CHEMISTRY

Physical Chemistry
Inorganic Chemistry
Organic Chemistry

Blocks - 1- 8

DR. B.R. AMBEDKAR OPEN UNIVERSITY
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PREFACE

This course deals with the topics in Physical, Inorganic and Organic Chemistry inlcuded in the syllabus for the Third Year of B.Sc Course offered by the Andhra Pradesh Open University. The syllabus is for the sake of convenience divided into Blocks, each of which comprises a number of Units. Each Block generally covers a specific area of the subject. The units are prepared by specialists in accordance with a format so designed as to enable the student read and understand them without much difficutly. Each unit begins with a statement of its aims and objectives and has at its end Model examination questions intended to test the students comprehension of its subject matter. Generally technical terms with which the student may not be familiar are given at the end of each unit under the head Glossary or Appendix wherever necessary.

In part-A dealing with physical Chemistry, it is attempted to explain the important aspects of thermodynamics, Electrochemistry, Chemical Kinetics, Surface Chemistry and Phase Rule. It is hoped that this part will help the student to acquire the necessarry knowledge in these areas.

In part-B delaing with Inorganic Chemistry efforts are made to describe the necessary aspects of the topics on crystal structure, Chemistry of d-block elements and general principles of metallurgy. These topics will enable the students to understand the salient features of the crystal structure, properties and the metallurgy of metals with special reference to transition metals.

Part-C (Blocks 9-13 separate book) dealing with Organic Chemistry expalins chemistry of Nitrogen compounds, Alicyclic and Hetorocycilic compounds; Carbohydrates-to the needed extent. The organic functional group analysis included at the end gives the student some knowledge to identify functional groups of carbon compounds.

The University hopes that this course material will help the student to get acquainted with fairly advanced aspects of chemistry.

BLOCK - 1

THERMODYNAMICS

Thermodynamics deals with the relationship between heat and mechanical energy. It is also concerned with the interconversion of different forms of energy. Initially it was restricted to the efficiency of heat engines. But the applications of thermodynamics got increased enormously in due course. Thermodynamics also predicts the spontaneity of physical and chemical processes. Just like kinetic theory of gases, thermodynamics provides sufficient theoretical background for experimentally verified laws in physical chemistry.

UNIT - 1 ZEROTH AND FIRST LAW OF THERMODYNAMICS

Contents

1.1 AIMS AND OBJECTIVES

In this unit you learn about the first law of thermodynamics, its various statemnts and how it is useful in deriving relations between observable properties of gases.

Once you complete the reading and understnading of various aspects of this unit, you must be able to:

- Explain the first law of thermodynamics expressed in a number of ways.
- Realise that a new function enthlphy. H is introduced, $H = E+PV$
- Define heat capacities of gases veits equations and describe isothermal an adiabatic processes.
- Relaise that maximum work is obtained in the rullerssible isothermal expansion of a gas.
- Find out the difference between real and ideal gases.
- Relate mathematically the change in internal energy to the heat absorbed and work done by the equation $\Delta E = Q - W$.

1.2 INTRODUCTION

Although the name thermodynamics suggests that it delas with the relation betweeen heat and mechanical energy (work), it is concerned with the interconversion of all forms of energy. The laws of thermodynamics are based on experience and developed without any reference to the structure of atom or molecules or mechanism of their interaction. They are useful in obtaining many important relationships, in defining equilibrium and in predicting the direction of a reaction. Before we proceed with the proper study of the subject, it is necessary to define the meaning of some terms which are used frequently in thermodynamics.

1.3 SYSTEM

In thermodynamic discussion we often speak of a system and consider the changes taking place in it. **Any collection of material or apparatus which is required for a particular experiment or problem can be called a system.** The nature of the system thus depends upon the nature of the problem. Any portion of the objective world which is the subject of investigation is a system, the rest is surrounding. For our purpose a vessel in which a reaction or a process takes place is a system, the water bath in which it is placed is its surroundings. The system together with its surroundings is called an isolated system. We say that the state of a system is completely defined when all its measurable properties are known. For example, the state of a gas is determined by its pressure, volume, temperature and mass (the number of moles). However the state of a gas is completely defined if any **three** of these four variables are known since the fourth one is fixed by the equation of state for an ideal gas $PV = nRT$.

1.4 WORK

Work is the product of the distance a body is moved and the force acting in that direction. Work = force x distance. To lift an object vertically some work has to be done. This is equal to height 'h' through which the object has been moved, multiplied by the force applied to do the work. The force is the force of gravity because it is agians the force of gravity that work has to be done. This is equal to **mg** where **m** is the mass of the object and **g** the acceleration due to gravity. Hence the work done is equal to **mgh.** The unit of work is the amount of work done when a force of one dyne moves its point of application through a distance of one centimeter.

Work done in th eexpansion of a gas

Consider a gas enclosed in a cylinder by means of a piston. When the gas expands (say when it is heated) it has to push the piston upwards. It does work. Suppose the pistion moves through a distance 1 cm. Work done = Fx 1 where F is the force against which the gas has expanded.

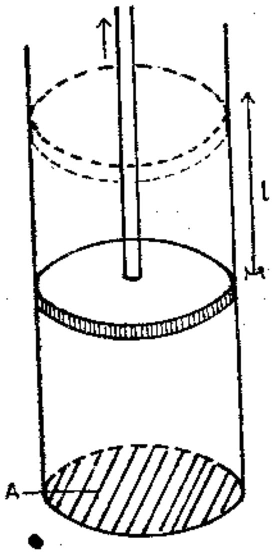

Fig: 1.1 Work done in the expansion of a gas

F is the external force acting on the gas. Here it is the weight of the piston. The above expression can also be written $\frac{F}{A} \times A \times 1$ where A is the area of cross section of the piston

$\frac{F}{A}$ is the force per unit area, therefore it must signify pressure P. Al has the dimentions of vlume, V.

Here it corresponds to the increase in volume of the gas. If the initial volume is V_1 and final volume V_2, this increase is equal to (V_2-V_1) Al is thereofe equal to V_2-V_1 .Substituting these, the expression for work becomes

$$W = P(V_2-V_1) - P.\Delta V$$

(the symbol Δ delta, denotes change in the value of the property following it. In this present case it denotes volume change)

Hence work of expanions is equal to the increase in volume multiplied by the pressure against which the gas expands.

