takes place. Thus with the increase of pressure the above equilibrium will be displaced towards the left forming more and more of S_R and since the formation of S_R is accompanied by an evolution of heat the transition temperature will be raised by the increase of pressure.

The transition curve BE terminates at the point E beyond which S_M disappears.

(5) **The curve CE, the fusion or melting point curve of S_M .** This curve is also inclined away from the pressure axis indicating that the melting point of S_M is raised by the increase of pressure. This is due to the fact that S_M melts taking its heat of fusion and expansion in volume follows, i.e., $S_M + Q$ (heat energy) $\rightleftharpoons S_L$.

According to Le Chatelier's Principle the increase of pressure will press the back-reaction and since this would result in the liberation of heat, the melting point would be raised.

The curves CE and BE are both inclined away from the pressure axis but since their inclinations are different they meet at the point E. This point corresponds to a temperature 151.6° and 1,288 atmospheres pressure. It is a triple point with three phases S_R , S_M and S_L in equilibrium. The curve CE ends at E as beyond this point S_M ceases to exist in a stable condition.

(6) *The curve (FE) EG, the melting point curve of rhombic sulphur.* The curve FE represents the melting point or fusion curve of metastable S_R . It passes through the triple point E and then becomes a stable fusion curve. Thus the curve EG is a continuation of FE but differs from it in as much as it is now a stable fusion curve of rhombic sulphur. This part of the curve is supported by experiment as follows :—

TABLE. THE SULPHUR SYSTEM : COMPONENT = 1
(Metastable systems are given in brackets)

Name of the System as represented in the diagram	Phases in equilibrium	Degree of freedom (Variance) $F = C - P + 2$
AREAS		
(i) ABEG	S_R	Two (<i>Bivariant</i>) $F = 1 - 1 + 2 = 2$
(ii) BEG	S_M	"
(iii) DCEG	S_L	"
(iv) ABCD	S_V	"
CURVES		
(i) AB (BF)	$S_R — S_V$	One (<i>Univariant</i>) $F = 1 - 2 + 2 = 1$
(ii) BC (BH)	$S_M — S_V$	"
(iii) CD (CF)	$S_L — S_V$	"
(iv) FE (EG)	$S_R — S_L$	"
(v) BE	$S_R — S_M$	"
(vi) CE	$S_M — S_L$	"
TRIPLE POINTS		
(i) B	$S_R — S_M — S_V$	Zero (<i>Invariant</i>) $F = 1 - 3 + 2 = 0$
(ii) C	$S_M — S_L — S_V$	"
(iii) E	$S_R — S_M — S_L$	"
(iv) (F)	$S_R — S_L — S_V$	"

It is well-known that under ordinary conditions it is S_M which appears as crystals when liquid sulphur is allowed to cool but at temperatures above 151° and under greater pressures than 1,288 atmospheres, only S_R crystallises. Thus the curve EG represents the effect of the increase of pressure on the true stable melting point of S_R which under ordinary conditions has no stable melting point.

TWO-COMPONENT SYSTEMS

In a 2-component system when both the components exist in one phase the degree of freedom becomes three, ($F = 2 - 1 + 2$).

In such a system not only the pressure and temperature but the composition of the phase may also alter. With three variable factors influencing the equilibrium, the question of graphic representation becomes much more complicated. Pressure, temperature, and composition could be represented by three axes at right angles yielding space models or solid equilibrium diagrams. For the sake of having simple plane diagrams we will consider only two of the variable factors at a time, the third one being regarded as constant. In this manner we can have

- (i) pressure-temperature (*p-t*) diagrams.
- (ii) temperature-composition (*t-c*) diagrams.
- (iii) composition-pressure (*c-p*) diagrams.

SYSTEM SILVER-LEAD

Molten silver and lead mix together in all proportions giving a homogeneous solution. They do not react chemically to form compounds and the **four possible phases** taking part in the equilibrium are (i) solid silver, (ii) solid lead, (iii) solution of silver and lead, and (iv) vapour.

Ag-Pb system is evidently a **two-component system** as the composition of the various phases can be represented by the two chemical individuals Ag and Pb.

Boiling points of the two metals being considerably high, in this system the gaseous phase is practically absent and, therefore, pressure can have no effect on equilibrium. Thus in such a case we need consider only the two remaining variables, the temperature and concentration. The complete *t-c* diagram of the system is given in Fig. 163.

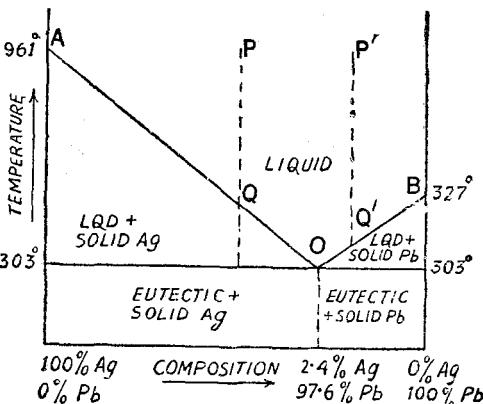


Fig. 163. *t-c* diagram of system Ag-Pb
(not drawn to scale).

The equilibrium diagram consists of two curves OA and OB. The curve OA shows the effect of the addition of lead on the melting point of pure silver and may be called as the *melting point or freezing point curve of silver*. The curve OB likewise shows the effect of the addition of silver on the melting point of pure lead and is named as the *melting-point or freezing point curve of lead*.

The Freezing Point Curve OA. The point A represents the melting point of silver where pure solid silver, liquid and vapour co-exist. The melting point of silver falls gradually along the curve AO with the continuous addition of lead. The lowest point attainable in this manner, is O as the solution now becomes saturated with respect to lead and further addition of lead causes no increase in the concentration of lead but simply separates as solid phase.

All along the curve AO there are 3 phases, solid silver, liquid and vapour in equilibrium, therefore, $F = C - P + 2 = 2 - 3 + 2 = 1$, that is, the system is univariant.

The Freezing Point Curve OB. The point B represents the melting point of lead with the continuous increase of silver in solution. The lowest point attainable in this manner, is O as the solution now is saturated with respect to silver and any more silver added deposits itself as the solid phase.

The curve OB represents a 2-component system consisting of the phases solid lead, solution and vapour. According to the phase rule equation, $F = C - P + 2 = 2 - 3 + 2 = 1$, and thus the system is univariant.

The Eutectic Point. The two curves OA and OB meet at the point O. Point O, being common to both the curves, represents the

conditions under which solid silver, solid lead, solution, and vapour co-exist. The degree of freedom here is zero, $F = 2 - 4 + 2 = 0$, and the system is non-variant. The point O lies at a temperature which is lower than the melting point of either component. Thus an alloy of silver and lead corresponding to point O (97.6% Pb., 2.4% Ag) will melt at 303°, a temperature lower than the melting point of silver (961°) and lead (327°). The point O which can be attained in the above manner for any two metals is called the *eutectic point* (Greek *eutectes* = easy melting). The temperature and composition corresponding to this point is called the **eutectic temperature** and **eutectic composition** respectively.

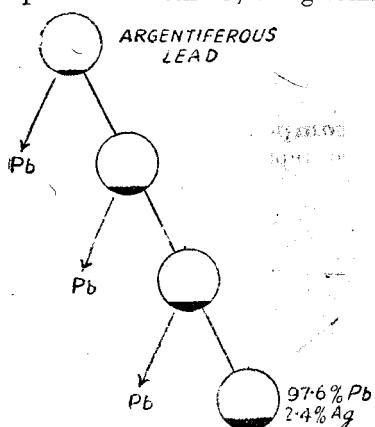


Fig. 164. Illustrating the gradual increase in the proportion of Ag on cooling of argentiferous lead.

Pattinson's process for the desilverisation of lead is based on the facts contained in the diagram (Fig. 164). Let P' represent the molten argentiferous lead containing a very small amount of silver in it. On cooling we travel along the dotted line P'Q' till the temperature corresponding to point Q' on the curve OB, is reached when lead begins to separate. On further lowering of temperature more of lead separates as solid phase till the eutectic point O is reached where an alloy containing about 2.4% of silver is obtained. This is then subjected to cupellation.

SYSTEM POTASSIUM IODIDE-WATER

Since potassium iodide does not form hydrates, the **four phases** taking part in the system KI—H₂O will be solid KI, solution, ice and vapour. It is clearly a **2-component system** as the two constituents KI and H₂O only can represent the composition of the various phases. There are **three degrees of freedom** as in addition to the

temperature and pressure, concentration of the solution may also be varied.

The equilibrium conditions are depicted in the *t-c* diagram (Fig. 165), pressure being considered constant at 1 atmosphere.

The curve AO shows the effect of the addition of KI on freezing point of water and may be called the *freezing point curve*. The curve OB indicates the increase of KI in saturated solution with rise of temperature and is named the *solubility curve* of KI. The area above the curves AO and OB represents a solution of KI in water.

The Freezing Point Curve AO. The point A is the freezing point of water under normal conditions. Here the equilibrium exists between ice, water and vapour.

If now a little KI is added the freezing point is lowered.

With further additions of KI the freezing point is lowered more and more till the point O is reached. Here the solution is saturated with respect to KI and any more KI added remains as solid salt. Since the progressive lowering of the freezing point depends on the continuous increase in the concentration of KI in solution the point O represents the lowest temperature attainable in this way.

Along the curve AO, ice, solution, and vapour are in equilibrium and there are two components, therefore, the degree of freedom is one,

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

The Solubility Curve OB. The curve OB represents the effect of the increase of temperature on the system solid KI—saturated solution—vapour. Looked at in another way this would be the solubility curve of KI as it also indicates the change of solubility of KI in water with rise of temperature. The solubility curve OB, however, cannot be carried to the 100% KI axis because it comes to an end at the boiling point of saturated solution. Thus the system at the point B is non-variant as the solubility of potassium iodide at the boiling point of saturated solution, a definite temperature, must be a fixed thing. Since the temperature and concentration both are fixed for the system at B, the degree of freedom here is zero. The point B if extended upwards, would be the melting point of potassium iodide.

The curve OB represents a 2-component system with phases solid KI, solution, and vapour in equilibrium. The degree of freedom

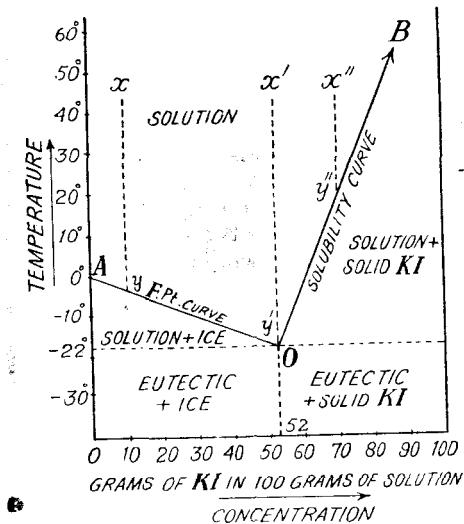


Fig. 165. *t-c* diagram for the system KI—H₂O (not drawn to scale).

as predicted from the phase rule equation would be 1,
 $F = C - P + 2 = 2 - 3 + 2 = 1$.

Cryohydric Point. The two curves, AO and OB meet at the point O which is known as the *eutectic point* and in systems in which the two components are a salt and water, it is termed as a *Cryohydric point*. Since the point O is common to both the curves AO and OB, there are four phases : solid KI, ice, solution and vapour in equilibrium and it is a *quadruple point*. We have here 4 phases and 2-components, therefore, the system is invariant. The composition and temperature both cannot be varied and are constant for the same 2-components.

Effect of Cooling KI solution

The effect of cooling KI solutions of varying composition can very well be interpreted by means of the diagram (Fig. 165). On withdrawing heat from a solution (x) less concentrated than the cryohydric point we travel along xy , till we reach y when solid ice separates. On further cooling, more of ice would separate till the cryohydric point is reached where solid KI would also appear. Similarly on withdrawing heat from a solution (x'') more concentrated than the cryohydric point, we travel along $x''y''$ till the curve BO is reached when solid KI separates. Now on further cooling we move along the curve BO till we reach O where solid ice would also appear. If a solution of cryohydric composition (x') be cooled, on reaching the point O, the solution will solidify as a whole.

Freezing Mixtures :

The facts contained in the above diagram explain the theory of freezing mixtures. When we add a salt, commonly sodium chloride, to melting ice, we follow along the curve AO. Thus the addition of salt to ice melts it and produces a lowering of temperature. The greater the proportion of salt added the greater will be the lowering produced. The lowest temperature which can be attained by means of a freezing mixture in this way will be the cryohydric temperature. On the other hand if we start with a saturated solution of salt and add ice to it we travel along the curve BO till the point O is reached. Thus the same minimum temperature can be attained with a freezing mixture whether we add salt to ice or ice to salt solution.

Some cryohydric temperatures

KI	+ ice	-22°
NH ₄ Cl	+ ice	-17°
NaCl	+ ice	-22°
CaCl ₂	+ ice	-37°
KNO ₃	+ ice	-2.6°
KCl	+ ice	-11.4°

THE SYSTEM FERRIC CHLORIDE-WATER

Water and ferric chloride form no less than four stable hydrates, namely, $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$; $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$; $\text{Fe}_2\text{Cl}_6 \cdot 5\text{H}_2\text{O}$; $\text{Fe}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$.

Evidently it is a **two-component system** as the composition of all the **eight phases**, viz., ice, 4 solid hydrates, anhydrous ferric chloride, solution and vapour can very well be represented by Fe_2Cl_6 and H_2O .

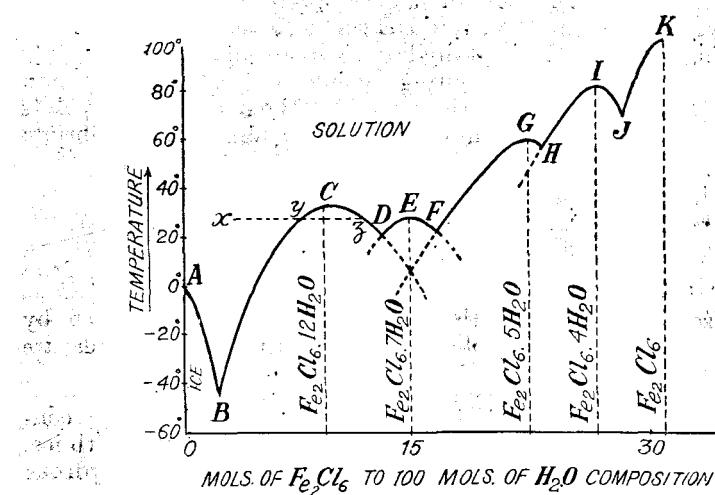


Fig. 166. The system Ferric Chloride-Water.

The *c-t* diagram plotted from Roozeboom's data, is given in Fig. 166.

The freezing point of pure water is represented by the point A. The freezing point of water is lowered by the addition of ferric chloride as indicated along the curve AB. When the point B (-55°) is reached the solution is saturated with the hydrate $12\text{H}_2\text{O}$ which then separates together with ice. At the cryohydric point B, ice, solid $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$, saturated solution, and vapour are in equilibrium and the system is invariant ($F=2-4+2=0$).

On further addition of ferric chloride, the ice phase vanishes, and the univariant system $\text{FeCl}_6 \cdot 12\text{H}_2\text{O}$ —Salt solution—Vapour results. This equilibrium is represented by the curve BC which can be regarded as the *solubility curve* of $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$. On addition of more chloride the temperature of the equilibrium rises until the point C (37°) is reached. Here the composition of the solution and the solid $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ in contact with it is identical and the temperature corresponding to this point may thus be regarded as the melting point of the dodecahydrate. This has been called **the congruent* melting point**.

Further addition of ferric chloride naturally lowers the melting point and the equilibrium shifts along the curve CD. The curve CD thus represents the melting point curve of $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$. The curve

*Congruent mean corresponding with.

CD terminates at the point D where a new solid phase, $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$, makes its appearance. It is a quadruple point, the four phases in equilibrium being $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$, $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$, saturated solution, and vapour. The eutectic point D may rightly be called the transition point. One further addition of ferric chloride to the system at the point D, we travel along the curve DE till at E we have the congruent melting point of the heptahydrate. In a similar manner points G and I represent the melting points of $\text{Fe}_2\text{Cl}_6 \cdot 5\text{H}_2\text{O}$ and $\text{Fe}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$ respectively. At the remaining three quadruple points which are also the transition points the four phases in equilibrium are :

Point	Phases
F (30°C)	$\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$, $\text{Fe}_2\text{Cl}_6 \cdot 5\text{H}_2\text{O}$, Sat. solution and vapour.
H (55°C)	$\text{Fe}_2\text{Cl}_6 \cdot 5\text{H}_2\text{O}$, $\text{Fe}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$, Sat. solution and vapour.
J (66°C)	$\text{Fe}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$, Fe_2Cl_6 anhyd., Sat. solution and vapour.

The solubility curve of the anhydrous salt is represented by the curve JK. Metastable solubility and melting point curves are represented by dotted lines.

The curves AB, BCD, DEF, FGH, HIJ and JK show the conditions under which solutions are in stable equilibrium with ice, $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$, $\text{Fe}_2\text{Cl}_6 \cdot 7\text{H}_2\text{O}$, $\text{Fe}_2\text{Cl}_6 \cdot 5\text{H}_2\text{O}$, $\text{Fe}_2\text{Cl}_6 \cdot 4\text{H}_2\text{O}$ and anhydrous Fe_2Cl_6 respectively.

The degree of freedom of the system at any time is given by the application of the phase rule equation $F = C - P + 2$. Along all the curves there are three phases, solid, solution and vapour in equilibrium and the degree of freedom, $F = C - P + 2 = 2 - 3 + 2 = 1$. At the quadruple points, the system is invariant, for $F = 2 - 4 + 2 = 0$.

Isothermal evaporation of dilute ferric chloride solution. Evaporation of a dilute ferric chloride solution means the continuous removal of water which results in the increase of the concentration of ferric chloride in solution. Thus the isothermal evaporation of a ferric chloride solution will produce the same effects as would be produced as a result of the addition of solid anhydrous chloride at the same temperature. Let us consider the isothermal evaporation of a dilute solution of ferric chloride between 30 — 32°C (say 31°C). Starting at the point x (Fig. 166) we observe that as water evaporates the solution becomes more concentrated until at the point y , $\text{Fe}_2\text{Cl}_6 \cdot 12\text{H}_2\text{O}$ begins to separate. On further evaporation more and more of the hydrate separates till at the vertical dotted line only solid hydrate is left behind. Further evaporation causes the solid hydrate to lose water which then begins to melt. At the point z the whole mass has been completely melted. Similar changes are noted if we continue the isothermal evaporation beyond z .

The phase rule thus interprets correctly the behaviour of a solution of ferric chloride on isothermal evaporation.

THE SYSTEM SODIUM SULPHATE-WATER

Sodium sulphate can form two hydrates, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, and the anhydrous salt can exist in two crystalline

forms, rhombic, and monoclinic. Since the composition of all the **four solid phases**, solution in water, and vapour can be represented by the two constituents Na_2SO_4 and H_2O , this is a **two-component system**. The system has got **three degrees of freedom** but pressure is left out of consideration as minor changes in pressure do not affect the equilibrium. The complete composition-temperature diagram is shown in Fig. 167.

At the point A (0°C), ice is in equilibrium with water and vapour. On adding anhydrous Na_2SO_4 to the system the melting point of ice is lowered along the curve AB, which represents a univariant system since 3 phases (ice, solution and vapour) are present. At B the fourth phase $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, appears and we have a quadruple point. Applying phase rule equation to the system at this point,

$$F = C - P + 2 = 2 - 4 + 2 = 0,$$

it is clear that here the system is non-variant.

It is possible with care to travel along BC if $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ fails to appear at B. C is a metastable quadruple point where the 4 phases ice, $\text{Na}_2\text{SO}_4 \cdot 7\text{H}_2\text{O}$, solution and vapour exist in metastable equilibrium. If now the temperature be raised and more of anhydrous Na_2SO_4 is added we get along the curve CD which is the *solubility curve of heptahydrate*. The curve CD represents the metastable

univariant system, the 3 phases, in equilibrium being $7\text{H}_2\text{O}$, solution and vapour. At D the fourth phase, anhydrous salt appears and thus it is a quadruple point. By lowering the temperature we travel along the dotted curve DE and it is theoretically possible to reach E where the tetrahydrate would separate. In practice, however, $4\text{H}_2\text{O}$ does not separate even on careful seeding as this hydrate is too soluble to be obtained in this way. It can, of course, be obtained in solid solution with isomorphous $\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$.

Returning now to the point B, further raising of temperature and continuous addition of Na_2SO_4 leads us to the solubility curve (BF) of $10\text{H}_2\text{O}$. This represents a stable univariant system up to the point F when rhombic sodium sulphate appears as one of the solid phases. Here the $10\text{H}_2\text{O}$, anhydrous Na_2SO_4 , solution and vapour are in equilibrium. F is thus a stable quadruple point or *transition point*. On warming, the $10\text{H}_2\text{O}$ disappears and we pass along FG, the *solubility curve of rhombic salt*. The curve FG shows a minimum

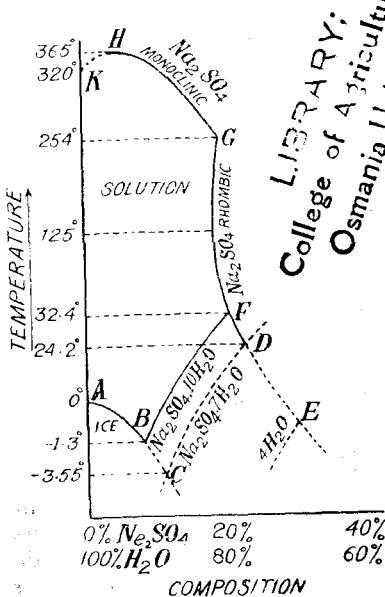


Fig. 167. c-t diagram of the system Sodium sulphate-Water.

at 125°C showing that the solubility first decreases with rise of temperature and then increases. Then we reach the point G where monoclinic Na_2SO_4 appears. This point differs from the previous quadruple points in that there are no water molecules present in the two solid phases. Since at G, rhombic Na_2SO_4 changes into monoclinic variety, it is called the transition point. On further raising the temperature, the solubility falls gradually to the critical point H where the liquid and vapour phase is identical. HK thus shows the solubility of anhydrous Na_2SO_4 in water vapour, the solubility decreases with the fall of temperature and finally becomes zero.

EXPERIMENTAL DETERMINATION OF TRANSITION POINT

(i) **The Dilatometric Method.** This method is based on the change in volume produced as a result of the transition of one form

into another because each form has a different density. The determination is carried out in a DILATOMETER (Fig. 168) which consists of a bulb A drawn out at the lower end B and having a capillary tube with a scale at the upper end. The substance is introduced from the lower end which is then sealed off and the bulb is filled with an inert liquid like paraffin. The dilatometer is now placed in a thermostat and the level of the paraffin in the capillary noted. The temperature of the thermostat is now raised degree by degree. So long as no change takes place in the solid, the rise in the paraffin level is regular and uniform. When the transition point is reached, a sudden change in the volume of the solid causes an abrupt rise or fall in the level. The same happens on cooling when the transition point is again reached. The cooling curve does not coincide, however, with the heating curve as there is always a lag. Usually a mean of the two temperatures is taken as the transition point.

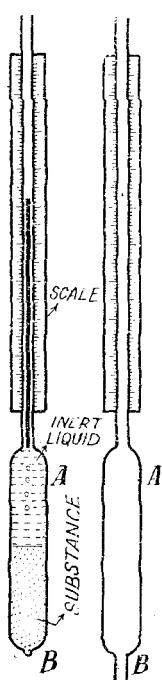


Fig. 168. The Dilatometer.

The dilatometer is used in another way as well. A mixture (1 : 1) of the two forms whose transition temperature is to be determined is placed in the bulb and then covered with the inert liquid and sealed as above. The dilatometer is now placed in a bath whose temperature can be regulated. If there is contraction, the temperature is altered till the small expansion is noticed. The transition temperature would lie between these two temperatures and at it there would be neither contraction nor expansion.

(ii) **The Solubility Method.** Each form has a different solubility at a given temperature but at the transition temperature both the forms have the same solubility. In this method, therefore, solubility curves for both the forms are plotted, and the transition temperature is given by the point at which the two curves cut each other.

Thus in Fig. 167. (Phase rule diagram for $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$) curve BF is solubility curve of $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and curve FG is the solubility curve of Na_2SO_4 , anhydrous. The two curves cut at F (32.4°C) which means that at this temperature both the forms have the same solubility, 32.4°C is, therefore, the transition temperature of sodium sulphate decahydrate.

(iii) **The Vapour Pressure Method.** This method is based on the fact that at the transition point the two forms possess the same vapour pressure. The vapour pressures are determined by any of the methods described already (See chapter VI).

A very convenient apparatus for this purpose was designed by Bremer and Frowein and is known as **Tensimeter**. It consists of a U-tube placed in front of a millimetre scale and ending in bulbs as shown in Fig. 169. The U-tube is filled with an oil or bromonaphthalene. Suppose we desire to determine the transition temperature of two isotopes. These are placed in the two side bulbs and these bulbs sealed. The liquid in the U-tube is now brought in the inner bulbs and the apparatus exhausted by a pump connected at F and then sealed at this point. The bulbs are now heated to the same temperature in a thermostat and transition point is given by that temperature at which the liquid stands at the same level in the two limbs of the U-tube.

(iv) **The Thermometric Method.** The method is based on the fact that each form has a different energy content. When a substance which can undergo transition is heated, its temperature rises gradually until the transition point is reached at which the temperature remains constant until its transformation into the other form is complete.

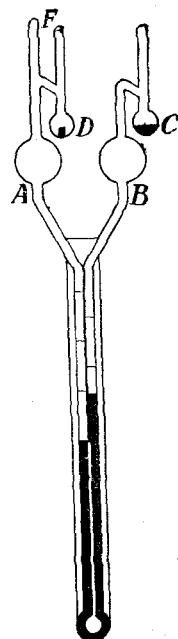


Fig. 169.
Tensimeter.

QUESTIONS AND PROBLEMS

- State Gibb's Phase Rule and explain the terms involved. Enumerate the number of phases in the following systems :
 - Freezing water,
 - Water above 0°C
 - NaCl and water,
 - Saturated solution of sodium sulphate at transition point.
- State the Phase Rule and apply it to a system of one component comprising more than one solid phase.
- State the Phase Rule and explain the terms involved. Discuss the applications of the Phase Rule to (i) Sulphur System, and (ii) Zinc Cadmium System.
- State the Phase Rule. Explain the terms used. Briefly show how it is applied to sulphur, or, explain how you will use the cooling curves of water to build up its phase diagram. *(Agra B.Sc., 1951)*
- State the Phase Rule and explain the different terms employed. Discuss the application of the rule to the equilibrium between different phases of water. *(Nagpur B.Sc., 1953)*
- State and explain the phase rule and illustrate its applications to the system sulphur and its modifications. *(Aligarh B.Sc., 1954)*

7. Explain clearly the terms (a) phase, (b) component, (c) degree of freedom. Apply the Phase Rule to the one-component system, with special reference to the equilibrium at high pressures and low temperatures.

(Punjab B.Sc., 1954)

8. Write a concise account of the various physical and allotropic forms of sulphur in terms of Phase Rule.

(Nagpur B.Sc., 1954)

9. State the Phase Rule and explain the terms involved. Discuss the applications of the rule to the sulphur system.

(Poona B.Sc., 1954)

10. State the Phase Rule ; define all the terms used. Illustrate the application of the rule with reference to a univariant system.

(Osmania B.Sc., 1953)

11. State the Phase Rule and explain clearly the terms involved in it. Discuss its application to a one-component system.

(Annamalai B.Sc., 1953)

12. Define the symbols in the equation $P+F=C+2$.

(Ceylon B.Sc., 1954)

13. Explain the following terms used in Phase Rule study of heterogeneous equilibria :—

- (i) Triple point, (ii) Transition point, (iii) Invariant system.

(Jammu & Kashmir B.Sc., 1953)

14. State the Phase Rule. Explain the terms "Component" and "Degree of freedom." Calculate with the aid of Phase Rule the numbers of degree of freedom of the following systems :—

- (i) Calcium carbonate—calcium oxide—carbon dioxide.

- (ii) Ice—water—water vapour.

(Mysore B.Sc., 1953)

15. Discuss Phase Rule and its application to (a) desilverization of lead, and (b) preparation of freezing mixtures.

16. Explain clearly with examples the terms : Components, Phase, Variance, as they are used in Phase Rule. Apply Phase Rule to the following equilibria :—

- (a) Sodium chloride solution in equilibrium with its vapour.

- (b) Potassium Iodide and Water.

17. What is Phase Rule ? Describe its applications to 'freezing mixtures.' What is the difference between a eutectoid, a solid solution and a cryohydrate ?

18. Define the terms phase, component and the degree of freedom. Discuss the application of Phase Rule to the systems given below :—

- (i) Zinc-Bismuth (ii) Lead-Silver.

(Andhra B.Sc., 1954)

19. Define (a) Phase (b) Equilibrium (c) Triple point (d) Degree of freedom with special reference to the system ferric chloride-water.

20. What is Phase Rule and of what value is it in studying heterogeneous equilibria ? Discuss its application to the existence of hydrates of ferric chloride.

21. Write an essay on Phase Rule and its applications.

(Banaras B.Sc., 1954)

22. Define the terms (i) phase, (ii) degree of freedom, (iii) component, as used in Gibbs' Phase Rule. Draw and discuss the phase diagram for sulphur system.

(Delhi B.Sc., 1954)

23. State the Phase Rule and explain fully the terms involved. Discuss the application of the Phase Rule to ice-water—water vapour system.

(Poona B.Sc., 1955)

24. Write a short note on Phase Rule and apply it to a one component system.

(Rajputana B.Sc., 1955)

25. Explain how Phase Rule is helpful in studying heterogeneous equilibria. What do you understand by the term 'degrees of freedom' ?

- Discuss the application of Phase Rule to the extraction of silver from lead.

(Punjab B.Sc., 1955)

26. State the Phase Rule and explain the terms used. Show and explain clearly with a diagram how you will apply it to a system of one component containing more than one solid phase.

(Delhi B.Sc., 1955)

27. Define the terms 'Phase', 'Component' and 'Degree of Freedom'. State Phase Rule and discuss its application to the system of water vapour, water and ice. (Punjab B.Sc., 1956)

28. Explain the terms used in Phase Rule. Discuss one component system with the application of Phase Rule. (Banaras B.Sc., 1956)

29. Explain with examples the terms used in Phase Rule. Discuss this rule for a one component system. (Lucknow B.Sc., 1956)

30. State the Phase Rule and explain the terms involved. Draw the equilibrium phase diagram for sulphur. Show that the four phases of sulphur cannot be in equilibrium. (Gujarat B.Sc., 1956)

31. State the Phase Rule and discuss its application to the study of sulphur system. (Allahabad B.Sc., 1957; Nagpur 1957; Aligarh 1956)

32. Discuss the system ice-water-vapour from the point of view of Phase Rule. (Allahabad B.Sc., 1957; Osmania 1956)

33. Mention the "Phase Rule" and discuss significance of the following terms :—

- (a) Degree of freedom,
- (b) Phase,
- (c) Component.

Apply Phase Rule to water system and explain it with a diagram.

(Delhi B.Sc., 1957)

34. What is the 'phase rule'? Discuss the $p-t$ diagram for the sulphur system from the point of view of Phase Rule. (Punjab B.Sc., 1958)

35. What is the objective purpose of phase rule? Explain the significance of the terms on which it is based. Explain how the degree of freedom in one component system varies with the number of phases; use the equation only. (Aligarh B.Sc., 1958)

36. Discuss the application of the phase rule to the system of salt-water. (Poona B.Sc., 1958)

37. What are (a) phase (b) component (c) degree of freedom?

Explain (a) transition point (b) melting point (c) triple point.

(Rangoon B.Sc., 1958)

38. State phase rule and apply it to the study of the lead-silver system. (Punjab B.Sc., 1959)

39. State the Phase Rule and explain the terms involved. Apply the rule to the water system. (Agra B.Sc., 1960; Aligarh B.Sc., 1959)

40. Explain clearly the term "degree of freedom" in the statement of the "Phase Rule". Discuss the application of the phase rule to the system consisting of molten mass of argentiferous lead. (Poona B.Sc., 1959)

41. State and explain the phase rule. Apply the rule to Sulphur system—rhombic, monoclinic, liquid and vapour. (Vikram B.Sc., 1959)

CHAPTER XIX

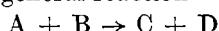
THERMOCHEMISTRY

GENERAL

Energy can manifest itself in many forms such as potential energy, kinetic energy, electrical energy and light energy. From the law of conservation of energy* it follows that when a certain amount of one form of energy disappears an equivalent amount of another form of energy makes its appearance.

For its existence as a chemical individual an element or a chemical compound is associated with a certain amount of internal energy which may be named as **chemical energy**, or **intrinsic energy**. Like other forms of energy this chemical energy may be converted into heat energy and vice versa. The study of the relation between these two forms of energy is known as **Thermochemistry** (*thermo* = heat).

Let us consider a general reaction



The substance A, B, C and D have their own intrinsic energy and usually the intrinsic energy of one substance is different from that of others. Let a , b , c and d stand for their individual intrinsic energies respectively. Comparing the total intrinsic energy before and after the reaction, either $(a + b) = (c + d)$

$$\text{or } (a + b) > (c + d)$$

$$\text{or } (a + b) < (c + d)$$

In the first case the total internal energy before and after the reaction being the same, no heat is evolved or absorbed. In the second case the internal energy before the reaction is greater than after the reaction, i.e., the difference $(a+b)-(c+d)$ is positive and an equivalent amount of heat will be liberated. In the third case an increase in internal energy takes place, i.e., $(a+b)-(c+d)$ is negative and an equivalent amount of heat will be absorbed from the surroundings. The chemical reactions which are accompanied by the evolution of heat are called **exothermic** and those which are accompanied by the absorption of heat are called **endothermic**.

HEAT OF REACTION

The number of calories† of heat liberated or absorbed during

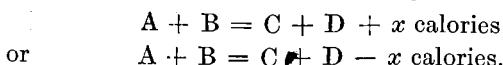
***Law of conservation of energy.** The energy of an isolated system is constant i.e., it cannot be altered in amount by interactions between the parts of the system.

†**Calorie** is the unit of heat. The so-called **small calorie** or **gram-calorie** is defined as the amount of heat required to raise the temperature of one gram of water through 1°C (15° to 16°C). The small calorie is recognised by being written with a small (c) or as 'cals'.

Large calorie or **kilogram calorie** is written with a capital 'C' and is defined as the amount of heat required to raise 1 kilogram of water from 15° to 16°C . That is $C = 1000 c$.

The temperature interval is specified because the specific heat of water varies with the temperature.

a reaction can be included in an ordinary chemical equation, thus

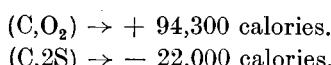


These equations indicate that, in the first case, one gram-molecule of A and one gram-molecule of B react together to form one gram-molecule of C and one gram-molecule of D, with the evolution of x calories; $+$ or $-x$ calories is then the heat of reaction represented by the above equations.

The **Heat of reaction** is defined as *the quantity of heat in calories evolved or absorbed when the number of gram-molecules of substances indicated by the chemical equation have completely reacted.*

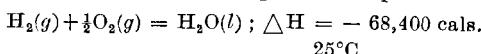
The equation $C + O_2 = CO_2 + 94,300$ calories, states that when 12 grams of carbon (graphite) react with 32 grams of oxygen to completion, 44 grams of carbon dioxide are produced and 94,300 calories of heat are evolved. It is an exothermic reaction. The equation : $H_2(g) + \frac{1}{2}O_2(g) = H_2O(l) + 68,400$ cals. indicates that when 2.016 gms. gaseous hydrogen react with 0.5 mol. (*i.e.*, 16 gms.) gaseous oxygen, 18.016 gms. liquid water are produced with the evolution of 68,400 calories of heat. Similarly, the equation, $C + 2S = CS_2 - 22,000$ calories shows that when 12 grams of carbon (graphite) react completely with 64 grams of sulphur, 76 grams of carbon disulphide are formed and 22,000 calories of heat are absorbed. This is an endothermic reaction.

For the sake of brevity the two reactions stated above may sometimes be written as



Modern or Thermodynamic Notation. This system of notation takes into consideration the *heat content* or *enthalpy* of the system (*See Chapter XXIV*) represented by H and the change in heat content by the symbol ΔH .

In the equation $H_2 + \frac{1}{2}O_2 = H_2O(l) + 68,400$ cals. mentioned above, the heat content of the system decreases by 68,400 cals. because this much amount of heat is evolved. The thermochemical equation is represented as



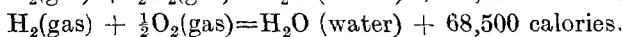
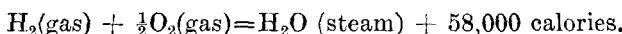
the subscript on ΔH showing the temperature at which the heat of reaction is measured.

In the case of $C + 2S = CS_2 - 22,000$ cals. $\Delta H = + 22,000$ cals.

Factors which affect the heat of reaction :

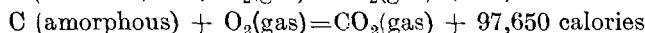
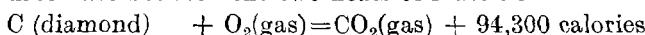
(i) **Reaction carried at constant volume or constant pressure.** If gases take part in a particular reaction it must be known whether the reaction is carried at constant volume or at constant pressure. If the volume be kept constant no work is done by or against the atmosphere. In case the system is allowed to expand during the reaction it does work against the atmosphere whereby some heat energy is consumed and the quantity of heat evolved would be less than at constant volume. If the system contracts, the heat of reaction would be greater than that at constant volume by an amount equal to the work done on the system by the surroundings.

(iii) **Physical state of reactants and products.** Since heat is produced or used up in many physical processes, such as evaporation, melting, solution or transformation from one modification to another, to make thermochemical equation quite definite *the physical state of substance taking part in the reaction must be explicitly defined.* Thus,

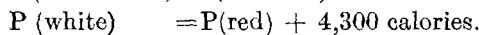
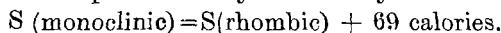


The second value of the heat of reaction in this case is higher as it includes latent heat evolved when steam condenses to water.

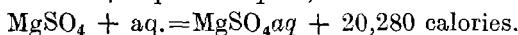
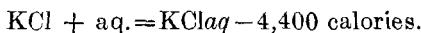
The difference between the two heats of reaction



is due to the heat difference when 12 grams of carbon change from diamond to amorphous variety. Similarly it has been shown



(iv) **Heat of solution.** Heat changes also take place when a substance is dissolved in a solvent. When a reaction takes place in solution, *the heats of solution of the reactants and the products must be taken into consideration.* The **heat of solution** may be defined as *the heat evolved or absorbed when one gram-molecule of a solute is dissolved in a large excess of water, so that the further dilution of the solution produces no heat exchange.* Heat of solution, may be expressed as



The symbol aq. (*aqua*=water) implies that the substance indicated is in aqueous solution and that the quantity of water is so large that the addition of more water would cause no further heat exchange.

The heat of solution of an electrolyte may be due to energy change involved during its ionisation or some hydrate formation as in the case of sulphuric acid. Usually heat is absorbed when ions are torn apart from each other in the process of solution and heat is evolved during hydrate formation. With salts as sodium chloride the heat of separation of ions just equals the heat of hydration and there is very little heat effect.

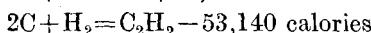
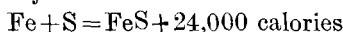
(v) **Temperature.** Heat changes accompany the change in the temperature of a gas, due to the variations in its specific heat. *The heat of a reaction, therefore, depends on the temperature at which it is carried out.* When no temperature is given, it is understood that the reaction takes place at room temperature.

In certain cases different names are given to the heat evolved in a chemical reaction. Thus we have the heat of formation, the heat of combustion and the heat of neutralisation.

HEAT OF FORMATION

The **heat of formation** of a compound is defined as the *quantity of heat in calories evolved or absorbed when one gram molecule of the*

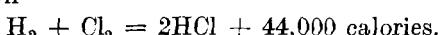
compound is formed from its elements. Thus the equations



indicate that the heat of formation of iron sulphide and acetylene is 24,000 calories and -53,140 calories respectively.

*Compounds which are formed from their elements with the evolution of heat are called **Exothermic Compounds** and those which are formed with the absorption of heat are called **Endothermic Compounds**.*

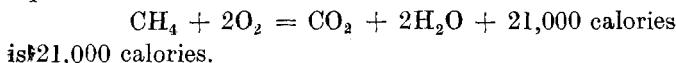
The formation of hydrochloric acid from elements may be shown by the equation



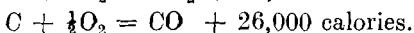
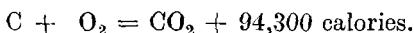
It may be noted that in this case 44,000 calories is not the heat of formation of hydrochloric acid because this much heat is liberated when two gram molecules of the acid are formed. The heat of formation of hydrochloric acid would, therefore, be $\frac{44,000}{2} = 22,000$ calories.

HEAT OF COMBUSTION

The **Heat of Combustion** of a substance is *the quantity of heat evolved when one-gram-molecule of the substance is completely oxidised.* As for example, the heat of combustion of methane as shown by the equation



We have,



It should be noted that 94,300 calories and not 26,000 calories is the heat of combustion of carbon as the combustion is complete only in the first reaction. In the second case, oxidation has converted carbon to carbon monoxide and is by no means complete as carbon monoxide can further be oxidised to carbon dioxide.