Let us calculate the work done when a gas expanding against a constant pressure of one atmosphere increases its volume by one litre.

Here $\Delta V = 1$ litre and $P = 1$ atmosphere.

$W = P. \Delta V = 1$ atmosphere x 1 litre.

To calculate the work done in ergs we must express pressure and volume in C.G.S. units.

1 atmosphere = 1.013×10^6 dyness cm^{-2} (= 76 x 13.6 x 981)

1 litre = 1000 = 10^3 cm^3

Work = 1.013×10^6 dyne $cm^{-2} \times 10^3$ cm^3

= 1.013×10^9 dyne cm. = 1.013×10^9 erg.

This is equal to 1.013×10^2 joules since 1.0×10^7 ergs = 1 joule.

In calories, since 4.184 joules = 1 calorie work done is equal to

$$1.013 \times 10^2 \text{ joules} \times \frac{1 \text{ calorie}}{4.184 \text{ joules}} = 24.21 \text{ calories}$$

The conversion factors are given below:

litre atmosphere	erg	calorie
1	1.013×10^9	24.21
9.871×10^{-10}	1	2.39×10^{-8}
4.13×10^{-2}	4.184×10^7	1

1.5 ENERGY

Energy is any property that can be produced from or converted into work. Hence energy has the same units as work.

You are familiar with two kinds of energy - Kinetic energy and potential energy. Kinetic energy is the energy possessed by bodies in motion. For example, the kinetic energy of an object of mass m and moving with a velocity v is $1/2\ mv^2$. It is the work done to increase the velocity of an object of mass m from zero to v. The energy possessed by objects in virtue of their position is called potential energy. Its value depends upon the force responsible for keeping it in that position. When an object of mass m is lifted through a height h its potential energy increases by mgh which is the work done in the lifting.

1.6 HEAT, TEMPERATURE AND ZEROTH LAW OF THERMODYNAMICS

From the definition of energy given above, heat must also be regarded as form of energy since it can be converted into work (expansion of gases) and work can be converted into heat (compression of gases) Our sense of touch can distinguish between different degrees of hotness and coldness qualitatively. This is relative because warm water may feel hot to a cold hand and cold to a warm hand. However one can establish an order between two objects, either A is warmer than B, A > B or vice versa. From our experience we can also put a number of objects in sequence such that when A > B and B>C it follows that A > C, that is A is hotter than C. When two objects A and B of different degrees of hotness are brought into thermal contact, heat may flow from one another until themal equirlibrium is established. Now it is a fact of experience that if two objects ;A and B are in thermal equilibrium separately with a third body, they (A& B) must be in thermal equilibrium with each other. This is regarded as the zeroth law of thermodynamics, a belated addition (1931) to the existing laws of thermodynamics. Though too obvious to be stated as a law it is not. This statement cannot be applied to any type of equilibrium. For example ammonia and hydrogen chloride gas may be separetely in chemical equilibrium wiht nitrogen but they are not in equilibrium with each other.

The zeroth law, may be represented mathematically by introducing a scalar quantity (some numerical value) to each substance which is measure of its degree of hotness. This may be the temperature. Hotter objects may be represented by larger values of temperature and colder objects smaller. The fact that A is warmer than B can now be represented by the mathematical inequality $T_A > T_B$. The introduction of temperature is a direct consequence of zeroth law. Any two substances in thermal equilibrium are characterised by the same vlaue of T. We can choose a reference substance in which the degree of hotness can be expressed in terms of a scale of temperature, so that any substance which is in thermal equilibrium with it has the same temperature. Such a refernece substance is a thermometer.

In a thermometer some property of the thermometric substance, may be correlated with temperature. Since the volumes of liquids and gases change appreciably with temperature, this is a convenient property. Gases are ideal for this purpose because the behaviour of different gases is alike over a range of temperatures, particularly at low pressures, strictly the product PV is measured at different pressures and extrapolated to zero pressure. This extrapolated value is then directly proportional to the absolute temperature. The triple point of water, (where water, ice and water vapour are in equilibrium) is taken as 273.16 K (Oc) and the temperature T of any substance is given in terms of the PV product of the gas extrapolated to zero pressure as that temperature T.

$$T = 273.16 \times \frac{\underset{P \to O}{\text{Limit}}\ (PV)}{\underset{P \to O}{\text{Limit}}\ (PV)_{\text{Triple point}}}$$

1.7 SPECIFIC HEAT AND HEAT CAPACITY

The unit of heat is the calorie. It is the heat required to raise the temperature of one gram of water by one degree in the range 14 to 15°c. The temperature is specified (as 14 to 15°c) since the heat required depends upon temperature.

Water is a peculiar liquid which requires a large amount of heat to increase its temperature. For other substances it is much less. The number of calories of heat required to raise temperature of 1g of the substance by 1° is called its specific heat. Values of specific heat in calories per gram for some metals are lead 0.031, Copper 0.093, Iron 0.11, Aluminium 0.215.

The amount of heat required to increase the temperature of m gm of a substance from T_1 to T_2 is ms $(T_2 - T_1)$ where S is the specific heat of the substance. The product ms is called the heat capacity of the substance. For gases it is convenient to take the unit mass as one mole instead of one gram. The heat required to increase the temperature of one mole of gas by 1° is called the molar heat capacity and is represented by the symbol C. Since the volume of a gas changes significantly on heating, gases have two different specific heats measured under different conditions-constant volume, constant pressure. These are C_v and C_p respectively.

1.8 MECHANICAL EQUIVALENCE OF HEAT

The first law of thermodynamics is based on a series of experiments carried out by James P. Joule during 1840-1850. The object of these experiments was to establish the exact equivalence between work and heat, to show that a given amount of work always produces the same amount of heat. With this object in view Joule performed a number of experiments in which work is converted into heat. The most important of these is his famous paddle wheel experiment. In this he caused falling weights to drive a series of paddles which in turn stirred vigorously water in a vessel. He found that water became warmer showing that the mechanical energy of the falling weights was converted into heat. From the height through which the weight has fallen and from the rise in temperature of water, he was able to calculate the amount of heat produced.