Applications of the heat of combustion :

(i) *Calculation of the heat of formation.* Since the heats of combustion of organic compounds can be determined with considerable ease, they are employed to calculate their heats of formation, the direct determination of which is often impossible.

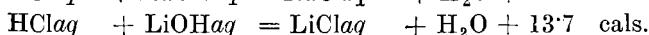
(ii) *Heating value of fuels.* Heating value of a fuel is an important matter. The purchaser of coal should be interested in the heat of combustion as well as its weight. The dietician must know the calories of heat obtainable from various food-stuffs.

(iii) *Deciding constitution.* Heat of combustion of organic compounds is to a large extent an additive property, as is shown by the fact that in a homologous series the difference between the heats of combustion of successive numbers is nearly constant and is equal to 158 cals. Constants corresponding to the heats of

combustion of various atoms and linkages have been worked out. The heat of combustion of an organic substance can be calculated from its probable structural formula by adding up the values of the constants corresponding to the atoms and linkages involved therein. If the value so obtained comes out to be the same as the experimental value of the heat of combustion of the compound, the assumed formula must be correct. In this way Kekule's formula for benzene with alternate double and single linkages has been supported as the calculated value of the heat of combustion of benzene according to this formula agrees with the actual heat of combustion. Heat of combustion of organic compounds has thus proved very valuable in deciding their chemical constitution.

HEAT OF NEUTRALISATION

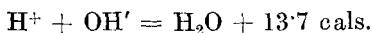
The **Heat of Neutralisation** is defined as *the amount of heat evolved when one gram-equivalent of an acid neutralizes one gram-equivalent of a base in dilute solution*. The following may be considered as the typical examples.



It may safely be concluded from the above data that the heat of neutralisation of a strong acid and a strong base is 13.7 cals., no matter what acid or base is employed. This regularity has been explained satisfactorily with the help of the theory of electrolytic dissociation. If HA and BOH represent any strong acid and any strong base respectively and equivalent amounts of these are dissolved in water we have :

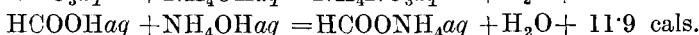
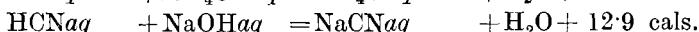


Disregarding the ions which occur on both sides of the reaction



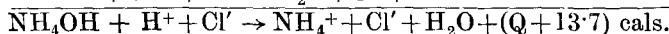
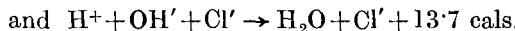
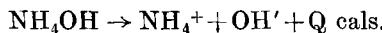
Thus the heat of neutralisation of an acid and a base is merely the heat of formation of water from hydroxyl and hydrogen ions.

When weak acids or weak bases are neutralised by strong bases and strong acids respectively, the heat of neutralisation may differ widely from 13.7 cals. This is shown by the following examples :



In such cases the neutralisation process involves not only the union of hydrogen and hydroxyl ions but also the dissociation of a weak acid or a weak base. The measured heat of neutralisation, therefore, is equal to the heat given out in the union of OH' and H+, plus the heat accompanying the dissociation of the weak acid or base. Neutralisation of ammonia by hydrochloric acid for example can be

written as



But we know that measured heat of neutralisation is 12.3 cals.

$$\text{Therefore } Q + 13.7 = 12.3$$

or

$$Q = -13.7 + 12.3 = -1.4 \text{ cals.}$$

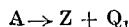
Hence the heat of dissociation of ammonium hydroxide into ions is -1.4 cals., i.e., 1.4 Cals., are absorbed when one gram molecule of ammonium hydroxide is dissociated into its ions.

HESS'S LAW OF CONSTANT HEAT SUMMATION

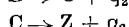
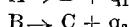
We have already seen that the heat evolved or absorbed in a certain reaction is equivalent to the difference of intrinsic energy of the reactants and the products, no matter in what manner the reaction is carried. Thus **Hess's Law** (1840) states :

If a chemical change can be made to take place in two or more different ways, whether in one or several steps, the amount of heat evolved or absorbed in the total change is the same no matter by which method the change is brought about.

The law also follows as a mere consequence of the Law of Conservation of Energy. Let us suppose that a substance A can be changed to Z directly.



where Q_1 is the heat evolved in the direct change. When the same change is brought about through intermediate stage.



the total evolution of heat $= q_1 + q_2 + q_3 = Q_2$

According to Hess's Law, $Q_1 = Q_2$.

If it is not so, let $Q_2 > Q_1$. Then by transforming A to Z through stages and retransforming directly back to A there would be a gain of heat $= Q_2 - Q_1$. By repeating this process again and again an unlimited heat will be developed in an isolated system. This goes against the Law of Conservation of Energy. Hence Q_1 must be equal to Q_2 .

Hess's Law has been tested experimentally and found to be true.

It may be illustrated by the following examples :—

Example 1. Carbon can be burnt to carbon dioxide directly or it may first be changed to carbon monoxide and then oxidised to carbon dioxide :

1st way

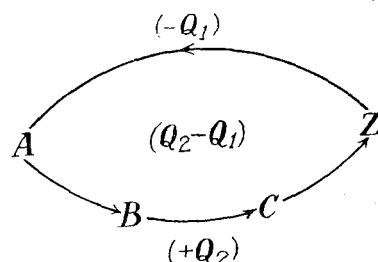
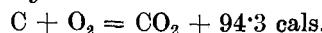
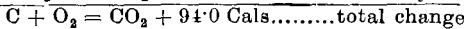
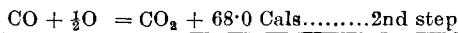
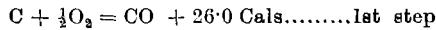


Fig. 170.

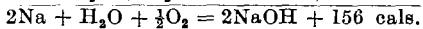
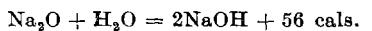
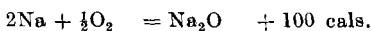
2nd way



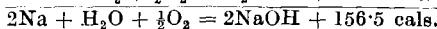
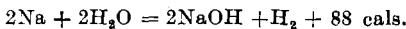
It will be seen that the total heat evolved is the same in the two cases.

Example 2. Another example of Hess's law is furnished by the formation of sodium hydroxide from metallic sodium. This process can be carried out in two ways :

1st way



2nd way



It may be observed that the total heat evolved in carrying the reaction in two different ways is the same, the difference of 0.5 cals. being within experimental error.

It may also be noted from the above examples that by the addition of a series of chemical equations we can obtain not only resultant products of this series of reactions, but also the net heat effect. It is, therefore, clear that **thermochemical equations may be multiplied, added or subtracted like ordinary algebraic equations.** For this reason Hess's law has been of great service in the indirect determination of the heat of formation.

THERMOCHEMICAL CALCULATION

The heat of formation can be determined either directly or indirectly. In the direct determination, weighed quantities of substances are allowed to react in a vessel surrounded by a known quantity of water and the rise in temperature recorded. This direct method can be used only in cases in which the reaction takes place rapidly and completely. If, for example we want to determine the heat of formation of methane, the direct method is impossible since carbon and hydrogen do not combine direct except very incompletely and at very high temperature. The indirect determination of the heats of formation can be made by the application of

(i) the Hess's law

and (ii) the concept of intrinsic energy.

Calculation of the heat of formation by the application of Hess's Law. We have already pointed out as a deduction from Hess's law that *thermochemical equations may be multiplied, added or subtracted like ordinary algebraic equations.* Let us see how this fact can be employed to solve thermochemical problems.

Example 1. Calculate the heat of formation of potassium hydroxide from the following :

- $K + H_2O + Aq = KOH_{aq} + \frac{1}{2}H_2 + 48,000$ calories,
- $H_2 + \frac{1}{2}O_2 = H_2O + 68,500$ calories,
- $KOH + Aq = KOH_{aq} + 14,000$ calories.

We should aim at the equation $K + \frac{1}{2}O_2 + \frac{1}{2}H_2 = KOH + Q$

where Q is the heat of formation of KOH .

Adding up equation (a) and (b) and subtracting the equation (c) will give
 $K + H_2O + H_2 + \frac{1}{2}O_2 - KOH = KOH_{aq} + \frac{1}{2}H_2 + H_2O - KOH_{aq}$
 $+ 48,000 + 68,500 - 14,000$

or

$$K + \frac{1}{2}H_2 + \frac{1}{2}O_2 - KOH = 102,500$$

or

$$K + \frac{1}{2}H_2 + \frac{1}{2}O_2 = KOH + 102,500 \text{ calories}$$

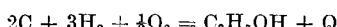
Hence Q , the heat of formation of KOH , is **102,500 calories**.

Example 2. The heat of combustion of ethyl alcohol is 330,000 calories. If the heat of formation of carbon dioxide and water is 94,300 calories and 68,500 calories respectively, calculate the heat of formation of alcohol.

We are given

- $C_2H_5OH + 3O_2 = 2CO_2 + 3H_2O + 330,000$ calories.
- $C + O_2 = CO_2 + 94,300$ calories.
- $H_2 + \frac{1}{2}O_2 = H_2O + 68,500$ calories.

We have to manipulate these equations in such a way as to get the required equation



where Q would be equal to heat of formation.

Multiplying equation (b) by 2 and equation (c) by 3 we have

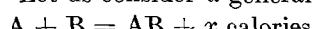
$$\begin{aligned} 2C + 2O_2 &= 2CO_2 + 2 \times 94,300 \\ 3H_2 + \frac{3}{2}O_2 &= 3H_2O + 3 \times 68,500 \end{aligned}$$

Now adding these up and subtracting equation (a) we get

$$2C + 3H_2 + \frac{1}{2}O_2 = C_2H_5OH + 64,100 \text{ calories.}$$

Thus Q , the heat of formation of alcohol, is **64,100 calories**.

Concept of intrinsic energy and the calculation of the heat of formation. Let us consider a general reaction



The total energy before and after reaction must be the same (*Law of conservation of energy*). Therefore

$$E_A + E_B = E_{AB} + x \text{ calories}$$

where E_A , E_B and E_{AB} are the intrinsic energies of A , B , and the compound AB respectively. Knowing the intrinsic energy of A , B and AB we could have at once written the value of x . But we have no means to know the absolute value of the intrinsic energy of a substance. The heat of a reaction, however, is related to intrinsic energy in as much as it is equivalent to the difference of total intrinsic energy before and after the reaction. Surely this relation should form a basis of our calculation. Hence we assume that **the intrinsic energy of an element is zero**, although we know such is not the case since elements like carbon and oxygen react to form carbon dioxide with the evolution of heat. Making this assumption, let us now write the energy equation for the reaction $A+B = AB+x$ calories.

$$E_A + E_B = E_{AB} + x \text{ cals.}$$

Since A and B are elements, their intrinsic energy is zero and therefore

$$0 + 0 = E_{AB} + x \text{ cals.}$$

or $E_{AB} = -x \text{ cals.}$

The intrinsic energy of a compound is, therefore, equal to its heat of formation but with the sign reversed. It may be carefully noted that the intrinsic energy of a compound as talked here is the additional amount of energy (in calories) which one gram molecule of a compound possesses above that of its constituent elements. The concept of intrinsic energy is extremely helpful in solving thermochemical problems in a simple way.

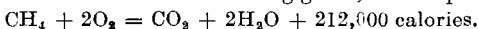
Example 1. The heat of combustion of methane was found to be 212,000 calories. If the heats of formation of carbon dioxide and water are 94,300 and 68,500 calories respectively, calculate the heat of formation of methane.

Since the intrinsic energy of a compound = -(heat of formation)

$$E_{CO_2} = -94,300 \text{ calories}$$

$$E_{H_2O} = -68,500 \text{ calories}$$

The heat of combustion of methane being given, we can put down



Writing the corresponding energy equation

$$E_{CH_4} + 2E_{O_2} = E_{CO_2} + 2E_{H_2O} + 212,000 \text{ calories.}$$

Putting intrinsic energy of the element oxygen as zero and substituting the intrinsic energy of CO_2 and H_2O

$$E_{CH_4} + 2 \times 0 = -94,300 + 2(-68,500) + 212,000$$

Therefore, $E_{CH_4} = -19,300 \text{ calories}$

Hence the heat of formation of methane is **19,300 calories**.

Example 2. Calculate the heat of formation of sulphur trioxide from the following data :

$$(a) SO_3 + H_2O = H_2SO_4 + 21,320 \text{ calories.}$$

$$(b) \text{heat of formation of anhydrous sulphuric acid} = 192,000 \text{ cal.}$$

$$(c) \text{heat of formation of water} = 68,500 \text{ calories.}$$

or $SO_3 + H_2O = H_2SO_4 + 21,320$

Therefore, $E_{SO_3} + E_{H_2O} = E_{H_2SO_4} + 21,320$

Substituting the given values

$$E_{SO_3} + (-68,500) = (-192,000) + 21,320$$

$$E_{SO_3} = -102,180$$

Heat of formation of SO_3 , therefore, is **102,180 calories**.

HEAT OF REACTION AT CONSTANT VOLUME AND PRESSURE

Heats of reaction are usually given for conditions of constant pressure because most reactions are studied at constant pressure. Heats of combustion, however, are measured at constant volume and if it is desired to find the heat evolved at constant pressure a correction must be applied.

When a gaseous reaction proceeds at constant volume, no work is done by the gas in expansion or upon it by the atmosphere in contraction. If the reaction proceeds at constant pressure and there is

an increase of volume of the gaseous mixture, work will be done by the gas in expanding and the heat which is equivalent to this work will come from the heat of reaction, which will thus appear too low. If the reaction on the other hand involves a contraction, work will be done on the gas and the heat of reaction will be too high.

When one gram molecular volume expands to two gram molecular volumes, the work done by the gas is

$$\begin{aligned} &= \text{Pressure} \times \text{Increase of volume} \\ &= P(2V - V) = PV = RT \end{aligned}$$

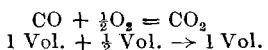
where R is gas constant and T is the temperature of the reaction on absolute scale. But the value of R is 2 cals. approximately. There will, therefore, be an absorption of $2T$ calories for every gram molecular volume increase in the reaction mixture. For every gram molecular volume of a gas which might disappear during a reaction, $2T$ calories of heat will be evolved. Hence we can write

$$H_p = H_v - 2nT \dots \dots \dots \text{for expansion}$$

$$\text{and } H_p = H_v + 2nT \dots \dots \dots \text{for contraction}$$

where H_p is the heat of reaction at constant pressure, H_v is the heat of reaction at constant volume, and n is the number of molecules decreased or increased during the reaction.

Example 1. Heat of combustion of carbon monoxide at constant volume and at 17°C is 67,710 cals. Calculate its heat of combustion at constant pressure.

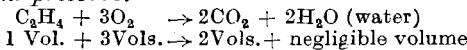


Since in this case decrease of volume takes place

$$\begin{aligned} H_p &= H_v + 2nT \\ &= 67,710 + 2 \times \frac{1}{2} \times (273 + 17) \\ &= 67,710 + 290 = 68,000 \text{ calories.} \end{aligned}$$

Hence the heat of combustion of carbon monoxide at constant pressure at 17°C is **68,000 calories**.

Example 2. The heat of combustion of C_2H_4 at 17° to CO_2 and liquid H_2O at constant volume is 332,190 cals. Find the heat of combustion at constant pressure.



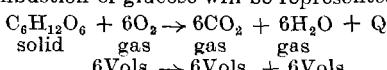
Thus a decrease of volume takes place and, therefore,

$$\begin{aligned} H_p &= H_v + 2nT \\ &= 332,190 + 2 \times 2 \times (273 + 17) \\ &= 333,190 + 4 \times 290 = 333,350 \text{ cals.} \end{aligned}$$

The heat of combustion at constant pressure at 17° is 333,350 calories.

Example 3. Heat of combustion of glucose ($\text{C}_6\text{H}_{12}\text{O}_6$) at constant pressure at 17°C was found to be 651 Cals. Calculate the heat of combustion of glucose at constant volume.

Heat of combustion of glucose will be represented by the equation



In this case since an increase of volume takes place

$$\begin{aligned} H_p &= H_v - 2nT \\ 651,000 &= H_v - 2 \times 6 \times 290 \\ \text{or} \quad H_v &= 651,000 + 3,480 \\ &= 654,480 \text{ calories} \end{aligned}$$

Hence the heat of combustion of glucose at constant volume at 17°C is **654,480 calories**.

EXPERIMENTAL DETERMINATION OF THE HEAT OF REACTION

The heat given out or absorbed in a chemical reaction is measured in a suitable apparatus called a *calorimeter* (Latin *calor*=heat).

The most common types are :

- (i) the water calorimeter,
- (ii) the vacuum flask,
- (iii) the adiabatic calorimeter, and
- (iv) the bomb calorimeter.

The water calorimeter. This is a convenient apparatus for finding the heat change accompanying a chemical reaction taking place in solution. The reaction is allowed to take place in a test-tube immersed in a known quantity, W , of water. The rise of the temperature, t , of the water is recorded with a sensitive thermometer. As the apparatus itself, *viz.*, vessels, thermometer, stirrer etc., is heated along with the water it contains, its water equivalent, W , *i.e.*, the quantity of the water which has the same heat capacity as the apparatus, must be determined and added to the quantity of water actually employed in the experiment. Heat given out in a reaction can thus readily be calculated.

$$Q = t(W+w)$$

Allowance must, of course, be made for the heat capacity of the solution in the tube. For dilute solutions, it is sufficiently accurate to assume that the heat capacity of the solution is the same as that of water.

The chief source of error in the measurement is the loss of heat by radiation.

The Vacuum Flask. The reactants which have been previously cooled to room temperature are mixed in a vacuum flask and the rise in temperature noted. In this case the loss of heat by conduction and radiation through the walls is very slight. The specific heat of the resulting solution is usually unknown, therefore, the flask is provided with a heating coil and the electric energy required to produce the same rise of temperature is determined. This gives directly the heat developed during the reaction and it is not at all

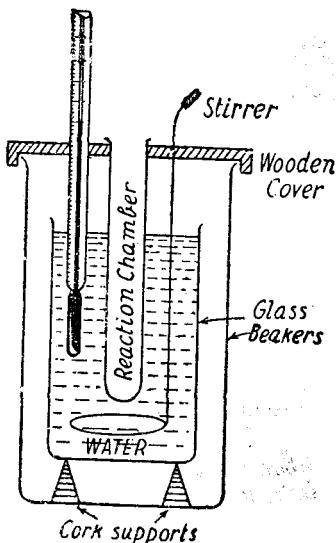


Fig. 171. The Water Calorimeter.

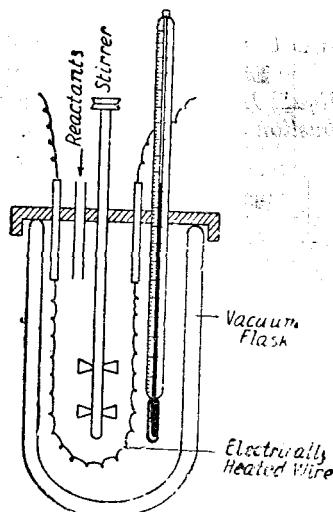


Fig. 172. The Vacuum Flask.

necessary to determine the heat capacity* of the calorimeter.

The Adiabatic Calorimeter. In this apparatus the surroundings of the reaction chamber are maintained at the temperature of the interior so that there is no tendency to lose or gain heat. The vessel in which the reaction is carried out is immersed in a bath of water or oil which can be electrically heated. During the reaction, this vessel is maintained as near as possible to the temperature of the enclosure. By suitable arrangements the control can be made automatic, and it is then merely necessary to record the difference between the initial and the highest temperature. The heat given out during the reaction is measured by heating the reaction mixture by a measured quantity of electric energy. Since the loss of heat from the inner enclosure is practically nil, the calorimeter is specially suitable for reactions which take a long time.

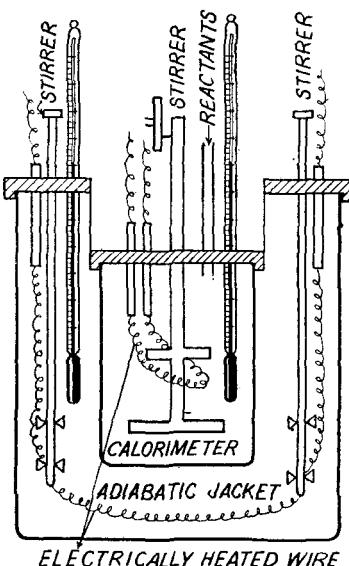


Fig. 173. The Adiabatic Calorimeter.

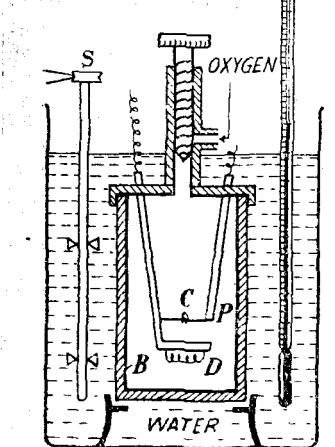


Fig. 174. The Bomb Calorimeter
S=stirrer ; B=Bomb ; D=Dish ;
OC=Cotton thread ; L=Lid ;
P=Platinum wire.

of the bomb and the calorimeter is found by burning in the bomb a

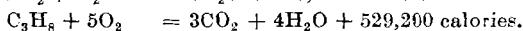
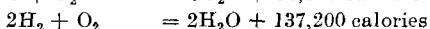
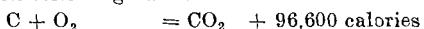
*Heat Capacity is the number of calories required to raise its temperature through 1°C.

The Bomb Calorimeter. This apparatus was devised by Berthelot (1881) to measure the heat of combustion of organic compounds. The bomb, B, shown in the figure is a strong steel vessel gilded or enamelled on the inside to resist the chemical attack of oxygen. A weighed amount of the substance is placed in a platinum dish, D, inside the bomb. The bomb is then filled with oxygen at a pressure of 25 atmospheres or so and immersed in a calorimeter provided as usual with suitable stirrers and thermometers. The temperature of the water is noted and combustion started with the help of a cotton thread, C, placed just above the sample which can be ignited by a current. The rise in temperature of water in the calorimeter is noted, and allowance made for the heat of combustion of the cotton thread. The heat capacity

known weight of a compound whose heat of combustion is already known.

QUESTIONS AND PROBLEMS

1. What are exothermic and endothermic reactions ? Give examples.
2. Define the heat of formation of a compound. What are endothermic and exothermic compounds ?
3. What is the intrinsic energy of a compound ? How has it proved useful in the indirect determination of the heats of formation ?
4. Calculate the heat of the reaction, $\text{Cu} + \text{N}_2\text{O} = \text{CuO} + \text{N}_2 + \text{Q}$ Cals. The heat of formation of N_2O is -17,700 calories and that of CuO is + 37,200 calories.
5. Calculate the heat of formation of propane (C_3H_8) at constant pressure from the following data :



All measurements being made at constant pressure and at 17°C .

6. Find out the heat of formation of hydrogen sulphide from the following data :—

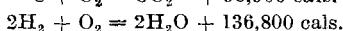
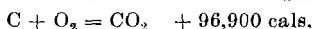
heat of combustion of hydrogen sulphide = 136.71 Cals.

heat of formation of water = 68.36 Cals.

heat of formation of sulphur dioxide = 71.08 Cals.

(Banaras B.Sc., 1956)

7. Calculate the heat of formation of methane, given that



8. What do you understand by the heat of formation of a compound ? How is the heat of formation determined ?

If the heat of formation of CO_2 is 94.3 Cal. and of water 68.4 Cal., calculate the heat of formation of ethyl alcohol, given that the heat of combustion of ethyl alcohol is 326.7 Cal. (Banaras B.Sc., 1953)

9. Define the terms : (1) heat of reaction, (2) heat of neutralization, (3) heat of solution, (4) heat of combustion. (Mysore B.Sc., 1954)

10. Define the term 'Heat of formation'. How is the heat of formation of an organic compound determined ? (Travancore B.Sc., 1954)

11. Write a note on the heats of combustion of organic compounds. What is their importance ?

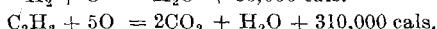
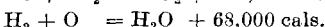
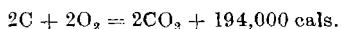
12. Determine the heat of formation of formic acid from the following data :—

heat of combustion of formic acid = 62,900 calories.

heat of formation of carbon dioxide = 96,600 calories.

heat of formation of water = 68,400 calories.

13. Calculate the heat of formation of acetylene from the following data :—



14. Explain with illustrations the following terms :—

(a) Heat of solution, (b) Heat of formation, (c) Heat of dilution, (d) Heat of neutralisation.

15. Define "heat of formation", "heat of solution" and "heat of neutralization." Calculate the heat of formation of water from the following data :—

Oxygen and hydrogen were exploded in a bomb in an ice calorimeter. For 2.0 gms. of hydrogen 838 gms. of ice melted. The latent heat of fusion of

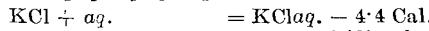
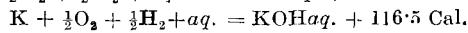
ice is 80 grams calories per degree. Ostwald has shown that a correction of 970 grams. cal. must be added ($H = 1.008$). (Punjab B.Sc., 1943 Suppl.)

16. The heat evolved during the formation of a given compound could not be determined directly. How would you proceed to measure the heat of formation of such a compound ?

Given that the heat of combustion of CS_2 is 256.1 cals. and heat of formation of CO_2 and SO_2 respectively are 94.3 and 71.0 cals., calculate the heat of formation of CS_2 .

17. The heats of neutralisation of NaOH and NH_4OH by HCl are 13,680 and 12,270 cals. respectively. What is the heat of dissociation of NH_4OH , if it is assumed to be practically undissociated ?

18. Calculate the heat of formation of potassium chloride from the following data :—



(Aligarh & Lucknow B.Sc., 1959)

19. Explain the terms exothermal and endothermal reactions. What relation exists between the thermochemical nature of a reaction and the stability of its products ?

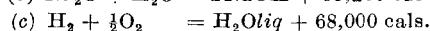
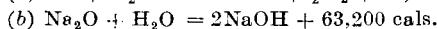
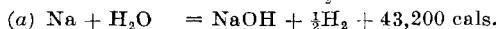
On dissolving 100 gms. anhydrous copper sulphate in water the heat evolved amounted to 9,900 cals. The same amount of crystalline substance $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, on dissolving gave an absorption of heat amounting to 1,100 calories. Calculate the heat of hydration of the gram-molecule of CuSO_4 into $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. (Rajputana B.Sc., 1954)

20. Write a note on Hess's Law of constant heat summation.

(Delhi B.Sc., 1953)

21. State and explain Hess's Law. Define heat of formation and heat of combustion.

22. What is Hess's Law ? How was it deduced ? From the following data calculate the heat of formation of Na_2O .



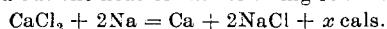
23. State Hess's Law and show how it could be used to evaluate the heat of formation in those cases where a direct determination is not possible. The heat of combustion of methane is 210,800 cals. The heat of formation of CO_2 and H_2O are 94,300 cals. and 68,300 cals. respectively. Calculate the heat of formation of methane. (Bombay B.Sc., 1936)

24. Write an account of Hess's Law in thermochemistry and illustrate it with examples.

Calculate the heat of formation of benzene, given that the heats of combustion of benzene, carbon and hydrogen are 754,300 cals., 94,380 cals., and 68,380 cals. respectively. (Agra B.Sc., 1944)

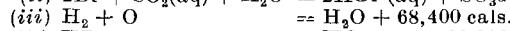
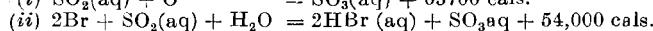
25. State and explain Hess's Law of constant heat summation. Illustrate its application with the help of a few examples.

Find out the heat of the following reaction :



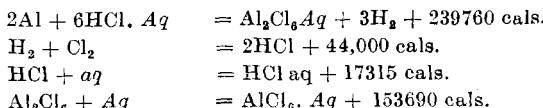
Given the heats of formation of CaCl_2 and NaCl as 191 cals. and 97.7 Cals. respectively.

26. Calculate the heat of formation of anhydrous hydrobromic acid from the following data :—



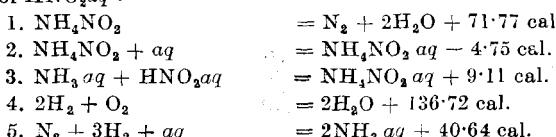
(Nagpur B.Sc., 1953)

27. From the following data calculate the heat of formation of anhydrous Al_2Cl_6 ,



(Poona B.Sc., 1956)

28. States Hess's Law. From the following data, calculate the heat of formation of HNO_3aq :—

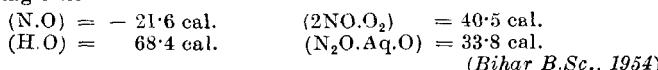


Given 1 cal. = 1000 calories.

(Andhra B.Sc., 1952)

29. Explain the meaning of the term 'heat of formation' and 'heat of combustion' and state Hess's law of heat summation. What differences are to be noted between chemical compounds according as they are formed with evolution or absorption of heat ?

Deduce the heat of formation of nitric acid in dilute solution ($\text{HNO}_3\text{. Aq}$) from the following data :—



(Bihar B.Sc., 1954)

30. (a) State and explain with illustration Hess's law of heat summation.

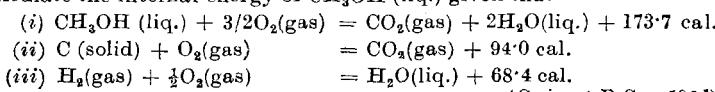
(b) Calculate the heat change accompanying the following reaction :—



Given the heat of formation of CaCl_2 = 191,000 calories and of NaCl = 97,700 calories. (Calcutta B.Sc., 1954)

31. State Hess's Law of constant heat summation and discuss its applications.

Calculate the internal energy of CH_3OH (liq.) given that



(Gujarat B.Sc., 1954)

32. (a) State and explain Hess's Law of constant heat summation.

(b) Heats of formation of carbon dioxide and water are 97.0 and 68.4 cals. respectively. If the heat of combustion of Benzene is 783.4 cals., calculate the heat of formation of Benzene. (Jammu & Kashmir B.Sc., 1954)

33. State Hess's law of constant heat summation and point out its usefulness.

At $T^\circ\text{K}$ heat evolved in the reaction $(\text{H}_2) + \frac{1}{2}(\text{O}_2) = (\text{H}_2\text{O})$ is $57,539 + 1.08T + 0.00145T^2 + 0.00000074T^3$ cal. and the heat evolved in the reaction $\text{C} + \frac{1}{2}(\text{O}_2) = \text{CO}$ is $27070 - 2.05T + 0.00255T^2 - 0.0000005 T^3$ cal. Calculate the amount of heat that will be evolved or absorbed when the reaction



is carried at 1000°K . (Lucknow B.Sc., 1954)

34. What is the difference in the heats of reaction at constant volume and constant pressure ? Given the heat of certain reaction at constant volume, what correction will you make to convert it into heat of the same reaction at constant pressure ?

35. By the combustion at constant pressure of 2 grams of hydrogen with oxygen to form liquid water at 17°C , 68,360 cals. are evolved. What is the heat evolved at constant volume ?

36. What do you understand by the terms "heat of reaction", "heat of formation" and "thermo-chemical equation" ? What is the relation between

heat of reaction at constant pressure and heat of reaction at constant volume ? Illustrate with an example how the heat of reaction is determined indirectly.

37. How would you determine the heats of reaction at constant volume and at constant pressure ? Give the relation between the two.

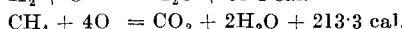
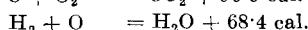
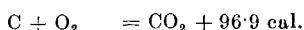
The heat of formation of C_2H_4 at $17^\circ C$ and at constant pressure is -2710 cals. What is its heat of formation at constant volume ? (Andhra B.Sc., 1953)

38. Explain with illustration any two of the following : (a) heat of solution, (b) heat of neutralisation, (c) heat of formation, and (d) heat of dilution.

The heat of combustion of 1 gm. mol. of methane is 213.8 kilo cals. and the heats of formation of CO_2 and of water are 94.3 and 68.3 kilo cals. respectively. Calculate the heat of formation of methane. (Utkal B.Sc., 1952)

39. Explain (a) endothermic and exothermic reactions, (b) heat of combustion and neutralization and (c) intrinsic energy.

Calculate the heat of formation of methane (CH_4) from the following data :—



(Allahabad B.Sc., 1955)

40. Explain what is meant by the heat of formation of a compound. Calculate the heat of formation of benzene, given that the heats of combustion of benzene, carbon and hydrogen are 754,300 cals., 94,380 cals. and 68,380 cals. respectively. (Banaras B.Sc., 1955)

41. Define heat of reaction and describe a method for its determination. What are exothermic and endothermic compounds ? (Delhi B.Sc., 1955)

42. Explain the terms 'heat of reaction', 'heat of formation', 'thermochemical equation'. What is the relation between the heat of reaction at constant pressure and heat of reaction at constant volume ? Illustrate with an example how the heat of a reaction can be determined indirectly.

(Andhra B.Sc., 1955)

43. State Hess's law and show that it follows from the first law of thermodynamics. Give two examples to illustrate the use of Hess's law in finding the heat of formation of compounds. (Osmania B.Sc., 1955)

44. What do you understand by the intrinsic energy of a compound ?

Calculate the heat of formation of carbon disulphide, given that the heats of combustion of CS_2 , sulphur and carbon are 265,100 cals. 710,80 cals. and 94,300 cals. respectively. (Rajputana B.Sc., 1955)

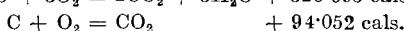
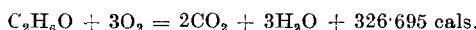
45. The heat evolved during the formation of a given compound could not be determined directly. How would you proceed to measure the heat of formation of such a compound ?

Given that the heat of combustion of carbon disulphide is 256.1 cals., and heat of formation of carbon dioxide and sulphur dioxide respectively are 94.3 and 71.0 Cals. Calculate the heat of formation of carbon disulphide.

(Punjab B.Sc., 1955)

46. Explain (a) Hess's law of constant heat summation (b) heat of solution (c) heat of neutralisation.

Calculate the heat of formation of ethyl alcohol from the following data :—



(Rangoon B.Sc., 1956)

47. What is the relation between heat of reaction at constant pressure and heat of reaction at constant volume ?

The heat of combustion of C_2H_4 at $17^\circ C$ at constant volume is 332,190 calories. What is the heat of combustion at constant pressure ?

(Rajputana B.Sc., 1956)

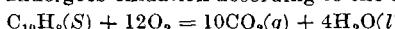
48. State Hess's law and show how it could be used to find the heat of formation of an organic compound. The heat of combustion of methane is

210,800 cals. The heats of formation of CO_2 and H_2O are 91,300 cals. and 68,300 cals. respectively. Calculate the heat of formation of methane.

(Aligarh B.Sc., 1955)

49. Define the terms 'heat of formation' and 'heat of combustion'. Show how Hess's law relates these two together.

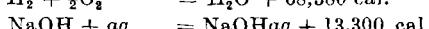
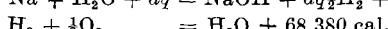
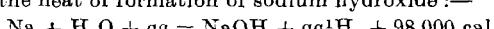
Naphthalene undergoes oxidation according to the equation :



and its heat of combustion is 1232.5 k. cals. Given that the heat of formation of carbon dioxide gas is 97.0 K. cals. and of liquid water is 68.4 cals. calculate the heat of formation of naphthalene.

(Osmania B.Sc., 1956)

50. State Hess's law of constant heat summation. From the following data, calculate the heat of formation of sodium hydroxide :—



(Bombay B.Sc., Subs., 1956)

51. State and explain Hess's Law of Constant Heat Summation. From the following data calculate the heat of formation of benzene from the elements in their standard state :

Heat of formation of water = - 68 K. cals.

Heat of formation of carbon dioxide = - 96.75 K cals.

Heat of combustion of benzene = - 799.3 K. cals.

(Travancore B.Sc., 1956)

52. The heats of combustion of one gram-atom of carbon and one-gram molecule of carbon monoxide are 97,000 & 68,000, cals. respectively at constant pressure and at 18°C. Calculate the heat of formation of carbon monoxide at constant pressure and at constant volume.

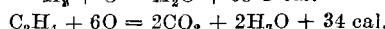
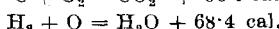
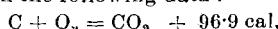
(Aligarh B.Sc., 1957)

53. State and discuss the laws of thermochemistry.

Liquid ethanol burnt in oxygen at 25°C shows $\Delta H = +325.0$ K. cals. Heat of formation of $\text{CO}_2(\text{gas})$ and $\text{H}_2\text{O}(l)$ are - 94.3 K. cals. and - 68.3 K. cals. respectively at the same temperature. Calculate the heat of formation of ethanol at 25°C.

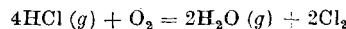
(Jammu & Kashmir B.Sc., 1958)

54. Discuss Hess's law of thermochemistry. Calculate the heat of formation of ethylene from the following data :—



(Punjab B.Sc., 1959)

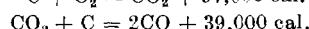
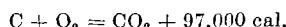
55. If the heats of formation of water vapour and hydrochloric acid gas are 57.8 and 22.0 kg. calories respectively, calculate the heat of the following reaction :



(Rangoon B.Sc., 1958)

56. Explain Hess's law and give a short account of its applications.

Calculate the heat of combination of carbon monoxide given the following heats of reaction :—



(Patna B.Sc., 1958)

57. State and explain Hess's law of constant heat summation.

Calculate the heat of formation of a hydrocarbon C_2H_4 with the help of this law if its heat of combustion is a calories and the heats of formation of carbon dioxide and water are b and c calories respectively. (Agra B.Sc., 1959)

58. What are the laws of thermochemistry? Describe a method of determining the heat of neutralisation of an acid by a base.

(Vikram B.Sc., 1959)

59. State Hess's law of Constant Heat Summation.

If the heats of combustion of benzene, carbon and hydrogen are q_1 , q_2 and q_3 calories respectively, what will be the heat of formation of benzene.

(Rajasthan B.Sc., 1959)

60. State the Hess's law of constant heat summation. Explain with examples the uses of this law in thermochemistry. (Venkateswara B.Sc., 1959)

61. The heat evolved during the formation of a given compound could not be determined directly. How would you proceed to measure the heat of formation of such a compound ? (Osmania B.Sc., 1959)

ANSWERS

- | | |
|---|---------------------------------|
| 4. 54,900 cals. | 5. 35,000 calories. |
| 6. 2.73 cals. | 7. 21,700 cals. |
| 8. 67.1 cal. | 12. 102,100 calories. |
| 13. -48,000 cal. | 15. 68,058 calories. |
| 16. -19.8 cals. | 17. 1,410 cals. |
| 18. 105.5 cals. | 19. 18,535 cals. |
| 22. 91,200 cals. | 23. 20,100 cals. |
| 24. 17,120 cals. | 25. 4.4 cals. |
| 26. 9,350 cals. | 27. 321,960 cals. |
| 28. 30.77 cals. | 29. 49.75 cals. |
| 30. 4,400 calories. | 31. -57.1 cal. |
| 32. 3.8 cals. | 33. 32,259 cals. absorbed. |
| 35. 67,490 cals. | 37. -3,290 cals. |
| 39. 17.1 Kilo cals. | 39. 20.4 cals. |
| 40. 17,120 cals. | 44. -28,640 cals. |
| 45. -19.8 cals. | 46. 66.09 cals. |
| 47. 332,190 cals. | 48. 17,100 calories. |
| 49. 11.1 K. cals. | 50. 153,080 calories. |
| 51. -14.8 K. cals. | 52. 29,291 calories. |
| 53. 718.5 K. cals. | 54. 296.6 calories. |
| 55. -27.6 cals. | 56. 58,000 cals. |
| 57. $-\frac{1}{2}(2a - 2bx - cy)$ cals. | 59. $(6q_2 - 3q_3 - q_1)$ cals. |

CHAPTER XX

ELECTROLYSIS AND ELECTRICAL CONDUCTIVITY

ELECTROLYTES AND ELECTROLYSIS

It is a common observation that solutions of acids, bases or salts as well as certain fused substances behave differently than metallic conductors when a current of electricity is passed through them. The passage of electricity through a *metallic conductor* e.g., copper or silver is not accompanied by any chemical transformation while the conduction of electricity through the solution of an acid, base or salt is invariably accompanied by chemical decomposition. A substance which decomposes as a result of the passage of electric current is called an **electrolyte** and this phenomenon of decomposition by electricity is called **electrolysis**. The products of electrolysis appear only at the electrodes, i.e., the two points where the current enters or leaves the solution.

Electrolytes Obey Ohm's Law. Electrolytes obey **Ohm's Law** to the same extent as the metallic conductors. According to this law the current C flowing through a conductor is given by the relation E/R where E is the electromotive force, i.e., the difference of potential at the two ends of the conductor, and R is resistance.

$$C = E/R.$$

The current strength is generally expressed in amperes. The **ampere** is defined, as the current which deposits 0.001118 gm. of silver per second from a 15 per cent solution of silver nitrate in a voltameter of definite dimensions. Quantity of electricity passing through a conductor is the product of current strength and time and is generally expressed in **coulombs**, a **coulomb** being the amount of electricity which passes in one second with a current strength of one ampere.

The unit of electrical resistance is **ohm** and is defined as the resistance at 0°C of a column of mercury 106.3 cm. long and weighing 14.4521 gms. The electromotive force is measured in volts, the **volt** being the difference in potential required to send a current of one ampere through a one ohm resistance.

These three units of electrical measurement are, therefore, related to each other by Ohm's Law as :

$$\text{Ampere} = \frac{\text{Volt}}{\text{Ohm}}$$

Faraday's Laws of Electrolysis. The decomposition of electrolytes by an electric current is governed by two laws first enunciated by Faraday in 1834. According to these laws :

(i) *The amount of chemical decomposition is proportional to the quantity of electricity which passes through an electrolyte (First Law of Electrolysis).*

(ii) When the same quantity of electricity is passed through different electrolytes, the amounts of the products obtained are proportional to their chemical equivalents (**Second Law of Electrolysis**).

It follows from the first law that under normal conditions chemical decomposition is in no way influenced by the form of the

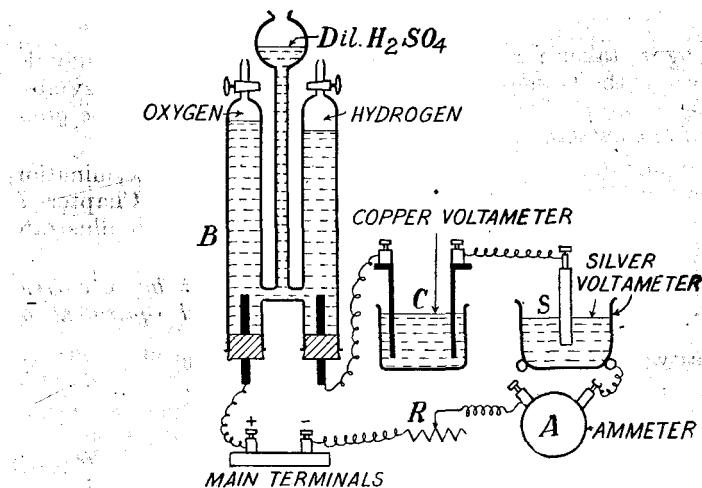


Fig. 175. Illustrating Faraday's Second Law of Electrolysis.

electrodes or the cell and that it is also independent of temperature or the current density.

If W is the weight of substance deposited by a current strength of C amps. in a time t seconds, the first law may be mathematically expressed as :

$$W \propto Ct$$

or

$$W = C \times t \times z$$

where z is a constant known as the **Electro-Chemical Equivalent**. When $C = 1$ and $t = 1$, $W = z$, from this it follows that the electro-chemical equivalent is the amount of a substance deposited by 1 ampere current passing for 1 second (i.e., 1 coulomb).

If we take an arrangement of the type shown in Fig. 175 and pass the same quantity of electricity through three voltameters containing solutions of dilute H_2SO_4 , $CuSO_4$ and $AgNO_3$ respectively and calculate the amounts of hydrogen, copper and silver liberated at the cathodes by one coulomb of electricity, we find these always to be :

$$\text{Hydrogen} = 0.00001036 \text{ gm.}$$

$$\text{Copper} = 31.78 \times 0.00001036 = 0.003692 \text{ gm.}$$

$$\text{Silver} = 107.88 \times 0.00001036 = 0.001118 \text{ gm.}$$

Since the chemical equivalents of hydrogen, copper and silver are respectively 1, 31.78 and 107.88, it follows that the electro-chemical equivalents are proportional to the chemical equivalents.

Now, since the electro-chemical equivalent weight is deposited by one coulomb of the current, the quantity of current needed to

deposit the equivalent weight will be :

$$\text{Hydrogen} = \frac{1}{1.00001036} = 96,515 \text{ coulombs}$$

$$\text{Copper} = \frac{31.78}{0.003292} = 96,537 \text{ , , }$$

$$\text{Silver} = \frac{107.88}{0.001118} = 96,494 \text{ , , }$$

The round figure taken for the quantity of current is 96,500 coulombs and is known as the *faraday*. The **Faraday**, denoted by the symbol F is thus *the quantity of current required to deposit or dissolve one gram equivalent of any substance.*

The importance of Faraday's Second Law in the determination of equivalent weights has already been discussed (See Chapter I, p. 14). Some solved examples are given below in order to illustrate the laws more fully :

Example 1. 0·1978 gm. of copper were deposited by a current of 0·2 amp. in 50 mts. What is the electro-chemical equivalent of copper ?

$$\begin{aligned} \text{Quantity of current passed} &= 0.2 \times 50 \times 60 \\ \text{Copper deposited by } 600 \text{ coulombs} &= 600 \text{ coulombs} \\ \therefore 1 \text{ coulomb will deposit } \frac{0.1978}{600} \text{ gm.} &= 0.1978 \text{ gm.} \\ \therefore \text{Electro-chemical eqvt. of copper} &= 0.0003296. \end{aligned}$$

Example 2. What current strength in amperes will be required to liberate 10 gms. of iodine from potassium iodide solution in one hour ?

96,500 coulombs will liberate the gm. equivalent of iodine = 127 gms.

$$\therefore 10 \text{ gms. iodine will be liberated by } \frac{96,500}{127} \times 10 \text{ coulombs.}$$

Let the current strength be C

Time in seconds = $1 \times 60 \times 60$.

$$\therefore \text{Quantity of current} = C \times 60 \times 60 = \frac{96,000}{127} \times 10$$

or $= 2.1 \text{ amps.}$

Example 3. An electric current is passed through three cells in series containing respectively solutions of copper sulphate, silver nitrate and potassium iodide. What weights of silver and iodine would be liberated while 1·25 gms. of copper is being deposited.

$$\begin{aligned} \frac{\text{Wt. of copper}}{\text{Wt. of iodine}} &= \frac{\text{Eqvt. of Cu}}{\text{Eqvt. of iodine}} \\ \text{or} \quad \frac{1.25}{x} &= \frac{31.7}{127} \end{aligned}$$

$$\text{Whence } x = 4.99 \text{ gms. of iodine}$$

$$\text{Also } \frac{\text{Wt. of copper}}{\text{Wt. of silver}} = \frac{1.25}{y} = \frac{\text{Eqvt. of Cu (31.7)}}{\text{Eqvt. of Ag. (108)}}$$

$$\therefore \text{Wt. of silver (y)} = \frac{108 \times 1.25}{31.7} = 4.25 \text{ gms.}$$

CONDUCTIVITY OF ELECTROLYTES

Specific Conductivity. The resistance offered by a conductor to the passage of electricity through it is proportional to its length *l* and inversely proportional to the area of cross-section *s*, so that the resistance R is given by the relation

$$R = \frac{\rho \times l}{s}$$

where ρ is a constant, the value of which depends upon the material of the conductor and is known as its **specific resistance**. When l and s are both equal to unity, $R = \rho$ from which it follows that *the specific resistance of an electrolyte is the resistance in ohms which a centimeter cube of it offers to the passage of electricity.*

It is evident that a substance which offers very little resistance to the flow of current allows more current to pass through it so that the power to conduct electricity is the converse of resistance. *The reciprocal of specific resistance is termed specific conductivity and is usually denoted by the symbol κ .*

Thus

$$\kappa = \frac{1}{\rho}.$$

Specific conductivity is generally expressed in *reciprocal ohms (r.o.)* or mhos.

In measuring the specific conductivity of the aqueous solution of an electrolyte, the volume of the water in which a certain weight of the electrolyte is dissolved, is always measured in cubic centimeters (c.cs.) and is known as the **dilution**. If the volume of a solution is V c.cs., the specific conductivity of such a solution at this dilution V is written as κ_v . It is the conductivity of one centimeter cube of the solution as shown in Fig. 176.

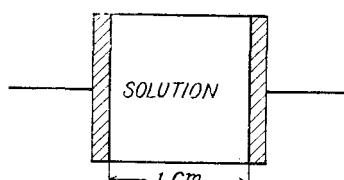


Fig. 176. Diagrammatic illustration of specific conductivity.

Equivalent and Molecular Conductivity. For comparison of conductivities, a definite fundamental weight of the electrolyte must be dissolved in the same volume of water. This weight is either the equivalent or the molecular weight.

If one gram equivalent weight of an electrolyte be dissolved in V c.cs., of the solution, the conductivity of all the ions produced from one gram equivalent is known as the **Equivalent Conductivity** at the dilution V and is written as λ_v . It is equal to the product of the specific conductivity κ_v and the volume V in c.cs., containing one gram equivalent of the electrolyte.

$$\lambda_v = \kappa_v \times V$$

This is illustrated diagrammatically in Fig. 177. A solution having 1 gm. mol. of the electrolyte dissolved in say, 9 c.cs. when placed between two plates 1 cm. apart

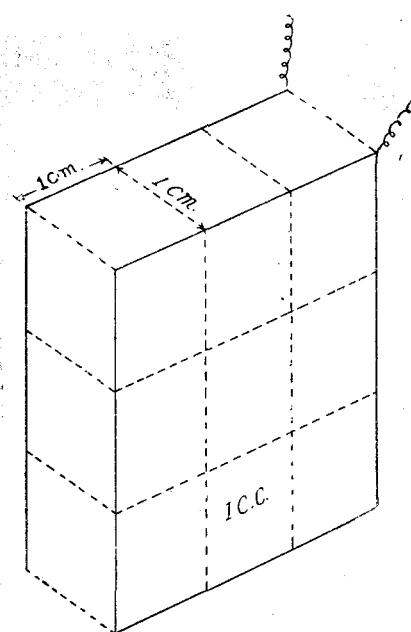


Fig. 177.

will consist of nine cubes each of which has a conductivity κ_v . Thus, total conductivity of the solution will be $9 \times \kappa_v$. Similarly, V c.cs., of solution will form V cubes and hence the total conductivity will be $\kappa_v \times V$.

Similarly, the **molecular conductivity** of a solution is the conductivity of all the ions produced by the dissociation of one gram molecular weight of an electrolyte when dissolved in a certain volume V c.cs. It is written as μ_v and for the same reasons is obtained by multiplying the specific conductivity κ_v by the volume in c.cs. containing one gram molecular weight of the electrolyte.

$$\mu_v = \kappa_v \times V$$

Effect of Dilution on Conductivity. As the solution becomes dilute, the number of current carrying particles or ions present per c.c. of the solution becomes less and less. Since specific conductivity is the conductivity of one centimetre cube of the solution it is to be expected that its value will fall with dilution.

The value of equivalent or molecular conductivity will, however, increase with dilution as it is the product of κ_v and the volume of the solution and on dilution more and more of the electrolyte ionises. When the whole of the substance has ionised, further addition of water produces little or no change in the value of λ_v or μ_v . This is illustrated in the tables below :

TABLE I. SPECIFIC AND MOLECULAR CONDUCTIVITIES OF
NaCl SOLUTION AT 18°C.

Volume V in c.cs. containing 1 gm. mol.	Specific conductivity	Molecular conductivity
1,000	0.0744	74.4
5,000	0.01780	88.2
20,000	0.00479	95.9
500,000	0.000213	106.7
1000,000	0.0001078	107.3
2000,000	0.0000542	108.5
5000,000	0.0000218	109.2
10000,000	0.00001097	109.7

TABLE II. EQUIVALENT CONDUCTIVITIES OF SOME COMMON
ELECTROLYTES AT 18°C.

Volume in c.cs. containing one gm. eqvt.	NaOH	KCl	HCl	CH ₃ COOH	CH ₃ COONa
1,000	160	98.3	301	1.32	41.2
2,000	172	120.4	327	2.01	49.4
10,000	183	112.0	351	4.60	61.1
20,000	190	115.9	360	6.48	64.2
100,000	200	122.4	370	14.3	70.2
200,000	203	124.4	373	20.0	72.4
500,000	206	126.3	376	30.2	74.3
∞	210	127.3	377	41.0	75.2

It is evident from the results given above that the equivalent or molecular conductivity tends to acquire a maximum value with increasing dilution. The maximum value of *equivalent conductivity at infinite dilution* is represented by the symbol λ_∞ and the molecular conductivity at infinite dilution by μ_∞ .

Classification of Electrolytes. A glance at Table II given above shows that electrolytes behave on dilution in two ways:

(i) Electrolytes like NaOH, KCl and HCl have a high value of conductivity even at low dilutions and there is no rapid increase in their equivalent conductivity on dilution. Such electrolytes are called **Strong Electrolytes**. Mineral acids, alkali and alkaline earth hydroxides and most of the salts belong to this type.

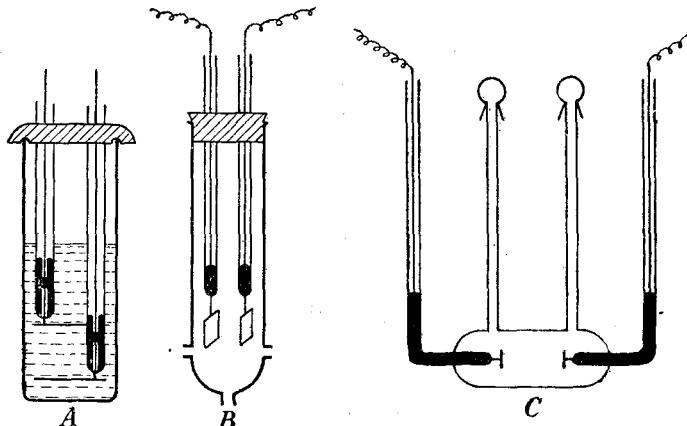
(ii) Substances like acetic acid have a low value of equivalent conductivity at higher concentrations and there is a *rapid increase* in their equivalent conductivity on dilution. Such electrolytes are termed **Weak electrolytes**. Most of the organic acids and bases belong to this class.

It must be remembered, however, that this division is not very sharp but is very convenient for most practical purposes.

Measurement of conductivity. Conductivity is the reciprocal of resistance and the value of latter can be determined by comparing it with known resistances in a Wheatstone bridge circuit.

The solution whose conductivity is to be determined is placed in a special type of cell known as *conductivity cell*. Fig. 178-A shows the type of cell employed for solutions of low conductivity while 174-B and 174-C is employed for highly conducting solutions.

The electrodes consist of platinum discs coated with finely divided platinum black and welded to platinum wires fused in two glass tubes. The glass tubes contain mercury and are firmly fixed in the ebonite cover of the cell so that the distance between the electrodes



DIPPING CELL FOR LIQUIDS OF HIGH CONDUCTANCE

Fig. 178.A, B and C. Conductivity cells.

may not alter during the experiment. Contact with the platinum

is made by dipping the copper wires of the circuit in the mercury contained in the tubes.

The main difficulty in determining the resistance of the solution of an electrolyte is that electrolysis of the solution takes place simultaneously with the conduction of the current and this produces two complications :

- (i) Polarisation soon sets in and causes the resistance to vary.
- (ii) The concentration of the solution alters.

To avoid these complications, an *alternating current* is employed and the galvanometer of the Wheatstone bridge circuit is replaced by a head telephone.

The arrangement is shown in Fig. 179. AB is a wire of *platinoid* or *manganin* having a uniform thickness and tightly stretched over

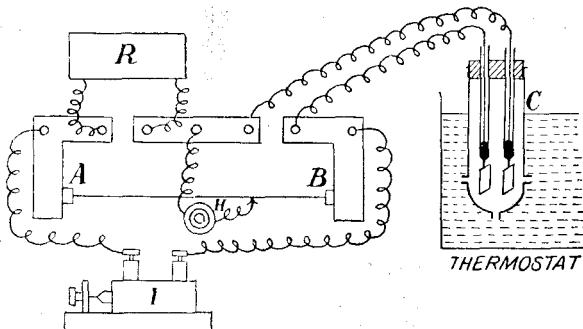


Fig. 179. Apparatus for the measurement of the conductivity of the solution of an electrolyte.

a meter rule graduated in millimetres. A sliding contact H (shown by the arrow head) moves along this wire. R is a resistance box. C is the conductivity cell containing the solution and is placed in the thermostat T for constant temperature measurement. I is the induction coil from which the current is led as shown in the diagram. When the current is flowing, any resistance is unplugged in the resistance box R and the sliding contact H is moved until the sound in the head telephone is the minimum. When this occurs, we have the relation :

$$\frac{\text{Resistance of } C}{\text{Resistance of } R} = \frac{\text{Resistance } BH}{\text{Resistance } AH} = \frac{\text{Length } BH}{\text{Length } AH}$$

or $\text{Resistance of } C = \frac{BH}{AH} \times \text{Resistance of } R.$

Cell Constant. Since the electrodes are not exactly 1 cm. apart and may not possess a surface area of 1 sq. cm. the reciprocal of the resistance C does not give the specific conductivity but a value proportional to it. Its exact value can be determined by measuring the distance between the electrodes and their area of cross-section. Actual measurements of these dimensions being very inconvenient,

1. Since the wire is of uniform material and thickness, the ratio of lengths read on the scale gives the ratio of resistances.

an indirect method is employed to calculate the specific conductivity from the observed value $1/C$.

When l is the distance between the electrodes and s , the area of cross section, the resistance R of the column of liquid enclosed between the electrodes is

$$R = \rho \times \frac{l}{s} \quad \dots(i)$$

or

$$R = \rho \times x$$

The ratio $\frac{l}{s}$ which we have put equal to x is known as the

Cell Constant.

From (i),

$$\text{Cell Constant } x = \frac{R}{\rho} = \frac{\frac{1}{\text{observed conductivity}}}{\frac{1}{\text{specific conductivity}}} = \frac{\kappa}{\text{obs. conductivity}}$$

$\therefore \text{Specific conductivity } \kappa = x \times \text{obs. conductivity.}$

Determination of the Cell Constant. According to the accurate measurements of Kohlraush, the specific conductivity of N/50 KCl solution at $25^\circ C$ is 0.002765 mhos. An N/50 solution of KCl is, therefore, obtained by dissolving 0.372 gm. analytically pure KCl in a 250 c.c. flask in **conductivity water*** and its conductivity determined as explained by placing the cell containing the solution in a thermostat maintained at $25^\circ C$. Then :

$$\text{Cell constant } x = \frac{0.002765}{\text{observed conductivity}}$$

Once the value of cell constant has been determined, great care must be taken not to alter the distance between the electrodes during subsequent measurements in any way.

Example 1. The specific conductivity of an $\frac{N}{50}$ solution of KCl at $25^\circ C$ is 0.002765 mhos. If the resistance of a cell containing this solution is 400 ohms, what is the cell constant?

$$\begin{aligned}\text{Cell constant } x &= \frac{0.002765}{\text{observed conductivity}} \\ &= 0.002765 \times \text{Resistance} \\ &= 0.002765 \times 490 \\ &= 1.106\end{aligned}$$

Example 2. The resistance of decinormal solution of a salt occupying a volume between two platinum electrodes 1.80 cms. apart and

***Conductivity water** is obtained by distilling an acid solution of KMnO_4 in ordinary distilled water through an alkaline solution of KMnO_4 and condensing the vapours by a tin condenser in a jena glass flask provided with a soda lime guard tube. The specific conductivity of such a water is near about 1×10^{-6} mhos.

5.4 sq. cm. in area was found to be 32 ohms. Calculate the equivalent conductivity of the solution.

Here $l = 1.80$ cm. and $s = 5.4$

$$\therefore \text{Cell constant } x = \frac{l}{s} = \frac{1.80}{5.4} = \frac{1}{3}$$

$$\text{Observed conductivity } s = \frac{1}{32} \text{ mhos.}$$

Since the solution is N/10, V = 10,000 c.cs.

Now, specific conductivity = $x \times$ obs. conductivity

or $\kappa = \frac{1}{3} \times \frac{1}{32} = \frac{1}{96}$ mhos.

and Eqvt. conductivity = $\kappa \times V$

$$= \frac{1}{96} \times 10,000 \\ = 104.1 \text{ mhos.}$$

QUESTIONS AND PROBLEMS

1. State and explain Faraday's Laws of Electrolysis. How may these laws be verified ?

2. What is the relation between the quantities of substances liberated at the electrodes when the same quantity of current is passed through different electrodes ? What use is made of this relation ?

3. Explain the terms : (a) Ampere, (b) Coulomb, (c) Faraday. 500 coulombs of electricity were passed through a solution of stannic chloride. What weight of tin would be deposited ?

4. During the electrolysis of brine in a Castner Kellner Cell, 1,000 gms. of chlorine were liberated. What quantity of electricity is required to do this ? Calculate the weight of caustic soda produced

5. The passage of current of electricity through acidulated water and a solution of copper sulphate liberates 203 c.cs. of hydrogen at N.T.P and deposits 0.571 gm. of copper. Calculate the equivalent weight of copper.

6. How can you determine the specific conductivity of the solution of an electrolyte ? How is specific conductivity related to the molecular and equivalent conductivity ?

7. The same current is passed through acidulated water and the sulphate of a metal M. The volume of a hydrogen liberated was 9.87 litres and the weight of the metal deposited 28 gms. The specific heat of the metal is 0.093. Find the formula of the sulphate.

8. Define 'electro-chemical equivalent.' How is it related to the chemical equivalent ?

5 amperes current passing for 30 minutes deposited 10.07 gms. of silver from a silver nitrate bath. Calculate the electro-chemical equivalent of silver.

9. What is cell constant and how is it determined ?

The specific conductivity of an $\frac{N}{50}$ solution of KCl at 25° is 0.002765

mhos. If the resistance of the same solution placed in the cell is 2,000 ohms, what is the cell constant ?

10. 0.5 normal solution of a salt occupying a volume between two platinum electrodes 1.72 cm. apart and of area 4.5 sq. cms. has a resistance of 25 ohms. Calculate the equivalent conductivity of the solution.

11. What is meant by the specific conductivity and the molecular conductivity of a solution of an electrolyte ? Why does the former decrease and the latter increase with dilution ?

12. Explain what do you mean by molecular conductivity. Describe the method of determining the molecular conductivity of an electrolyte, say potassium chloride, and its degree of ionization at a certain dilution.

13. State Faraday's Law of Electrolysis.

14. What do you understand by the term 'molecular conductivity'? Describe the method for the determination of the molecular conductivity of acetic acid at infinite dilution.

15. State how you would proceed to determine experimentally the specific conductivity of a solution of acetic acid.

16. Explain what is meant by equivalent conductivity of an electrolyte. Describe the method you would adopt to measure this quantity. (Agra, 1940)

17. What factors determine the conductivity of a solution? Explain, (i) equivalent conductivity, (ii) molecular conductivity, (iii) specific conductivity. (Agra B.Sc., 1951)

18. What do you understand by the term 'molecular conductivity'? Describe the method for the determination of molecular conductivity of acetic acid at infinite dilution. (Banaras B.Sc., 1953)

19. How is the specific conductivity of an electrolyte determined? Describe carefully the precautions to be observed in the accurate determination of specific conductivity of an electrolyte. How will you obtain equivalent conductivity at infinite dilution of (a) a strong electrolyte and (b) a weak electrolyte. (Bombay B.Sc., 1953)

20. Explain what is meant by equivalent conductivity of an electrolyte. Describe a method you would adopt to measure this quantity. (Agra B.Sc., 1954)

21. How is molecular conductivity of a solution determined? What is the relationship between the molecular conductivity and the degree of ionisation of an electrolyte in solution? (Nagpur B.Sc., 1955)

22. Explain in specific and equivalent conductivities of a solution of an electrolyte and deduce the relation between the two. Describe the determination of the equivalent conductivity of a solution of a salt. (Rangoon B.Sc., 1955)

23. Define (a) Equivalent conductivity; (b) Molecular Conductivity; (c) Cell Constant; and (d) Degree of hydrolysis. (Madras B.Sc., 1955)

24. What is meant by the equivalent conductivity of a substance? Describe how the equivalent conductivity of a substance is experimentally determined. (Mysore B.Sc., 1955)

25. Explain clearly the terms specific conductivity, equivalent conductivity and molecular conductivity. Outline the method that can be used for determining the solubility of a sparingly soluble salt by conductivity method. (Travancore B.Sc., 1956)

26. Describe the conductivity methods of determining (a) the solubility of a sparingly soluble salt and (b) the end points in acid base titrations. (Mysore B.Sc., 1958)

27. 0.5 N solution of a salt surrounding two platinum electrodes 2.1 cms. apart and 4.2 sq. cms. in area was found to offer a resistance of 25 ohms. Calculate the equivalent conductivity of the solution. (Osmania B.Sc. 1959)

28. Explain the terms specific conductivity and equivalent conductivity. Describe how you will obtain the equivalent conductivity of acetic acid in infinite solution from the conductivity measurements. Indicate the precautions which should be observed for accurate determination of specific conductivity. (Vikram B.Sc., 1959)

ANSWER

- | | |
|----------------|--------------------------------------|
| 3. 0.1537 gm. | 4. 2,719,400 coulombs ; 1,126.7 gms. |
| 5. 31.50 | 7. M. SO ₄ |
| 8. 0.001118 | 9. 5.53 |
| 10. 30.56 mhos | 27. 80 mhos. |

CHAPTER XXI IONISATION

THE MECHANISM OF ELECTROLYSIS

Grotthus' Chain Hypothesis. In 1805, Grotthus suggested a scheme of electrolytic action in order to explain the phenomenon of electrolysis. The molecules of an electrolyte which are made up of positive and negative radicals were supposed by him to be present in an haphazard way in solution. On switching the current, however, they arrange themselves in such a way that all the positive constituents face the cathode while the negative constituents face the anode and their free movements in different directions stop.

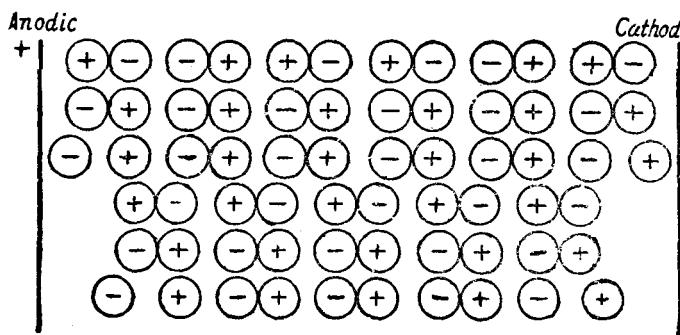


Fig. 180. Grotthus Chain Hypothesis

The molecules nearest to the electrodes then break up under the electrostatic influence of charges on the electrodes on which a radical possessing the opposite charges is deposited. One positive radical is thus left without a partner in the anodic area while one negative radical similarly is left in the cathodic area. These two radicals then decompose the neighbouring molecules and in this manner a *change of partners* takes place throughout the solution. The current again exerts a directive influence which is followed by decomposition and a change of partners.

Objections to Grotthus' Chain Hypothesis. A serious objection, however, arises if we accept this chain mechanism. It follows from the above hypothesis that a certain amount of energy is needed to disrupt the molecules, the value of which should vary with the solute. But we find that electrolytes obey Ohm's Law ($\frac{E}{I} = R$) which implies that the whole of the current is used in overcoming the resistance of the electrolyte and no part of it is utilised in tearing apart the molecules. Moreover a current of even very small electromotive force can cause electrolysis. This can happen only if the ions are present in solution before electrolysis but the hypothesis of Grotthus conceives of no such state.

The Theory of Claussius. In order to explain the electrolysis of the solution of an electrolyte by a current of even very small E.M.F., Claussius suggested in 1857 that the molecules of an electrolyte in solution are in a state of constant agitation and as a result of collisions between them a very small fraction of the solute undergoes disruption into ions.

These ions remain in the free condition only momentarily and reform the molecules of the electrolyte by combining with oppositely charged ions. There is thus a state of equilibrium between the unionised and the ionised molecules, though the number of ions present at any time is extremely small even at high dilutions.

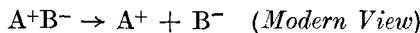
When the electrodes are immersed in the solution, the ions simply move towards the opposite electrode, no electrical energy being required to separate the molecules. As these ions are deposited at the opposite electrodes, their place is taken up by fresh ions produced by the disruption of other molecules and in this way, a current of very small E.M.F. can cause the electrolysis.

The theory of Claussius was only qualitative in character and though it gave a satisfactory mechanism of electrolytic conduction, it failed to explain quantitatively, the various allied phenomena, especially the abnormal behaviour of electrolytes in solution, viz., their higher values of osmotic pressure, depression of freezing point elevation of boiling point, etc., and their increase with dilution.

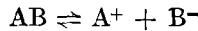
Arrhenius' Theory of Electrolytic Dissociation. In 1884, as a result of quantitative measurements on the electrical conductivity of solutions, Arrhenius put forth a comprehensive theory of ionisation which has been supported and further developed by later work. It gives us not only a simple mechanism of electrolytic conduction but a clear explanation of the conductivity data and the abnormal behaviour of electrolytes observed in dilute solutions. The main points of this theory in its modern form (**Ionic Theory**) may be summed up as follows :

(1) When dissolved in water, salts, bases and acids yield two kinds of particles, one carrying a positive charge and the other equal but negative charge. These charged particles are called **Ions**.

In its most modern form, the theory assumes that the solid electrolyte is a combination of charged ions which are held together by electrostatic lines of force. In the process of solution, these lines of force are cut off and the ions separate.



(2) Ions present in solution constantly reunite to form neutral molecules and thus there is a state of equilibrium between the ionised and the non-ionised molecules. Thus :



Applying the Law of Mass Action to the ionic equilibrium;

$$\frac{[A^+][B^-]}{[AB]} = K \text{ (Ionisation constant.)}$$

(3) When an electric current is passed through the solution of an electrolyte, the positive ions move towards the cathode and the negative ions move towards the anode.

The movements of the ions in this way constitute the electric current through the solution and also explains the phenomenon of electrolysis. The electrical conductivity of a solution depends upon the number of ions present in solution. The fraction of the total number of molecules present in solution as ions is known as the degree of ionisation.

(4) The ions act like molecules in depressing the freezing point, elevating the boiling-point, lowering the vapour pressure and establishing the osmotic pressure. Thus a substance yielding two ions per molecule exerts twice the normal effect of the solute, and one yielding three ions per molecule about thrice the normal effect.

(5) The properties of electrolytes in solution are the properties of the ions. In aqueous solution, acid properties are due to H^+ ions, basic properties due to OH^- ions, and the chemical properties of salts due to the ions constituting them.

FACTORS WHICH INFLUENCE IONISATION

The degree of ionisation of an electrolyte in solution depends upon the following factors :—

1. Nature of Solute. The nature of the solute is the chief factor which determines its degree of ionisation in solution. Strong acids and strong bases, and the salts obtained by their inter-action are almost completely ionised in solution. On the other hand, weak acids and weak bases and their salts are feebly ionised.

2. Nature of the Solvent. The nature of the solvent affects ionisation to a marked degree. It cuts the lines of force binding the two ions and thus separates them. This effect of the solvent is measured by its 'dielectric constant'. The **Dielectric Constant** of a solvent may be defined as its capacity to weaken the force of attraction between the electrical charges immersed in that solvent.

The dielectric constant of vacuum is the minimum and is taken as the standard. The dielectric constant of any solvent is evaluated considering that of vacuum as unity. As shown in the table below, water having a high dielectric constant is a good strong ionising solvent.

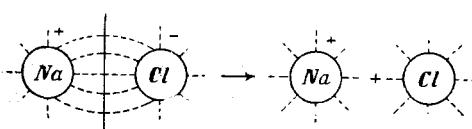


Fig. 181. Ionisation of $NaCl$.

Solvent	Dielectric Constant	Ionisation
Vacuum	...	None
Benzene	2.3	Extremely small
Ether	4.1	Small
Alcohol	25	Moderately strong
Water	80	Very strong

3. Concentration. The extent of ionisation of an electrolyte is inversely proportional to the concentration of its solution. The less concentrated the solution, the greater will be the ionisation of the electrolyte. This is obviously due to the fact that in a dilute solution the ratio of solvent molecules to the solute molecules is large, and the greater number of solvent molecules will separate more molecules of the solute into ions.

4. Temperature. The ionisation of an electrolyte in solution also depends on temperature. The higher the temperature, greater is the ionisation. At high temperature the increased molecular velocities overcome the forces of attraction between the ions and consequently the ionisation is great.

MIGRATION OF IONS

Electricity is carried through the solution of an electrolyte by a migration of the ions. The ions can exist independently in

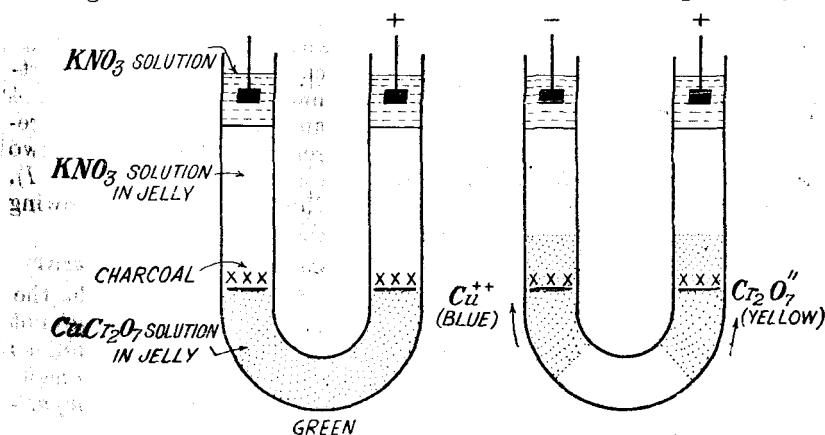


Fig. 182. Migration of ions.

solution and with the passage of the current they move through the solution in opposite directions towards the oppositely charged electrodes and usually at different rates. The phenomenon of ionic migration can be demonstrated by the following experiment :—

The lower part of a U-tube is filled with an aqueous solution of 5 per cent of agar agar and a small amount of copper dichromate. Since this salt is not easily available, a mixture of copper sulphate and pot. dichromate is used instead. This solution, which is dark green in colour, sets to a jelly on cooling. The position of the surface of green solution in the two limbs of the U-tube is

marked by means of a small amount of charcoal scattered on it. In both the limbs is then placed a layer of solution of pot. nitrate and agar agar. This is also allowed to set. Over this second layer is placed some solution of pot. nitrate in pure water in which are inserted the electrodes. As the current is turned on, the blue colour of copper ions rises into the jelly under the negative electrode. The reddish yellow dichromate ions move up in the second arm of the tube towards the anode. After some time the two types of ions are seen moving with well-defined boundaries. The use of jelly in the above experiment prevents the mixing of the solutions by diffusion.

Relative Speeds of Ions during Electrolysis :

It has been pointed out earlier that during electrolysis the ions are liberated in equivalent amounts at the two electrodes. It might be thought, therefore that they move at the same rate. This, however, is not so, for the **the ions are always discharged in equivalent amounts, no matter what their relative speed is.**

The following scheme will make the point clear.

In Fig. 183, A is the anode and C the cathode, α and c are two porous diaphragms which prevent convection currents but allow the

ions to pass. They also divide the cell into an *anodic* and a *cathodic compartment* as shown. The sign + represents a cation while the sign - represents an anion.

Before electrolysis let there be 13 molecules in all. The number of molecules in the two compartments is the same *viz.*, 4 and 5 molecules are present between the two diaphragms α & c : (See I). Now consider the following cases :-

(i) Let the anions (-) alone be capable of movement.

When, say, two anions, have crossed diaphragms towards the anode, we get the position as shown in II. The cations have not moved at all but in spite of that the number of discharged anions and cations is the same, *viz.*, 2. The concentration, in the anodic compartment, however, has not altered while in the cathodic compartment it has fallen by two molecules.

(ii) Let the anions and cations move at the same rate.

When two ions of each type have crossed the diaphragms towards the opposite electrode we get the condition as shown in III. The number of discharged anions and cations is the same, *viz.*, 4. The concentration of both the compartments has also fallen to the same extent *viz.*, by two molecules.

(iii) Let the cations move at twice the speed of the anions.

In this case, when two cations have passed the diaphragms to the right, one anion passes these to the left and we get the state of

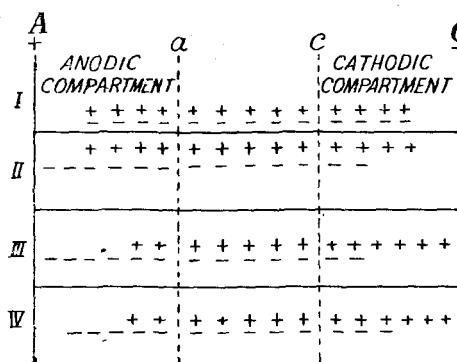


Fig. 183. Scheme showing the equivalence of discharge for any relative rate of motion of the two ions.

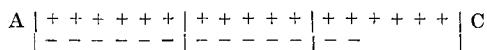
affairs as shown in IV. The total number of discharged anions and cations is again the same, *viz.*, 3, although the concentration in the cathodic compartment has fallen by one while that in the anodic compartment has gone down by 2 molecules.

It is evident from the above considerations that ions are always discharged in equivalent amounts, the effect of difference in their speed causing only a change of concentration around electrodes. It is also obvious that **the loss of concentration around any electrode is proportional to the speed of the ion moving away from it.**

$$\text{or } \frac{\text{Fall round anode}}{\text{Fall round cathode}} = \frac{\text{Speed of cation}}{\text{Speed of anion}}$$

In deriving the above relation, an important assumption has been made, namely, that the discharged ions do not react with the material of the electrodes. In many cases, however, they do combine with the electrodes and an increase of concentration occurs around such an electrode rather than a decrease.

Migration Velocity of Ag^+ and NO_3^- ions. If we study the electrolysis of a solution of silver nitrate in a cell of the type described above but using silver electrodes we find that instead of a fall, the concentration of silver nitrate increases around the anode as the current passes through the solution. This is due to the fact that every nitrate ion that arrives at the anode dissolves from it one ion of silver to form silver nitrate. Supposing that the ions move at the same rate, the state of affairs would have been as shown in Fig. 179 III if the electrodes were of some metal like platinum, *i.e.*, in each compartment a fall of concentration by 2 should have taken place. With silver electrodes, however, we have the condition shown below :



It is clear that the concentration around the cathode has fallen from 4 to 2 as before, but around the anode it has increased from 4 to 6. It is very easy to calculate the speed ratio of the ions in this case as well, by putting a silver voltameter in the circuit which would give us the total current passed or *increase in concentration round the anode that would have been if no silver ions had migrated towards the cathode.* The difference between this total increase and the actual increase around the anode gives the fall in concentration around the anode due to the migration of silver ions.

Example. In an experiment, the increase in concentration of AgNO_3 round the silver anode was 5·6 mgs. of silver. 10·73 mgs. of silver were deposited by the same current in the silver voltameter placed in series. Find the speed ratio of the silver and nitrate ions.

Fall of concentration round cathode (= rise of concentration round anode) = 5·6 mg.

If no silver ions had migrated from the anode, the increase in concentration round the anode would have been 10·78 mgs. silver. But the actual increase is 5·6 mgs.

\therefore Fall round anode due to migration of $\text{Ag}^+ = (10.73 - 5.6)$
 $= 5.13$

$$\frac{\text{Speed of } \text{Ag}^+}{\text{Speed of } \text{NO}_3^-} = \frac{\text{Fall round anode}}{\text{Fall round cathode}} = \frac{5.13}{5.6} = 0.916.$$

Transport Numbers :

During the electrolysis, the current if carried by the anions and the cations and the amount carried by each is proportional to its speed. If u represents the speed of migration of the cation and v that of the anion, $\frac{u}{u+v}$ represents the share taken by the cation in the transport of the current and is called its **Transport number or Hittorf's Number**.

Similarly, $\frac{v}{u+v}$ is the fraction of the total current carried by the anion or its *transport number*. The transport number of the anion ($-$) is generally represented by n , so that the transport number of the cation will be $1-n$.

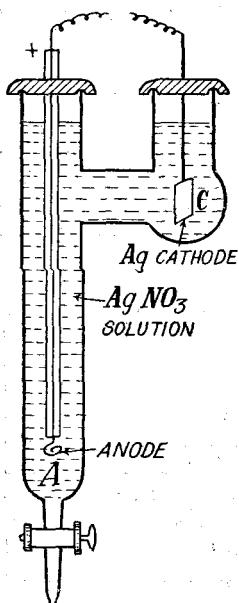


Fig. 184.
Transport Apparatus.

$$n = \frac{v}{u+v} \text{ and } 1-n = \frac{v}{u+v}$$

$$\text{or } \frac{u}{v} = \frac{1-n}{n}$$

If the speed ratio $\frac{u}{v}$ be denoted by r , we have

$$r = \frac{1-n}{n} \text{ or } n = \frac{1}{1+r}.$$

Determination of transport number of silver and nitrate ions. The transport numbers are generally determined in an apparatus of the type shown in Fig. 184. It has two limbs, one much longer than the other and connected to it by a short wide tube. The silver anode is placed in the longer limb and is sealed in a glass tube in such a way that only a small portion of it bent in the form of a spiral is in contact with the solution well below in the limb. The lower end of the limb is in the form of a tap. The cathode C is a piece of freshly silvered silver foil. The apparatus is filled up with a standard solution of silver nitrate and a steady current about 0.01 amperes is passed for two to three hours. It is an important precaution to pass the current only for a short time so that the concentration alters only in the lower part of the anode limb. The transport apparatus is connected with a copper or silver voltameter in series as depicted in Fig. 185, which shows the circuit for the experiment.

When the current has been passed for about three hours, a suitable quantity of the solution is very carefully drawn from the lower

portion of the anode limb in a weighed flask and its weight determined. Its silver content is determined by titration against a

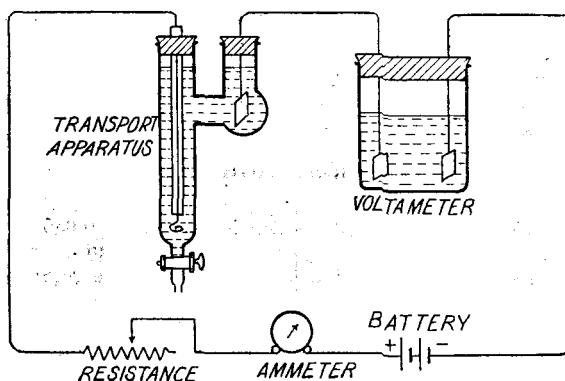


Fig. 185. Experimental measurement of transport numbers.

standard solution of potassium thiocyanate. The weight of silver deposited in the silver voltameter is also noted or if a copper voltameter is used the weight of silver equivalent to the copper deposited there is calculated by multiplication with $\frac{108}{31.5}$.