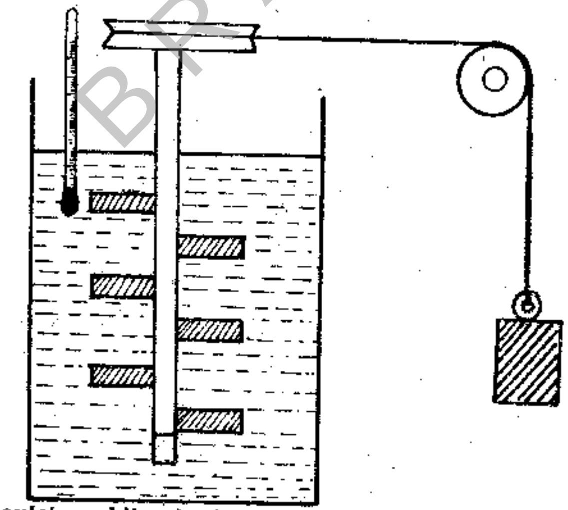

Fig: 1.2. Joule's paddle wheel apparatus

Other methods of conversion of work into heat used by him were electrical heating, compression of gases and forcing of liquids through fine holes: In all these experiments the heat produced was measrued by finding the rise in temperature of a known weight of water. In every case he found that each calorie of heat produced corresponds to the disappearence of 4.18 X 10^7 ergs of work. This is called mechanical equivalent of heat. Thus he was able to establish that "a given amount of work no matter what its origin always produces the same amount of heat". This must be regarded as a preliminary formulation of the first law of thermodynamics.

1.9 LAW OF CONSERVATION OF ENERGY

If work and heat are regarded as two different forms of energy, their equivalence can be extended to include all forms of energy and Joule's statements may be developed into a wider generalization. This was done by Helmholtz who stated the first law of ther-modynamics as follows.

"Although energy may be converted from one form into another it cannot be created or destroyed". In other words, "Whenever a quantity of one kind of energy disappears an exactly equivalent amonut of some other kind must be produced".

These statements are referred to as the law of conservation of energy. No direct proof can be given for the first law in the sense that no reason.can be given why energy must be conserved in a process. The law is based purely on experience- the experience that no one has been able to produce energy out of nothing or produce more energy from a given quantity of work than is requiried to produce back the work. If this were possible then it is easy to see that a perpetual motion machine (a machine that can produce more energy than is required to run it) can be constructed. In our experience nobody has been able to show that such a construction is theoretically possible. This is the reason why we believe in the validity of the first law of themodynamics. Our inability to violate the law forms another statement. It is impossible to construct a machine which could produce work continuously without supplying an equivalent amount of energy to it from some other source."

1.10 INTERNAL ENERGY OF SYSTEM AND THE FIRST LAW

Every system has some energy contained in it. It is called its internal energy and represented by the symbol E. This energy is a function of the state of the system and is independent of its previous history (that is how the system has been brought to that state). Let us suppose a system in a particular state represented by a set of values of pressure, volume and temperature (P_1 V_1 and T_1) is changed to another state of values (P_2 V_2 and T_2). If the internal energy is a function of state then change in its internal energy due to this change of state must be independent of the path by which this change is brought about. Otherwise the first law of themodynamcis would be violated. Of the numerous paths available for this change, let us select two paths I & II (see figure 1.3) Let the increase in internal energy in the path I Δ be E_I and in the second path Δ E_{II}. Law of conservation of energy requires that $\Delta E_I = \Delta E_{II}$.

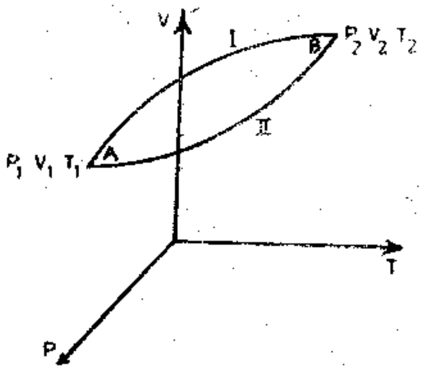

Fig 1-3 Change in internal energy

To prove this let us suppose $\Delta E_I > \Delta E_{II}$. If the system is taken by path I the increase in energy is ΔE_I. If it is brought back to starting point in path II there will be a decrease in energy ΔE_{II}. The net change in energy in this cycle would be equal to $\Delta E_I - \Delta E_{II}$. At the end of the cycle the system is in its initial state with a gain in its energy equal to $\Delta E_I - \Delta E_{II}$. Since the pressure, volume and temperature are the same as before, it implies that energy has been created. If the cycle is repeated a number of times, enormous amounts of energy can be produced which can be used to run a perpetual machine. Since our experience shows that energy cannot be ceated, ΔE_I cannot be greater than ΔE_{II}. In the same way it can be shown that DE_I cannot be less than ΔE_{II}. Hence ΔE_I must be equal to ΔE_{II} and therefore the change in energy is independent of path by which the change is brought about. These conclusions are stated in the form of another statement of the first law.

(i) The change in internal energy of system depends only on the initial and final states of the system and not on path by which the change is brought above.

$$\Delta E = E_{Final} - E_{Initial.}$$

(ii) In a cyclic process there is no change in the internal energy of the system. This can be expressed as follows.

$$\Sigma \Delta E = O \text{ or } \oint dE = O$$

$$A \rightarrow B$$

$$B \rightarrow A$$

Such a property is called a state function. Internal energy of a system is a state fucntion.

We have not so far tried to analyse the nature of this internal energy. It consists of the kinetic energy of the moving particles within the system and the potential energy arising out of the forces of attraction between them. Thermodynamics does not recognize them as we are not interested in the absolute value of internal energy. We are interested only in changes in internal energy.

For our present discussion we can consider two ways in which the internal energy of a system can change (i) by absorbing heat from the surroundings or giving out heat to it (ii) by doing any external work or when any work is done on it. Heat absorbed by the system is taken as positive and the heat escaping from the system as negative. When a system performs work (as in the expansion of a gas) 'W' is taken as negative. This convention about work is not a happy one, because one would expect work done on the system as positive in the same way as heat entering a system is termed positive-such a change in convention has been suggested by IUPAC and some authors are already adopting it. However we have for various reasons decided to retain the older convention of treating the work done by the system as positive.

Mathematical expression of the first law

Consider what happens when Q calories of heat is supplied to a gas enclosed in a cylinder by means of a piston. Part of the heat may increase the internal energy of the gas ΔE_I and part of it may cause the gas expand and do some work 'W' by pushing the piston upwards. Since the energy has to be conserved in every change, we write $Q = \Delta E + W$ or $\Delta E = Q - W$. Change in internal energy ΔE is the algebraic sum of the heat absorbed Q and Work done (W). This is the mathematical epxression of the first law of thermodynamics.

1.11 'Q' AND 'W' ARE NOT STATE FUNCTIONS

In the above equation, E alone is a state funciton: the value of ΔE depends only on the initial and final states and not on the path by which the change is brought about. Though the compositie quantity Q-W is always constant in a given change, the individual properities Q and W are not functions for state. For a given change in state their values depend upon the manner in which the change is brought about. For example the amount of work a system has to perform depends upon the opposition the system experiences.

Consider the work done in the expansion of a gas. It is given by the expression P_{ex} x ΔV where ΔV is th ehcange in volume and P_{ex} is pressue against whch the gas expands. Thus for the same change in volume work done by the gas depends upon the opposing pressure.

Let the initial state of a gas be represented by 5 atmospheres pressure and 2 litres volume and final state 2 atmospheres pressures and 5 litres volume There are many ways in which this change can be brought about and the work done will be different in each path. The gas may expand into an evacuated vessel until its final volume is five litres. In this expansion the gas does not meet with any resistnace. P_{ex} is equal to zero. Hence work done is zero. Below we give two specific paths by which the change is brought about where the work done is different as shown by the shaded areas.

In the path I. the gas is first allowed to expand against a constant pressure of 5 atmospheres until its volume is 5 litres. The pressure may be kept constant by continusly supplying heat to the gas.

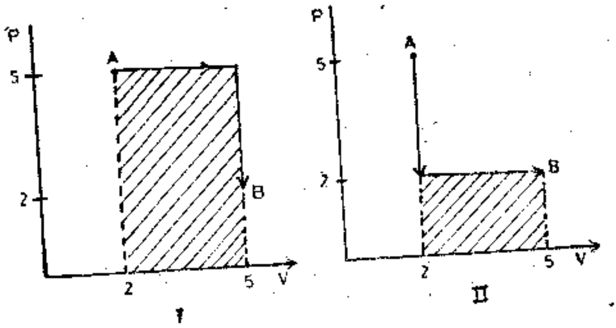

Fig 1.4 The work done in different paths

In this change work done by the gas is equal to $P_{ex}\ \Delta V$ =S X (5-2) = 15 litres atmosphere. Next keeping the volume constant at 5 litres the gas is allowed to cool until the pressure drops to 2 atmospheres. No work is done in this stage as the volume is constant. Next the gas is allowed to expand agianst a constant pressure of 2 atmospheres until the volume is 5 litres. Here againt he pressure is maintained constant by continuous supply of heat. The work done in this operation is 2 x (5-2) = 6. Thus in the change from state A to state B by the path II the total work done is that obtained in the second operation namely 2 x (5-2) = 6 litre atmospheres. Thus for the same change of state (A → B) the wrok done in the two paths is different.

Therefore we conclude that work is not a state function. In the expression $\Delta V = Q - W$. ΔE is a fixed quantity for a given change of state. If W changes with the path followed , Q must also change. Hence Q is also not a state function.

1.12 APPLICATION OF THE FIRST LAW TO GASES

When the system is a gas we may assume no work done other than that involving change in volume (ΔV)

$W = P_{ex}\ (V_2 - V_1)$: V_1 and V_2 are the initial and final volumes of the gas. If $V_2 > V_1$ there is expansion and the work is done by the gas and W is positive. If $V_2 < V_1$ there is compression of the gas and work is done on the gas. W is negative. Substituting the vlaue of work, the first law equation becomes.

$$Q = \Delta E + P_{ex}\ \Delta V$$

This equation takes different forms depending upon the conditions of experiment.

1.12.1 Constnat volume

If the volume of the gas is kept constant say by locking the piston in place by a screw' no work is possible as $\Delta V = 0$ and hence $P_{ex}\ \Delta V = 0$. On introducing this condition the equation becomes

$$Q_v = \Delta E.$$

This means that all the heat absorbed goes to increase the internal energy of the gas. The subscript V denotes condition of constant volume.

1.12.2 Constant pressure

If the gas absorbs heat under contant pressure the volume can change hence

$$Q_v = \Delta E + P \Delta V$$

$$= E_2 - E_1 + P(V_2 - V_1)$$

$$= (E_2 + PV_2) - (E_1 + PV_1)$$

Thus the heat absorbed at constant pressure is equal to the increase in the value of the composite quantity E + PV in going from the initial state to the final state.

It has been found convenient to define a new quantity by the relation

$$H = E + PV$$

H is called the enthalpy or heat content of the system. Since E,P & V are state functions H is also a state function.

$$\Delta H = H_2 - H_1 = (E_2 + P_2 V_2) - (E_1 + P_1 V_1)$$

At constant pressure

$$\Delta H = (E_2 + PV_2) - (E_1 + PV_1) \ Q_p$$

Thus the heat absorbed at constant pressure goes to increase the enthalpy of a gas.