In an actual experiment, let W grams be the weight of silver deposited in the silver voltameter and let a gms. of the anode solution contain b gms. of silver nitrate.

$$\therefore \text{Wt. of water} = (a - b) \text{ gms.}$$

Let the weight of silver nitrate associated with $(a - b)$ gms. of water at the beginning of the experiment be c .

$$\therefore \text{Increase in wt.} = (b - c) \text{ gms. } \text{AgNO}_3$$

$$= (b - c) \times \frac{108}{170} \text{ gms. Ag.}$$

$$= w \text{ gms silver.}$$

If no silver had migrated from the anode, increase would have been W gms.

\therefore fall in concentration due to

$$\text{migration of silver ions} = (W - w) \text{ gms.}$$

$$\text{Hence, Transport No. of } \text{Ag}^+ = \frac{W - w}{W}$$

$$\text{and that of nitrate ion} = 1 - \left(\frac{W - w}{W} \right).$$

Calculation of Transport Numbers. The following two cases arise :

CASE I. When the electrodes are unattackable

Example 1. The original strength of a solution of caustic soda was 0.059 gm. per 100 c.c. After electrolysis between platinum electrodes 100 c.cs. of the cathode solution contained 0.06315 gm. NaOH and the same current deposited 0.05216 gm. silver in a silver voltameter. Find the transport numbers of Na^+ and OH' ions.

The current which deposits 0.05216 gm. silver in the voltameter

$$\begin{aligned}\text{would decompose NaOH} &= 0.05216 \times \frac{40}{108} \\ &= 0.01932 \text{ gm.}\end{aligned}$$

$$\begin{aligned}\text{Increase in NaOH round the cathode} &= 0.06315 - 0.059 \\ &= 0.00415 \text{ gm.}\end{aligned}$$

If no hydroxyl ion had migrated from the cathode, the increase would have been equal to 0.01932 gm.

\therefore Fall round cathode due to the migration of hydroxyl ions

$$\begin{aligned}&= 0.01932 - 0.00415 \\ &= 0.01517\end{aligned}$$

$$\begin{aligned}\text{Hence Transport number of OH}' \text{ ion} &= \frac{0.01517}{0.01932} \\ &= 0.785\end{aligned}$$

$$\begin{aligned}\therefore \text{Transport No. of Na}^+ \text{ ion} &= 1 - 0.078 \\ &= 0.215\end{aligned}$$

CASE II. When the electrodes are attackable

Example 2. In an electrolysis of copper sulphate between copper electrodes the total mass of copper deposited at the cathode was 0.153 gm. and the masses of copper per unit volume of the anode liquid before and after electrolysis were 0.79 and 0.91 gm. respectively. Calculate the transport numbers of the Cu^{++} and $\text{SO}_4^{''}$ ions.

Wt. of copper in the anode liquid before electrolysis = 0.79 gm.

Wt. of copper in the anode liquid after electrolysis = 0.91 gm.

Increase in weight = 0.91 - 0.79 = 0.12 gm.

Increase in wt. of copper cathode in the voltameter = 0.153 gm.

This means that if no copper had migrated from the anode, increase in weight would have been 0.153 gm.

But actual increase = 0.12.

Fall in concentration due to migration of Cu^{++} ions = 0.153 - 0.12
= 0.033

\therefore Transport number of Cu^{++} ion = $\frac{0.033}{0.153} = 0.215$

and Transport number of $\text{SO}_4^{''}$ ion = $(1 - 0.215) = 0.785$.

Example 3. The speed ratio of the silver and nitrate ions in a solution of AgNO_3 electrolysed between silver electrodes is 0.916 (See example pp. 359-60). Find the transport number of the two ions.

$$\frac{\text{Speed of } \text{Ag}^+}{\text{Speed of } \text{NO}_3'} = \frac{u}{v} = r = 0.916$$

Now $r = \frac{u}{v} = \frac{1 - n}{n}$ when n is the transport number of the anion

$$n = \frac{1}{1+r}$$

$$\therefore \text{Transport No. of } \text{NO}_3' \text{ ion} = \frac{1}{1 + 0.916} = 0.521$$

and Transport No. of Ag^+ ion = $(1 - 0.521) = 0.479$.

KOHLRAUSH'S LAW

An examination of the equivalent conductivity of electrolytes at infinite dilution reveals an interesting relationship between conductivity and transport numbers. At 25°C the values λ_∞ for some electrolytes are given below :

Electrolyte	λ_∞ 25°C	Difference	Electrolyte	λ_∞ 25°C	Difference
NaBr NaCl	128·51 126·45	2·06	KBr NaBr	151·92 128·51	23·41
KBr KCl	151·92 149·86	2·06	KCl NaCl	149·86 126·45	23·41
LiBr LiCl	117·09 115·03	2·06	KNO ₃ NaNO ₃	144·96 121·55	23·41
NH ₄ Br NH ₄ Cl	151·80 149·74	2·06	KOH NaOH	271·52 248·11	23·41

It is clear from the above figures that when the bromide ion is replaced by the chloride, a constant difference of 2·06 is produced in the value of the conductivity at infinite dilution. Similarly, the replacement of potassium by sodium causes a difference of 23·41 units when the anion remains the same. *In other words, each ion makes a certain definite contribution to the conductivity of the solution. This regularity was first of all noticed by Kohlraush (1875) and is known as Kohlraush's Law, which may be stated as follows:—*

The equivalent conductivity at infinite dilution is for different electrolytes, the sum of two values, one depending upon the cation and the other on the anion

$$\text{or } \lambda_\infty = \lambda_a + \lambda_c$$

The values λ_a and λ_c are called the **Ionic mobilities** of the anion and cation respectively.

Applications of Kohlraush's Law

For each ion, the ionic mobility possesses a constant value at a fixed temperature and is the same no matter of which electrolyte it forms a part. It is expressed in ohms⁻¹ cms² and is directly proportional to the speeds of the ions

$$\lambda_a \propto v \text{ or } \lambda_a = k \times v$$

$$\lambda_c \propto u \text{ or } \lambda_c = k \times u$$

$$\text{Also } \lambda_\infty = (\lambda_a + \lambda_c) = k(u + v)$$

$$\therefore \frac{\lambda_a}{\lambda_\infty} = \frac{kv}{k(u+v)} = \frac{v}{u+v} = n \quad \dots(i)$$

$$\text{and } \frac{\lambda_c}{\lambda_\infty} = \frac{ku}{k(u+v)} = \frac{u}{u+v} = (1-n) \quad \dots(ii)$$

Dividing (i) by (ii) we have

$$\frac{\lambda_a}{\lambda_c} = \frac{n}{1-n}.$$

The above relationship between ionic mobilities and transport numbers helps us to determine ionic mobilities from the experimental values of the transport number of ions.

(1) **Calculation of λ_∞ for Weak Electrolytes.** Weak electrolytes do not ionise to a sufficient extent in solution and are far from being completely ionised even at very great dilution. The practical determination of λ_∞ in such cases is, therefore, not possible but it can be calculated with the help of Kohlraush's Law. Thus :

$$\frac{\lambda_a}{\lambda_c} = \frac{n}{1-n}$$

or $\lambda_a - n\lambda_a = n\lambda_c$

or $\lambda_a = n(\lambda_a + \lambda_c)$
 $= n\lambda_\infty$

or the mobility of an ion is obtained by multiplying the equivalent conductivity at infinite dilution of any **strong electrolyte** containing that ion by its transport number. In this manner the ionic mobilities of the two ions present in the weak electrolyte can be calculated and we get its equivalent conductivity at infinite dilution by adding up these two values.

Example. At $18^\circ C$, the equivalent conductivity at infinite dilution for HCl and CH_3COONa are 383.5 and 78.4 respectively. If the transport numbers of hydrogen and acetate ions are 0.841 and 0.46 respectively, calculate the ionic mobilities of the acetate and hydrogen ions as well as the equivalent conductivity of acetic acid at infinite dilution.

$$\begin{aligned}\text{Mobility of } H^+ &= \lambda_\infty \text{ for HCl} \times \text{Transport No. of } H^+ \\ &= 383.5 \times 0.841 \\ &= 322.52 \text{ mhos}\end{aligned}$$

$$\begin{aligned}\text{Mobility of acetate ion} &= \lambda_\infty \text{ for } CH_3COONa \times \text{Tr. No. of acetate ion} \\ &= 78.4 \times 0.46 \\ &= 36.06 \text{ mhos}\end{aligned}$$

$$\begin{aligned}\therefore \text{Conductivity of acetic acid at infinite dilution} &= \lambda_a + \lambda_c = 36.06 + 322.52 \\ &= 358.58 \text{ mhos.}\end{aligned}$$

(2) **Calculation of Absolute Ionic Mobilities.** The **absolute ionic mobility** or the absolute velocity of an ion represents its velocity in centimetres per second under a potential gradient of one volt per centimetre. (Potential gradient = applied E.M.F./distance between the electrodes). For example, if the velocity of the ion at infinite dilution is u cms. per second when the distance between the electrodes is 20 cms. and voltage is 100, the potential gradient is

$100/20$ i.e., 5 volts per cm. and the absolute mobility is $\frac{u}{5}$ cms./sec.

It has been shown that under a potential gradient of 1 volt/cm., the value of the constant k referred to above viz., in $\lambda_a = k \times v$ and

$\lambda_e = k \times u$ is the charge on one gm. equivalent of the ion i.e., 96,500 coulombs (= 1 Faraday). The absolute ionic mobility is, therefore, obtained by dividing the ionic mobility by 96,500.

Example. The molecular conductivity at infinite dilution of KCl is 130.1. The Hittorf number, n , of the chlorine ions in very dilute solution is 0.505. Calculate the mobilities in cm./sec. of potassium and chlorine ions.

$$\begin{aligned}\text{Ionic mobility of chlorine ion, } (\lambda_a) &= \lambda_\infty \times n \\ &= 130.1 \times 0.505\end{aligned}$$

$$\begin{aligned}\text{Ionic velocity of chlorine ion } (v) &= \frac{130.1 \times 0.505}{96,500} \\ &= 0.000681 \text{ cm./sec.}\end{aligned}$$

$$\text{Ionic mobility of } K^+ = \lambda_\infty \times (1-n) = 130.1 \times 0.495$$

$$\text{Absolute Ionic mobility of } K^+ \text{ i.e., } u = \frac{130.1 \times 0.495}{96,500} = 0.000667 \text{ cm./sec.}$$

(3) Calculation of the solubility of sparingly soluble salts.

Substances like $AgCl$ or $PbSO_4$ which are ordinarily called insoluble do possess a definite value of solubility in water, the value of which can be determined from conductivity measurements of their saturated solutions (See chapter XXI). Since a very small amount of solute is present, it must be completely dissociated into ions even in a saturated solution so that the equivalent conductivity κV is equal to equivalent conductivity at infinite dilution which according to Kohlraush's Law is the sum of the ionic mobilities.

$$\text{i.e., } \kappa V = \lambda_\infty = \lambda_a + \lambda_e$$

knowing κ and λ_∞ , V can be found out which is the volume in c.c. containing 1 gm. eqvt. of the electrolyte.

Example. The specific conductivity of a saturated solution of silver chloride at $18^\circ C$ is 1.24×10^{-6} mhos. after subtracting that of water. The mobilities of Ag^+ and Cl^- ions at this temperature are 53.8 and 65.3 respectively. Calculate the solubility of silver chloride in grams per litre.

Here

$$\kappa = 1.24 \times 10^{-6} \text{ mhos}$$

and

$$\lambda_\infty = \lambda_{Ag} + \lambda_{Cl} = 53.8 + 65.3 = 119.1$$

Now

$$\lambda_\infty = \kappa \times V$$

or

$$119.1 = 1.24 \times 10^{-6} \times V$$

∴

$$V = \frac{119.1}{1.24 \times 10^{-6}} \text{ c.cs.}$$

i.e.,

$$\frac{119.1}{1.24 \times 10^{-6}} \text{ c.cs. contain } AgCl = 1 \text{ gm. eqvt.}$$

$$= 143.5$$

$$\therefore 1000 \text{ c.cs. contain } AgCl = \frac{143.5 \times 1.24 \times 10^{-6}}{119.1} \times 1000$$

$$= \frac{143.5 \times 1.24}{119.1} \times 10^{-3}$$

$$= 1.494 \times 10^{-3} \text{ gm.}$$

(4) Calculation of the Apparent Degree of Ionisation or Conductivity Ratio. The apparent degree of ionisation, α , of an

electrolyte at the dilution V is given by $\alpha = \frac{\lambda_v}{\lambda_\infty}$ where λ_v is the equivalent conductivity of the electrolyte at the dilution V and λ_∞ is its equivalent conductivity at infinite dilution and this according to Kohlraush's Law is the sum of λ_a and λ_c .

Example 1. The mobility of silver ion at 18° is 55.7 and of the nitrate ion 60.8. If the specific conductivity of $AgNO_3$ in a decinormal solution at 18° is 0.00947 mhos., what will be the percentage of dissociation of the salt at this concentration?

$$\text{Specific conductivity } (\kappa) \text{ in } \frac{N}{10} \text{ solution} = 0.00947 \text{ mhos.}$$

$$\text{Volume containing 1 gm. equivalent} = 10,000 \text{ c.cs.}$$

$$\therefore \text{Eqvt. Conductivity at this dilution} = 0.00947 \times 10,000 \\ = 94.7 \text{ mhos.}$$

$$\text{Eqvt. Conductivity at infinite dilution} = 55.7 + 60.8 = 116.5$$

$$\therefore \alpha = \frac{94.7}{116.5} = 0.8128$$

Hence the salt is 81.28% dissociated.

Example 2. The equivalent conductivity at 18° of a normal solution of KCl is 98.2, and for infinite dilution at the same temperature

131. Calculate the degree of ionisation of KCl at this dilution.

$$\text{We know } \frac{\lambda_v}{\lambda_\infty} = \alpha$$

$$\text{Here, } \lambda_v = 98.2; \lambda_\infty = 113.$$

$$\therefore \frac{\lambda_v}{\lambda_\infty} = \frac{98.2}{113} = 0.75$$

Hence the degree of ionisation of KCl in normal solution is 0.75.

(5) **Calculation of the Ionic product for water.** The observed specific conductivity of the purest water at $25^\circ C$ is 5.54×10^{-8} mhos. The conductivity of one litre of water containing 1 gram eqvt. of it would be

$$\lambda_{H_2O} = 5.54 \times 10^{-8} \times 1000 = 5.54 \times 10^{-5} \text{ mhos.}$$

At the same temperature the mobilities of H^+ ions and OH^- ions are

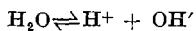
$$\lambda H^+ = 349.8 \text{ mhos.}$$

$$\lambda OH^- = 198.5 \text{ mhos.}$$

According to Kohlraush's Law

$$\begin{aligned} \lambda_{H_2O} &= \lambda_{H^+} + \lambda_{OH^-} \\ &= 349.8 + 198.5 = 548.3 \text{ mhos.} \end{aligned}$$

Since one molecule of water gives one H^+ ion and one OH^- ion,



and assuming that ionic concentration is proportional to conductivity, we have

$$[H^+] = [OH^-] = \frac{5.54 \times 10^{-5}}{548.3} = 1.01 \times 10^{-7} \text{ gm. ion per litre}$$

The ionic product of water is then

$$K_w = [H^+] [OH^-] = 1.02 \times 10^{-14} \text{ at } 25^\circ C.$$

For most purposes, the value of K_w is generally taken to be 10^{-14} .

QUESTIONS AND PROBLEMS

- Give a brief account of the Ionic Theory and show how it explains the phenomenon of electrolysis.
- Give a short account of the theory of electrolytic dissociation, and indicate what explanation it gives of (a) electrolysis and (b) the heat of neutralisation of a strong acid by a strong base.
- Give a short account of the theory of electrolytic dissociation, and show that it provides an explanation for the abnormal osmotic pressure observed in the case of electrolytes.
- (a) Discuss the mechanism of conduction of electricity through an aqueous solution of sodium chloride.
(b) Explain the following terms :—(i) cations, (ii) anions, (iii) electrochemical equivalents and (iv) Faraday. *(Calcutta B.Sc., 1954)*
- What are the fundamental facts on which the dissociation theory of Arrhenius is based ? State the usefulness of this theory. *(Lucknow B.Sc., 1954)*
- Give an account of the theory of electrolytic dissociation and indicate what explanation it gives of
(a) electrolysis, and
(b) the heat of neutralisation of a strong acid and a strong base. *(Aligarh B.Sc., 1953)*
- What are ions and in what respect do they differ from atoms ? Describe an experiment to illustrate the existence of ions and their relative speed.
- Show that the ions are always discharged in equivalent amounts no matter what their speed is and that the loss of concentration round any electrode is proportional to the speed of the ion moving away from it.
- "The transport numbers of the Ag and NO_3^- ions are 0.474 and 0.526 respectively." Explain this statement and describe an experimental method of obtaining the figures.
- What do you understand by the mobility of an ion ? At 18° the velocity of migration of silver ion is 0.00057 cm./sec. and the nitrate ion 0.00063 cm./sec. What is the value of λ_∞ for silver nitrate at 18° ?
- At 15°C the mobility of Na^+ ion is 43.4 and that of the Cl^- ion is 65.5. Calculate the equivalent conductivity of NaCl at infinite dilution and the transport numbers of Na^+ and Cl^- ions.
- From the electrolysis of HCl in a cell with a cadmium anode, the following results were obtained. Change in concentration of chlorine at anode and cathode respectively ± 0.00545 gm. Silver deposited in a Voltameter connected in series with the cell, 0.0986 gm. Calculate the transport number of H^+ and Cl^- ions.
- A solution of AgNO_3 containing 0.510 gm. of the salt in 60.40 gms. of the solution was electrolysed, under silver electrodes. After electrolysis, 54 gms. of the anode solution was found to contain 0.56 gm. of AgNO_3 . A current of 0.04 amps. was passed for 2950 seconds. Calculate the transport numbers of silver and nitrate ions.
- What evidence can you offer that in a solution of an electrolyte undergoing electrolysis the ions move towards the electrodes at different speeds ?
- What do you understand by the term "transport number" of an ion and how is it experimentally determined ?
- A solution of silver nitrate containing 1.06 milligram. of silver per gram of the solution was electrolysed between silver electrodes and the anode liquid after electrolysis contained 42.94 m. gm. of silver in 25 gms. of the solution. In a silver voltameter in series 31.10 m. gms. of silver were deposited. Calculate the transport number of silver ion. *(Karnatak B.Sc., 1955)*
- Explain the significance and inter-relationship of the following :—
Transport number ; equivalent conductance at infinite dilution ; ionic mobilities.

The velocity of migration of silver ion at 18°C is $0\cdot000577$ cm. per sec. and of the NO_3^- ion $0\cdot000630$ cm. per sec. The specific conductance of $\text{N}/10$ AgNO_3 solution at 18°C is $0\cdot00947$ reciprocal ohm. What is the degree of dissociation of silver nitrate?

17. What is meant by "Transport number" of an ion? Describe the outlines of a method for determining the transport number of Ag^+ and NO_3^- ions in a solution of silver nitrate?

A solution of silver nitrate having the composition $28\cdot435$ gm. H_2O , $0\cdot2099$ gm. AgNO_3 was electrolysed, using silver electrodes. The current passed deposited $0\cdot000792$ gm. equivalent of silver. At the conclusion of the electrolysis the solution around the anode was found to have the composition $28\cdot435$ gms. of H_2O , $0\cdot2874$ gm. of AgNO_3 . Calculate the transport number of the nitrate ion. (Punjab B.Sc., 1950)

18. What do you understand by transport number of ions? Describe a method for the determination of transport number of silver and nitrate ions. (Banaras B.Sc., 1952)

19. The transport numbers of silver and nitrate ions are $0\cdot474$ and $0\cdot526$ respectively. Explain this statement and describe an experimental method for obtaining these numbers. (Nagpur B.Sc., 1953)

20. In a transport number experiment a solution of silver nitrate containing $0\cdot0074$ gm. per gram of water was used. During the experiment $0\cdot0785$ gm. of silver was deposited in silver voltameter placed in series with the transport apparatus. After the experiment 25 gms. of the anode solution contained $0\cdot2553$ gm. of silver nitrate. Find the transport numbers of silver and nitrate ions. The electrodes were of silver. (Delhi B.Sc. 1953)

21. Derive the equation relating the mobility of an ion to its absolute velocity. Outline one method of measuring the absolute velocity of an ion. (Ceylon Final, 1954)

22. Define the term transport number of an ion and describe the method employed to determine it.

During the electrolysis of a solution of CuSO_4 in which $5\cdot047$ gms. CuSO_4 were dissolved in $94\cdot95$ gms. of water, $1\cdot548$ gms. of silver were deposited in Coulometer placed in series with the copper sulphate solution. After electrolysis $137\cdot7$ gms. of the anode solution was found to contain $7\cdot702$ gms. CuSO_4 . Calculate (i) the relative velocities of migration of the copper ion and the sulphate ion, and (ii) the transport number of the sulphate ion. (Poona B.Sc., 1954)

23. How would you determine the transport number for silver and nitrate ions in a silver nitrate solution?

The transport number of silver ion is $0\cdot466$ and that for nitrate ion $0\cdot534$ at 18°C . The molecular conductivity of a very dilute solution of silver nitrate is $115\cdot8$ at the same temperature. Calculate the ionic mobilities of silver and nitrate ions. (Nagpur B.Sc., 1954)

24. State and explain Kohlrausch's Law. How would you measure the conductance at infinite dilution of acetic acid? If the conductance at infinite dilution of NaCl , HCl and CH_3COONa are $126\cdot45$, $426\cdot16$ and $91\cdot0$ respectively, what will be that of CH_3COOH ? (Lucknow B.Sc., 1954)

25. What is meant by equivalent conductivity? How can it be determined experimentally for a decinormal solution of acetic acid and how would you apply Kohlrausch's law to determine its dissociation constant? (Aligarh B.Sc., 1954)

26. Explain Kohlrausch law of migration of ions and the following terms:—(a) Specific conductivity, (b) equivalent conductivity and molecular conductivity at infinite dilution. (Calcutta B.Sc., 1954)

27. At 18° the equivalent conductivity of centinormal solution of HCl , NaCl , CH_3COONa and CH_3COOH is $369\cdot3$, $101\cdot7$, $71\cdot7$ and $14\cdot3$ respectively. Calculate the degree of dissociation of centinormal acetic acid, assuming that the other electrolytes mentioned above are completely ionised. (Agra B.Sc., 1951)

28. At 15° , the conductivity at infinite dilution of HCl and CH_3COONa is 380 and 80 respectively. The transport numbers of hydrogen and acetate-

ions in these electrolytes are 0·84 and 0·56 respectively. Calculate the equivalent conductivity at infinite dilution for acetic acid.

(Agra B.Sc., 1946; Baroda 1956)

29. The equivalent conductance of ammonium chloride at infinite dilution is 149·7 mhos and the ionic conductance of OH⁻ and Cl⁻ ions are 198 and 76·3 mhos respectively. Calculate the equivalent conductance of ammonium hydroxide at infinite dilution. (Bombay B.Sc., 1953)

30. The equivalent conductivity of a deinormal solution of a weak acid is 8·0 mhos. If the equivalent conductivity at infinite dilution of the acid is 400·0 mhos, calculate the dissociation constant.

(Jammu and Kashmir B.Sc., 1953)

31. It was required to find the degree of dissociation of a solution of hydrochloric acid of strength 1·37N at 18°C. Its specific resistance was found to be 2·54 ohms. The equivalent conductivity at infinite dilution of hydrochloric acid is 384 rec. ohms. Calculate the degree of dissociation. (Cl=35·5)

(Patna B.Sc., 1953)

32. State concisely the Arrhenius Theory of electrolytic dissociation pointing out the evidence in favour of the theory.

A solution of BaCl₂ containing 9·0 gms. of the anhydrous salt per litre boils at 100·056°C, under a pressure of 760 mm. Calculate the degree of dissociation of the salt.

Molar elevation, 5·2; Ba, 137·4; Cl, 35·5. (Utkal B.Sc., 1955)

33. In the electrolysis of a solution of hydrochloric acid between cadmium electrodes the following results were obtained :—gain in chlorine round the anode and loss in chlorine round the cathode, 0·00665 gram; silver deposited in a voltameter in a series with the cell, 0·1190 gram. Find the transport numbers of the hydrogen and chlorine ion. (Cl=35·5, Ag=108).

(Andhra, B.Sc., 1955)

34. What do you understand by transport number of an ion? Describe the method for the determination of transport number of Ag⁺ and NO₃⁻ ions.

The equivalent conductivity of a very dilute solution of sodium nitrate at 18°C is 105·2 mhos. Being given that the ionic conductivity of nitrate ion in the same solution is 61·7, calculate the transport number of sodium ions.

(Banaras B.Sc., 1955)

35. Explain the term (a) Transport numbers, (b) Equivalent conductivity at infinite solution, (c) Ionic mobilities, and show their inter-relationship.

The velocity of migration of the silver ion is 0·00577 cm. per sec. and of the nitrate ion 0·000630 cm. per sec. The specific conductivity of N/10 silver nitrate is 0·00947 reciprocal ohms. Find the degree of dissociation of silver nitrate. (Osmania B.Sc., 1955)

36. State and explain Kohlrausch's law of ionic mobility. How does it help in determining the equivalent conductivity at infinite dilution of weak electrolytes?

At 18°C the conductivities at infinite dilution of NH₄Cl, NaOH and NaCl are 129·8, 217·4 and 108·9 mhos respectively. If the equivalent conductivity of N/1000 solution of NH₄OH is 9·33 mhos, calculate the degree of dissociation of ammonium hydroxide at this dilution. (Agra B.Sc., 1955)

37. What is transport number of ions? How will you determine the dissociation constant of NH₄OH by the application of Kohlrausch's law?

(Rajputana B.Sc., 1956)

38. State as clearly as you can the Arrhenius theory of electrolytic dissociation, pointing out the evidence in its favour and also some facts which it fails to explain. How would you define an acid, base and salt in terms of the above theory. (Agra B.Sc., 1956)

39. A solution of silver nitrate containing 1·139 mgs. of silver per gram of solution was electrolysed between silver electrodes and the anode liquid after electrolysis contained 39·66 mgs. silver in 20·09 grams of solution. In a silver voltameter in series with the electrolytic cell 32·10 mgs. of silver was deposited. Calculate the transport numbers of silver and chloride ions.

(Madras B.Sc., 1955)

40. State Kohlrausch's law of independent migration of ions.

Explain the terms 'ionic mobility' and 'absolute velocity of an ion'.

How will you demonstrate the movement of hydrogen ions ?

(Osmania B.Sc., 1956)

41. Describe a method for determining the transport number of silver ion from a silver nitrate solution.

A dilute solution of silver nitrate has an equivalent conductivity of 115.2 and the transport number of silver ion is 0.47. Calculate the mobilities of silver and nitrate ions. (Lucknow B.Sc., 1956)

42. Define the term "transport number" of an ion and describe one method to determine it.

A current which deposited 0.047 gram of copper in a voltmeter containing copper sulphate was passed through a solution of silver nitrate using silver electrodes. The liquid from the cathode contained, before the experiment 1.315 grams of silver, and after the experiment 1.231 grams of silver. Calculate the transport number of the ions in solution. (Baroda B.Sc., 1956)

43. What is meant by the term "transport number of an ion"? Indicate two methods which differ in principle by which the transport number can be determined. How is the transport number influenced by dilution and by changes of temperature? (Travancore B.Sc., 1956)

44. What do you understand by the mobility of an ion?

At 18°C the velocity of migration of silver ion is 0.00057 cm./sec. and that of the nitrate ion 0.00063 cm./sec. What is the value of λ_∞ for silver nitrate at 18°C? (F, Faraday = 96,5000 Coulombs). (Banaras B.Sc., 1956)

45. State clearly what you understand by (a) Transport number and (b) Kohlrausch's law. What important result is obtained by the application of the former to the latter? The equivalent conductivity of ammonium chloride at infinite dilutions is 149.7 mhos and the ionic conductance of OH⁻ and Cl⁻ ions are 198 and 76.3 mhos respectively. Calculate the equivalent conductivity of ammonium hydroxide at infinite dilution. (Nagpur B.Sc., 1957)

46. Explain what you understand by the transport number of an ion. How may the transport number of silver ion in a solution of silver nitrate be determined experimentally? (Jammu & Kashmir B.Sc., 1957)

47. Describe the experimental method for the determination of transport numbers of silver and nitrate ions. (Mysore B.Sc., 1958)

48. What is Hittorf's number? How is it related to the mobilities of ions? Describe with details the determination of Hittorf's number for nitrate ion from a silver nitrate solution. (Allahabad B.Sc., 1958)

49. At 25° the equivalent conductivity of maleic acid at a dilution of 30 litres is 180 r.o. At infinite dilution it is 390 r.o. Calculate the dissociation constant of the acid. (Bombay B.Sc., 1958)

50. The specific conductivity of a solution of acetic acid containing 1 gm. equivalent in 1000 litres of the solution is 4.1×10^{-5} mhos. Calculate the equivalent conductivity of acetic acid and also the degree of dissociation of acetic acid at that dilution. Equivalent conductivity at infinite dilution of acetic acid is 350 mhos. (Rangoon B.Sc., 1958)

51. The velocity of migration of silver ion is 0.00057 cm. and of nitrate ion 0.00063 cm. per second. The specific conductivity of N/10 AgNO₃ is 0.00947 mho. Find the degree of dissociation of AgNO₃ at this dilution. (Aligarh B.Sc., 1958)

52. The specific resistance of a solution of sulphuric acid containing 14.5 gms. of H₂SO₄ per litre is 18 ohms. The equivalent conductivity at infinite dilution is 384 reciprocal ohms. What is the concentration of hydrogen ions in the solution? (Utkal B.Sc., 1959)

53. Define the transport number of an ion. How is it experimentally determined?

A solution of silver nitrate was electrolysed between silver electrodes. Before electrolysis, solution contained 26.50 m.gms. of silver per 25 gms. of the solution. After electrolysis the anode liquid contained 42.94 m.gms. of silver in 25 gms. of solution. 32.10 m.gms. of silver were deposited in a silver voltameter in series. Calculate the transport number of silver ion.

(Karnatak B.Sc., 1959)

ANSWERS

- | | |
|--|--|
| 10. 115.8 | 32. 0.747 |
| 11. 108.9 ; $\text{Na}^+ = 0.399$ and $\text{Cl}' = 0.601$ | 33. 0.83 and 0.17 |
| 12. $\text{H}^+ = 0.832$; $\text{Cl} = 0.168$ | 34. 0.4135 |
| 13. $\text{Ag}^+ = 0.489$; $\text{NO}_3' = 0.511$ | 35. 0.813 |
| 15. 0.488 | 36. 0.03915 |
| 16. 0.813 | 37. $\text{Cl}' = 0.525$; $\text{Ag}^+ = 0.475$ |
| 17. 0.576 | 41. $\text{Ag}^+ = 54.14$; $\text{NO}_3' = 61.60$ |
| 20. $\text{Ag}^+ = 0.4158$; $\text{NO}_3' = 0.584$ | 42. $\text{Ag}^+ = 0.478$; $\text{NO}_3' = 0.522$ |
| 22. (i) 0.4371 : 1 ; (ii) 0.6944 | 44. 115.8 |
| 23. $\text{Ag}^+ = 53.59$; $\text{NO}_3' = 61.85$ | 45. 271.4 |
| 24. 390.71 | 49. 0.0132 |
| 27. 0.04214 | 50. 0.117 |
| 28. 364.0 | 51. 81.8% |
| 29. 271.4 | 52. 0.1447 gm. ion/litre |
| 30. 4.08×10^{-5} | 53. $\text{Ag}^+ = 0.482$; $\text{NO}_3' = 0.518$. |
| 31. 0.7485 | |

CHAPTER XXII

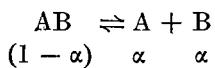
IONIC EQUILIBRIA

APPLICATIONS OF THE IONIC THEORY

OSTWALD'S DILUTION FORMULA

The Ionic Theory visualizes a state of equilibrium between the ionised and the unionised molecules in solution and it was noticed by Ostwald that the Law of Mass Action can be satisfactorily applied to the solution of *weak electrolytes*, i.e., substances which ionise to a very small extent and whose molecular conductivity does not attain a steady value even at high dilutions.

Consider 1 gm. mol. of such an electrolyte AB to be dissolved in V litres of the solution. If α be the degree of ionisation, we have at equilibrium :



i.e., $(1-\alpha)$ gm. mol. of AB and α gm. mol. of each A and B. The active mass of unionised AB is $\frac{1-\alpha}{V}$ while that of A and B is $\frac{\alpha}{V}$ each.

$$\text{Rate of ionisation} = k_1 \times \frac{1-\alpha}{V}$$

$$\text{Rate of combination} = k_2 \times \left(\frac{\alpha}{V} \right)^2$$

At equilibrium :

$$k_1 \times \frac{1-\alpha}{V} = k_2 \times \left(\frac{\alpha}{V} \right)^2$$

$$\text{or} \quad \frac{\alpha^2}{(1-\alpha)V} = \frac{k_1}{k_2} = K$$

The expression $\frac{\alpha^2}{(1-\alpha)V} = K$ is known as **Ostwald's Dilution**

Formula and K is called the **Ionisation constant**. A constant value of K is obtained only in case of weak electrolytes and generally the value of α is very small as compared with 1 so that in most of the calculations we can take V instead of $(1-\alpha)V$. The formula in such cases assumes the form $\frac{\alpha^2}{V} = K$ which implies that the degree of ionisation of a weak electrolyte is proportional to the square root of the dilution, i.e., $\alpha = K' \sqrt{V}$.

Verification of Ostwald's Formula. The dilution formula is derived on the assumption that the Law of Mass Action applies to the ionisation occurring in solution. Its verification, therefore, may be done in the same way as for the Mass Law (p. 232, Chapter XIV) viz., by substituting the values of α at different dilutions V in the

expression $\frac{\alpha^2}{(1-\alpha)V}$ and finding out if the value of K comes out to be constant within reasonable limits.

The value of α is determined by conductively measurements and is obtained by dividing the eqvt. conductivity at a certain dilution (λ_v) by the conductivity at infinite dilution (λ_∞)

$$\alpha = \frac{\lambda_v}{\lambda_\infty}$$

The dilution is effected by withdrawing a certain volume of the solution from the conductivity cell by means of a pipette and adding the same volume of conductivity water. The results obtained in case of acetic acid are summarised in the table below :

TABLE.—Ionisation of Acetic acid in aqueous solution at 25°C
 $\lambda_\infty = 387$

V (litres)	λ_v	$\alpha = \lambda_v/387$	$K = \alpha^2/(1-\alpha)V$
8	4.63	0.012	18.1×10^{-6}
16	6.50	0.0168	17.9×10^{-6}
32	9.20	0.0238	18.1×10^{-6}
64	12.9	0.033	18.0×10^{-6}
128	18.1	0.0468	17.9×10^{-6}
256	25.4	0.0656	18.0×10^{-6}

It is seen that the value of the ionisation constant is very nearly the same.

The ionisation constants for some weak acids and bases at 25°C are given below :

Hydrocyanic Acid	1.3×10^{-9}
Acetic Acid	1.82×10^{-5}
Chloracetic Acid	1.4×10^{-3}
Formic Acid	2.0×10^{-4}
Ammonium hydroxide	1.80×10^{-5}
Methylamine	4.0×10^{-4}
Citric Acid	8.4×10^{-4}
Tartaric Acid	1.1×10^{-3}
Propionic Acid	1.4×10^{-5}

USES OF OSTWALD'S FORMULA

(i) Calculation of Ionisation Constant

Example 1. Formic acid is 4.5% dissociated in a 0.1 N solution at 20°C. Calculate the dissociation constant of the acid.

Let K be the dissociation constant. Then, according to Ostwald's formula :

$$\frac{\alpha^2}{(1-\alpha)V} = K$$

Here if we start with 1 gm. mol.

$$\alpha = 0.045; (1-\alpha) = 0.955 \text{ and } V = 10$$

$$\therefore K = \frac{0.045 \times 0.045}{0.955 \times 10} = 2.1 \times 10^{-4}$$

Example 2. The equivalent conductivity of $\frac{N}{32}$ solution of a weak acid is 9.2 mhos. If the conductivity at infinite dilution is 389 mhos, what is the dissociation constant of the acid?

(Oxford Open Scholarship)

$$\text{Degree of dissociation } \alpha = \frac{9.2}{389} = 0.0236$$

$$(1 - \alpha) = 0.9764 \text{ and } V = 32$$

$$\therefore K = \frac{0.0236 \times 0.0236}{0.9764 \times 32} = 1.8 \times 10^{-5}$$

(2) Calculation of Degree of Dissociation

Example. At 25° the degree of ionisation of propionic acid in $\frac{N}{10}$ solution is 0.01133. What would be the degree of ionisation of this acid at the same temperature in $N/100$ solution?

Using the simplified Ostwald dilution formula :

$$\text{Ionisation constant } K = \frac{\alpha^2}{V} = \frac{0.01133 \times 0.01133}{10}$$

Let α be the degree of ionisation when the dilution is $N/100$ i.e., when $V = 100$ we have

$$K = \frac{\alpha^2}{100}$$

$$\frac{0.01133 \times 0.01133}{10} = \frac{\alpha^2}{100}$$

or

$$\alpha^2 = (0.01133)^2 \times 10$$

or

$$\alpha = 0.01133 \sqrt{10} = 0.036$$

ANOMALY OF STRONG ELECTROLYTES

Ostwald's Dilution Formula fails to give satisfactory results when applied to solutions of *strong electrolytes* i.e., those electrolytes which are highly ionised in solution. The value of ionisation constant K , far from remaining constant, rapidly falls with dilution. In the table below are given the values for potassium chloride in order to illustrate the point.

TABLE.—Ionisation of KCl at 18°C
 $\lambda_\infty = 129.9$

V	λ	$\alpha = \lambda / 129.9$	$K = \alpha^2 / (1 - \alpha)V$
1	98.27	0.7565	2.35
2	102.41	0.7883	1.434
5	107.96	0.831	0.8154
20	115.75	0.891	0.3642
	119.96	0.9234	0.2221
	124.41	0.9577	0.1084

A number of empirical dilution formulae have been suggested by different workers but these again do not fully accord with the behaviour of the electrolytes and some of them have even no theoretical basis. Some of the empirical formulae are :

$$\text{Van't Hoff : } \frac{\alpha^3}{(1 - \alpha)^2 V} = K$$

$$\text{Walker : } \frac{\alpha^2}{(1-\alpha)V} = \frac{K(1-\alpha)}{\alpha}$$

$$\text{J. C. Ghosh : } \sqrt[3]{V} \log \alpha = K$$

$$\text{Kohlrausch : } (\lambda_\infty - \lambda_v) \sqrt{V} = K$$

$$\text{or } \lambda_\infty - \lambda_v = K \sqrt{C}$$

The cause of breakdown may be sought in one or more of the following factors :—

- (i) The concentration of the ions is very high and the presence of charges on the ions appreciably affects the equilibrium. Consequently the law of Mass Action in its simple form cannot be strictly applied.
- (ii) The ions may get hydrated and affect the active mass.
- (iii) The degree of dissociation α cannot be accurately determined by conductivity measurements by using the relation λ_v/λ_∞ which gives the conductivity ratio only represented by f_c .

THEORY OF STRONG ELECTROLYTES

In 1906, Sutherland suggested that all strong electrolytes are almost completely ionised at all dilutions. The charged ions are already present in the solid electrolyte before it is dissolved in water but they have no freedom of movement and are, therefore, ineffective in conducting electricity. On fusing or dissolving the electrolyte in water, they acquire freedom of movement towards the opposite electrode when electrolysed.

While Arrhenius maintained that the increase in conductivity on dilution is due to an increase in the number of ions, Sutherland contended that the number of ions does not alter, it being the maximum already and that the increase in conductivity is due to an increase of the ionic velocities u and v (or the mobilities λ_a and λ_v). The ionic velocities increase partly due to a change in the viscosity of the solution and partly due to the weakening of the inter-ionic forces, each ion having in its neighbourhood a large concentration of ions of the opposite sign.

Not much notice was, however, taken of this view.

Ghosh's Formula. In 1918, J. C. Ghosh revived the above theory. He assumed that though the electrolyte is completely ionised, all the ions are not free to move owing to the influence of electric charges and it is only the *mobile ions* which contribute to the conductivity of the solution. The value α represents the "active" proportion of the salt and can be determined by purely electrical data, the Law of Mass Action playing no part whatsoever. His formula

$$\sqrt[3]{V} \log \alpha = K$$

was applicable to univalent strong electrolytes.

Debye-Hückel Theory. In 1923, Debye and Huckel and in 1926, Onsager put forward the *Modern Theory of strong electrolytes*. Without going into mathematical details, a brief outline of the main

idea is given below :—

- (i) The strong electrolyte is completely ionised at all dilutions.

The present position as it has emerged from the study of Ram spectra, X-ray analysis of crystals, Distribution co-efficients and vapour pressures is that there is a very small amount of unionised substance also present and that instead of saying completely ionised we should say 'almost completely ionised'.

- (ii) The ratio λ_v/λ_∞ does not give the degree of ionisation α for strong electrolytes but only conductivity ratio or conductivity co-efficient f_c .
- (iii) The increase in conductivity on dilution is due to an increase in the mobility of the ions.
- (iv) Around each ion, there exists an "ionic atmosphere" of oppositely charged ions and to these the solvent molecules are also attached.

A positive ion is on the average surrounded by more negative than positive ions and *vice versa*.