Heat capacities of gases C_p and C_v

we can now define the heat capacities of gases in terms of ΔE and ΔH. C_v is the molar heat capacity of a gas at constant volume. When one mole of a gas is heated at constant volume from T_1 to T_2 the heat absorbed will be equal to $C_v (T_2 - T_1) = C_v \Delta T$. This means $Q_v = C_v \Delta T_T$ But heat absorbed at constant volume Q_v has been shown to be equal to ΔE. Hence

$$\Delta E = C_V \Delta T \text{ or } C_V = \frac{\Delta E}{\Delta T}$$

For an infinitestimal chnage $C_V = \left(\frac{dE}{dT}\right)_V$

In the same way the heat absorbed to increase the temperature of one mole of a gas at constant pressure from T_1 to T_2 is $C_p (T_2 - T_1)$ or $C_p \Delta T$ where C_p is the molar heat capacity of a gas at constant pressure.

$$Q_P = C_P \Delta T \text{ Since } Q_P = \Delta H, \text{ we have}$$

$$\Delta H = C_P \Delta T \text{ and } C_P = \frac{\Delta H}{\Delta T}$$

For infinitesimal change in temperature $C_P = \left(\frac{dH}{dT}\right)_P$

These two equations may be used to find ΔE and ΔH for a gas when it is heated under constant pressure or constant volume.

$$\Delta H = \int_{T_1}^{T_2} dH = \int_{T_1}^{T_2} C_p dT = C_p (T_2 - T_1)$$

$$\Delta E = \int_{T_1}^{T_2} dE = \int_{T_1}^{T_2} C_v dT = C_v (T_2 - T_1)$$

In writing these equations it has been assumed that C_p and C_v do not chnage with temperature which is true for only small ranges of temperature C_p and C_v for an ideal gas.

$C_p - C_v$ for an ideal gas

$$H = E + PV \text{ ----- (1)}$$

$$\frac{dH}{dT} = \frac{dE}{dT} + \frac{d(PV)}{dT} \text{ -------(2)}$$

For an ideal gas PV = RT.

$$\therefore \frac{d(PV)}{dT} = \frac{d(RT)}{dT} = R \text{ ----- (3)}$$

Substituting the results in (3) into (2), we have

$$\frac{dH}{dT} = \frac{dE}{dT} + R \text{ ---- (4)}$$

$$\text{But } C_p = \frac{dH}{dT} \text{ and } C_v = \frac{dE}{dT}$$

Substituting these results in (4), We have

$$C_p = C_v + R$$

$$C_p - C_v = R$$

Two more restrictions can be applied to the first law equation besides these of constant volume and constant pressure.

1.12.3 Isothermal processes

These are processes taking place at constant temperature. The vessel containing the gas is kept in a constant temperature both or a thermostat which contains a thermoregulator to maintian the temperature constant at any desired value. Ordinarily a large reservoir of water may be taken as a constant temperature bath. When the temperature is constant the internal energy of a gas cannot change $(\Delta E)_T = 0$ because all forms of energy are dependent on temperature in some way or other. Therefore under isothermal conditions $Q = \Delta E + W$ becomes $Q = W$. When a gas does work (say by expansion) under isothermal conditions, the conservation law requires that an equivalent amount of heat be absorbed from the surrounding (here the thermostat).

Check your progress 1.

What do you mean by an isothermal process?

....

....

....

....

....

1.12.4 Adiabatic processes

If a process is allowed to take place in such a way that heat can neither enter the system nor leave it, the process is said to be an adiabatic process. Thus in an adiabatic process there is no exchange of heat with the surroundings (Q = O). This can be realised by allowing the process to take pla e in a vessel whose walls are made of perfect thermal insulating material. However materials which are hundred per cent thermal insulators do not exist, we can only make a process as nearly adiabatic as possible. A vacuum flask or a thermos bottle is a suitable container for an adiabatic process. Often a process taking place very rapidly may be considered adiabatic because in such rapid changes there is no sufficient time for heat exchange to take place with the surroundings.

In an adiabatic process since Q = O the first law equaion beocmes $O = \Delta E + W = -\Delta E$

When a gas does work by adiabatic expansion, work is done at the expense of internal energy of the gas which decreases. Hence in an adiabatic expansion the gas cools. On the other hand when a gas is compressed adiabatically, work is done on the gas (considered negative). Hence to keep the term on the right hand negative in the above euqaiton Δ E must be positive. Internal energy of the gas increases and so does the temperature. In an adiabatic compression therefore a gas warms up.

Problem 1

A gas absorbs 150 calories of heat and expands against a constant pressure of one atmosphere until its volume increases from 10 litres to 15 liters. Calculate the change in the internal energy of the gas in this process.

Heat absorbed Q = 150 calories

Work done, W = 1 atm. x (15 - 10) litres = 5 litre atmospheres

$$= \frac{5 \text{ x } 24.2 \text{ cal.}}{1 \text{ let atm.}} = 121.05 \text{ cal.}$$

$$\Delta E \; Q - W = 150 - 121.05 \text{ cal.} = 28.95 \text{ cal.}$$

Problem 2

What is the work done when one mole of water is converted into steam at 1 atm. pressure and 100°c?

Work done is the product of external resistance (pressure) and the increase is volume. When water is converted into steam, it pushes the atmosphere above it and does work. Neglecting the volume of water converted into steam, the increase in volume may be taken as the volume of steam, produced by the evaporation of one mole water. Volume of steam at 100°c and 1

$$\text{atmosphere} = 22.4 \text{ l mole}^{-1} \text{ x } \frac{373 \text{ degrees}}{273 \text{ degrees}} \quad \text{this is equal to 30.6 litres mole}^{-1}$$

$W = P \text{ x } \Delta V = 1 \text{ atm. x } 30.6 \text{ lit mole}^{-1} = 30.6 \text{ lit. atm. mole}^{-1} \; 740.8 \text{ cals}$

Alternatively

If it is assumed that steam behaves as an ideal gas P x vol of steam = RT

Therefore $W = RT = 0.0821 \text{ lit atm. deg}^{-1} \text{ mole}^{-1} \text{ x } 373 \text{ degrees} = 30.62 \text{ lit atm mole}^{-1}$

$$30.62 \text{ lit. atm. mole}^{1-} = 30.62 \text{ x mole}^{-1} \text{ x } \frac{24.21 \text{ cal}}{1 \text{ lit} = \text{atm}} = 740.8 \text{ cal}$$

Thus we find that the work done in this process depends only on the temperature and nothing else.

Problem 3

calculate the change in internal energy in the above process. In the process of conversion of one mole of water into steam at its boiling point, heat necessary is the latent heat of vaporisation per mole. Since the latent heat of vaporisation per gram of water is equal to 540 cals, its molar latent heat = 18.02 x 540 = 9730 cals. mole $^{1-}$ work done has been shown to be 740.8 cals.

$$\therefore \Delta E = Q - W = 9730 - 740.8 = 8989.2 \text{ cals.}$$

Problem 4

Two litres of an ideal of gas at O° and 4 atm pressure is expanded isothermally against a constant pressure of 1 atm. Until the pressure of the gas is also 1 atm. what are the values of W, Δ, E, Δ and Q for this process.

Since it is an isothermal process Δ E = O Hence Q = W.

W = external pressure x change in volume.

Initial volume is two litres at 4 atm. Final volume can be obtained from

$P_1V_1 = P_2V_2$ .4 atm x 2 litres = 1 atm x V_2 litres. V_2 = 8 litres.

W = 1 x (8 - 2) = 6. lit atm = 6 x 24. 21 = 145.26 cal

Δ H = Δ E + (PV). At constant temperature

PV = constant ∴ Δ (PV) = O. Since Δ E = O,

Δ H = + o = o

1.13 MAXIMUM WORK DONE IN THE EXPANSION OF A GAS

For an infinitesimal (infinitely small) increase in volume the work done by the gas is P_{ex} d v. Here P_{ex} is the external pressure agianst which the gas expands. For a finite change in volume from V_1 to V_2 the work done is obtained by integrating the above expression between these two limits $W = p_{ex} \int_{v1}^{v2} p_{ex} dv$

If the external pressure is constant throughout the expansion, P_{ex} can be taken out of the integral, otherwise it should be expressed as a function of volume of the gas. Thus for constant pressure.

$$W = P_{ex} \int_{V_1}^{V_2} dv = P_{ex} (V_2 - V_1)$$

The value of the integral is given by shaded area in the figure 1.5

For a given change in the volume, the work depends upon the opposing pressure. Higher the pressure greater would be the work done for the same change in volume. When a gas expands into an evacuated vessel the opposing pressure is P_{ex} = O. Hence no work at all is done by the gas which means with no opposition during expansion. As the opposing pressure is increased from zero more and more work has to be done as the pressure approaches the pressure of the gas itself. Once this pressure is reached there cannot be any change in its volume as the driving pressure (of the gas) becomes equal to the opposing pressure. Further increase in opposing pressure will cause the gas to contract in volume and work is done on the gas instead of by the gas. For expansion to occur at all, it is necessary that the opposing pressure is less than the driving pressure of the gas. From what has been said above, it is obvious that maximum work can be obtained when the opposing pressure differs from the pressure of the gas by as small a quantity as possible. P should be (p-dp) where P is the pressure of the gas. The volume of the gas then increases by an infi-nitesimal amount dv, so that W = (P-dp) dv ~ Pdv, since the product dp.dv (of two infinitesimal quantities) is negligibly small.

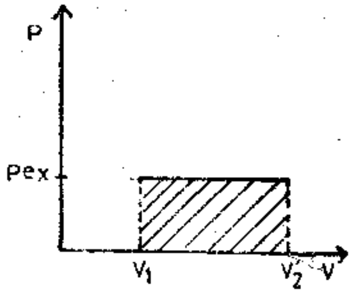

Fig: 1.5 mimimum work

To obtain maximum work in a given expansion, at every stage of the expansion the external pressure must be adjusted to differ from the pressure of ~~the~~ gas by an infinitesimal amount. Such an expansion is called a reversible expansion. Reversible because at any stage the expansion can be reversed by altering the opposing pressure only slightly. A reversible process is one in which the driving forces differ only infinitesimally from the opposing forces. Every stage is only infinitesimally away from equilibrium which can be restored from either side by infinitesimal change. Ofcourse in actual processes such a condition can never be realised because it is impossible to have a machine whose parts are completely frictionless. Hence opposing force can never be adjusted to differ only infinitesimally from the driving forces. Although maximum work in the e;xpansion of a gas cannot be realised in practice, it is of considerable theoretical importance to find its value.

We have seen that for an infnitesimal change in volume the maximum work obtained is Pdv, where P is the pressure of the gas. In a reversible expansion from volume the work done is given by the sum of infinite steps dv. The sum is given by the integral $\int_{v1}^{v2} pdv$

Here P is the pressure of the gas which changes continuously. Hence it is expressed as a function of its volume. For an ideal gas $P = \frac{nRT}{V}$

Hence $W = \int_{V_1}^{V_2} \frac{nRT}{V} dv$ For an isothermal process T is constant

$$W \text{ becomes } = nRT \int_{V_1}^{V_2} \frac{1}{V} dv = nRT \ In \frac{V_2}{V_1}$$

In common logarithms $W_{max} = 2.303 \ nRT \log \frac{V_2}{V_1}$

The value of the integrall $\int_{V_1}^{V_2} Pdv$ is obviously given by the area under the curve when P is plotted agianst V. Since P is the pressure of the gas itself the curve is a hyperbola as requried by Boyle's law (see figure 1.6). In natural processes the opposing forces are small compared to the driving forces. They are irreversibe processes because equilibrium cannot be restored by infinitesimal change in the reverse direction. Maximum work can never be obtained in such processes.

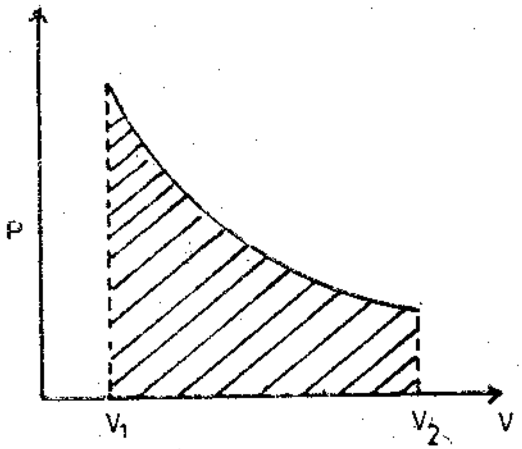

Fig: 1.6 P-V Curve - Hyperbola

Let us consider how the work is done in the irrevesible expansion of a specific gas. This differs from that in reversible expansion in change in volume.