- (v) In spite of complete ionisation, λ_v is much less than λ_∞ . This is due to the following two causes :—

(i) **The relaxation effect.** Suppose that a central negative ion moves to the right under the influence of the E.M.F. applied. The 'ionic atmosphere' of positive ions is thus left behind to die away whilst a new ionic atmosphere of positive ions is under formation towards the right. Now the formation of the new 'ionic atmosphere' does not take place at the same rate at which the old one decays and the latter lags behind or takes more time, known as '*relaxation time*'. During this interval there is a preponderance of positive ions to the left of the central negative ion which is under move and these drag it back. Moreover, the central ion moves into a place where there is an excess of ions of its own sign and this has also a retarding effect.

(ii) **The electrophoretic effect.** The solvent molecules attached to the 'ionic atmosphere' moving in the opposite direction, produce friction and retard the motion of the central ion.

Both the above causes reduce the velocity of the ion. They disappear at infinite dilution but at any other dilution their effect is proportional to the square root of the concentration i.e., \sqrt{C}

$$\lambda_v = \lambda_\infty = K\sqrt{C}$$

where K is a constant for the given solvent depending upon its viscosity and dielectric constant. This relation agrees with the empirical dilution formula put forward earlier by Kohlrausch on the basis of his experimental work.

The above equation may also be written in the form

$$\lambda_\infty - \lambda_v = K\sqrt{C}$$

or $1 - \frac{\lambda_v}{\lambda_\infty} = \frac{K}{\lambda_\infty}\sqrt{C}$

$$\text{or } 1 - f_c = \text{Constant } \sqrt{C}$$

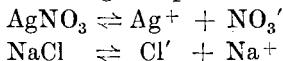
In its exact mathematical form the Debye-Hückel equation is given as :

$$1 - f_c = \sqrt{\frac{4\pi^2}{\epsilon kT} \left[\frac{e^2}{6kT} w_1 + bw_2 \right] nc}$$

when e is the charge, ϵ is the dielectric constant of the solvent, k is Boltzmann constant, T is the absolute temperature, w_1 and w_2 are valency factors, b is the mean ionic diameter and nc is ionic concentration. While retaining the main form, the equation was slightly modified by Onsagar in 1926, Sheldovsky in 1932 and Jones and Bickford in 1934 in order to get good results at all dilutions.

IONIC REACTIONS

The tests in qualitative analysis are the tests for radicals which the ionic theory identifies with the ions. Radicals can be tested in solution only as long as they exist in the form of ions. Thus silver in solution can be detected by the addition of a soluble chloride when a white precipitate of AgCl is produced.

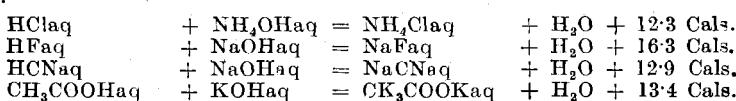


If silver ceases to exist in solution in the form of an ion as a result of the formation of a complex ion as, for instance, in sodium argento cyanide $\text{NaAg}(\text{CN})_2$, the test for silver is not given. Similarly $\text{K}_4\text{Fe}(\text{CN})_6$ does not give test for iron and $\text{K}_3\text{Cu}(\text{CN})_4$ gives no usual qualitative test for copper.

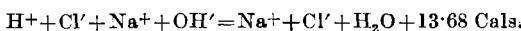
Again an acid which gives all the tests of a hydrion in an aqueous solution will not give the same tests when dissolved in an organic solvent, say toluene, because the acid does not ionise in the latter type of solvents to give hydrogen ions.

HEAT OF NEUTRALISATION

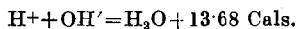
In the chapter on *Thermochemistry* it has been pointed out that the heat of neutralisation of a strong acid and a strong base is always nearly equal to 13.7 Cals., no matter what acid or base is employed. With weak acids or weak bases, the heat of neutralisation varies widely and may be less or greater than 13.7 Cals. Thus :



The Ionic Theory offers a decent explanation of this behaviour. Strong acids and bases according to this theory are almost completely ionised in solution. They combine to form a strongly ionised salt and water which is very feebly ionised. Considering the neutralisation of HCl by NaOH, we may write the ionic equation in the form,

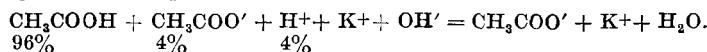


Eliminating the common ions on both sides, we have



i.e., the heat of neutralisation in this case is the heat of formation of water. The same applies to all other similar cases and consequently the heat of neutralisation is always nearly the same.

When, however, a weak acid or base is involved, besides the heat of formation of water the heat of ionisation of the weak acid or base also determines the heat of neutralisation. Thus heat of neutralisation = 13·7 Cals. + Q Cals., where Q is the heat of ionisation of the acid or base. The heat of neutralisation is more than 13·7 Cals., if Q is positive and less than 13·7 Cals., if Q is negative. For example consider the neutralisation of acetic acid by KOH. Let the ionisation of CH_3COOH be 4% and that of KOH complete. Writing the ionic equation, we have :



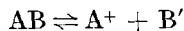
When the H^+ ions (4%) are removed in the form of unionised water, more of CH_3COOH ionises i.e., $\text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COO}' + \text{H}^+ + \text{Q}$ and this process continues until the neutralisation is complete. Q is negative in this case (-300 cal.) and, therefore, the heat of neutralisation is less than 13·7 Cals. by 0·3 Cals. i.e., 13·4 Cals.

COLOUR AND SOLUTION

Salt solutions owe their colour to the coloured ions which they produce when dissolved in water. Thus Cu^{++} , CrO_4'' , MnO_4' and Co^{++} ions are blue, yellow, purple and pink respectively and any solution of a salt containing one of these ions will show the true specific colour of the ion at sufficient dilution and will have the same absorption spectrum. If the coloured ion is removed from solution by the formation of a colourless complex ion, the solution will lose its colour, e.g., addition of KCN to CuSO_4 .

COMMON ION EFFECT

In the solution of an electrolyte in water, there exists an equilibrium between the ions and the unionised molecules to which the Law of Mass Action can be applied. Considering the ionisation of an electrolyte AB, we have :

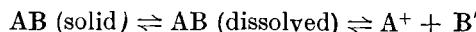


$$\text{and} \quad \frac{[\text{A}^+] [\text{B}']}{[\text{AB}]} = K \text{ (ionisation constant)}$$

If now another electrolyte yielding the A^+ or B' ions be added to the above solution, it will result in the increase of concentration of the ions A^+ or B' and in order that K may remain the same, the concentration (AB) must evidently increase. In other words the degree of ionisation of an electrolyte is suppressed by the addition of another electrolyte containing a common ion. Thus the ionisation of NH_4OH is diminished by the addition of NH_4Cl which furnishes the common NH_4^+ ion and that of CH_3COOH is suppressed by the addition of CH_3COONa which furnishes the common acetate ion.

SOLUBILITY PRODUCT

In the saturated solution of an electrolyte in contact with the solid, we have the equilibrium



By the Law of Mass Action,

$$\frac{[A^+] \times [B']}{[AB]} = K$$

Since the solution is saturated and in contact with the solid, the factor $[AB]$ must be constant at a fixed temperature.

Hence $[A^+] \times [B'] = \text{a constant}$

In other words, the product of the ionic concentrations in a saturated solution of a soluble electrolyte at a given temperature is a constant quantity. It is denoted by S and is known as the **Solubility Product**.

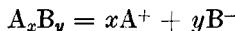
Example 1. Taking the m. wt. of AgCl as 143.5 and its solubility as 0.0014 gm. per litre at 18°C , calculate its solubility product at this temperature.

$$\text{Solubility in gm., mols} = \frac{0.0014}{143.5} = 1.0 \times 10^{-5}$$

Since AgCl is sparingly soluble, it must be completely dissociated. In other words, the eqvt. concentration of each ion is 1.0×10^{-5} gm. ions/litre.

$$\begin{aligned} \text{i.e., } [\text{Ag}^+] &= 1.0 \times 10^{-5} \quad \text{and} \quad [\text{Cl}^-] = 1.0 \times 10^{-5} \\ \therefore \text{Solubility product of AgCl at } 18^\circ\text{C} &= [\text{Ag}^+] \times [\text{Cl}^-] \\ &= 1.0 \times 10^{-5} \times 1.0 \times 10^{-5} \\ &= 1.0 \times 10^{-10}. \end{aligned}$$

In the case of an electrolyte yielding more than two ions in solution as for instance

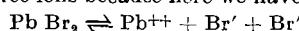


the expression for solubility product S , becomes $S = [\text{A}^+]^x [\text{B}^-]^y$

Example 2. The solubility product of lead bromide is 8×10^{-5} . If the salt is 80% dissociated in saturated solution, find the solubility of the salt.

$$\text{Solubility product} = 8 \times 10^{-5}$$

This is the product of three ions because here we have the equilibrium :



i.e.,

If x be the number of gm. molecule ionised

$$S = [\text{Pb}^{++}][\text{Br}'][\text{Br}']$$

$\therefore x = \sqrt[3]{S} = \sqrt[3]{8 \times 10^{-5}}$

\therefore we have 2.714×10^{-2} gm. molecules ionised per litre.

$$\begin{aligned} \therefore \text{Total no. gm. molecules per litre} &= 2.714 \times 10^{-2} \times \frac{100}{80} \\ &= 3.392 \times 10^{-2} \end{aligned}$$

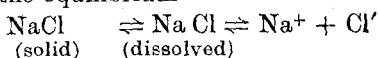
$$\text{Mol. wt. of PbBr}_3 = 207 + 160 = 367$$

$$\begin{aligned} \therefore \text{Solubility} &= 3.392 \times 10^{-2} \times 367 \\ &= 12.448 \text{ gms. per litre.} \end{aligned}$$

APPLICATIONS OF SOLUBILITY PRODUCT

Since the ionic product is equal to the solubility product when the solution is saturated, it follows that (i) when the ionic product exceeds the solubility product, the solution is supersaturated and precipitation will occur; (ii) when the ionic product is less than the solubility product, the solution will be unsaturated. This concept of the solubility product finds a number of applications some of which are described on the next page :

(1) Purification of common salt. In the purification of common salt, a saturated solution of it freed from suspended impurities is taken and HCl gas passed through it. In the saturated solution we have the equilibrium



On passing HCl gas, the concentration of Cl⁻ ions is increased because HCl is highly ionised. The ionic product $[Na^+] \times [Cl^-]$ thus considerably increases so much so that it *exceeds the solubility product of sodium chloride at the given temperature*. The result is a supersaturated solution of sodium chloride from which solid sodium chloride precipitates out in order to restore the equilibrium.

(2) **Salting out of Soap.** Ordinary soap is a mixture of the sodium salts of higher fatty acids and is obtained in the form of a concentrated solution as a result of saponification. From this solution soap precipitates out on the addition of a saturated common salt solution because the concentration of $[Na^+]$ ions increases and the ionic product $[Na^+] \times [C_n H_{2n+1} COO']$ far exceeds the solubility product of soap at that temperature.

(3) **Solvay's Ammonia-Soda Process.** When NH_4HCO_3 is added to a saturated NaCl solution we get in solution the four ions Na^+ , Cl' , NH_4^+ , and HCO_3' . These can give rise to four different compounds but out of these the solubility product of NaHCO_3 is the lowest and is easily exceeded. It, therefore, separates out in the form of a precipitate.

(4) Using Excess of Reagent. In quantitative analysis an excess of the precipitating reagent is always employed to ensure complete precipitation. For example, in the precipitation of barium sulphate $\text{BaCl}_2 + \text{H}_2\text{SO}_4 = \text{BaSO}_4 + 2\text{HCl}$, a small quantity of BaSO_4 may be left in solution if equivalent amounts of the two reactants are employed, for though BaSO_4 is an insoluble substance it possesses a measurable solubility. If a little excess of H_2SO_4 is employed, the ionic product $[\text{Ba}^{++}] \times [\text{SO}_4^{--}]$ far exceeds the solubility product of BaSO_4 and it is precipitated more completely.

(5) **Precipitation of the Sulphides of Group II and IV.**
In qualitative analysis, the sulphides of group II are precipitated in presence of dil. HCl while those of Group IV precipitate only in the presence of an alkali. The reason of this will become clear from the values of some solubility products at 18°C given below:

TABLE. Solubility products of some common sulphides
at 18°C

Sulphides of Group IV	Sulphides of Group II
Manganese Sulphide	$1 \cdot 4 \times 10^{-16}$
Zinc Sulphide	$1 \cdot 2 \times 10^{-23}$
Nickel Sulphide	$1 \cdot 4 \times 10^{-24}$
Cobalt Sulphide	3×10^{-26}
Lead Sulphide	$3 \cdot 4 \times 10^{-28}$
Cadmium Sulphide	$3 \cdot 6 \times 10^{-29}$
Copper (ic) Sulphide	$8 \cdot 5 \times 10^{-45}$
Mercuric Sulphide	41×10^{-53}

It is evident that the solubility product of the sulphides of Group II

is much lower than that of Group IV. When sulphuretted hydrogen is passed into the solutions of the various salts, precipitation of the sulphide can occur only when the ionic product $[M^{++}][S^{- -}]$ exceeds the solubility product of the sulphide at that temperature.

In the presence of acid, the ionisation of H_2S ($H_2S \rightleftharpoons 2H^+ + S^-$) is suppressed due to an increase of H^+ ions so that there are few S^- ions in solution and the solubility product of the sulphides of Group IV is not reached. It is, however, enough to cause the precipitation of CuS etc., which possess a low solubility product. In the presence of NH_4OH , the hydroxyl ions unite with the H^+ ions produced from H_2S to give unionised water, so that more of H_2S ionises and thus the concentration of S^- ions in solution increases. Eventually it becomes so high that the solubility product of ZnS , etc., is exceeded and these precipitate out.

(6) **Precipitation of the Hydroxides of Group III.** Ammonium hydroxide is a weak base and ionises in solution to a very small extent ($NH_4OH \rightleftharpoons NH_4^+ + OH^-$). In presence of highly ionised NH_4Cl , due to an increase in the number of NH_4^+ ions, the ionisation of NH_4OH is further suppressed so that the concentration of OH^- ions falls very low. Under these conditions the solubility product of the hydroxides of Al, Fe and Cr alone is reached and these precipitate out while the hydroxides of Zn, Mn, Ni, Mg, Co, etc., (which possess a comparatively higher value of solubility product) are not precipitated from their salt solutions which would otherwise have precipitated in the absence of NH_4Cl .

TABLE. Solubility products of some common hydroxides
at 18°C.

$Fe(OH)_3$	$1 \cdot 1 \times 10^{-36}$	$Zn(OH)_2$	$1 \cdot 8 \times 10^{-14}$
$Al(OH)_3$	$8 \cdot 5 \times 10^{-23}$	$Mn(OH)_2$	$4 \cdot 0 \times 10^{-13}$
		$Mg(OH)_2$	$3 \cdot 4 \times 10^{-11}$

ISOHYDRIC SOLUTIONS

Solutions of electrolytes are said to be *isohydric* if the concentration of the common ion present in them is the same and on mixing such solutions, there occurs no change in the degree of ionisation of either of the electrolytes.

Consider two isohydric solutions of acids HA_1 and HA_2 , and let v_1 and v_2 be their dilutions at which their degrees of ionisation are a_1 and a_2 respectively.

$$\text{For } HA_1, \text{ we have } \frac{a_1^2}{(1-a_1)v_1} = k_1 \quad \dots (i)$$

$$\text{For } HA_2, \dots, \frac{a_2^2}{(1-a_2)v_2} = k_2 \quad \dots (ii)$$

On mixing, the total volume becomes $(v_1 + v_2)$ while the concentration of the hydrogen ion (the common ion) becomes $\frac{(a_1 + a_2)}{(v_1 + v_2)}$.

Applying Ostwald's law to the acid HA_1 in the mixture, we have :

$$\frac{(a_1 + a_2) \cdot a_1}{(1 - a_1)(v_1 + v_2)} = k_1 \quad \dots (iii)$$

Dividing equation (ii) by equation (i), we get

$$\frac{(a_1 + a_2)v_1}{(v_1 + v_2)a_1} = 1$$

or $\frac{a_2 v_1}{a_1 v_2} = 1$

or $\frac{a_1}{v_1} = \frac{a_2}{v_2} \quad \dots (iv)$

From equation (iv) it is possible to calculate the relative dilutions of two acids at which they would be isohydric.

Example. Dissociation constant for acetic acid is 0.000018 and for cyanacetic acid 0.0037 at 25°C. What should be the relative dilution of the two acids so that the solutions may be isohydric?

(Agra B.Sc., 1952)

$$k_1 \text{ (acetic acid)} = 0.000018$$

$$k_2 \text{ (cyanacetic acid)} = 0.0037$$

For solution to be isohydric :

$$\frac{a_1}{a_2} = \frac{v_1}{v_2} \quad \dots (i)$$

For Ostwald's formula,

$$a_1^2 = k_1 v_1 = 0.000018 v_1$$

and $a_1^2 = k_2 v_2 = 0.0037 v_2$

Substituting these values in equation (i)

$$\frac{v_1}{v_2} = \frac{0.000018}{0.0037} \cdot 10$$

or $\frac{v_1}{v_2} = \frac{0.000018}{0.0037} = \frac{18}{3700}$

∴ the relative dilution of acetic acid and cyanacetic acid is 1 : 205.5.

RELATIVE STRENGTH OF ACIDS

From the point of view of the classical Ionic Theory, an acid is a substance which furnishes H^+ ions by itself or when dissolved in water and all the acid properties of an acid, viz., corrosive action, sour taste, action of litmus etc., are due to these hydrons.

The extent to which an acid property is given by an acid is a measure of its strength. **The strength of an acid solution does not depend upon its concentration but upon the number of free H^+ ions present**, which as we know are determined by its degree of ionisation. On dilution, the ionisation increases and more of free H^+ ions come in the solution with the result that the strength of the acid increases. At infinite dilution, the ionisation is nearly complete and all acids tend to be equally strong so that it is necessary that in comparing the strengths, all measurements be made with equi-normal solutions.

Some of the methods used for the determination of the relative strengths of acids are described below :

(1) **Thomson's Thermal Method.** Suppose we want to compare the relative strengths of HCl and H₂SO₄. Let the heat of neutralization of HCl and NaOH be x cals. and that of H₂SO₄ and NaOH be y cals. Now take a mixture containing one gram equivalent of each acid and add to it a solution containing one gram equivalent of NaOH. The two acids will take up NaOH in the ratio of their strengths, the stronger acid neutralising more of it. Suppose that n gm. equivalents of NaOH is neutralised by HCl and the rest ($1-n$) by H₂SO₄. The heat evolved in case of HCl would be nx cals. while in case of H₂SO₄ it would be $(1-n)y$ calories. Let the actual evolution of heat be z cals. Then, $z = nx + (1-n)y$.

$$\text{Whence } n = \frac{z-y}{x-y}.$$

The ratio $n/(1-n)$ gives the strength of HCl as compared with that of H₂SO₄.

(2) **Ostwald's Volume Method.** In this case, the change in volume is noted instead of the change in heat content when a base distributes itself between two acids. By the same reasoning, we shall have :

$$n = \frac{z-y}{x-y}$$

where : n = fraction of 1 gm. equivalent of NaOH neutralised by HCl.

z = change in volume when 1 litre of a solution containing 1 gm. equivalent of HCl and 1 gm. equivalent of H₂SO₄ is neutralised by 1 litre N.NaOH.

x = change in volume when 1 litre N.HCl is neutralised by 1 litre N.NaOH.

and y = change in volume when 1 litre N.H₂SO₄ is neutralised by 1 litre N.NaOH.

(3) **The Catalytic Method.** The hydrolysis of esters and the inversion of cane-sugar (See Chap. XV for details of following the progress of these reactions) are catalysed by H⁺ ions. This means that the rate of reaction is proportional to the number of H⁺ ions present in solution and a stronger acid would cause greater hydrolysis in unit time.

The velocity constant for such reactions which are of the *first order* is given by the expression

$$k = \frac{2.303}{t} \log \frac{a}{a-x}.$$

For the same interval of time t the value of x (amount transformed) will be comparatively larger and $(a-x)$ consequently smaller and this would give a larger value of k if the acid is strong.

To compare the strengths of any two acids, therefore, the velocity constants of the above reactions are determined in the presence of different acids, the hydrogen ions furnished by them catalysing the reactions. The one which gives a larger value of k is the stronger of the two.

(4) **The Conductivity Method.** It has already been pointed out that the strength of an acid at any dilution depends upon the number of free H^+ ions it can give in solution at that dilution, i.e., its degree of ionisation. It has also been shown that for weak acids, the conductivity ratio $\frac{\lambda_v}{\lambda_\infty}$ gives with fair accuracy the degree of ionisation of the acid.

$$\text{For acid No. I, } \alpha_I = \frac{\lambda_v^I}{\lambda_\infty^I} \quad \dots (i)$$

$$\text{and for acid No. II, } \alpha_{II} = \frac{\lambda_v^{II}}{\lambda_\infty^{II}} \quad \dots (ii)$$

At infinite dilution, all weak acids have almost the same value of λ_∞

$$\text{i.e., } \lambda_\infty^I = \lambda_\infty^{II}$$

\therefore From equations (i) and (ii),

$$\frac{\alpha_I}{\alpha_{II}} = \frac{\lambda_v^I}{\lambda_v^{II}}$$

The equivalent conductivities at the same dilution give us, therefore, an idea of the relative strengths of the two acids.

(5) **By Comparing the dissociation constants of Weak Acids.** For an acid in solution, we have the equilibrium



Its dissociation constant is the ratio of the velocity of its dissociation (k_1) to the velocity of the recombination of the ions (k_2) to form the undissociated acid

$$\text{i.e., } \frac{[H^+] \times [A']}{[HA]} = \frac{k_1}{k_2} = K$$

For an acid HA_1 ,

$$\frac{[H^+] \times [A_1']}{[HA_1]} = K_1$$

and for another acid HA_2 ,

$$\frac{[H^+] \times [A_2']}{[HA_2]} = K_2$$

Since $[H^+]$ is the measure of the acidity, the ratio $\frac{K_1}{K_2}$ would give us the relative strengths of the two acids. The dissociation constants of some weak acids are given below at $25^\circ C$.

Formic acid	... 1.774×10^{-4}
Acetic acid	... 1.752×10^{-5}
Benzoic acid	... 6.31×10^{-5}
Chloracetic acid	... 1.33×10^{-3}
Boric acid	... 5.75×10^{-10}

Example. The electrolytic dissociation constants of formic acid and acetic acid are 21.4×10^{-5} and 1.8×10^{-5} respectively. What are the relative strengths of the acids? (Punjab B.Sc. 1936, 1942 Suppl.)

$$\frac{\text{Strength of formic acid}}{\text{Strength of acetic acid}} = \frac{\text{Dissociation constant of HCOOH}}{\text{Dissociation constant of CH}_3\text{COOH}}$$

$$= \frac{21.4 \times 10^{-5}}{1.81 \times 10^{-5}} = \frac{11.82}{1}$$

∴ Formic acid is 11.85 times stronger than acetic acid.

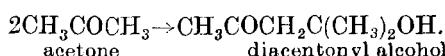
Hydrochloric acid is one of the strongest acids and is generally employed as a standard of comparison. In the Table that follows, the relative strengths of some of the common acids are given.

TABLE : Relative Strengths of Acids

Acid	METHOD				
	Thermal	Volume	Sugar Inversion	Ester hydrolysis	Ioni- sation
HCl	100	93	100	100	100
HNO ₃	100	100	100	91.5	99.6
H ₂ SO ₄	49	...	53.6	54.7	65.1
CH ₃ COOH	3		1.4	1.74	1.4

RELATIVE STRENGTH OF BASES

A base is a substance which furnishes OH' ions when dissolved in water and the basic properties of a base are due to these hydroxyl ions. The relative strength of bases is measured in the same manner as the relative strength of acids and the methods more often employed are (1) the thermal method, (2) the conductivity method, (3) the catalytic method on the reaction :



Caustic soda and caustic potash are very strong bases while ammonium hydroxide is, in comparison, very weak.

SCALE OF ACIDITY = pH VALUE

Instead of stating in a vague manner that a solution is weakly acidic or strongly alkaline, we can now express the acidity of a solution on a scale of acidity in the same way as we express the temperature on a thermometer scale. This is brought about as follows:

Pure water ionises to a very small degree though to a measurable extent so that we have the equilibrium,



$$\therefore \frac{[\text{H}^+] \times [\text{OH}']}{(\text{H}_2\text{O})} = K$$

The concentration of unionised water may be taken as practi-

cally constant as only one molecule out of nearly 550 water molecules ionises.

$$\therefore [H^+] \times [OH'] = K_w$$

This **ionic product of water** is roughly taken as 1×10^{-14} when the concentrations are expressed in gm. ions per litre. This means that in pure water the concentration of H^+ ions and OH' ions is 1×10^{-7} gm. ions per litre each. If the concentration of H^+ ions is more than 10^{-7} the solution is acidic, if less, the solution is alkaline.

The hydrogen ion concentrations are generally expressed in terms of the numerical value of the negative power to which 10 must be raised in order to express the required concentration and is denoted by the symbol pH^* . Thus we can have a scale in which degree of acidity is expressed in pH values.

Acidic	$[H^+]$	$\rightarrow 10^{-6} \quad 10^{-5} \quad 10^{-4} \quad 10^{-3} \quad 10^{-2} \quad 10^{-1} \quad 10^{-0}$
Solutions	pH value	$\rightarrow 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad 5 \quad 6$
Alkaline	$[H^+]$	$10^{-14} \quad 10^{-13} \quad 10^{-12} \quad 10^{-11} \quad 10^{-10} \quad 10^{-9} \quad 10^{-8}$
Solutions	pH value	$14 \quad 13 \quad 12 \quad 11 \quad 10 \quad 9 \quad 8$

Expressed mathematically, pH is the logarithm of the reciprocal of the hydrogen ion concentration.

$$[H^+] = 10^{-pH}$$

$$\log [H^+] = -pH \log 10$$

$$\text{or} \quad pH = \frac{-\log [H^+]}{\log 10}$$

$$\therefore \log 10 = 1$$

$$\therefore pH = -\log [H^+]$$

Example 1. Calculate the pH value of a solution whose hydrogen ion concentration is 0.005 gm. per litre

$$\begin{aligned} pH &= -\log [H^+] \\ &= -\log [0.005] = -(3.699) \\ &= -(-2.301) = 2.301. \end{aligned}$$

Example 2. The pH value of a solution of caustic soda is 9. Calculate the hydroxyl ion concentration per litre assuming complete ionisation.

$$-\log [H^+] = 9$$

$$[H^+] = 1 \times 10^{-9}$$

$$\text{But } [H^+] \times [OH'] = 1 \times 10^{-14}$$

$$\therefore [OH'] = \frac{1 \times 10^{-14}}{1 \times 10^{-9}} = 1 \times 10^{-5}$$

BUFFER SOLUTIONS

It has been mentioned above that pure water has a pH value equal to 7. But even the purest form of water cannot retain this value for long. It gradually changes either due to the solution of the carbon dioxide of the air in the water or as a result of the silicates dissolved from the glass container. The same is the case with the solutions of single salts.

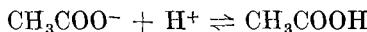
*It was first proposed by Sorenson in 1909.

It is noticed, however, that a solution containing a weak acid and the salt of it with a strong base (*e.g.*, $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$) or a weak base and the salt of it with a strong acid (*e.g.*, $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$) possesses the following characteristics :—

- (i) It has a definite pH value.
 - (ii) Its pH value does not alter either on keeping for long or on dilution.
 - (iii) Its pH value is very slightly altered by the addition of a strong acid in the first case viz., $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ and a strong base in the second case viz., $\text{NH}_4\text{Cl} + \text{NH}_3\text{OH}$.

Such solutions with reserve acidity or alkalinity are called **Buffer Solutions**.

Consider the case of a solution of acetic acid containing sodium acetate. Since acetic acid is a weak acid, there will be very few H^+ ions in solution but due to the presence of the strong electrolyte sodium acetate, we have an excess of Na^+ and CH_3COO^- ions. When a strong acid is added, the H^+ ions of it combine with the CH_3COO^- ions to form the feebly ionised CH_3COOH with the result that the pH value does not alter to any considerable extent.



Similarly, when a strong base is added to a buffer solution containing NH_4Cl and NH_4OH , the OH^- ions combine with NH_4^+ ions to form the feebly ionised NH_4OH .

USE OF INDICATORS

An **indicator** is employed to determine the end point in a titration. In the titration of acids with alkalies the *indicators used are organic substances which change colour when a certain pH value is reached.* In the table given below, the range of some of the important indicators is shown :

Indicator	Colour change	pH range
Phenolphthalein	Colourless to pink (acid) (alkali)	8-9.5 ; Colourless upto 8. Attains deep pink colour at 9.5.
Litmus	Red to blue (acid) (alkali)	5.5-7.5 ; Red upto 5.5. Attains blue colour at 7.5.
Methyl Red	Red to yellow (acid) (alkali)	4.5-6.5 ; Red upto 4.5. Attains deep yellow colour at 6.5.
Methyl Orange	Pink to yellow (acid) (alkali)	3.2-4.5 ; Deep pink upto 3.2. Attains yellow colour at 4.5.
Phenol Red	Yellow to red (acid) (alkali)	6.8-8.4 ; Yellow upto 6.8; Attains red colour at 8.4.

It is evident from a study of the above table that phenolphthalein which becomes colourless when $\text{pH}=8$, will indicate a solution to be acidic while it is actually a bit alkaline. Similarly methyl orange shows a yellow alkali colour when pH value is $4\cdot 5$ i.e., when the solution is appreciably acidic. Thus the selection of a suitable indicator for a particular titration is extremely important.

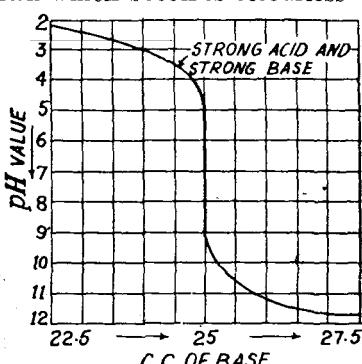


Fig. 186. Variation of pH during titration of strong acid and strong base.

noticed that in the region of the neutral point, a very sharp change in pH value occurs on the addition of a very small quantity of the base, the curve being practically a straight line as the value of pH changes from 4 to 10. In such a case then, any indicator with range $3\cdot 5$ – $10\cdot 5$ would serve the purpose, so that **methyl orange**, **phenolphthalein** or litmus, all the three can be employed.

Weak Acid and a Strong Base :

Fig. 187 shows the variation of pH when a weak acid is titrated against a strong base, say acetic acid against caustic potash. It is clear from the curve that there is very little change in the pH value until the neutral point is reached when the value suddenly alters from $6\cdot 5$ to 10 for

the solution at the end point is slightly alkaline due to the hydrolysis of the salt produced. In such a case, we should employ an indicator with a colour range $6\cdot 5$ to 10 and from the study of the table given earlier, it is clear that **phenolphthalein** is the suitable indicator for it has its working range on the alkaline side (8 – $9\cdot 5$). Moreover in such a case, the base should be put in the burette.

Strong Acid and a Weak Base :

When a strong acid like hydrochloric acid is titrated against a weak base a NH_4OH , the salt produced at

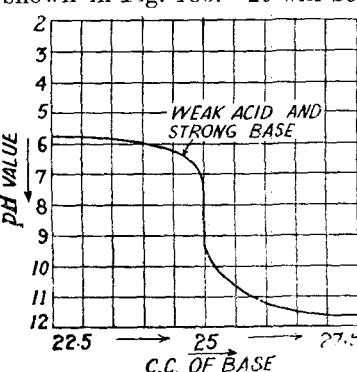


Fig. 187. Variation of pH during titration of a weak acid with a strong base.

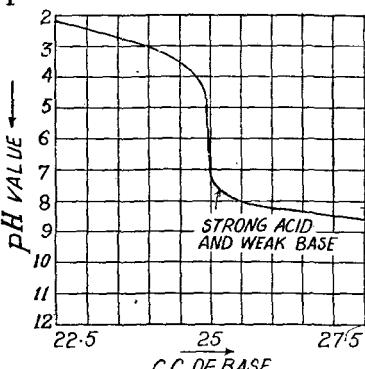


Fig. 188. Variation of pH during titration of a strong acid with a weak base.

the end point will show a slightly acid reaction due to hydrolysis. The variation of pH in this case, as seen in the curve in Fig. 188, takes place in the neutral point region from pH = 3.5 to pH = 7. The best indicator to be employed in such a case then would be one which has its working range on the acid side so that methyl red or methyl orange would serve the purpose well, its colour range being 4.5–6.5. The acid should be put in the burette.

Weak Acid and Weak Base :

It will be observed in Fig. 189 that when a weak acid is titrated against a weak base, no sharp change in the pH value takes place so that a titration is not possible. The pH varies very slowly between 6 and 8, so that if at all a titration is to be done, an indicator with this range e.g., **Phenol red** (6.8—8.4) will have to be employed.

Use of Indicators in determining pH value. Indicators are also employed in the determination of the hydrogen ion concentration by the **calorimetric method**. For this purpose the B. D. H. Universal indicator (which is a mixture of several indicators) is commonly employed. Its range is from pH 3–11 i.e., it gives different shades of colour as the pH of the solution is varied from 3 to 11. *Buffer solutions* of known pH value from pH 3–11 are prepared and a drop of indicator added to each when in each buffer solution a different colour is produced. With these colours, the colour produced by the indicator in the unknown solution is then matched and the pH value of the solution determined.

THEORY OF INDICATORS

As we have already defined, an indicator is a substance which possesses one colour in acid solution and a different one in alkaline solution. Two theories have been put forward to explain this colour change of indicators. We will discuss these with reference to the two important acid-base indicators, namely, Phenolphthalein and Methyl Orange.

1. **Ostwald's Theory based on Ionisation.** It has already been explained in Chap. XXI that the colour of a solution is due to the presence of coloured ions which are produced when a salt is dissolved in water. Ostwald maintained that an indicator is a weak electrolyte whose undissociated molecule gives rise to a large number of coloured ions under the influence of a strong acid or a strong base.

For example, **Phenolphthalein** (which for convenience we shall write as HPh) is a weak acid. Its undissociated molecule is colourless. On dissociation, it gives the H^+ ions which are also colourless and the rest of the molecule Ph^- which possesses a deep pink colour.

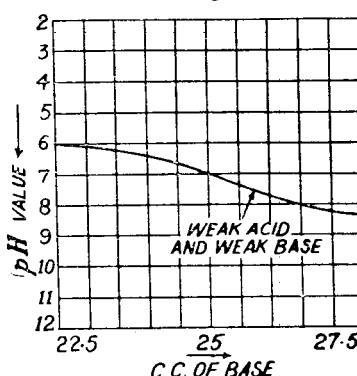
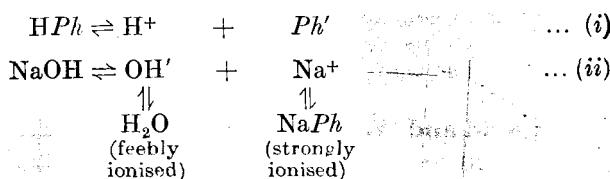


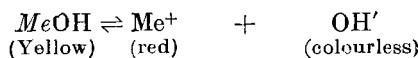
Fig. 189. Variation of pH during titration of a weak acid and a weak base.

In the presence of an acid, due to an increase in the concentration of hydrogen ions, the dissociation of HPh is practically nil so that the solution would remain colourless. On the addition of a strong alkali like $NaOH$, the OH' ions from it combine with the H^+ ions from phenolphthalein to form the feebly ionised water so that the equilibrium (i) is disturbed and more of the phenolphthalein ionises to restore this equilibrium.

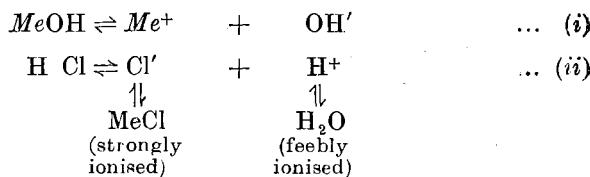


The Ph' ions so produced combine with Na^+ ions to form the strongly ionised sodium salt $NaPh$ and thus remain in solution in the ionic state and impart a pink colour to it.

The action of **Methyl Orange** is explained in a similar manner. It is a weak base represented for convenience as $MeOH$ whose undissociated molecule is *yellow*. On ionisation it gives the colourless OH' ions and *red* coloured Me^+ ions,

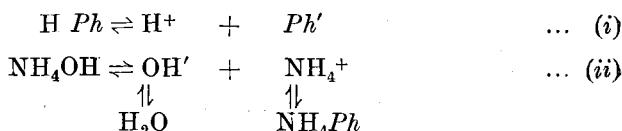


In the presence of an alkali, due to an excess of OH' ions, the ionisation of $MeOH$ is suppressed so that solution is yellow in colour. When the acid is in slight excess, we have the equilibria shown below :



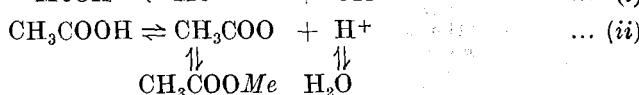
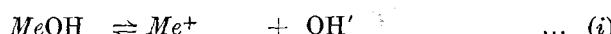
The H^+ ions from the acid combine with the OH' ions of methyl orange to form the feebly ionised water. This disturbs the equilibrium (i) so that more of methyl orange ionises to form the coloured Me^+ ions which remain in solution in the ionic state because the salt $MeCl$ formed with them is strongly ionised. In acid solution, therefore, methyl orange gives a pink red colour.

This theory also explains why phenolphthalein is not a suitable indicator in the titration of a strong acid with a weak base like NH_4OH . Firstly, the base being weak, it furnishes very few OH' ions with which the H^+ ions of phenolphthalein can combine.

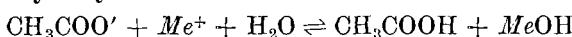


The equilibrium (i) is not, therefore, sufficiently disturbed. Secondly the salt NH_4Ph produced by the combination of NH_4^+ and Ph' gets hydrolysed; $\text{NH}_4^+ + \text{Ph}' + \text{H}_2\text{O} \rightleftharpoons \text{HPh} + \text{NH}_4\text{OH}$ and because of this, the pink colour does not appear until sufficient excess of NH_4OH has been added.

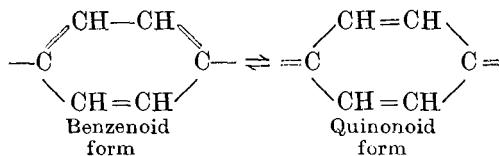
For a similar reason, methyl orange is not a suitable indicator in titrating a strong base against a weak acid. The equilibria involved are :



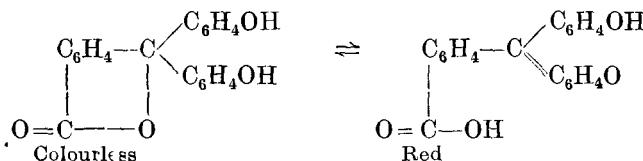
Acetic acid being a weak acid does not furnish sufficient H^+ ions to disturb the equilibrium (i) and the salt CH_3COOMe formed, though strongly ionised does not furnish sufficient red Me^+ ions because of hydrolysis.



2. The Quinonoid Theory. As most of the acid-alkali indicators are organic aromatic derivatives, the quinonoid theory attempts to explain the colour changes on the basis of intramolecular change rather than ionisation. It is believed that an indicator consists of an equilibrium mixture of at least two tautomeric forms, *one of which can exist in an acid solution and the other in alkaline solution*. The two forms possess different colours and as the pH of the solution containing such an indicator alters, *the solution shows a change of colour due to the passing of one form in the other*. The quinonoid form is usually deeper in colour than the benzenoid form.

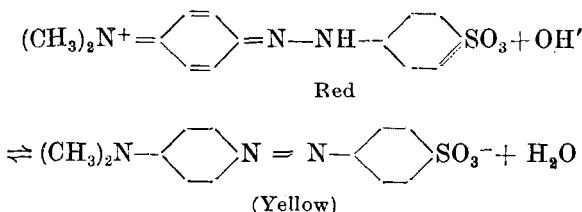


The indicator phenolphthalein is colourless in the acid form (benzenoid structure) but possesses a red colour in the tautomeric form which exists in an alkaline solution (quinonoid structure).



It gives, therefore, a pink to deep red colour in the alkaline solution while it is colourless in the acidic solution.

Similarly, we have the two tautomeric forms of methyl orange, the red form existing in the acidic solution but passing to the yellow form as the pH value alters to the alkaline side.



QUESTIONS AND PROBLEMS

1. Apply the Law of Mass Action to the electrolytic dissociation of acetic acid. How will you determine the degree of dissociation of acetic acid?
2. What is Ostwald's Dilution law? How will you determine experimentally the dissociation constant of acetic acid?
3. How can you determine the dissociation constant of acetic acid? Explain the principles involved and say why the dissociation constant of a strong acid like HCl cannot be determined in the same manner.
4. Explain what is meant by the dissociation constant of an acid and point out how it can be determined in case of acetic acid. The equivalent conductivity of an N/10 solution of an acid is 45 and at infinite dilution is 380. Calculate the dissociation constant of the acid.
5. Describe how you will ascertain whether an organic acid, say propionic acid, obeys Ostwald's dilution law. Is this law always applicable?
(Nagpur B.Sc., 1954)
6. What is meant by the anomaly of strong electrolytes? How is it removed on the basis of the theory of complete ionisation?
7. Give an account of the Debye-Huckle theory of strong electrolytes.
(Bombay B.Sc., 1953)
8. What is the basis for the classification of electrolytes into two groups, 'Strong' and 'Weak'? How would you proceed to determine the dissociation constant of acetic acid?
(Nagpur B.Sc., 1953)
9. Discuss the important applications of the ionic theory of electrolytes to analytical Chemistry.
10. Write notes on (a) Solubility product, (b) Ostwald's Dilution Law.
11. On the basis of the electrolytic dissociation theory, explain clearly the use of dilute hydrochloric acid in the second group and of ammonium chloride in the third group of systematic qualitative analysis of inorganic bases.
12. Define solubility product and give a method of determining it experimentally.
(Andhra B.Sc., 1953)
13. Define the terms "Solubility" and "Solubility product" of a substance. Explain giving three examples, how solubility product is used in Qualitative analysis.
The solubility of BaSO_4 at 20°C is 2.33×10^{-4} gm. per c.c. Calculate the solubility product of BaSO_4 assuming that it is completely ionised.
(Annamalai B.Sc., 1953)
14. What do you understand by the term 'Solubility product'? Describe a method by which the solubility product of a difficultly soluble salt may be determined.
(Gujarat B.Sc., 1954)
15. Comment on the fact that magnesium hydroxide is soluble in a solution of ammonium chloride but not either in sodium or potassium chloride solution.
16. Write an essay on the various methods employed for determining the relative strength of acids.