$$P \times \Delta V = 1 \times (10-2) = 8 \text{ litre atmosphers}$$

$$= 8 \times 24.21 = 193.68 \text{ calories}$$

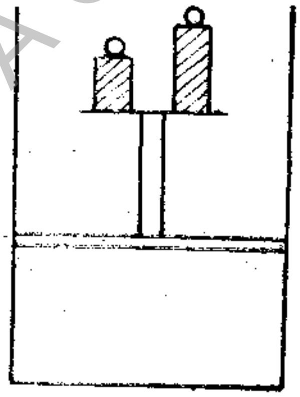

Fig: 1.7 The gas at requried pressure

(from say 2 litres to 10 litres) of one mole of a gas. Suppose 2 litres of a gas is orginally under a pressure of 5 atmospheres. This can be arranged by placing appropriate weights on piston as shown in the figure 1.7

In one instance of an irriversible expansion, let the weights be removed in one step. The pressure on the gas suddenly drops to one atmosphere. The gas expands against this external pressure of 1 atmosphere until its own pressure becomes equal to one atmosphere and the volume ofcourse to 10 litres. The changes are indicated in the figure 1.8. The work done is given by the area udner the figure.

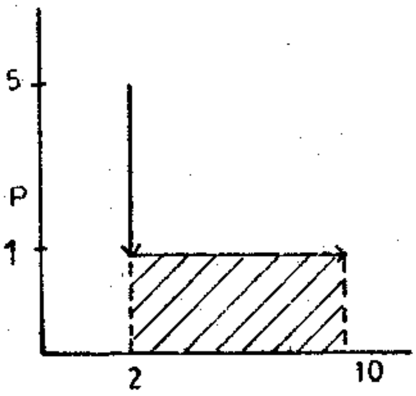

Fig: 1.8 change in volue at constant pressure.

In the reversible expansion the pressure infinitelyshow form 5 atmospheres to one atmosphere when the volume changes from 2 litres to 10 litres. Maximum work is obtained.

This is given by the expression $W_{max} = 2.303 \text{ n RT} \log\frac{V_2}{V_1}$. At 25° c this value would be $= 2.303 \times 1 \times 1.987 \times 298 \times \log\frac{10}{2} = 2.303 \times 1.987 \times 298 \times 0.6990$

= 953.2 calories which is much higher than the work done in an irreversible process.

Since in an isothermal process $P_1 V_1 = P_2 V_2$ or $\frac{V_2}{V_1} o= \frac{P_1}{P_2}$

Substituting this in equation

$\Delta W = Q - E$ (First Law) (1)

We have $W = - \Delta E$ (2)

1.14 ADIABATIC PROCESSES IN AN IDEAL GAS

Since in an adiabatic process $Q = 0$.

Substituting the value $\Delta E = nC_v T$ and $W = P_{ex} \Delta V$ which is the only work assumed for a gas, in equation (2) wehave

$$P_{ex} \Delta V = - n C_v . \Delta T \qquad (3)$$

For an infinitesimal change

$$P_{ex} dv = -n C_v dT \qquad (4)$$

For reverisble expansion of a gas $P_{ex} \approx$ where P is the presussure of the gas. Then

$$Pdv = - n C_v . dT \text{ For an ideal gas } P = \frac{nRT}{V} \qquad (5)$$

$$\therefore n\frac{RT}{V} dv = - n C_v . dT$$

∴ eliminating 'n' and rearranging (6)

$$\frac{R}{C_v} \times \frac{1}{V} d V = - \frac{1}{T} dT \qquad (7)$$

$$\text{But } R = C_p - C_v \qquad (8)$$

Integrating between the limits V_1 at temperature T_1 and V_2 at temperature T_2

Substituting (8) in (7)

$$\text{We have } \frac{C_p - C_v}{C_v} \frac{1}{v} dv = - \frac{1}{T} dt \qquad (9)$$

$$\text{ie } \left(\frac{cp}{cv} - 1\right) \frac{dv}{v} = - \frac{1}{T} dT$$

$$(\gamma - 1) - \frac{dv}{v} = - \frac{1}{T} . dT \qquad (10)$$

$$(\gamma - 1) \int_{V_1}^{V_2} \frac{1}{V} d V = - \int_{T_1}^{T_2} \frac{1}{T} dt \text{ --- } (11)$$

$$(\gamma - 1) \ln \frac{V_2}{V_1} = \ln \frac{T_1}{T_2} \quad \ln \frac{T_1}{T_2} \text{ ---- } (12)$$

Taking antilogs on both sides

$$\left(\frac{V_2}{V_1}\right)^{\gamma - 1} = \frac{T_1}{T_2} \quad - (13)$$

The above expression relates the temperature change with volume change in an adiabatic expansion.

For an ideal gas we have another set of relations

$$P_1 V_1 = n RT_1$$

$$\text{and} \quad P_2 V_2 = n R T_2 \qquad \text{from which we get } \frac{T_1}{T_2} = \frac{P_1 V_1}{P_2 V_2}$$

$$\text{Substituting this in 13 we get } \left(\frac{V_2}{V_1}\right)^{\gamma - 1} = \frac{P_1 V_1}{P_2 V_2} \text{ ---- } (14)$$

$$\text{or } P_2 V_2 . V_2^{\gamma 1} = P_1 V_1 . V_1^{\gamma 1}$$

$$P_2 V_2^{\gamma} = P_1 V_1^{\gamma} \text{ ------ } (15)$$

In general Pv = constant in an adiabatic expansion of a gas

$$\text{i.e } \frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma}$$

It is interesting to compare this pressure change with that in an isothermal expansion for the same volume change V_1 to V_2. For an isothermal expansion, since the temperature is constant the relation $P_1 V_1 = T_2 V_2$ holds

$$\text{and hence } \frac{P_2}{P_1} = \frac{V_1}{V_2}$$

Since $\gamma > 1$ and in expansion $V_2 > V_1$

$$\left(\frac{V_1}{V_2}\right)^{\gamma 1} = \frac{V_1}{V_2} \left[\text{For example} \left(\frac{2}{3}\right)^{2} < \frac{2}{3}\right]$$

Therefore $\frac{P_2}{P_1}$ adiabatic is less than $\left(\frac{P_2}{p_1}\right)$ isothermal

If the initial pressure is the same in the two expansions (P final) adiabatic < (P final) isothermal.