17. What do you understand by 'strength of an acid'? Describe the methods for comparing the relative strengths of two acids.

18. Explain the term "strength of an acid" and outline the methods that may be employed to compare the relative strengths of two acids.

How would you account for the effect of sodium acetate on the strength of aqueous acetic acid solution? (Madras B.Sc., 1952)

19. What are the important methods of determining the strength of an acid? (Lucknow B.Sc., 1953)

20. Discuss the generalised concept of an acid and a base. Give a short outline of the different methods by which the strength of an acid may be determined. (Rajputana B.Sc., 1954)

21. State and explain the theory of electrolytic dissociation. What are strong electrolytes? Give examples.

What is meant by solubility product? (Gauhati B.Sc., 1953)

22. Explain the principles underlying the following: (i) The use of excess of the precipitant in chemical analysis to obtain more complete precipitation. (ii) Why a sharp end point is not obtained when acetic acid is titrated with ammonium hydroxide? (Punjab B.Sc., 1937)

23. Explain in words all that is implied in the expression

$$[\text{H}^+] = [\text{OH}^-] = \sqrt{10^{-13.8}} = 10^{-6.9}$$

and hence define the pH of a solution. (Punjab B.Sc., 1941 Suppl.)

24. What do you understand by the term pH number? What is the pH number of solutions whose hydrogen ions concentrations are (a) 0.00038, and (b) 0.0000975.

25. The hydrogen ion concentration of a solution is 1.7×10^{-5} mole per litre. Calculate its pH.

26. The pH of a solution is 9.6. Calculate its hydrogen and hydroxyl ion concentrations.

27. Write short notes on:

(i) Ionisation constant of water, (ii) Hydrogen ion concentration, (iii) Acidity of acids. (Agra B.Sc., 1944)

28. What are buffer solutions? Given that the dissociation constant of a weak monobasic acid at 25°C is 10^{-5} , show how the solutions of pH 4.0, 5.0, and 6.0 may be prepared? Derive any equation you may use. (Ceylon Final, 1954)

29. Explain the theory of indicators and state what is meant by the statement that a certain solution has pH=5. (Punjab B.Sc., 1944 Suppl.)

30. Give a brief account of the theory of indicators. (Delhi B.Sc., 1954; Agra B.Sc., 1954)

31. Write clearly an account of theory of indicators. (Aligarh B.Sc., 1954; Agra 1960)

32. Write all you know about the theory of indicators, with methyl orange and phenolphthalein as your examples.

To a solution of sodium carbonate, two drops of methyl orange and two drops of phenolphthalein are added. It is then completely neutralised by adding sulphuric acid drop by drop. What colour changes take place during neutralization and why? (Agra B.Sc., 1954)

33. Write notes on:—

Solubility product, theory of indicators, pH value. (Nagpur B.Sc., 1953)

34. What is pH value? Explain its significance and describe how it is determined. (Osmania B.Sc., 1953)

35. Write short notes on:—

(a) Ostwald Dilution law.

(b) Theory of Indicators. (Jammu and Kashmir B.Sc., 1954)

36. Name the indicators you will use in titrating (i) a solution of ammonia with hydrochloric acid and (ii) a solution of acetic acid with caustic soda. Give reasons for your answers. (Calcutta B.Sc., 1954)

37. Write short notes on any two of the following :—
 (a) Solubility product.
 (b) Theory of Indicators.
 (c) pH value and its determination. (*Allahabad B.Sc., 1954*)
38. (a) Discuss the theory of indicators.
 (b) Describe a method of determining pH of a solution.
39. Explain what you understand by the pH value of a solution. Discuss the methods usually employed in determining it. (*Agra B.Sc., 1955*)
40. What do you understand by the term 'Solubility Product'? Discuss its applications to the separation of copper, zinc and manganese from the mixture of their salts. (*Punjab B.Sc., 1955*)
41. Describe briefly the principles of various theories which have been put forward to explain the anomalous behaviour of strong electrolytes. (*Karnatak B.Sc., 1955*)
42. Explain why :—
 (a) Cadmium sulphide is not precipitated when H_2S is passed through $CdCl_2$ in strong acid solution ;
 (b) Ammonium chloride solution is acid to litmus and ammonium acetate solution is neutral ;
 (c) Methyl orange is not a suitable indicator when oxalic acid is titrated against caustic soda solution. (*Banaras B.Sc., 1955*)
43. Explain the underlying physical principles of four of the following :—
 (a) A sharp end point is not obtained when acetic acid is titrated against ammonium hydroxide.
 (b) Zinc sulphide is precipitated by hydrogen sulphide from an ammonia solution but not from a strong hydrochloric acid solution.
 (c) Methyl orange is not used as an indicator for titrating acetic acid against caustic soda solution.
 (d) Ammonium chloride is acid to litmus.
 (e) The precipitation of magnesium hydroxide by NH_4OH is prevented by the addition of NH_4Cl but its precipitation by $NaOH$ is not prevented by the addition of $NaCl$. (*Allahabad B.Sc., 1953*)
44. Write a note on the Theory of Indicators. (*Delhi B.Sc., 1955*)
45. Write an essay on the various methods employed for the determination of relative strengths of acids. (*Banaras B.Sc., 1955*)
46. What is meant by pH value of a solution? What are indicators? Show how they can be used to determine the pH value of a solution.
 (a) What is the pH value of a solution whose hydrogen ion concentration is 2.36×10^{-8} gm. ion per litre ?
 (b) What is the hydrogen ion concentration of a solution whose pH value is 6.58 ? (*Rangoon B.Sc., 1955*)
47. What is meant by the strength of an acid? Explain any method that may be employed to compare the relative strengths of acetic acid and nitric acid. Why is the strength of acetic acid affected by the addition of sodium acetate to its aqueous solution. (*Andhra B.Sc., 1956*)
48. Explain fully Ostwald's dilution law and show how the following can be explained on the basis of this law :
 (a) Use of ammonium chloride for the precipitation of hydroxides of the aluminium group of metals in qualitative analysis.
 (b) Why the aqueous solution of sodium acetate reacts alkaline to litmus. (*Delhi B.Sc., 1956*)
49. Discuss the anomaly of strong electrolytes. (*Rajputana B.Sc., 1956*)
50. What do you understand by the solubility product? Illustrate the application of the knowledge of solubility product in analytical and industrial chemistry. (*Rajputana B.Sc., 1956*)
51. The dissociation constant of acetic acid at 18° is 1.8×10^{-5} . Calculate the degree of dissociation and H ion concentration in
 (a) 0.25 normal acetic acid solution.

- (b) 0·25 normal acetic acid solution containing 0·25 normal sodium acetate, if the sodium acetate is assumed to be completely dissociated. (Madras B.Sc., 1955)
52. What is Ostwald's dilution law ? Give a brief account of the method for determining the dissociation constant of acetic acid. (Lucknow B.Sc., 1956)
53. What is Ostwald's dilution law ? Under what conditions is it applicable to solutions of electrolytes ? How would you determine the dissociation constant of acetic acid ? (Aligarh B.Sc., 1956)
54. What is Ostwald's dilution law and discuss its limitations. A concentrated solution of formic acid is ionized to the extent of eight per cent. Find the ionization constant of the acid. (Mysore B.Sc., 1957)
55. Define solubility product. Discuss its applications in qualitative analysis. (Madras B.Sc., 1955)
56. What is solubility product ? Discuss its applications. (Allahabad B.Sc., 1957)
57. Explain the principles underlying the following :—
- (a) Calcium oxalate is soluble in HCl although it is almost insoluble in acetic acid.
 - (b) Why a sharp end-point is not obtained when acetic acid is titrated with NH₄OH.
 - (c) Magnesium hydroxide is not precipitated by NH₄OH in the presence of NH₄Cl.
 - (d) Sodium carbonate solution is alkaline to litmus. (Banaras B.Sc., 1956)
58. Explain clearly the Solubility Product and Common Ion Effect. Discuss their importance in chemical analysis. (Aligarh B.Sc., 1957)
59. Explain what you understand by the dissociation constant of an acid. Describe how you will determine the dissociation constant of acetic acid. The electrolytic dissociation constants of formic and acetic acids are $21\cdot40 \times 10^{-5}$ and $1\cdot80 \times 10^{-5}$ respectively. Calculate the relative strength of the two acids. (Poona B.Sc., 1957)
60. What do you understand by the term 'Strength of an acid' ? Describe the methods for comparing the strengths of two acids. (Nagpur B.Sc., 1956)
61. Write notes on any two of the following :—
- (a) Buffer solution
 - (b) Strength of acid
 - (c) Theory of indicators. (Nagpur B.Sc., 1957)
62. Write a note on the theory of Indicators. (Jammu & Kashmir B.Sc., 1957)
63. Write a clear account of the theory of Indicators. (Aligarh B.Sc., 1957)
64. What is pH ? How may (i) neutral (ii) acidic and (iii) alkaline aqueous solutions be defined in terms of pH ? Calculate the pH of a mixture containing 50 c.cs. of normal hydrochloric acid and 30 c.cs. of normal sodium hydroxide assuming both to be completely dissociated in normal solutions. (Poona B.Sc., 1957)
65. Write a note on pH value. What would be the pH value of 0·1 N Hydrochloric acid solution ? (Jammu & Kashmir B.Sc., 1958)
66. What is an acid-base indicator ? Explain its mechanism with reference to phenolphthalein. What type of indicator will you employ in titrating (a) a strong acid and a strong base, (b) a strong acid and a weak base, and (c) a weak acid and a strong base ? Give reasons. (Travancore B.Sc., 1957)
67. What is Ostwald's dilution law ? Explain how the dissociation constant of acetic acid can be determined. (Allahabad B.Sc., 1958)
68. Give an ionic theory of solutions and explain why hydrochloric acid and nitric acid have the same heat of neutralisation. Why is the heat of neutralisation of hydrocyanic acid much smaller ? (Rajputana B.Sc., 1958)

69. Why does the colour of an indicator change with the hydrogen ion concentration? What indicators would you use for titrating (a) hydrochloric acid, and (b) acetic acid, by a strong base? Given reasons for your answer.

(Rajputana B.Sc., 1958)

70. Derive Ostwald's dilution law and state its limitation. How will you determine the value of ionic mobility?

(Aligarh B.Sc., 1958)

71. How is Hydrogen ion concentration measured and how is it expressed?

72. Find out the pH of 0.002 N acetic acid and 0.002 N caustic soda solutions if the former is 2.3% and the latter is 100% ionised. ($K_w = 10^{-14}$).

(Patna B.Sc., 1958)

73. What do you understand by 'Solubility product'? Discuss its applications in quantitative analysis.

(Punjab B.S., 1959)

74. Explain the term : Weak and strong electrolytes. Discuss how (a) the theory of solubility product and (b) Ostwald's dilution law are based on the theory of electrolytes dissociation.

(Venkateswara B.Sc., 1959)

75. What do you understand by the term 'strength of an acid or a base'. Given two acids, how will you compare their strengths?

The electrolytic dissociation constants of formic acid and acetic acids are 21.4×10^{-5} and 1.8×10^{-5} respectively. What are the relative strengths of the two acids?

(Osmania B.Sc., 1959)

76. The heat of neutralisation of a strong acid by a strong base in dilute solution has been found to be practically constant. How do you account for this phenomenon?

(Delhi B.Sc., 1959)

77. Explain the modern concept of acids and bases.

Describe various methods employed to determine the relative strength of acids.

(Vikram B.Sc., 1959)

78. Give a short account of the theory of indicators. How is pH determined with the help of indicators?

(Lucknow B.Sc., 1959)

79. Write notes on :—

(a) Buffer solution;

(b) Indicators;

(c) Solubility product.

(Utkal B.Sc., 1959)

80. Explain the theory of indicators and state what is meant by the statement that a certain solution has pH = 5.

(Marthwada B.Sc., 1959)

81. You are given a number of indicators and solutions of known hydrogen ion concentration. How would you proceed to determine the hydrogen ion concentration of an unknown solution?

Will 0.1 N solutions of hydrochloric acid and acetic acid have the same hydrogen ion concentration? Give reasons for your answer.

(Rajasthan B.Sc., 1959)

ANSWERS

4. 0.0016·7

13. 1.0×10^{-12}

24. (a) 3.42 (b) 5.125

25. ·47

26. $[H^+] = 2.51 \times 10^{-10}$; $[OH^-] = 3.98 \times 10^{-5}$

46. (a) 7.627 (b) 2.63×10^{-7} .

51. (a) 8.49×10^{-3} ; 2.12×10^{-3} ; (b) 7.19×10^{-5} ; 17.97×10^{-6} .

54. 6.95×10^{-5} .

59. 11.88.

60. 4.3372; 11.301.

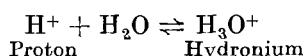
75. Formic acid is 11.82 times stronger than acetic acid.

CHAPTER XXIII

ACIDS AND BASES—SALT HYDROLYSIS

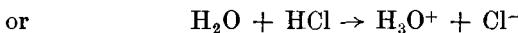
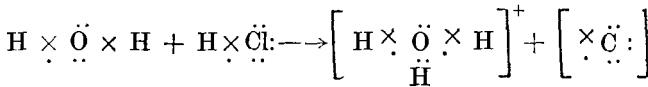
PROTON CONCEPT OF ACIDS

During recent years a new concept of acids and bases has been gradually developing itself based on the work of Bronsted and T. M. Lowry (1923) which is able to explain the ionic equilibria in solutions in a much more satisfactory manner. According to this concept, an **acid** is regarded as a **substance which gives off a proton $[H^+]$ in solution**. This proton is always *solvated* i.e., combined with one or more molecules of the solvent. In aqueous solution, it is supposed to be combined with at least one water molecule to give the **Hydronium ion**.

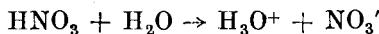


The ease with which this proton is given off in solution is a measure of the 'strength' of the acid.

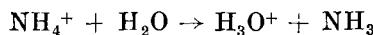
For the acid properties of an acid to exhibit themselves, *the presence of a solvent is absolutely necessary*. Dry hydrochloric acid, dry H_2SO_4 , dry HNO_3 and dry $HClO_4$ do not turn blue litmus red or react with metals. They develop their acidic properties only in the presence of a solvent. Thus in the presence of water, hydrochloric acid gives a proton to water forming the hydronium ion and the anion chloride.



Nitric acid and chloric acid behave in a similar way, their molecules being covalent just like that of HCl.



It must be clearly understood that it is not necessary for an acid to be a non-ionised molecule. *Any neutral molecule or even an ion will be regarded as an acid so long as it can give a proton in solution.* Thus ammonium ion $\text{[NH}_4^+]$ is an acid and so is bisulphate ion $\text{[HSO}_4^-]$.



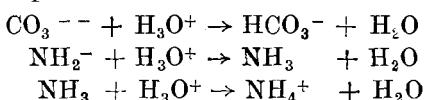
BASE AS PROTON ACCEPTOR

The classical definition of a base as a substance which gives hydroxyl ions (OH^-) in solution which combine with the hydrogen ions furnished by an acid serves the purpose only in aqueous

solutions. It is now well-known that there are other solvents besides water in which oxygen is not a part of the solvent molecules and in which non-oxygen containing molecules ionise and exhibit basic properties. Sodamide NaNH_2 dissolved in liquid ammonia is an interesting example of this type in which the basic properties are determined by the NH_2^- ion instead of the OH^- ion. To cover such cases, our definition of a base must be extended. A **base** is now regarded as a molecule or an ion which can accept a proton given off by an acid in solution. The strength of a base is determined by the firmness with which it can hold the proton to it in solution.

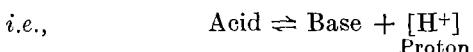
According to this concept of a base, substances like NaOH , KOH and $\text{Ca}(\text{OH})_2$ which are electrovalent in nature should be regarded as 'salts', the real base being OH^- . In fact, hydroxyl $[\text{OH}]^-$ is the strongest base for it combines with a proton to form water and holds the proton so firmly to it that water ionises to a very feeble extent, one molecule out of 550 million ionising. The chloride ion Cl^- is also a base because of the change $\text{Cl}^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{HCl} + \text{H}_2\text{O}$ but a very weak base because in the presence of water, the proton easily parts company with it and combines with water to form the hydronium ion H_3O^+ .

CO_3^{2-} , CH_3COO^- , NH_2^- and ammonia molecule (NH_3) are some other examples of bases.



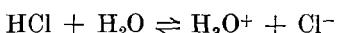
ACID-BASE RELATIONSHIP

When an acid loses a proton in solution to act as an acid, the remaining part of its molecule which is an anion will have tendency to gain the proton back and thus act as a base.

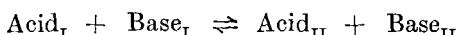


Such an acid and a base which differ by a proton and are formed one from the other by the gain or loss of it are said to form a **Conjugate pair** e.g., NO_3^- is the base conjugate to the acid HNO_3 and NH_4^+ is the acid conjugate to the base NH_3 .

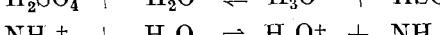
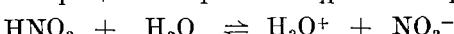
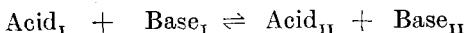
In the reaction :



Cl^- is the base conjugate to the acid HCl and H_3O^+ is the acid conjugate to the base H_2O . This behaviour is in fact general so that when an acid reacts with a base the products are an acid conjugate to the base and a base conjugate to the acid i.e.,



Base_{II} is the conjugate of Acid_I and Acid_{II} is the conjugate of Base_I .

Examples :

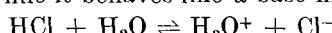
Strong acids always possess weak conjugate bases and are highly ionised in solution while weak acids have strong conjugate bases and are, therefore, feebly ionised.

WATER AS AN ACID AND A BASE

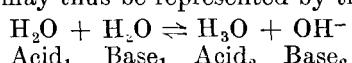
Water which is the most common solvent shows a unique behaviour for it can give off a proton as well as receive one. In reactions like



it acts as an acid while it behaves like a base in reaction of the type



Its dual role may thus be represented by the equation

**SALT HYDROLYSIS**

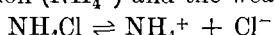
Pure water is neutral in character because in the above change OH^- and H_3O^+ exactly balance each other. If we remove, however, either one or the other, a change is produced in the system and the solution becomes alkaline or acidic. This is exactly the change produced during the phenomenon known as *salt hydrolysis*.

Salt Hydrolysis may be defined as *a reaction in which the anion or the cation of a salt react with the solvent water to produce acidity or alkalinity*.

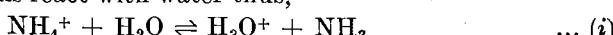
Evidently, it is the nature of the anion or cation constituting the salt which will determine whether the solution produced as a result of hydrolysis will be acidic or alkaline. If the subject is examined from this point of view, the following four different cases can arise :—

1. Salt of a Strong Acid and a Weak Base. Salts like FeCl_3 , AlCl_3 , NH_4Cl , CuSO_4 etc., are formed from a strong acid and a weak base. In such cases, the acid cation is strong i.e., possess a greater tendency to give protons $[\text{H}^+]$ when in contact with water, while the weak base anion cannot accept all the protons. As a result, the ionisation equilibrium of water is disturbed and there is an excess of $[\text{H}^+]$ in solution. *Such salts give, therefore, solutions which are acidic.*

Let us consider the case of ammonium chloride formed from the strong acid cation (NH_4^+) and the weak base anion (Cl^-).



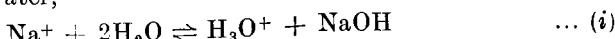
The two ions react with water thus,



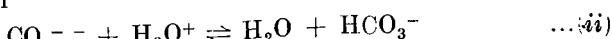
The cation NH_4^+ being a strong acid *the reaction (i) proceeds to a considerable extent*, the protons (H^+) having a tendency to part company with NH_4^+ and get into solution where they combine with water in sufficient number to form acid hydronium ions. The anion Cl^- is a weak base which implies that it has very little tendency to accept the protons and form HCl . *The reaction (ii) consequently does not proceed to any considerable extent* and the solution exhibits an acid reaction due to the excess of H_3O^+ ions contributed by reaction (i).

2. Salt of a Weak Acid and a Strong Base. Salts like Na_2CO_3 , CH_3COONa , NaHCO_3 and NaCN are produced by the combination of a weak acid and a strong base. In such cases the acid cation is weak and has very little tendency to give off $[\text{H}^+]$ by reaction with water. The same anion, on the other hand, is strong and is able to fix up a large number of protons (H^+) from water. This upsets the normal equilibrium obtained in water and due to an excess of OH^- in solution, the latter is *alkaline in behaviour*.

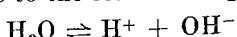
Consider the case of sodium carbonate Na_2CO_3 . The acid cation Na^+ is very weak and has little or no tendency to give off protons by action with water,



The strong anion base CO_3^{2-} accepts, however, a large number of H^+ from water



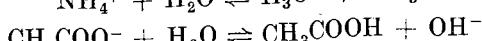
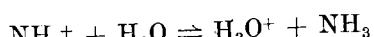
i.e., reaction (ii) proceeds to a relatively much larger extent than reaction (i) and due to the removal of protons from the equilibrium



there occurs an excess of OH^- and the solution is alkaline.

3. Salt of a Weak Acid and a Weak Base. Examples of this type of salts are ammonium acetate, ammonium carbonate, etc. As both the acid and the base are weak, their conjugate acids and bases are strong and will appreciably react with water. Such salts are, therefore, considerably hydrolysed in aqueous solution and the ultimate nature of the solution will depend upon the relative hydrolysis of the anion. If both react to the same extent the solution is neutral. If the cation reacts to a large extent, the solution is slightly acidic and if the anion is comparatively a little more active, the solution is alkaline.

In the case of $\text{CH}_3\text{COONH}_4$, for example, the reactions which occur are :



As the cation acid and the anion base are both equally strong the two reactions occur to the same extent and the ionic equilibrium of water is not altered. The solution is, therefore, neutral.

4. Salt of a Strong Acid and a Strong Base. In this case, the conjugate acid of the base and conjugate base of the acid are

both weak and thus have no tendency either to give off protons in solution or to accept them. There is consequently no reaction worth the name with water and the ionic equilibrium $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$ is not upset. *The solutions or salts like NaCl, KNO₃, Na₂SO₄ etc., are, therefore, neutral.*

DEGREE OF HYDROLYSIS

The extent to which hydrolysis proceeds is expressed as the **Degree of hydrolysis** and may be defined as *the fraction of the total salt hydrolysed when the equilibrium has been attained*. It is denoted by the symbol h .

Consider the hydrolysis of a salt BA derived from a weak acid (HA) and a strong base (BOH). The equilibrium in this case is represented as already explained as :



Suppose we start with one gram mol. of the salt dissolved in V litres and h be the degree of hydrolysis. When the equilibrium is attained, we have :

$$\text{Active mass of free acid} = [\text{HA}] = \frac{h}{V}$$

$$\text{,, , , free base} = [\text{OH}^-] = \frac{h}{V}$$

$$\text{,, , , unhydrolysed salt} = [\text{A}^-] = \frac{1-h}{V}$$

Active mass of water is taken as constant,

\therefore By the Law of Mass Action :

$$\frac{[\text{HA}] \times [\text{OH}^-]}{[\text{A}^-] \times [\text{H}_2\text{O}]} = K$$

$$\text{or } \frac{\frac{h}{V} \times \frac{h}{V}}{\frac{1-h}{V}} = \frac{h^2}{(1-h)V} = K_H$$

The constant K_H is called the **Hydrolysis Constant**. When h is very small, $(1-h)$ may be considered as equal to one and we have in such a case

$$K_H \times V = h^2$$

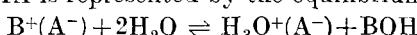
$$\text{or } h = K_H \sqrt{V}$$

i.e., the degree of hydrolysis is proportional to the square root of the dilution.

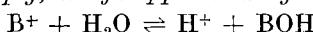
Relation between the Hydrolysis and Ionisation Constants

Case I. Salt of a Weak Base and a Strong Acid

The hydrolysis of a salt BA, formed from a weak base BOH and a strong acid HA is represented by the equilibrium



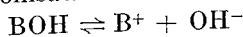
or *more simply, though approximately as :*



Applying the Law of Mass Action

$$\frac{[\text{BOH}] \times [\text{H}^+]}{[\text{B}^+]} = K_H ; [\text{H}_2\text{O}] \text{ being constant}$$

From the ionisation of the base BOH ;



$$\text{we have, } \frac{[\text{B}^+] \times [\text{OH}^-]}{[\text{BOH}]} = K \quad \left[\begin{array}{l} \text{Ionisation constant of} \\ \text{the base} \end{array} \right] \dots (ii)$$

The Ionic product of water

$$[\text{H}^+] \times [\text{OH}^-] = K \quad \dots (iii)$$

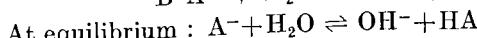
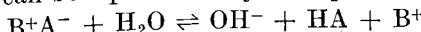
Dividing (iii) by (ii), we have :

$$\begin{aligned} \frac{K_w}{K_B} &= \frac{[\text{H}^+] \times [\text{OH}^-] \times [\text{BOH}]}{[\text{B}^+] \times [\text{OH}^-]} \\ &= \frac{[\text{H}^+] \times [\text{BOH}]}{[\text{B}^+]} \\ &= K_H \end{aligned}$$

$$\therefore \frac{K_w}{K_B} = K_H$$

Case II. Salt of a Weak Acid and a Strong Base

The hydrolysis of a salt BA formed from a weak acid HA and a strong base BOH can be represented by the equilibrium,



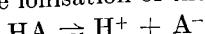
Applying the Law of Mass Action

$$\frac{[\text{HA}] \times [\text{OH}^-]}{[\text{A}^-] [\text{H}_2\text{O}]} = K$$

Since the active mass of water is constant in a dilute solution

$$\frac{[\text{HA}] [\text{OH}^-]}{[\text{A}^-]} = K_H \quad \dots (i)$$

From the ionisation of the acid HA ;



$$\text{we have : } \frac{[\text{H}^+] \times [\text{A}^-]}{[\text{HA}]} = K_A \quad \left[\begin{array}{l} \text{Ionisation constant} \\ \text{of the acid} \end{array} \right] \dots (ii)$$

The ionic product of water as usual is

$$[\text{H}^+] \times [\text{OH}^-] = K_w \quad \dots (iii)$$

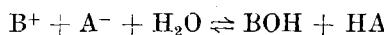
Dividing (iii) by (ii), we get :

$$\begin{aligned} \frac{K_w}{K_A} &= \frac{[\text{H}^+] \times [\text{OH}^-] \times [\text{HA}]}{[\text{H}^+] \times [\text{A}^-]} \\ &= \frac{[\text{OH}^-] \times [\text{HA}]}{[\text{A}^-]} \\ &= K_H \end{aligned}$$

$$\therefore \frac{K_w}{K_A} = K_H$$

Case III. Salt of a Weak Acid and a Weak Base

Let the weak acid be HA and weak base BOH. The salt BA from these two is fully ionised in water and as explained already gives us the equilibrium :



$$\therefore \text{At equilibrium ; } \frac{[BOH] \times [HA]}{[B^+] \times [A^-]} = K_H \quad \dots (i)$$

$$\text{Also, } \frac{[H^+] \times [A']}{[HA]} = K_A \quad (\text{Ionisation constant of the acid}) \quad \dots (ii)$$

$$\frac{[B^+] \times [OH^-]}{[BOH]} = K_B \quad (\text{Ionisation constant of the base}) \quad \dots (iii)$$

$$\text{and } [H^+] \times [OH'] = K_w \quad (\text{Ionic product of water}) \quad \dots (iv)$$

From (ii), (iii) and (iv)

$$\frac{K_w}{K_A \times K_B} = \frac{[H^+] \times [OH'] \times [HA] \times [BOH]}{[H^+] \times [A'] \times [B^+] \times [OH']}$$

$$\therefore \frac{K_w}{K_A \times K_B} = K_H$$

DETERMINATION OF THE DEGREE OF HYDROLYSIS

A number of methods are available for determining the degree of hydrolysis of a salt. Some of these are described below :

(1) **From the ionisation constant.** From a knowledge of K_A , K_B and K_w , the value of K_H can be calculated with the help of the expressions :

$$K_H = \frac{K_w}{K_B}; \quad K_H = \frac{K_w}{K_A}; \quad K_H = \frac{K_w}{K_A \times K_B}$$

Knowing the hydrolysis constant, h can be found by the application of the Law of Mass Action

$$K_H = \frac{h^2}{(1-h)V}$$

Since h is very small

$$K_H = \frac{h^2}{V}$$

or

$$h^2 = K_H \times V$$

$$h = \sqrt{K_H \times V}$$

where V is the volume in litres that contains 1 gram molecule of the salt.

Example 1. What is the percentage hydrolysis of NaCN in N/80 solution when the dissociation constant for HCN is 1.3×10^{-9} and $K_w = 10^{-14}$? (Punjab B.Sc., 1935)

Since NaCN is the salt of a strong base and a weak acid (Case ii above)

$$K_H = \frac{K_w}{K_A} = \frac{1 \times 10^{-14}}{1.3 \times 10^{-9}} = 7.7 \times 10^{-6}$$

$$\text{If } h \text{ is the degree of hydrolysis we have } K_H = \frac{h^2}{(1-h)V}$$

$$\text{Since } h \text{ is very small we have, } \frac{h^2}{V} = K_H$$

$$\text{or } h^2 = K_H \times V = 7.7 \times 10^{-6} \times 80$$

$$\therefore h = \sqrt{7.7 \times 10^{-6} \times 80} = 2.48 \times 10^{-2}$$

∴ Percentage hydrolysis in N/80 solution is 2.48.

Example 2. Calculate the hydrolysis constant and degree of hydrolysis of NH_4Cl in a 0.001 M solution. $K_B = 1.8 \times 10^{-5}$; $K_w = 10^{-14}$.

Since NH_4Cl is the salt of a weak base and a strong acid,

$$K_H = \frac{K_w}{K_B}$$

$$\text{or } K_H = \frac{10^{-14}}{1.8 \times 10^{-5}} = 5.5 \times 10^{-10}$$

If h be the degree of hydrolysis,

$$K_H = \frac{h^2}{(1-h)V}$$

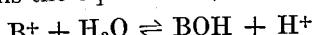
Since h is very small

$$K_H = \frac{h^2}{V} \quad \text{or } h^2 = K_H \times V \\ = 5.5 \times 10^{-10} \times 10^3 = 55 \times 10^{-2} \\ \therefore h = 7.4 \times 10^{-4} \text{ or } 0.00074.$$

(2) **From Conductivity Measurements.** For the determination of the degree of hydrolysis of a salt by the conductivity method, three different measurements of conductivity are necessary. These are :

- (i) The equivalent conductivity λ_v of the solution at a certain dilution V .
- (ii) The equivalent conductivity of the strong acid or base at infinite dilution i.e., λ_∞ .
- (iii) The equivalent conductivity of the salt solution in presence of excess of weak acid or base. Let it be λ'_v . This measurement gives the conductivity of the salt solution if no hydrolysis had occurred for the presence of excess of weak free acid or base prevents the hydrolysis of the salt and reduces it nearly to zero.

Consider the hydrolysis of the salt of a strong acid and a weak base. We have in this the equilibrium,



The equivalent conductivity λ_v is due to the H^+ ions and the ions B^+ only, BOH being very weak does not appreciably affect the conductivity.

If h is the degree of hydrolysis when one gram equivalent is dissolved in V litres, the unhydrolysed salt will be $(1 - h)$.

\therefore Conductivity due to $[H^+]$ ions = $h\lambda_\infty$

and " " " $[B^+]$ ions = $(1 - h)\lambda'_v$

$$\text{or } \lambda_v = (1 - h)\lambda'_v + h\lambda_\infty$$

$$\text{or } h(\lambda_\infty - \lambda'_v) = \lambda_v - \lambda'_v$$

$$\text{or } h = \frac{\lambda_v - \lambda'_v}{\lambda_\infty - \lambda'_v}.$$

Example. The equivalent conductivity of a solution of aniline hydrochloride was found to be 144 at a certain dilution and at $25^\circ C$. In the presence of excess of aniline, the value of conductivity is 103.6. If λ_∞ for HCl at this temperature is 383, calculate the degree of hydrolysis.

In this case :

$$\lambda_\infty = 383$$

$$\lambda_v = 144$$

$$\lambda'_v = 103.6.$$

Now, as shown above :

$$h = \frac{\lambda_v - \lambda'_v}{\lambda_\infty - \lambda'_v}$$

$$= \frac{144 - 103.6}{383 - 103.6} = 0.144$$

\therefore The degree of hydrolysis is 14.4 %.

(3) **Farmer's Distribution Method.** Suppose we want to determine the degree of hydrolysis of aniline hydrochloride. Shake a known weight of it with benzene and water and find the weight of aniline in the benzene layer by passing dry HCl through it and weighing the hydrochloride formed. The weight in the aqueous layer can be calculated if the distribution ratio of aniline between water and benzene is known. This is determined by a separate experiment (See *Distribution Law*). Knowing the weight of aniline in aqueous layer, the degree of hydrolysis can be calculated.

Total free aniline = aniline in benzene + aniline in water.

Free hydrochloric acid will also have the same concentration in gm. mols. per litre and the concentration of the unhydrolysed salt is (initial concentration—hydrolysed concn.)

$$\text{Now } K_H = \frac{[\text{free acid}] \times [\text{free base}]}{[\text{unhydrolysed salt}]}$$

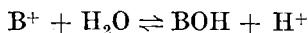
Knowing K_H ; h can be calculated for

$$K_H = \frac{h^2}{(1 - h)V}$$

(4) **From the Depression of Freezing Point.** The depression of freezing point depends upon the number of particles present and

when the number increases as a result of ionisation or hydrolysis, the observed depression is higher than the normal value.

Consider the hydrolysis of salt BA formed from a weak base and a strong acid. The equilibrium attained is



Neglecting water, it can be seen that for every B^+ ion used up, one H^+ ion and one BOH molecule is produced. If h be the degree of hydrolysis and we start with 1 gm. mol. of the salt, the number of particles after hydrolysis is $(1+h)$. If i be the Van't Hoff factor for the salt and the acid, unionised molecules of the weak base not affecting the depression we shall have :

$$\frac{\text{Observed Depression}}{\text{Normal Depression}} = (i + h)$$

This method has been found to give satisfactory result only when the hydrolysis is sufficiently large so that the value of $(i + h)$ is markedly different from i .

(5) **The Indicator Method.** This method is used only when hydrolysis does not take place to a great extent. We determine in this case the pH value of the solution by the calorimetric method. The pH value depends upon the H^+ or OH^- ions produced as a result of hydrolysis.

Suppose we start with a gm. mols. of the salt of strong acid and a weak base. Let h be the degree of hydrolysis when the equilibrium $B^+ + H_2O \rightleftharpoons BOH + H^+$ has been attained. The concentration of $[H^+]$ at equilibrium is :

$$[H^+] = h \times A$$

The value hA is equated with the hydrogen ion concentration calculated from the pH value. Knowing (H^+) and A , the degree of hydrolysis h can be calculated.

QUESTIONS AND PROBLEMS

- What is the modern conception of an 'acid' and a 'base'? Arrange some acids and bases in the order of their strength.
- Give an account of the proton transfer theory of acids and bases. (*Gujarat B.Sc., 1953*)
- Explain the phenomenon 'Salt hydrolysis' taking your examples from (a) the salt of a weak base and a strong acid, (b) the salt of a strong acid and a weak base, and (c) the salt of a weak base and a weak acid.
- What is meant by the term 'degree of hydrolysis'? How would you determine the degree of hydrolysis of aniline hydrochloride?
- What is salt hydrolysis? Explain clearly why an aqueous solution of sodium chloride is neutral towards indicators, a solution of sodium acetate alkaline and a solution of ferric chloride acidic? Why is a solution of ammonium acetate almost neutral towards indicators?
- Explain what you understand by hydrolysis taking for your illustration the behaviour of a solution of potassium cyanide. Calculate the degree of hydrolysis of a decinormal potassium cyanide solution at 25°C. The dissociation constant of HCN at 25°C is 1.3×10^{-10} and the ionic product of water 1×10^{-14} .
- Explain and apply the Law of Mass Action to the hydrolysis of a salt of a strong acid and a weak base. The dissociation constant of aniline as a

base at 25°C is 5.93×10^{-10} . The ionic product of water at 25°C is 1.2×10^{-14} . Calculate the percentage hydrolysis of aniline hydrochloride in 0.1 N solution at 25°C .

8. Why is a solution of sodium carbonate alkaline?

9. Develop equations showing the necessary relationships for the hydrolysis of salts of weak acids and strong bases.

At 25°C , the ionisation constant of acetic acid is 1.8×10^{-5} and the ionic product of water is 1.2×10^{-14} . Calculate the percentage hydrolysis of a normal solution of sodium acetate. (*Osmania B.Sc., 1953*)

10. Write a note on hydrolysis. Describe two methods of determining the degree of hydrolysis. (*Lucknow B.Sc., 1953*)

11. Why do certain salts hydrolyse in solution? Give examples of salt hydrolysis. Describe a method for measuring the degree of hydrolysis in any one case. (*Travancore B.Sc., 1953*)

12. Write a note on the hydrolysis of salts. Calculate the degree of hydrolysis of $\text{N}/100$ solution of ammonium chloride. The dissociation constant of ammonium hydroxide is 1.7×10^{-5} and ionisation constant of water is 1.0×10^{-14} at 25°C . (*Banaras B.Sc., 1951*)

13. What is meant by the term 'hydrolytic constant'? The degree of hydrolysis of a decinormal solution of potassium cyanide is one per cent. What is the value of the hydrolytic constant of the salt? (*Nagpur B.Sc., 1953*)

14. Outline a method by which the ionic product of water may be determined. Obtain equations to show how this quantity is involved in the hydrolysis of the salt of a strong acid and a weak base. (*Ceylon Final, 1953*)

15. Describe two methods by which you can calculate the dissociation constant K_w of water. (*Agra B.Sc., 1954*)

16. Describe the different methods employed for the determination of the degree of hydrolysis of a salt. (*Poona B.Sc., 1954*)

17. Explain the terms hydrolysis constant, and the degree of hydrolysis.

Derive an expression for the degree of hydrolysis of potassium cyanide.

Calculate the degree of hydrolysis of $\text{N}/10$ KCN at 20°C , given that the dissociation constant of HCN is 7.2×10^{-10} and ionic product of water, 10^{-14} , both at 20°C . (*Annamalai B.Sc., 1954*)

18. Describe with reference to typical examples, how the hydrolysis of a salt is explained on the basis of the theory of electrolytic dissociation.

Discuss the principles of the several methods used for the determination of the degree of hydrolysis of a salt. (*Indian Administrative Services, 1950*)

19. At 18°C the degree of hydrolysis of 0.01 N aniline acetate is 54%. Calculate the dissociation constant of aniline given that K_A for acetic acid is 1.8×10^{-5} and $K_w = 1.0 \times 10^{-14}$ at 18°C . (*Baroda B.Sc., 1955*)

20. Describe the relation between the hydrolysis constant of a salt of a weak acid and a weak base and their dissociation constants. Show that the degree of hydrolysis of such a salt is independent of dilution.

At 25°C the dissociation constant of aniline is 4.8×10^{-10} and of acetic acid 1.8×10^{-5} . The ionic product of water is 1.0×10^{-14} . What is the degree of hydrolysis of 0.01 N and 0.02 N solutions of aniline acetate, if the unhydrolysed aniline acetate is assumed to be completely dissociated?

(*Poona B.Sc., 1955*)

21. Derive the expression for the hydrolysis of a salt of a weak base and a weak acid and show that in this case the extent of the hydrolysis is independent of the dilution. (*Andhra B.Sc., 1956*)

22. Comment on the following statements:—

(i) degree of hydrolysis of a salt of a weak acid and a weak base is independent of dilution.

(ii) heat of neutralisation of a strong acid and a strong base is constant and is independent of the nature of the acid or base.

(iii) The ions are discharged in electrolysis, in equivalent amounts independent of their migration velocities. (*Baroda B.Sc., 1956*)

23. Describe the principles of the different methods employed in the determination of the degree of hydrolysis of a salt. (*Karnatak B.Sc., 1956*)

24. What is meant by the terms 'Degree of hydrolysis', and 'Hydrolysis constant'? Deduce in the case of a salt of a strong acid and weak base, the relation between the hydrolysis constant and the dissociation constant of the base. How will you determine the degree of hydrolysis of aniline hydrochloride solution? (*Punjab B.Sc., 1956*)

25. Develop necessary equations showing the relationships for the hydrolysis of a salt of a strong base and a weak acid. At 25°C the degree of hydrolysis of sodium acetate is 0.00008 in N/10 solution. If the ionic product of water at 25°C is 1.2×10^{-14} , find the ionization constant of acetic acid. (*Osmania B.Sc., 1956*)

26. Why do salts hydrolyse in solution? Give examples of salt hydrolysis. Derive equations showing the necessary relationships for hydrolysis of salts of (a) weak acid and strong base (b) weak acid and weak base. (*Nagpur B.Sc., 1957*)

27. Explain clearly the terms 'hydrolysis' and 'ionization'. Assuming that the specific conductivity of pure water is $0.50 \times 10^{-7} \text{ ohm}^{-1}$, calculate the ionic product of water. The mobilities of the hydrogen ion and the hydroxyl ion are 317 and 180 respectively. (*Delhi B.Sc., 1958*)

28. What is meant by the degree of hydrolysis?

Calculate the percentage hydrolysis of sodium acetate in 0.1 N solution at 25°C from the following data, assuming that the salt is completely dissociated:—

Dissociation constant of acetic acid at 25° = 1.8×10^{-5} .

Ionic product for water = 1.21×10^{-14} . (*Punjab B.Sc., 1958*)

29. Discuss salt hydrolysis and show that for a salt of weak base and weak acid the hydrolysis constant is given by

$$k_h' = \frac{k_w}{k_a k_b}$$

where k_w is the ionization constant for water, and k_a , k_b are the dissociation constants of the weak acid and the weak base. (*Allahabad B.Sc., 1958*)

30. What is hydrolysis? Explain clearly why an aqueous solution of sodium chloride is neutral towards indicators, a solution of sodium acetate alkaline and a solution of ferric chloride acidic? Why is a solution of ammonium acetate almost neutral towards indicators. (*Aligarh B.Sc., 1959*)

31. Give an account of the methods employed for the determination of the degree of hydrolysis of a salt. Calculate the degree of hydrolysis of 0.01 N solution of sodium acetate. (The ionic product of water is 10^{-14} and the dissociation constant of acetic acid is 1.8×10^{-5}). (*Karnatak B.Sc., 1959*)

32. Deduce an expression for the hydrolysis of a salt of a weak acid and a weak base.

From the following data calculate the degree of hydrolysis of such a salt.

$$K_a = 2 \times 10^{-5}, K_b = 6 \times 10^{-10} \text{ and } K_w = 1.2 \times 10^{-14}.$$

(*Poona B.Sc., 1959*)

33. Describe a method of determining the ionic product of water.

Shields found that an 0.1 molar solution of sodium acetate is 0.008 per cent. hydrolysed at 25°C. The ionization constant of acetic acid is 0.000018 at 25°C. Taking the salt and the sodium hydroxide formed to be completely dissociated, calculate the ionization constant of water. (*Lucknow B.Sc., 1959*)

ANSWERS

6. 0.02774

25. 1.875×10^{-5}

7. 0.0449

27. 1.01×10^{-14}

9. 0.002582%

28. 8.19×10^{-3}

12. 0.0002425

31. 0.0002379

17. 0.0118

32. 75.97%

19. 8.765×10^{-8}

33. 1.15×10^{-14}

20. 1 and 0.98

CHAPTER XXIV

CHEMICAL THERMODYNAMICS

DEFINITIONS

Energy is defined as *capacity of a system to do work*. It may be present in a system either in the form of *kinetic energy* or *potential energy* or both. Kinetic energy is the energy which a system possesses by virtue of its motion while potential energy is the energy which it possesses by virtue of its position. The absolute value of the total energy present in a system is known as its **intrinsic** or **internal energy**. It depends upon the pressure, volume and temperature and cannot be measured by any known method although it is possible to measure the energy change (ΔE) which the system undergoes. When energy is absorbed, ΔE is positive otherwise negative and is expressed in the usual units of work.

When the energy of a system is not in equilibrium with its surroundings, the balance of energy only is available for doing work and is known as its **free energy**. A system is said to be **isolated** when it can neither give energy nor receive energy from its surroundings.

The various changes and transformations which occur in nature are accompanied by energy change. The energy is of many kinds, mechanical, electrical, radiant, heat etc., and when one kind of energy disappears, another kind takes its place which means that the various kinds of energy are inter-convertible. The quantitative treatment of the relationship between different forms of energy is called **thermodynamics**.

FIRST LAW OF THERMODYNAMICS

Failure to construct a perpetual motion machine, i.e., a machine which could produce more mechanical work than the equivalent of energy used by it led to the universal acceptance of the principle of **conservation of energy**. Accordingly, *energy can neither be created nor destroyed even though it may be changed from one form to another* and the **first law of thermodynamics** enunciated in 1842 by Julius Robert Mayer and more accurately defined in 1847 by Helmholtz states that :

For an isolated system, the sum of all the forms of energy is constant at all times.

In other words, if a system changes from a given state A to another given state B, the total energy of the system and its surroundings remains unaltered.

Let a quantity of heat q be absorbed by a system whose internal energy in the given state A is E_1 . As the result of the absorption of heat, let the system do work equal to w on its surroundings and let its final energy in the state B be E_2 .

Increase in the internal energy of the system $= E_2 - E_1 = \Delta E$

According to the first law of thermodynamics,

$$\Delta E + w = q$$

or

$$\Delta E = q - w \quad \dots (1)$$

In a cyclic process, where the initial and the final states of a system are the same, $E_1 = E_2$, and in such cases ΔE being zero,

$$q - w = 0$$

or

$$q = w$$

i.e., the work done is equal to the heat absorbed.

Due attention must be paid in thermodynamic treatment to the signs. If work is done by the system, w is positive while if work is done on the system by the surroundings as for instance in the compression of a gas, w is negative. Similarly, q is positive if the system absorbs heat but if it evolves heat, q is negative.

Heat changes at constant pressure and at constant volume. When the work w is only mechanical work involving expansion or contraction, it may be replaced in equation (1) by $P \cdot \Delta V$ where P is the constant external pressure and ΔV is the increase in volume.

$$\text{or} \quad \Delta E = q - P \cdot \Delta V \quad \dots (2)$$

For a process conducted at **constant volume**, ΔV is zero

$$\therefore \quad \Delta E = q_v$$

i.e., the whole of the heat absorbed by a system at constant volume is utilized to increase the internal energy.

Similarly, under adiabatic conditions, when the system neither takes in nor gives out any heat during the process $q = 0$ and equation (1) reduces itself to

$$-\Delta E = w$$

i.e., decrease in internal energy in an adiabatic system is equal to the work done by the system.

HEAT CONTENT OR ENTHALPY

To evaluate the heat transferred in a **constant pressure** process, it is more convenient to make use of a function known as **enthalpy** or **heat content** denoted by the symbol H . Constant pressure processes are more common in Chemistry as a majority of the reactions are performed in open vessels.

At constant pressure, equation (2) may be written as

$$q_p = \Delta E + P \Delta V \quad \dots (3)$$

$$\text{Here,} \quad \Delta E = E_2 - E_1$$

$$\text{and} \quad \Delta V = V_2 - V_1$$

$$\therefore \quad q_p = (E_2 - E_1) + P(V_2 - V_1) \\ = (E_2 + PV_2) - (E_1 + PV_1) \quad \dots (4)$$

Just as the internal energy E is characterised by the state of a system only and is independent of the amount by which it is achieved, so is the product $PV(E + PV)$, therefore, is also

dependent only on the state of the system and is known as *enthalpy* or heat content (H).

$$\text{or } H = E + PV \quad \dots (5)$$

Using this value in equation (4), we get

$$q_p = H_2 - H_1 = \Delta H \quad \dots (6)$$

Combining equation (3) and (6), we have

$$\Delta H = \Delta E + P \Delta V \quad \dots (7)$$

i.e., the change in heat content at constant pressure is equal to the sum of the increase in internal energy and the mechanical work of expansion.

Combining equation (7) with (3), we have

$$q_p = \Delta H \quad \dots (8)$$

i.e., Enthalpy measures heat content at constant pressure and the heat of reaction of a process at constant pressure is equal to the change in enthalpy ΔH .

Heat of Reaction at Constant Volume and Constant Pressure.

Though heats of reaction are usually measured at constant pressure, it is also sometimes necessary to carry out the reaction at constant volume as for instance in the measurement of the heat of combustion. But in such cases, it is possible to convert the heat of reaction at constant volume to one at constant pressure.

$$\text{For, } q_v = \Delta E$$

and from equation (3), we have

$$\Delta E = q_p - P \cdot \Delta V$$

Combining the above two equations, we get

$$q_v = q_p - P \cdot \Delta V \quad \dots (9)$$

For an ideal gas, therefore,

$$q_v = q_p - nRT \quad \dots (10)$$

where n represents the change in the number of moles present.

HEAT CAPACITY

The heat capacity of a substance is defined as the amount of heat required to raise the temperature of one mol. of a substance through 1°C and is denoted by the symbol C . In the case of gases, it has two values, one at constant volume C_v and the other at constant pressure C_p .

At constant volume, no P-V work is done by the gas and the whole quantity of heat added goes to raise the temperature of the system. Let a small quantity of heat dq produce in one mol. of a gas a temperature rise dT as the internal energy increases by dE .

We have in such a case,

$$dE = C_v dT \quad \dots (11)$$

where C_v is the heat capacity at constant volume.

From equation (11), we get the thermodynamic definition of the heat capacity at constant volume as

$$\left(\frac{\delta E}{\delta T} \right)_v = C_v \quad \dots (12)$$

At constant pressure, the heat supplied is utilized in two ways :

(i) In raising the internal energy of the system and

(ii) In performing external work done by the expanding gas i.e., P-V work

$$\therefore dE + PdV = C_p dT \quad \dots(13)$$

From the above it follows that :

$$C_p = \left[\frac{\delta(E + PV)}{\delta T} \right] = \left[\frac{\delta H}{\delta T} \right]_p \quad \dots(14)$$

The difference $C_p - C_v$ for ideal gases. From equation (11) and (13) we have

$$C_p - C_v = \left(\frac{\delta H}{\delta T} \right)_p - \left(\frac{\delta E}{\delta T} \right)_v \quad \dots(15)$$

According to equation (5), $H = E + PV$

Differentiating this with respect to temperature at constant pressure, we get

$$\left(\frac{\delta H}{\delta T} \right)_p = \left(\frac{\delta E}{\delta T} \right)_p + P \left(\frac{\delta V}{\delta T} \right)_p \quad \dots(16)$$

Substituting the value in equation (15), we have

$$C_p - C_v = \left(\frac{\delta E}{\delta T} \right)_p + P \left(\frac{\delta V}{\delta T} \right)_p - \left(\frac{\delta E}{\delta T} \right)_v \quad \dots(17)$$

Taking internal energy as a function of two independent variables V and T , the increase dE may be expressed as :

$$dE = \left(\frac{\delta E}{\delta T} \right)_v dT + \left(\frac{\delta E}{\delta V} \right)_T dV \quad \dots(18)$$

Dividing both sides by dT , when the pressure is kept constant ;

$$\left(\frac{\delta E}{\delta T} \right)_p = \left(\frac{\delta E}{\delta T} \right)_v + \left(\frac{\delta E}{\delta V} \right)_T \cdot \left(\frac{\delta V}{\delta T} \right)_v \quad \dots(19)$$

Substituting the value of equation (19) in equation (17), we have

$$\begin{aligned} C_p - C_v &= \left(\frac{\delta E}{\delta T} \right)_v + \left(\frac{\delta E}{\delta V} \right)_T \left(\frac{\delta V}{\delta T} \right)_v + P \left(\frac{\delta V}{\delta T} \right)_v - \left(\frac{\delta E}{\delta T} \right)_v \\ &= \left(\frac{\delta E}{\delta V} \right)_T \left(\frac{\delta V}{\delta T} \right)_p + P \left(\frac{\delta V}{\delta T} \right)_p \quad \dots(20) \end{aligned}$$

Now for an ideal gas

$$PV = RT$$

$$\text{or } P \left(\frac{\delta V}{\delta T} \right)_p = RT \quad \dots(21)$$

$$\text{and } \left(\frac{\delta E}{\delta V} \right)_T = 0 \quad \dots(22)$$

i.e., the internal energy is independent of the volume. Substituting the values of equations (21) and (22) in equation (20), we have

$$C_p - C_v = R \quad \dots(23)$$

Adiabatic Expansion and Compression of Ideal Gases.

We have already seen that under adiabatic conditions, the decrease in internal energy is equal to the work done by the system.

or

$$-\Delta E = \Delta w$$

Let one mol. of a gas expand adiabatically from a volume V to $(V + dV)$ under a constant pressure P . Let the temperature fall by dT when the work done is $P.dV$

$$\therefore -\Delta E = P.dv = -C_v dT.$$

Dividing both sides by the absolute temperature T , we get

$$\frac{P}{T} dV = -C_v dT$$

But

$$\frac{P}{T} = \frac{R}{V} \quad \dots(24)$$

$$\therefore R \frac{dV}{V} = -C_v \frac{dT}{T}$$

When the volume changes from V_1 to V_2 , the temperature falls from T_1 to T_2

$$\therefore \int_{V_1}^{V_2} R \frac{dV}{V} = - \int_{T_1}^{T_2} C_v \frac{dT}{T}$$

$$\text{or} \quad R \log_e \frac{V_1}{V_2} = C_v \log_e \frac{T_2}{T_1}$$

$$\text{But} \quad C_p - C_v = R \quad \dots(\text{See eq. 23})$$

$$\therefore (C_p - C_v) \log_e \frac{V_1}{V_2} = C_v \log_e \frac{T_2}{T_1}$$

$$\text{or} \quad \log_e \frac{T_2}{T_1} = (\gamma - 1) \log_e \frac{V_1}{V_2}$$

$$\text{or} \quad \frac{T_2}{T_1} = \left(\frac{V_1}{V_2} \right)^{\gamma-1} \quad \dots(25)$$

Since $P_1 V_1 = RT_1$ and $P_2 V_2 = RT_2$, we get by eliminating T_1 and T_2

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2} \right)^\gamma$$

$$\text{or} \quad P_1 V_1^\gamma = P_2 V_2^\gamma \quad \dots(26)$$

$$\text{or} \quad PV^\gamma = \text{Constant} \quad \dots(27)$$

Similarly by eliminating V_1 and V_2 we get

$$\left(\frac{T_2}{T_1} \right)^\gamma = \left(\frac{P_2}{P_1} \right)^{\gamma-1} \quad \dots(28)$$

Depending upon the data given, equations (25), (26) and (27) may be utilised without serious error in case of *actual gases* to calculate the change in temperature, pressure etc. during an adiabatic compression or expansion.

Variation of Heat of Reaction with Temperature—

Kirchoff's Equation. It has already been pointed out that the change in enthalpy (heat of reaction) depends only on the initial and final states

$$\text{i.e., } \Delta H = H_2 - H_1$$

Differentiating this with respect to temperature at constant pressure, we have

$$\left[\frac{\delta(\Delta H)}{\delta T} \right]_p = \left(\frac{\delta H_2}{\delta T} \right)_p - \left(\frac{\delta H_1}{\delta T} \right)_p \quad \dots(29)$$

According to equation (14), we have

$$\left(\frac{\delta H}{\delta T} \right)_p = C_p$$

$$\therefore \left[\frac{\delta(\Delta H)}{\delta T} \right]_p = C_{p_2} - C_{p_1} = \Delta C_p \quad \dots(30)$$

or, change in the heat of reaction at constant pressure per degree change of temperature is equal to the difference in the heat capacities of the products and the reactants.

Integrating the above expression between the temperatures T_1 , T_2 when the difference of temperature is large, we have,

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p \cdot dT \quad \dots(31)$$

Equation (31) may be utilized for calculating the heat of reaction at a given temperature when it is known at some other temperature and when the heat capacities of the products and the reactants are known.

JOULE-THOMSON EFFECT

The change in temperature produced when a gas expands by flowing through some kind of obstruction (like a porous plug) from a region of higher pressure to one of lower pressure is known as

Joule-Thomson Effect.

A Joule-Thomson expression is characterised by the fact that :

- (i) it is irreversible
- (ii) it is adiabatic (i.e., $q = v$)

Suppose the high pressure is P_1 and the lower pressure is P_2 when the volumes per mol. are respectively V_1 and V_2 .

Work done on the gas in forcing it through the plug is $P_1 V_1$ while that done by the gas in expanding is $P_2 V_2$.

$$\therefore \text{Net work done by the gas} = w = P_2 V_2 - P_1 V_1$$

$$\text{But } E_2 - E_1 = q - w$$

$$= 0 - w$$

$$= (P_1 V_1 - P_2 V_2)$$

$$\text{or } E_2 + P_2 V_2 = E_1 + P_1 V_1$$

$$\text{or } H_2 = H_1$$

The investigation is, therefore, concerned with the change in temperature with pressure at constant enthalpy i.e., $(\frac{\delta H}{\delta T})_H$. It is represented by the symbol μ and is called **Joule-Thomson coefficient**.

A positive μ corresponds to cooling on expansion while a negative value suggests heating. When the value of $\mu=0$, the condition is called **inversion point**.

At normal temperature and pressure, a majority of gases show a positive Joule-Thomson coefficient and this fact is utilised in the liquefaction of gases by expansion.

REVERSIBLE PROCESSES

A thermodynamically reversible process is one which is carried out so very slowly that at every stage of it, the system is in temperature and pressure equilibrium with its surroundings. In such processes, the driving and opposing forces differ only infinitesimally and the process can be reversed completely by increasing the opposing force by an infinitesimal amount.

To understand this concept of reversibility, imagine a cylinder containing some water in equilibrium with its vapour and fitted with a weightless, frictionless piston. Let this cylinder be placed in a constant temperature bath. The driving force on the piston is the external pressure while the opposing force is the vapour pressure of water and as long as these are equal, the system is in perfect equilibrium. Now increase the external pressure by an infinitesimal amount. This will cause the vapour to condense but this condensation will take place so very slowly that the heat given off by this condensation is taken up by the bath and there is no change in the temperature and pressure and at all stages of the condensation of water vapour a state of equilibrium is maintained. In case, however, the external pressure is reduced by an infinitesimal amount below the vapour pressure of water, slow evaporation will start. Thus an infinitesimal change in pressure on either side of the equilibrium pressure causes the process to be reversed.

Although complete reversibility is more or less hypothetical and cannot be realised due to dissipation of energy in some form by friction etc., yet it can be approached and is determined by the difference between the driving and the opposing forces. Spontaneous processes like the expansion of a gas into a vacuum, the flow of heat from a hot body to a colder body in contact with it or the diffusion of one gas into another always proceed in a direction of greater stability and are, therefore, irreversible.

REVERSIBILITY AND MAXIMUM WORK

Consider a perfect gas enclosed in a cylinder provided with a weightless and frictionless piston. Let its pressure be p which in a state of equilibrium is equal to the external pressure on the piston.

Let the external pressure be reduced by an infinitesimal amount Δp and let the small increase in volume be dV which causes the piston to move up.

$$\text{Work done by the gas} = (p - dp).dV \quad \dots(32)$$

It is evident that smaller the value of dp , the greater is the work done or that the work that can be obtained from a system is the maximum when the external pressure differs infinitesimally from the internal pressure of the gas. Incidentally, the conditions of reversibility of a process are identically the same and it may, therefore, be stated that *maximum work can be obtained from a process only when it is carried out reversibly and isothermally*.

To calculate the maximum work done, when an ideal gas expands isothermally and reversibly from V_1 to V_2 , we have to add all the infinitesimally small amounts of work represented by equation

$$dw = (p - dp). dV$$

Neglecting the very small term $dp.dV$

$$dw = p.dV$$

$$w = \int_{V_1}^{V_2} p.dV \quad \dots(33)$$

If we have one gram mol. of a gas,

$$PV = RT$$

or

$$P = RT/V$$

$$\therefore w = \int_{V_1}^{V_2} RT \cdot \frac{dV}{V}$$

or

$$w = RT \log_e \frac{V_2}{V_1} \quad \dots(34)$$

Since $P_1V_1 = P_2V_2$, we may also have the alternative equation

$$w = RT \log_e \frac{P_1}{P_2} \quad \dots(35)$$

Equations (34) and (35) give the maximum work obtainable from an isothermal reversible expansion of one gram mol. of an ideal gas.

SECOND LAW OF THERMODYNAMICS

The first law of thermodynamics which is concerned with the equivalence of different forms of energy does not tell us anything about the ease or extent of convertibility of one form of energy into another. When we come to examine the relationship between heat and work, we notice that whereas different forms of energy can be readily and completely converted into heat, it is not possible to convert back heat completely into work. This limitation forms the basis of the second law of thermodynamics which states that :

It is impossible to convert heat into an equivalent amount of work without producing other changes in some parts of the system.

The flow of heat being unidirectional from a higher to a lower temperature, another way of stating the law according to Classius is :

"It is impossible for a self acting machine, unaided by any external agency, to transfer heat from a body at a low to one at a higher temperature."

THE CARNOT CYCLE

To calculate the maximum extent to which heat can be converted into work, we make use of the *Carnot Cycle* which consists of a series of operations on a perfect gas so that at the conclusion of the operations, the gas is restored to its original state.

First Operation—Isothermal Expansion. Let one mol. of a perfect gas be enclosed in a cylinder fitted with a frictionless piston and let its temperature, pressure and volume be T_2 , P_1 and V_1 respectively. The cylinder is placed in contact with a heat reservoir whose temperature remains constant at T_2 ° Abs.

Now let the gas expand isothermally and reversibly to the new volume V_2 (along AB in Fig. 191) taking in this process heat equal to Q_2 from the reservoir.

Work w_1 done by the gas in this process according to the eq. (34) is

$$w_1 = RT_2 \log_e \frac{V_2}{V_1} = Q_2 \quad \dots(36)$$

Second Operation—Adiabatic Expansion. The gas at B is now at a temperature T_2 and has a volume V_2 under the new pressure P_2 . It is now completely isolated and allowed to expand adiabatically (along BC in Fig. 191) to the new volume V_3 . Let the temperature drop to T_1 . Here $q = 0$ and work w_2 is done at the expense of the internal energy of the gas.

$$\therefore w_2 = -\Delta E$$

$$= C_v(T_2 - T_1)$$

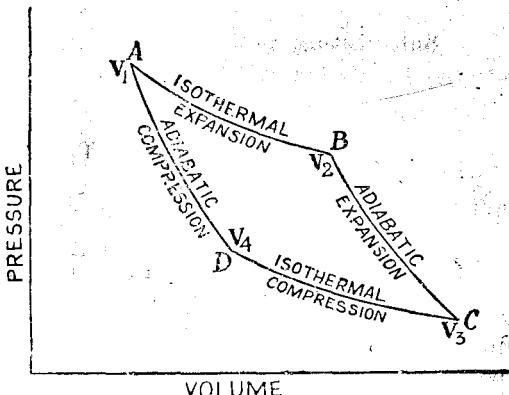


Fig. 191. The Carnot Cycle.

Third Operation—Isothermal Compression. The cylinder is now placed in contact with a heat reservoir at T_1 . The volume of the gas is V_3 and its pressure P_3 . It is now isothermally and reversibly compressed until the volume is V_4 . During this compression, the gas gives out heat to the reservoir. Let its value be Q_1 so that the work done on the gas w_3 is

$$w_3 = R T_1 \log_e \frac{V_3}{V_4} = -Q_1$$

Fourth Operation—Adiabatic Compression. The gas with volume V_4 and temperature T_1 is again isolated and compressed adiabatically until it regains its original state i.e., its volume becomes V_1 and its temperature T_2 .

Work done w_4 upon the gas is equal to the increase in the internal energy

$$\begin{aligned} w_4 &= -C_v(T_2 - T_1) \\ \text{Total work } W &= w_1 + w_2 + w_3 + w_4 \\ &= RT_2 \log_e \frac{V_2}{V_1} + C_v(T_2 - T_1) + RT_1 \log_e \frac{V_3}{V_4} \\ &\quad - C_v(T_2 - T_1), \\ &= RT_2 \log_e \frac{V_2}{V_1} + RT_1 \log_e \frac{V_3}{V_4} \\ W &= Q_2 - Q_1 \end{aligned} \quad \dots(37)$$

According to equation (25) governing the adiabatic changes :

$$\frac{T_2}{T_1} = \left(\frac{V_3}{V_2}\right)^{\gamma-1} \quad \dots \text{For adiabatic expansion}$$

$$\text{and} \quad \frac{T_1}{T_2} = \left(\frac{V_1}{V_4}\right)^{\gamma-1} \quad \dots \text{For adiabatic compression}$$

Combining the two equations :

$$\frac{V_3}{V_2} = \frac{V_4}{V_1}$$

$$\text{or} \quad \frac{V_3}{V_4} = \frac{V_2}{V_1}$$

Substituting these values in equation (37), we have

$$\begin{aligned} W &= Q_2 - Q_1 = RT_2 \log_e \frac{V_2}{V_1} - RT_1 \log_e \frac{V_3}{V_4} \\ &= R(T_2 - T_1) \log_e \frac{V_2}{V_1} \end{aligned} \quad \dots(38)$$

Dividing this equation by equation (36), we get

$$\frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2} = \frac{T_2 - T_1}{T_2}$$

The factor $\frac{W}{Q_2}$ is called the *thermodynamic efficiency* and gives the fraction of the heat which it is possible to convert into work. It is evident from the *Carnot equation* that the efficiency of a process depends only upon the temperature limits between which the cycle operates and is independent of all other factors. All reversible engines operating in cycles between the same temperature limits possess the same efficiency.

ENTROPY

In 1850, Claussius introduced a new function of the state of the system called **Entropy** and designated it by the symbol S. It is numerically defined by the equation $dS = \frac{dq}{T}$ where q is the heat

transferred reversibly and dS is the entropy change for an infinitesimal reversible process.

Any finite process may be considered to be made up of a number of such infinitesimal steps, all reversible and the total change in entropy is given by

$$\Delta S = \int \frac{dq}{T}$$

The difference in entropy ΔS between two points A and B depends entirely upon the state A and state B and can be calculated if the substance can be brought reversibly from one state to the other. It is independent of the path taken.

Entropy change in reversible process. According to the Carnot Cycle equation derived earlier

$$\begin{aligned} \frac{Q_2 - Q_1}{Q_2} &= \frac{T_2 - T}{T_2} \\ \therefore \quad \frac{Q_1}{T_1} &= \frac{Q_2}{T_2} \\ \text{or} \quad \frac{Q_2}{T_2} - \frac{Q_1}{T_1} &= 0 \end{aligned} \quad \dots (39)$$

The quantity $\frac{Q_2}{T_2}$ is the change in entropy at temperature T_2 and may be denoted by ΔS_2 . Similarly $\frac{Q_1}{T_1}$ is the decrease in entropy at temperature T_1 and is denoted by ΔS_1

$$\therefore \quad \Delta S_2 - \Delta S_1 = 0 \quad \dots (40)$$

It follows, therefore, that for a reversible process, the entropy of the system remains constant and $\Delta S = 0$ or $\int \frac{dq}{T} = 0$.

Entropy change in irreversible process. The efficiency of an irreversible Carnot Cycle is always less than that of a reversible one operating between the same two temperatures

$$\text{i.e.,} \quad \frac{Q_2 - Q_1}{Q_2} < \frac{T_2 - T_1}{T_2}$$

where Q_2 is the heat absorbed at temperature T_2 and Q_1 is the heat returned at temperature T_1 .

$$\text{or} \quad \frac{Q_2}{T_2} - \frac{Q_1}{T_1} < 0$$

In other words $\int \frac{dq}{T}$ for an irreversible cycle is always less than

zero and the entropy of the final state is always greater than that of the initial state. As most of the processes going on in nature are spontaneous and irreversible, it has been said that "the entropy of the universe always tends towards a maximum". (Claussius).

THE GIBBS-HELMHOLTZ EQUATION

The Gibbs-Helmholtz equation expresses a relationship between the internal energy and maximum work and is derived by combining the first law equation with the second law Carnot Cycle equation

According to the first law of thermodynamics

$$-\Delta E = w - q \quad \dots(i)$$

The maximum work obtainable from a Carnot Cycle operating between the temperatures T_2 and T_1 at a cost of a quantity of heat q_2 is

$$w = q_2 \frac{(T_2 - T_1)}{T_2}$$

For an infinitesimal change in temperature dT , when the amount of heat taken up is q , the maximum work dw' will be

$$dw' = q \cdot \frac{dT}{T}$$

or $q = T \cdot \frac{dw'}{dT} \quad \dots(ii)$

Eliminating q between the equations (i) and (ii) above, we get

$$-\Delta E = w - T \frac{dw'}{dT}$$

or $w + \Delta E = T \frac{dw'}{dT} \quad \dots(41)$

From the above equation, it follows that the decrease in internal energy of a system (or the heat of reaction) will be equal to the work done only if either T is zero i.e., the reaction is carried out at absolute zero or dw/dT is zero which means that the process is independent of temperature. In this respect, the Gibbs-Helmholtz equation finds application in the study of the Daniell Cell (or for the matter of that other reversible cells) for the temperature co-efficient of such a cell is almost zero.

THE CLAPEYRON EQUATION

A useful thermodynamic relation which gives us important information about a system consisting of any two phases of a single substance in chemical equilibrium is the Clapeyron equation. It is derived from the Gibbs-Helmholtz equation mentioned above.

Let the system studied be



Consider one gram mol. of a liquid confined in a cylinder by a frictionless piston. Let the volume of the liquid be V_1 and its vapour pressure equal to p . Now allow the liquid to evaporate reversibly at a constant temperature T and when the whole of it has vaporised, let the volume of the vapour be V_2

$$\therefore \text{Work done during evaporation } w = p(V_2 - V_1) \quad \dots(i)$$

Differentiating equation (i) with respect to temperature at constant $(V_2 - V_1)$ we get

$$\frac{dw}{dT} = (V_2 - V_1) \frac{dp}{dT} \quad \dots(ii)$$

Heat absorbed from the surroundings is the latent heat of vaporisation L which on substitution in the first law equation gives us

$$\Delta E = w - L \quad \dots(iii)$$

On substitution of expression (ii) and (iii) in the Gibbs-Helmholtz equation, we have :

$$w + \Delta E = T \frac{dw}{dT}$$

$$w + (L - w) = T (V_2 - V_1) \frac{dp}{dT}$$

or $L = T \frac{dp}{dT} (V_2 - V_1)$

or $\frac{dp}{dT} = \frac{L}{T(V_2 - V_1)} \quad \dots(42)$

This is the Clapeyron equation which in its general form may be written as

$$\frac{dp}{dT} = \frac{\Delta H}{T(V_2 - V_1)} \quad \dots(43)$$

where ΔH is the heat of transition when a volume V_1 of a definite weight of one form changes to a volume V_2 of the same weight of other form at the temperature T.

CLAUSIUS CLAPEYRON EQUATION

The above equation can be simplified by neglecting the small volume of the liquid in comparison with the volume of the vapour. Equation (43) in such a case becomes

$$\frac{dp}{dT} = \frac{\Delta H}{TV_2}$$

Supposing the vapour to obey the ideal gas laws

$$V_2 = \frac{RT}{p}$$

$$\therefore \frac{dp}{dT} = \frac{\Delta H p}{RT^2}$$

or $\frac{1}{p} \cdot \frac{dp}{dT} = \frac{\Delta H}{RT^2}$

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

$$\therefore d \log_e \frac{p}{dT} = \frac{\Delta H}{RT^2} \quad \dots(44)$$

Equation (44) is known as the **Claussius Clapeyron equation** and though approximate is of very great value.

If ΔH is regarded as constant, we may integrate the above equation

$$d \log_e p = \Delta H \frac{dT}{RT^2}$$

$$\int d \log_e p = \frac{\Delta H}{R} \int \frac{dT}{T^2}$$

or $\log_e p = \frac{-\Delta H}{RT} + \text{Constant}$

or $\log p = \frac{-\Delta H}{2.303 RT} + C$

If p_1 is the vapour pressure at T_1 and p_2 the vapour pressure at T_2 , we have

$$\log p_1 = \frac{-\Delta H}{2.303 RT_1} + C \quad \dots (i)$$

and $\log p_2 = \frac{-\Delta H}{2.303 RT_2} + C \quad \dots (ii)$

Subtracting (i) from (ii)

$$\log \frac{p_2}{p_1} = \frac{\Delta H}{2.303 R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \dots (45)$$

In this form the equation may be used to calculate the heat of vaporisation if the vapour pressure of the liquid at two different temperatures is given. Also knowing the vapour pressure at one temperature and the latent heat of vaporisation, we can calculate the vapour pressure at any other temperature.

FREE ENERGY AND MAXIMUM WORK

It has already been pointed out that the maximum work of the change of a substance from one state to the other depends entirely upon the initial and final states and is the maximum when the change is reversible.

If the maximum work function be denoted by A , then in passing from one state to another, this function will alter by a fixed amount ΔA and will be made up of (a) the work done by expansion and (b) all other work, for example, electrical work etc. denoted by W

$$\therefore -\Delta A = W + p\Delta V$$

(decrease in work
function)

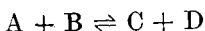
Since $p\Delta V$ is the work of expansion, it does not represent the available work and, therefore, W is that portion of the maximum work which is the net work of the change. It is represented by ΔF and is called the *change in free energy*, when F is the **free energy** function.

$$\therefore -\Delta A = -\Delta F + \Delta V$$

or $\Delta A = \Delta F - p\Delta V \quad \dots (46)$

Free energy change in Chemical Reactions—Van't Hoff Isotherm. The Van't Hoff Isotherm gives the net work that can

be obtained from a gaseous reactant at constant temperature when both the reactants and the products are at suitable arbitrary pressures. It can be derived by using the "equilibrium box" which is a theoretical device with the supposition that of its four walls, one is permeable to A, the second to B, the third to C and the fourth to D when the gaseous reaction to be considered is



Let the initial pressures of A and B be p_a and p_b and the final pressures of C and D be p_c and p_d respectively and let the equilibrium pressures of the four be P_A , P_B , P_C and P_D respectively.

The following theoretical operations may be performed :—

(i) Change the pressure on A from the initial pressure p_a to the equilibrium pressure P_A .

.. Work done by the gas

$$= RT \log_e \frac{p_a}{P_A}.$$

(ii) Change the pressure on B from p_b to P_B

Work done by the gas = $RT \log_e \frac{p_b}{P_B}$

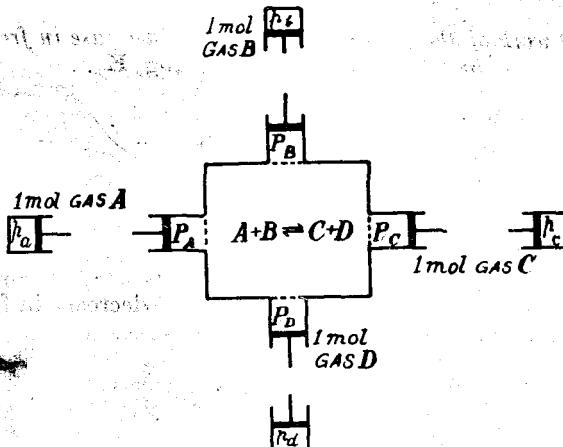


Fig. 192. Van't Hoff equilibrium box.

(iii) Introduce 1 gm. mol. of A and 1 gm. mol. of the gas B through their respective semi-permeable membranes into the equilibrium box which contains the reactants and the products at the equilibrium pressure. This will not involve any work as the partial pressures of A and B inside the box are equal to the pressure of the gases coming in. A and B react to form 1 gm. mol. of C and 1 gm. mol. of D.

(iv) Withdraw 1 gm. mol. of C and 1 gm. mol. of D from the equilibrium box through their respective semi-permeable walls. No work is done in this process as the gases come out at the equilibrium pressures P_C and P_D .

(v) Now alter the pressure on the gas from the equilibrium pressure P_C and P_D to the final pressure p_c and p_d .

$$\text{Work done by the gas C} = RT \log_e \frac{P_C}{p_c}$$

$$\text{Work done by the gas D} = RT \log_e \frac{P_D}{p_d}$$

As the change in free energy is equal to the total work done by the gases :

$$\begin{aligned} -\Delta F &= RT \log_e \frac{P_C \times P_D}{P_A \times P_B} - RT \log_e \frac{p_c \times p_d}{p_a \times p_b} \\ &= RT \log_e K_p - RT \log_e \frac{p_c \times p_d}{p_a \times p_b} \end{aligned}$$

If the reaction is started with reactants at a partial pressure of one atmosphere and the resulting products are also at 1 atmosphere pressure, we have :

$$-\Delta F = RT \log_e K_p - RT \log_e 1$$

$$\text{or } -\Delta F = RT \log_e K_p \quad \dots (47)$$

i.e., the net work of the reaction is equal to the decrease in free energy of the system and is given by the expression $RT \log_e K_p$.

VAN'T HOFF ISOCHEORE

The Van't Hoff Isochore is obtained by combining the Van't Hoff Isotherm with the Gibbs-Helmholtz equation according to which :

$$\Delta H + w' = T \left(\frac{dw'}{dT} \right)_p$$

Since the net work of a change is equal to the decrease in free energy of the system, i.e., $w' = -\Delta F$, we have :

$$\Delta H - \Delta F = -T \left(\frac{d(\Delta F)}{dT} \right)_p$$

Now, according to Van't Hoff Isotherm :

$$-\Delta F = RT \log_e K_p$$

$$\therefore -T \frac{d(\Delta F)}{dT} = RT \log K_p + RT \frac{d(\log K_p)}{dT}$$

Multiplying throughout by T, we have :

$$-T \frac{d(\Delta F)}{dT} = RT \log K_p + RT^2 \frac{d \log K_p}{dT}$$

$$= -\Delta F + RT^2 \frac{d \log K_p}{dT}$$

But according to Gibbs-Helmholtz equation,

$$\begin{aligned} -T \left(\frac{d(\Delta F)}{dT} \right)_p &= \Delta H - \Delta F \\ \therefore \Delta H - \Delta F &= -\Delta F + RT^2 \frac{d \log K_p}{dT} \\ \text{or } \frac{\Delta H}{RT^2} &= \frac{d \log K_p}{dT} \quad \dots (48) \end{aligned}$$

This equation is known as *Van't Hoff Isochore*.

For applying the Isochore to any particular reaction, it is essential to integrate it. If ΔH remains constant over a range of temperature, we have an integration,

$$\log K_p = \int \frac{\Delta H}{RT^2} dT = \frac{-\Delta H}{RT} + \text{Const.}$$

If we integrate the above expression between two temperatures T_1 and T_2 at which the equilibrium constants are K_{p_1} and K_{p_2} respectively, we have :

$$\begin{aligned} \log K_{p_1} - \log K_{p_2} &= \frac{-\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \\ &= \frac{-\Delta H}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right) \quad \dots (49) \end{aligned}$$

Knowing the equilibrium constants at two different temperatures, it is possible, therefore, to calculate the change in heat content.

QUESTIONS AND PROBLEMS

1. Show that under adiabatic conditions, the decrease in internal energy of a system is equal to the work done.
2. State the first law of thermodynamics and obtain the relation $pV^\gamma = \text{constant.}$ (Agra M.Sc., Prev. 195)
3. What is meant by the heat capacity of a system? Show from thermodynamical consideration that $C_p - C_v = R.$
4. What do you understand by a thermodynamically reversible process? Show that maximum work can be obtained from a system only when it is reversibly and isothermally carried out.
5. State the second law of thermodynamics and prove that all reversible engines operating in cycles between the same temperature limits possess the same efficiency.
6. Deduce the equation of Gibbs and Helmholtz and mention its importance.
7. Derive Claußius-Clapeyron equation. What are its applications?
8. State the second law of thermodynamics in as many forms as possible and show that they are identical in significance. (Bombay B.Sc., 1956)
9. State the first and second laws of Thermodynamics. Use them to determine Gibbs-Helmholtz equation, and mention some uses of this equation. (Osmania B.Sc., 1956)
10. State the second law of thermodynamics and explain the condition under which heat can be converted into work. (Poona B.Sc., 1956)
11. Derive an expression for the efficiency of a Carnot's engine working between two temperatures T_1 and T_2 and use it to derive the Guldberg-Helmholtz equation. (Karnatak B.Sc., 1956)

CHAPTER XXV

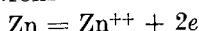
ELECTROMOTIVE FORCE

GALVANIC CELLS

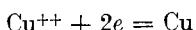
A galvanic cell is a device for converting chemical energy into electrical energy. The electromotive force (e. m. f.) of such a cell is directly proportional to the intensity of chemical reaction taking place in it and the process going on in a galvanic cell is the reverse of that of electrolysis in the electrolytic cell.

A typical galvanic cell is the **Daniell Cell** which is shown in Fig. 193. It consists of an outer copper vessel containing a concentrated solution of copper sulphate. Inside it is a porous pot containing a zinc rod dipping in a dilute solution of zinc sulphate.

The zinc passes into solution as zinc ions liberating two electrons



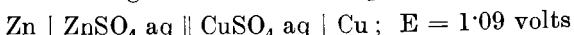
The cupric ions gain these electrons and are discharged as metallic copper.



Thus, we can suppose that the electrons set free at the zinc electrode travel along the external circuit and are used at the copper electrode for the discharge of Cu^{++} . The cell reaction can be represented as



and the cell according to convention is represented as



i.e., the negative electrode is on the extreme left whilst the positive electrode is on the extreme right. A double vertical line between the two liquids signifies that the liquid junction e.m.f. has either been reduced to the minimum by suitable means or that the value of e.m.f. does not include the liquid junction e.m.f.

REVERSIBLE AND IRREVERSIBLE CELLS

In the case of Daniell Cell described above, the e.m.f. is 1.09 volts and the cell reaction is



If to such a cell an external e.m.f. exactly equal to 1.09 volts is applied, the cell reaction stops but if it is increased infinitesimally beyond 1.09 volts, we notice that the cell reaction is reversed and

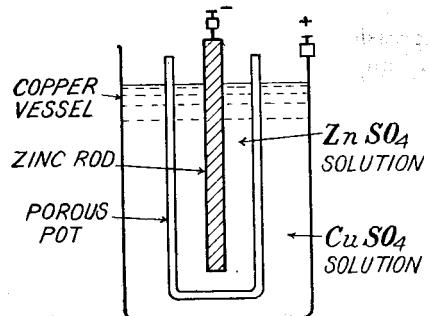
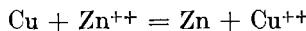


Fig. 193. Daniell Cell.

we have



By maintaining this external e.m.f. it is possible to restore the cell to its original state.

Neglecting the small diffusion that might occur across the boundaries of the two liquids, such a cell is the nearest approach to reversibility. A cell of this type is called a **reversible cell** and the conditions of reversibility as explained in Chapter XXIV are :

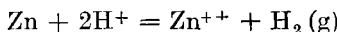
(i) If an e.m.f. exactly equal to its own is applied from some external source, the chemical reaction going on inside the cell will stop.

(ii) If the external e.m.f. is infinitesimally greater than that of the cell, the current will begin to flow in the opposite direction and at the same time the cell reaction is reversed.

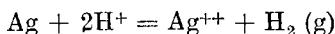
Any other cell which does not satisfy these conditions is irreversible. For example, the cell



is irreversible. Here the cell reaction is



But when the cell is connected with an external source of potential slightly greater than its own, the reaction becomes



RELATION BETWEEN ELECTRICAL ENERGY AND CHEMICAL ENERGY

It is only in case of reversible cells that thermodynamic principles can be employed to obtain a definite relation between electrical energy and chemical energy. When the cell is working reversibly, it is at each moment in a state of equilibrium and gives out the maximum work which according to equation (34) (Chapter XXIV) is

$$w = RT \log_e \frac{V_2}{V_1}$$

$$\text{or } w_e = RT \log_e \frac{C_1}{C_2} \quad \dots (i)$$

where w_e represents the electrical energy. The value of this electrical work done per gram ion is represented by nFE where E is the e.m.f. of the cell, n is the valency of the ion and F is 1 Faraday ($= 96,500$ coulombs). Substituting this value of work in equation (i), we have

$$nFE = RT \log_e \frac{C_1}{C_2}$$

$$\text{or } E = \frac{RT}{nF} \log_e \frac{C_1}{C_2}$$

$$\text{or } E = \frac{2.303RT}{nF} \log \frac{C_1}{C_2}$$

It has also been mentioned in connection with the Gibbs-Helmholtz equation (Chapter XXIV) that the decrease in internal energy of a cell (or its heat of reaction) is equal to the work done if $\frac{dw}{dT}$ is zero

$$\text{i.e., } w_e = -\Delta E = Q$$

where Q is the heat of reaction in calories

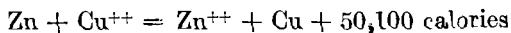
$$\text{or } nEF = Q$$

$$\text{or } E = \frac{Q}{nF}$$

Since 1 cal. = 4.185 joules or volt-coulombs

$$E = \frac{4.185 Q}{nF} \text{ volts}$$

In the case of Daniell Cell :



$$\therefore \text{e.m.f.} = \frac{4.185 \times 50100}{2 \times 96500} = 1.09 \text{ volts.}$$

SOURCE OF E.M.F. IN A GALVANIC CELL

We have mentioned above that the ultimate source of e.m.f. in a galvanic cell is the chemical reaction which proceeds when a current is flowing.

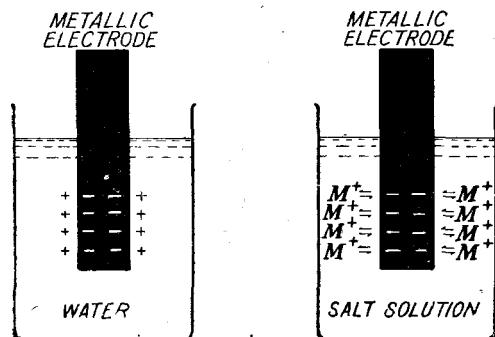


Fig. 194. (a) Formation of electrical double layer when a metal bar is dipped in water.

Fig. 194. (b) Equilibrium between solution pressure of a metal and its ionic pressure.

Nernst (1889) advanced a theory to explain the above phenomenon. According to the **Nernst Theory**, all metallic elements and hydrogen have a tendency to pass into solution in the form of positive ions. This property of the metals is known as *Solution Pressure*. Due to the migration of positive ions, the metallic electrode is left negatively charged and thus an electrical double layer is set up at the electrode.

If the metallic electrode is dipped in a solution of one of its salts, the position becomes slightly different. In such a case, the tendency of the metal to pass into solution as ions is opposed by a reverse tendency of the ions to be deposited back on the electrode. This backward reaction is attributed to the osmotic pressure of ions in solution. Thus the standard potential of a metal is equal to the difference between its solution pressure and the osmotic pressure of its ions. Two possibilities can arise :

(1) If the solution pressure of the metal exceeds the osmotic pressure of its ions, the cations pass into solution more rapidly leaving the electrode negative-charged e.g., zinc in zinc sulphate solution.

(2) If the solution pressure of the metal is less than the osmotic pressure of its ions, the cations will be driven out of the solution and deposited on the electrode making it positively charged e.g., copper sulphate solution.

In case of a galvanic cell e.g., Daniell cell, we have two electrodes dipping in the solution of their respective salts. Each electrode acquires a certain potential due to the difference in the rates of migration and return of cations. The e.m.f. of such a cell is then equal to the resultant of its two electrode potentials.

$$E_1 - E_2 = \frac{2.303 RT}{nF} \log \frac{C_1}{C_2}$$

where E_1 = Potential of (+) electrode dipping in a solution of concentration C_1 .

E_2 = Potential of (-) electrode in a solution of concentration C_2 .

R = Gas constant.

T = Absolute Temperature.

n = Valency of cation.

F = Faraday.

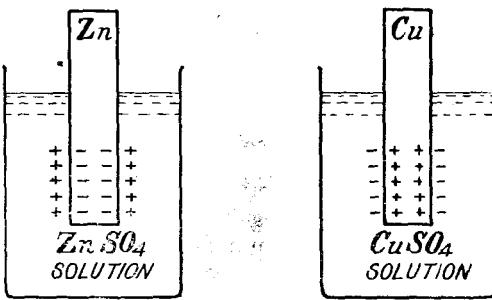
Substituting the value of R and F in the above equation and taking the temperature as 15°C , the above relation is simplified to

$$E_1 - E_2 = \frac{0.058}{n} \log \frac{C_1}{C_2}$$

MEASUREMENT OF ELECTRODE POTENTIALS

The **single electrode potential** e.g., the difference of potential between a metal and a solution of its salt, is generally measured in an indirect manner. The electrode whose potential is to be measured, is combined with a *reference electrode* of known potential and the e.m.f. of the resulting cell is noted experimentally. The potential of the unknown electrode is calculated from the fact that the e.m.f. of a cell is the algebraic difference between the potentials of its two electrodes. Thus

$$E = E_1 - E_2$$



(A) Fig. 195. Electrical double layers :

A : Zn in ZnSO_4 solution.

B : Cu in CuSO_4 solution.

where

E = Observed e.m.f. of the cell,

E_1 = Electrode potential of the (+) electrode,

E_2 = Electrode potential of the (-) electrode.

Knowing E and either E_1 or E_2 , the other electrode potential can be calculated.

Reference Electrodes .

The following reference electrodes are commonly used :—

(1) **Dropping Mercury Electrode.** We have seen that when a metal is dipped in a solution of its own salt, an electrical double layer is formed at the electrode-solution junction. Mercury being liquid at ordinary temperatures behaves differently. The exceptional behaviour of mercury is made use of in the direct measurement of its electrode potential.

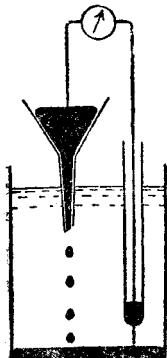


Fig. 196. Dropping Hg-electrode

Mercury is allowed to drop from a funnel through a solution of a mercurous salt. Since the mercury surface is continuously being replaced, no double layer is formed at the contact between mercury in the funnel and the solution. The potential of the mercury in the funnel is, therefore, the same as that of mercurous salt in solution. If now we connect the mercury layer in the funnel and that at the bottom of the beaker through a millivoltmeter, we can directly read the single mercury electrode potential.

(2) **Hydrogen Electrode.** It is the primary standard electrode. It consists of a small platinum strip P coated with platinum black to absorb the hydrogen gas. A platinum wire welded to the electrode and sealed through a glass tube makes contact with the outer circuit. The platinum strip is surrounded by an outer glass tube which has an inlet for hydrogen at the top, and a number of holes at the base for the escape of excess of gas. The electrode is placed in a dilute solution of an acid. Pure hydrogen gas is then admitted into it at one atmosphere pressure. A part of the gas is absorbed by the platinised electrode, while the excess escapes through the lower holes. There results an equilibrium between the absorbed hydrogen on the electrode surface and the hydrogen ions in the solution.



By convention the potential of this standard hydrogen electrode is arbitrarily fixed as zero. Thus when this electrode is coupled

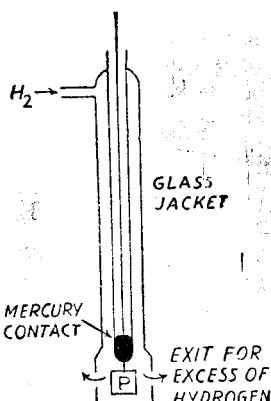


Fig. 197. Hydrogen electrode.

with any other, the observe e.m.f. of the cell will be numerically equal to the potential of the known electrode.

(3) **Calomel Electrode.** It consists of a glass tube having a layer of mercury at the bottom. The mercury surface is connected to the outer circuit by means of a glass tube. The mercury is covered with a paste of mercurous chloride (calomel) and mercury in potassium chloride solution. The electrolyte is also a solution of potassium chloride. This electrode can be connected to the other electrode by a salt bridge. The potential of this electrode depends upon the concentration of potassium chloride solution. When saturated potassium chloride solution is used, it comes to be +0.2458 volts at 25°C on hydrogen scale.

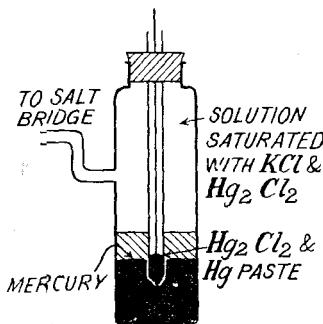


Fig. 198. Calomel electrode.

ELECTROCHEMICAL SERIES

The potentials measured with reference to hydrogen electrode are said to refer to **Hydrogen scale**. When the metals are arranged in the order of potentials with respect to normal solutions of their ions and measured on the hydrogen scale, the list is called the **Electrochemical series**. It is of great importance in the study of solutions. A metal with a negative potential will displace those following it in the series from solutions of their salts. This is so, because a negative potential indicates a comparatively higher tendency to ionise. Thus zinc (potential -0.76 volts) will displace copper (+0.34 volts) from a solution of copper sulphate.

ELECTROCHEMICAL SERIES

Metal	Ion	Potential	Metal	Ion	Potential
Li	Li ⁺	-3.00	Ni	Ni ⁺⁺	-0.23
K	K ⁺	-2.92	Sn	Sn ⁺⁺	-0.13
Ba	Ba ⁺⁺	-2.90	Pb	Pb ⁺⁺	-0.12
Na	Na ⁺	-2.71	H	H ⁺	0.00
Mg	Mg ⁺⁺	-1.87	Cu	Cu ⁺⁺	+0.34
Al	Al ⁺⁺⁺	-1.69	Ag	Ag ⁺⁺	+0.80
Zn	Zn ⁺⁺	-0.76	Hg	Hg ⁺⁺	+0.80
Fe	Fe ⁺⁺	-0.44	Au	Au ⁺⁺⁺	+1.36

HOW TO MEASURE THE E.M.F. OF A CELL

During the passage of an electric current, the e.m.f. of a cell is altered because (i) the internal resistance of the cell may absorb some of the available potential difference, and (ii) the chemical change involved may result in polarisation. Hence the e.m.f. of a cell cannot be determined directly by a voltmeter. It can, however, be measured accurately with the help of potentiometer. In this case we measure the external potential difference required to stop the passage

of current in the cell under examination. Since at the time of measurement, no current is flowing through the cell, the two above-mentioned sources of error are eliminated.

The apparatus used (potentiometer) consists of a wire AB of

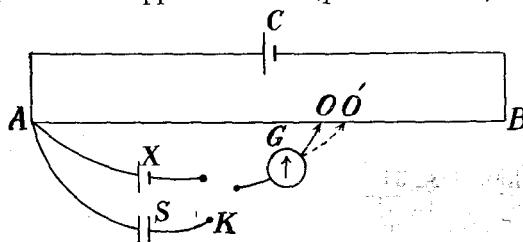


Fig. 199. Measuring the e.m.f. of a cell with the help of potentiometer.

uniform diameter and possessing high resistance. The two ends of this wire are connected to a storage battery C having a constant and larger e.m.f. than that to be measured. The cell X under examination is also connected to A, taking care that the

same poles of X and C are linked to A. The other terminal of the cell X is connected to a movable contact O through a galvanometer G. By using a two-way key K, the unknown cell in the circuit can be replaced by a standard cell S. The cell C sends a current through the galvanometer in a direction opposite to that in which the current is sent by the cell X. By moving to and fro, the position of the sliding contact O is so adjusted that no current flows through the galvanometer. The distance AO is measured. The experiment is then repeated with a standard cell S of known e.m.f. Again the new distance AO' arrived in this case is measured. Thus

$$\frac{\text{e.m.f. of cell } X}{\text{e.m.f. of cell } S} = \frac{\text{Pot. difference between A and O}}{\text{Pot. difference between A and O'}}$$

Since the wire is of uniform thickness, the fall of potential per unit length must be same. If e represents the fall of potential per unit length, the above relation is reduced to

$$\frac{\text{e.m.f. of cell } X}{\text{e.m.f. of cell } S} = \frac{AO \times e}{AO' \times e} = \frac{AO}{AO'}$$

Knowing the e.m.f. of cell S, we can calculate that of X, the unknown cell.

The Standard Cell. The most common standard cell is the **Weston cell**. It consists of an H-shaped glass vessel. The positive electrode is formed of a layer of pure mercury covered with a paste of solid mercurous sulphate and cadmium sulphate in mercury. The negative electrode is 12.5 per cent cadmium amalgam. The electrolyte is a solution of cadmium sulphate which is kept saturated by contact with

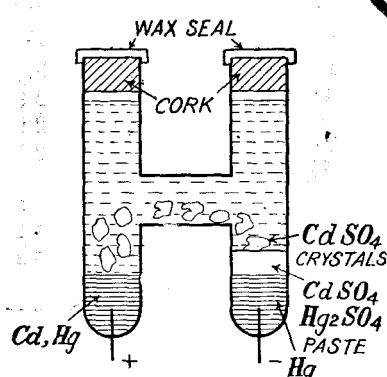


Fig. 200. Weston Standard Cell.

crystals of $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$. To prevent the loss of water by evaporation the limbs are sealed with wax. The cell reaction is represented by $\text{Cd} + \text{Hg}_2^{++} \rightleftharpoons \text{Cd}^{++} + 2\text{Hg}$. The Weston Cell has an e.m.f. of 1.0183 at 20°C . It varies only slightly (0.0000406 volt per degree C) by change in temperature. The e.m.f. remains constant for many years.

Potentiometric Titrations. More recently the measurement of e.m.f. by potentiometer has been used for recording the end-points in volumetric titrations. This method has several advantages over the ordinary indicator method. Thus,

- (1) It can be used in case of coloured solutions *e.g.*, vinegar or inks where ordinary titration with the help of indicators is out of question.
- (2) It can also be employed for the titrations of weak acids against weak alkalies.
- (3) In case of oxidation-reduction titrations, the use of external indicators is eliminated.
- (4) With slight modifications, the apparatus can be automatic.

The potentiometric titrations are based on the fact that near the end point, there is a sudden change in the e.m.f. of a hydrogen and another standard electrode. The apparatus used is shown in Fig. 201. The hydrogen electrode H and the calomel electrode C are placed in contact with the acid solution to be titrated. The cell thus formed is connected to the potentiometer (See Fig. 201) and its e.m.f. measured as described before. The standard alkali solution is then run from the burette gradually. After each addition the solution is stirred thoroughly and the e.m.f. of the cell measured. The volumes of alkali added are plotted against the e.m.f.s recorded. At the neutral point, there is an abrupt change in the e.m.f.

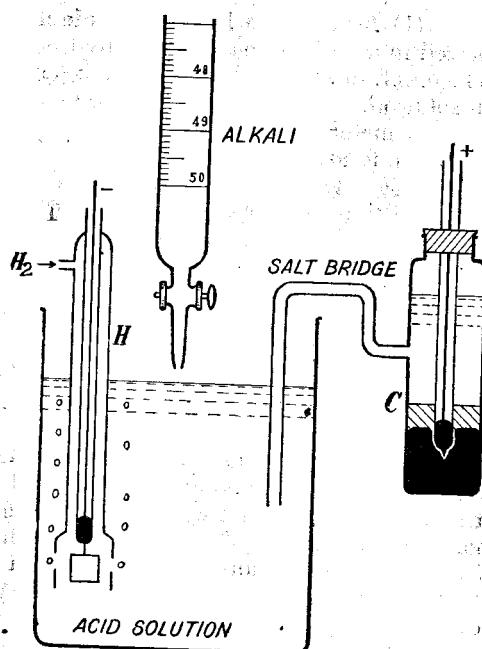


Fig. 201. Potentiometric titrations.

A similar procedure will determine the end-point in the case of oxidation-reduction titrations.

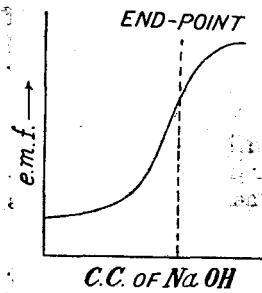


Fig. 202(a) End-point of acid-alkali titration.

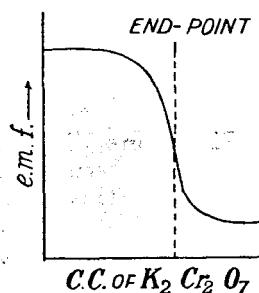


Fig. 202(b) End-point of oxidation reduction titration.

For example, ferrous sulphate solution is placed in the beaker and is titrated against standard potassium dichromate solution from the burette. As in the case of acid-alkali titrations, there is an abrupt change in the e.m.f. at the end-point.

Determination of pH of a solution

The conductivity and the *Indicator methods* for the determination of pH have already been described. A potentiometer may be used for the accurate determination of pH, by the following two methods :—

(1) **By using a hydrogen electrode.** The given solution is placed in a beaker having (a) hydrogen and (b) calomel electrodes. The e.m.f. of such a cell depends upon the concentration of H⁺ ions in solution. By noting the e.m.f. of the cell with the help of the potentiometer (See Fig. 199) we can calculate pH of the solution from the following relation :

$$\begin{aligned} E - E_c &= 0.002 \times T \times \log \frac{1}{[H^+]} \\ &= 0.002T \times pH. \end{aligned}$$

where

E = Observed e.m.f. of the cell.

E_c = Potential of the calomel electrode (*given*)

T = Absolute temperature.

(2) **By using a Glass Electrode.** The glass electrode is extremely useful for determining the pH value of a solution because it is not affected by oxidising or reducing agents and is not easily poisoned. It is based on the principle that when a glass membrane separates two solutions differing in pH, a potential difference is found to exist between the two surfaces of the glass which varies with the difference of pH of the two solutions.

The glass electrode consists of a thin walled glass bulb made out of special type of low melting glass. It is filled with normal hydrochloric acid solution saturated with quinhydrone or in contact with Ag/AgCl electrode. The platinum wire dipping in the electrolyte

passes out of the glass tube at G. The bulb is placed in the solution S of which the pH is to be measured and which is contained in the beaker B. The potential is measured against a standard calomel electrode C (Fig. 203).

An ordinary potentiometer cannot be used to measure the voltage of such a cell because of the high resistance of the glass membrane and for this reason valve electrometers which require very little current for their operation are made use of.

The potential E of the electrode is given by the relation

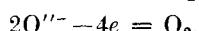
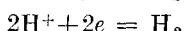
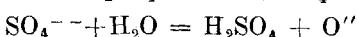
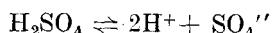
$$E = E_g^o + \frac{2.303RT}{F} \log_{10} [H^+]$$

E_g^o is determined by calibrating the apparatus by means of a buffer solution of known pH value.

The glass electrode gives very good results for pH value ranging between 0 to 9. For solutions of high alkalinity, high accuracy is not obtained.

POLARISATION

When an electric current is passed between platinum electrodes placed in dilute sulphuric acid, hydrogen and oxygen are evolved at the cathode and anode respectively.



Outside the solution, the current flows from cathode to anode while inside the solution it flows from anode to cathode. If now the battery is removed and the two electrodes are connected through a galvanometer, a small current will be seen to pass between the two electrodes. The direction of the current in this case, however, is opposite to that during electrolysis i.e., the current flows from anode to cathode outside the cell. It so happens because the platinum electrodes used during electrolysis are covered with bubbles of hydrogen and oxygen which constitute gas electrodes. Since the e.m.f. of these new electrodes is opposite to that of the battery, it is called the back e.m.f.

This phenomenon of back e.m.f. brought by the products of electrolysis is termed **Polarisation**. An exactly similar thing happens when

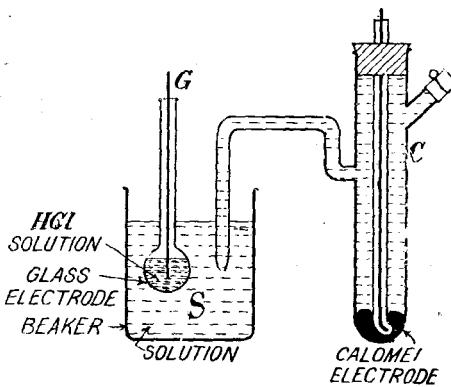


Fig. 203. Glass Electrode.

a voltaic cell consisting of a zinc and a copper electrode in dilute sulphuric acid, is set up. When used as a source of electric current,

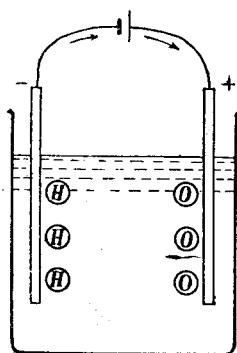


Fig. 204 (a) Polarisation during electrolysis.

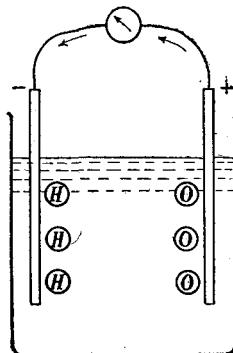


Fig. 204 (b) Polarised cell can supply electric current.

the e.m.f. of such a cell rapidly falls due to the covering of electrodes by gas bubbles.

Explanation of Polarisation. When the electrolysis stops as described above, the solution pressure exerted by absorbed hydrogen exceeds the ionic pressure of H^+ ions in the solution. Consequently hydrogen ions go into the solution, leaving the cathode negatively charged. Similarly at the other electrode O'' ions go into the solution leaving the anode positively charged. If these two electrodes are now connected, a current will flow from anode to cathode until the electrodes are completely depolarised.

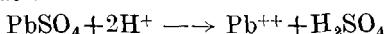
Accumulators or Secondary Cells.

From the above it is clear that a polarised voltaic cell can be used as a source of electric current. Such a cell is known as *accumulator*. Unlike the primary cell, the energy from an accumulator is not generated within itself but is previously stored in it from some outside source. Thus the electrical energy supplied by it is second hand and hence its name, **secondary cell**.

The platinum electrodes used in electrolysis of acidulated water possess only a small capacity to accumulate the products of electrolysis. Therefore, they can supply very little electrical energy while being discharged or depolarised. The capacity of such an accumulator can be increased many fold by replacing the platinum electrodes with perforated lead plates filled with a paste of litharge in dilute sulphuric acid.

During 'charge' an electric current is passed through the accumulators from a dynamo or mains. The electrolysis in the cell takes place and the electrical energy is converted into potential chemical energy. This can be represented by the following reactions :

At the cathode :



At the anode :



During charging the water is electrolysed and sulphuric acid is generated. Thus, the acid gets stronger and denser.

During 'discharge' the reverse action takes place and the chemical energy is converted into electrical energy.

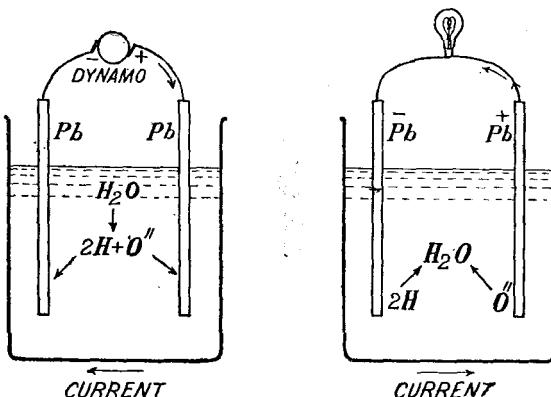
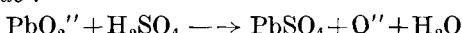


Fig. 205 (a) Charging. Fig. 205 (b) Discharging.



At the anode :



The acid gets weaker and lead sulphate is formed on both the plates. The specific gravity of the acid during charging gradually increases to 1.20. During discharge it slowly falls and the cell is sent for recharging when it has come down to 1.17. The e.m.f. of lead accumulator is 2.1 volts.

Decomposition Potential.

We have seen above that the products of electrolysis exert a back e.m.f. which counteracts the primary e.m.f. Obviously, the

electrolysis of a compound cannot be carried indefinitely, unless, the back e.m.f. is overcome. Thus if an external e.m.f. of one volt is applied to the two platinum electrodes dipping in dilute sulphuric acid, at once the electrolysis of water sets in but very soon it comes to a stop. This happens because the back e.m.f. has become greater than the applied e.m.f. If the applied e.m.f. is now gradually increased, a point is reached when the electrolysis commences.

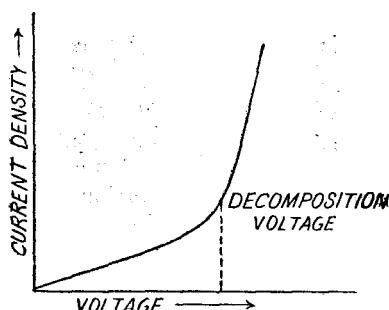


Fig. 206. Decomposition potential.

continues and does not stop even though the applied e.m.f. is increased no more. It is, therefore, clear that a certain minimum voltage must be applied before a continuous electrolysis commences.

This voltage which is just sufficient to overcome the back e.m.f. due to polarisation is called Decomposition potential of the given solution.

The decomposition potential varies from solution to solution. During electrolysis, the metallic ions travel towards the cathode. If the metal has a high solution pressure, it will try to send these ions back into the solution *i.e.*, the solution will have high decomposition potential. Thus, a metal with high solution pressure, *e.g.*, zinc, requires a higher e.m.f. to be deposited on the cathode than a metal like copper with low solution pressure. This fact is made use of in refining and electrometallurgy of metals. For example, copper and zinc can be separated electrically. The decomposition potentials of copper sulphate and zinc sulphate are 1.5 and 2.55 volts respectively with copper and zinc electrodes. When an e.m.f. of less than 2.5 volts is applied between copper electrodes, only copper will be deposited on the cathode while zinc remains in solution.

Overvoltage.

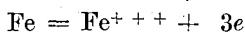
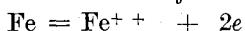
Theoretically the voltage required for the decomposition of an acid solution is equal to the e.m.f. of the reversible cell with hydrogen at one atmosphere. It is, however, found that the observed decomposition voltage is always higher than the theoretical (reversible) value. Thus with platinum and lead electrodes we require respectively a current of 1.7 and 2.2 volts for the electrolysis of dilute sulphuric acid against a theoretical value of 1.23 volts. This is explained by the fact that the passage of a small current is accompanied by relatively large polarisation which naturally depends on the nature of the electrode.

The difference between the voltage at which a gas is actually evolved during electrolysis and the theoretical value at which it ought to have been evolved, is known as overvoltage.

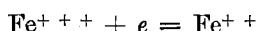
The working of the lead accumulator can be explained on the basis of overvoltage. It is due to the high overvoltage of lead during the charging that the metal is deposited on the cathode instead of the hydrogen being evolved. This view is further confirmed by the fact that if the lead electrodes are covered with a metal of low overvoltage like platinum, hydrogen gas is evolved and no lead is deposited.

OXIDATION-REDUCTION ("REDOX") POTENTIAL

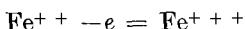
Metal ions act as oxidising or reducing agents as a result of their ability to gain or to lose electrons forming ions of lower or higher valency which represent different stages of oxidation. An atom of iron, for example, may lose two electrons to form the ferrous ion or three electrons to form the ferric ion :



A ferric ion acts as an oxidising agent because it can gain one electron and be converted into the lower state of oxidation, *i.e.*, ferrous



Similarly the ferrous ion acts as a reducing agent because it can lose one electron to be converted to the ferric ion



However, if we take a mixed solution of ferric and ferrous ions, the solution will possess reducing or oxidising properties according as whether it can lose or gain electrons. If a platinum plate be immersed in such a solution and the solution tends to oxidise the plate, electrons will be removed from the plate which will acquire a positive charge. If on the other hand, the solution tends to reduce the plate, it will give up electrons to it and the plate will acquire a negative charge. The magnitude and the sign of the charge given to the plate, therefore, measures the oxidising or the reducing power of the solution.

If we set up a cell of the type Pt | Fe⁺⁺ || Fe⁺⁺⁺ | Pt, and join the two electrodes by a wire, the ferrous ions will give electrons to the platinum electrode and thus pass into ferric state whereas these electrons will travel by the connecting wire and be taken up by the ferric ions to be reduced to the ferrous state. The potential difference so produced will go on developing until it puts a stop to this process.

The potential E of the platinum electrode dipping in a solution containing ferric and ferrous ions when measured against a standard electrode will be given by the expression

$$E = E_0 + \frac{2.303 RT}{nF} \log_{10} \frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]}$$

where n is the difference in the valencies of the ions.

When the ratio $\frac{[\text{Fe}^{+++}]}{[\text{Fe}^{++}]}$ = 1, the second term in the above equation becomes zero and E_0 is the potential which is set up when the platinum electrode dips in a 50% mixture of ferrous and ferric ions and is known as the "redox" potential.

A high positive "redox" potential indicates that the ion in the higher state of oxidation is acting as a strong oxidising agent whilst a high negative "redox" potential indicates the higher reducing power of the ion in the lower state of oxidation.

The "redox" potentials obtained from some well known reactions are given below :

<i>Reaction</i>	<i>Potential (volts)</i>
Co ⁺⁺⁺ → Co ⁺⁺	+ 1.82
Ce ⁺⁺⁺ → Ce ⁺⁺	+ 1.44
Tl ⁺⁺⁺ → Tl ⁺	+ 1.24
Fe ⁺⁺⁺ → Fe ⁺⁺	+ 0.76
Sn ⁺⁺⁺⁺ → Sn ⁺⁺	+ 0.15
V ⁺⁺⁺ → V ⁺⁺	- 0.2
Cr ⁺⁺⁺ → Cr ⁺⁺	- 0.4

REDOX INDICATORS

Certain organic dyestuffs like methylene blue, neutral red, Janus green, phenosafranine, indigo disulphonic acid etc., possess the property of being coloured in their oxidised form and colourless in the reduced state as "leuco" compounds. The reduction involves one or more hydrogen atoms and the colour change occurs at different "redox" potentials according to the *pH* value of the solution. As such these dyestuffs can be used as indicators of the oxidation potentials of solutions into which they are added. If the oxidation potential of the solution is more positive than the redox potential of the indicator, the latter will remain fully oxidised and thus show its full colour but as soon as the oxidation potential comes to the negative side of E_0 , the indicator will be reduced to the colourless form.

A variety of redox indicators with different E_0 values at a given *pH* are available and these are used in determining the approximate oxidation-reduction conditions prevailing in biological systems and for indicating the end points of oxidation-reduction reactions in volumetric analysis.

CONCENTRATION CELLS

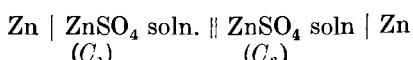
A concentration cell is a galvanic cell in which electrical energy is produced by the transference of a substance from a system of high concentration to one of low concentration. In general, there are two types of concentration cells :

- (1) Those having an electrolyte of two different concentrations but identical electrodes.
- (2) Those having electrodes of two different concentrations but the electrolyte of only one strength.

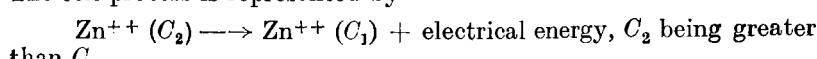
Of these, the first type is by far the most important.

When the concentration of an electrolyte is altered, there occurs a corresponding change in the potential of the electrode in contact with the electrolyte. Thus a cell can be constructed by dipping two identical electrodes in solutions of different concentrations of the same electrolyte. The source of electrical energy in the cell is the tendency of the electrolyte to diffuse from a solution of higher concentration to that of lower concentration. Thus with passage of time the two concentrations tend to become equal. For this reason the e.m.f. of a concentration cell is maximum at the start and it gradually falls to zero as the two concentrations become identical.

A concentration cell with zinc electrodes and the solutions of zinc sulphate of two different concentrations can be represented by



where C_1 and C_2 represent the concentrations of the two solutions. The cell process is represented by



It can be shown thermodynamically that the energy change in this process is equal to $RT \log_e \frac{C_1}{C_2}$ where R is gas constant and T, temperature on the absolute scale.

Suppose the valency of cation is n . When 1 gram atom of the metal is dissolved from one electrode and deposited on the other, the

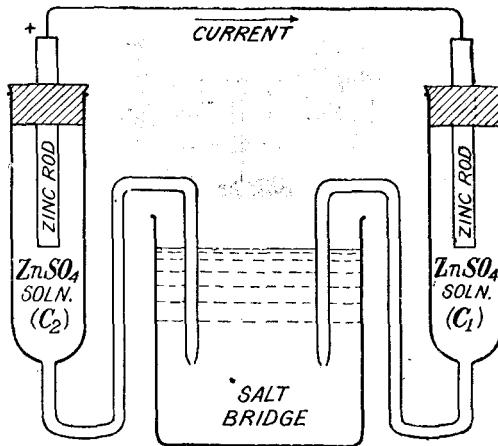


Fig. 207. Typical Concentration cell where $C_2 > C_1$

amount of electrical energy that has passed round the circuit = nF coulombs where F is faraday. Hence the electrical work done or free energy change = nFE where E represents the e.m.f. of the cell. Obviously

$$-nFE = RT \log_e \frac{C_1}{C_2}$$

or $E = -\frac{RT}{nF} \log_e \frac{C_1}{C_2}$

$$= \frac{2.303RT}{nF} \log_{10} \frac{C_2}{C_1}$$

By substituting the values of R ($= 8.318 \times 10^7$ ergs) and F ($= 96500$ coulombs), we can calculate the e.m.f. of the cell at any temperature (say 15°C).

$$E = \frac{2.303 \times 8.318 \times 10^7 \times (273 + 15)}{n \times 96500} \log \frac{C_2}{C_1}$$

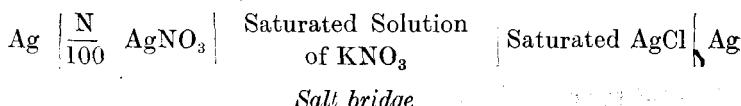
$$= \frac{0.058}{n} \log \frac{C_2}{C_1}$$

A usual form of the concentration cell is shown in Fig. 207. The two electrodes are connected by means of a salt bridge.

Applications of the Concentration Cells.

(1) *Determination of the Solubility of Sparingly soluble salts.* The ionic concentration of a solution can be calculated from the e.m.f. of a concentration cell. In case of sparingly soluble salts, the substance can be supposed to be completely ionised even in the saturated solution. Hence the ionic concentration is proportional to the solubility of the salt.

Suppose we want to find the solubility of silver chloride. This can be done by measuring the e.m.f. of the cell



The e.m.f. of the cell at 15° is given by the relation

$$E = \frac{0.058}{n} \log \frac{C_2}{C_1}$$

Here n , the valency of Ag is 1 and C_2 , the concentration of Ag in N/100 AgNO_3 solution is 0.01 gram ions of silver per litre.

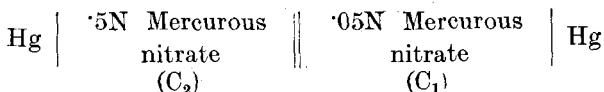
$$\text{Hence } E = \frac{0.058}{1} \log \frac{0.01}{C_1}$$

From the above expression, the concentration of AgCl in gram ions of silver per litre can be calculated. Multiplying this by 143.5, the molecular weight of silver chloride, we get the solubility of AgCl in grams per litre.

(2) *Determination of Valency.* In the equation for e.m.f. of a concentration cell

$$E = \frac{0.058}{n} \log \frac{C_2}{C_1}$$

Here, n represents the valency of cation. Thus Ogg determined the valency of mercurous ions by e.m.f. of the cell.



The observed e.m.f. was 0.029 volts. Substituting the various values, we have

$$0.029 = \frac{0.058}{n} \log \frac{0.5}{0.05}$$

$$= \frac{0.058}{n} \log 10 = \frac{0.058}{n}$$

$$\text{or } n = \frac{0.058}{0.029} = 2$$

(3) *Determination of Transition Point.* Let there be a concentration cell having electrodes of two allotropic forms of a metal, say grey tin and white tin. There will be a potential difference between these two electrodes except at the transition point. At this stage, the two forms of tin are in equilibrium and the e.m.f. will be zero. Hence, by changing the temperature of the cell, we can find out the transition point.

Cohen found that the cell having grey and white tin as electrodes in ammonium stannichloride solution, exhibited no e.m.f. at 18°C. This temperature must then be the transition point of the two allotropic forms of tin.

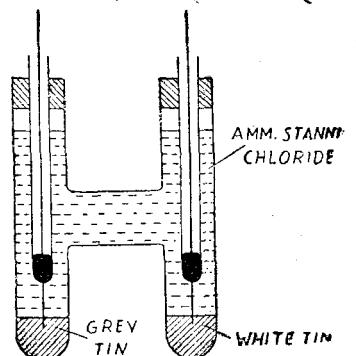


Fig. 208. Cell for determination of transition point of grey and white tin.

QUESTIONS AND PROBLEMS

1. Describe a simple galvanic cell. Explain the cell reaction.
 2. Describe a method commonly used for the measurement of the e.m.f. of a cell. Give the construction of the standard Weston cell needed in the above determination.
 3. Define polarisation of a cell. Explain the phenomenon and discuss its applications.
 4. Write notes on : Accumulators, Decomposition potential and Over-voltage.
 5. What do you understand by the term 'Electromotive series of Metals'?
 6. What is meant by the hydrogen electrode? How would you make use of this electrode for determining hydrogen ion concentration in a solution?
 7. What do you mean by (a) Single electrode potential, (b) Concentration cell?
- How would you measure single electrode potential? Indicate how on the basis of such measurements elements can be arranged in the order of decreasing electro-positiveness. (Madras B.Sc., 1944)
8. What is the theoretical explanation for the development of a potential difference when a metal dips in solution for one of its salts?
 - Explain why zinc is the positive and copper the negative electrode in a Daniell Cell.
 9. What is the origin of e.m.f. in a cell? What are concentration cells and for what purposes are they used?
 10. What is meant by the normal potential of an element? Explain how normal potentials are determined and used to calculate the e.m.f. of the voltaic cell. (Poona B.Sc., 1953)
 11. What is meant by normal electrode potential? Describe how the solubility product of silver chloride is determined. (Annamalai B.Sc., 1954)
 12. Write notes on (a) Concentration cells, (b) Over-voltage. (Bombay B.Sc., 1953)
 13. What are concentration cells? Give a brief account of the applications of e.m.f. measurements of the analytical chemistry. (Baroda B.Sc., 1953)

14. What is meant by *pH* of a solution ? Describe how *pH* of a solution is determined by using (a) Buffer solution, (b) Hydrogen electrode.

(Mysore B.Sc., 1954)

15. What are concentration cells ? How is the e.m.f. of a concentration cell measured by potentiometric method ?

What is the origin of e.m.f. in a cell ? (Karnatak B.Sc., 1955)

16. Describe theory of the concentration cells. Give a few of their applications. (Indian Administrative Service 1954)

17. Write an essay on concentration cells and their applications. (Madras B.Sc., 1955)

18. What are concentration cells ? Obtain an expression for the e.m.f. of the following cell :—



(Lucknow B.Sc., 1955)

19. How is the potential at the interface of a metal dipping in a solution of its salt explained ? Deduce the quantitative expression for it. Apply it to evaluate the e.m.f. of a concentration cell. (Travancore B.Sc., 1957)

20. How is the potential at the interface of a metal dipping in a solution of its salt explained ? Deduce the quantitative expression for it. Apply it to evaluate the e.m.f. of a concentration cell. (Kerala B.Sc., 1957)

21. What do you understand by electrode potentials and how are they determined ? What is the importance of these values ?

(Delhi B.Sc., Hons. 1959)

22. Explain what you understand by a concentration cell. Derive an expression for the electromotive force of a concentration cell. Show how you would proceed to determine the solubility of silver bromide by making use of a concentration cell. (Venkateswara B.Sc., 1959)

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