This means that for the same volume change, there is greater fall in pressure in an adiabatic expansion than in an isothermal expansion, as seen in the figure 1.9. The greater fall in pressure in an adiabatic expansion is due to the fact that there is a decrease in temperature as well.

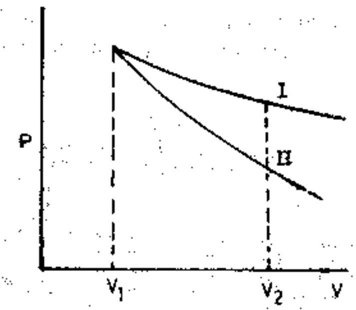

Fig. 1.9 Change in pressur in isothermal and adiabatic expansions

I = Isothermal

II = Adiabatic

Problem 5 0.5 mole of a monatomic gas $\left(C_v = \frac{3}{2} R\right)$ is confined in a vessel of volume onelitre under a pressure of 10 atmospheres. It is expanded reversibly under adiabatic conditions until a pressure of one atmosphere is reached. What are the final volume and temperature? What is the work done in the expansion?

In an adiabatic reversible expansion

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \quad \gamma = \frac{5}{3} \text{ for a mono atomic gas}$$

$$10 \times (1)^{5/3} = 1 \times (V_2)^{5/3} \quad \therefore (V_2)^{\frac{5}{3}} = 10 \text{ or } V_2 = (10)^{3/5} = 3.98 \text{ lit.}$$

Final pressure $P_2 = 1$ atm and final volume $V_2 = 3.98$ lit.

$$\text{Final temperature } T_2 = \frac{P_2 V_2}{n R} = \frac{1 \text{ atm} \times 3.98 \text{ lit}}{0.5 \times 0.0821 \text{ lit. atm deg}^{-1} \text{ mole}^{-1}} = 96.95 \text{ K}$$

$$\text{Initial temperature } T_1 = \frac{P_1 V_1}{n R} = \frac{10 \times 1}{0.5 \times 0.0821} = 243.6 \text{ degrees K}$$

Work done = $-\Delta E = -nC_v. \; \Delta T = -0.5 \times 3 \; (96.96 - 243.6) = 219.46$ cals.

Check your progress - 2

What do you mean by an adiabatic process?

....

....

....

....

....

By applying the first law, relationships are derived between the observable properties of gases under isothermal and adiabatic conditions. Heat capacities of gases are expressed in thermodynamic equations. Thermodynamic criterian of a perfect gas is, its internal energy should not chnage with the change of volume at constant temperature. An attempt has been made in this the unit to study the behaviour of real gases by the application of Joule-Thomson experiment.

1.18 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines.

1. The equation Q= $\Delta E + P \Delta V$ represents the first law of ther modynamics. What form would it assumes under (a) constant volume (b) constant pressure (c) isothermal conditions (d) adiabatic conditions?

2. Define the term reversible process and give one example (other than expansion of gases).

3. Derive an expression for the work done in an isothermal reversible expansion of a gas

4. Explian why a gas becomes warmer in an adiabatic compression and cooler in adiabatic expansion.

5. Give the thermodynamics criterion of a perfect gas.

II Answer the following in 30 lines.

1. Give the different forms in which the first law of thermodynamics can be exressed. Explain their significance. Do you consider evolution of energy in nuclear fission a violation of the first law?

2. Describe the experiment for Joule-Thomson effect. Why do some gases show warming in Joule-Thomson expansion. Explain how cooling in Joule-Thomson effect useful in the liquefaction of gases.

III Solve the following Problems.

1. In the expansion of a gas against constant pressure of atmospheres, its volume increases by 5 litres. Calculate the work done in this process in the following units (i) litre atmospheres (ii) ergs (iii) calories.

2. When one mole of zinc is dissolved in dilute HCl at 25$_0$c, the hydrogen gas evolved pushes the atmosphere above it. Calculate the work done in this process.

3. Find the amount of heat necessary to heat 5g of Argon from 0° to 25°c at constant volume and at constant pressure (Molar heat capacity C_v of a gas = 3 cals/mole^1; degree)

4. One mole of an ideal gas (C_v = 5 cal mole^{-1} degree^{-1}) at S.T.P. is heated to twice its initial temperature. Calculate ΔE and ΔH in this process. (1365 cals, 1911 cals)

5. One mole ofan ideal gas expands reversibly at constant temperature 0^0 c from 2 atmosphere pressure to one atmosphere. Calculate W, ΔE and Q in this change.

6. Calculate the minimum work that must be done at 25^0 c Tt on 2 moles of CO to compress it from a volume of 20 litres to a volume 1.0 litre. (Hint: Minimum work is done in isothermal reversible compression).

7. In a reversible isothermal expansion one mole of an ideal gas increases its volume from V_1 to 10 V_1 and does 5000 calories of work. If the initial pressure was 50 atmospheres calculate V_1. (1.79 liters)

8. One mole of CH_4 at 200°c and 10 atm. expanded adiabatically and reversibly until its temperature was 0°c. Assuming an average value of 7.5 cal $mole^{-1}$ $degree^{-1}$ for Cv of methane in this temperature range, calculate the work done by methane and its final pressure. (0.725 atm)

9. The volume of one mole of an ideal gas of monatomic initially at 2 atm and 25°c (V=12.21) is doubled by (a) isothermal expansion (b) adiabatic expansion. If both are reversible, calculate the final pressure, Q,W, and Δ E in each case.

1.19 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Any change brought about on a gaseous system at constant temperature is called an isothermal process. Here Q = W.

2. Any change brought about on a gas using its internal energy only is called as adiabatic process. Here Q = 0. Heat neither enters nor leaves the systems.

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UNIT - 2 THERMOCHEMISTRY

Contents

2.1 AIMS AND OBJECTIVES

In this unit you will learn about the heat changes accompanying chemical reactions and the application of the law of conservation of energy to such changes.

Once you complete the reading and understanding of different aspects of thermochemistry, you must be able to:

- differentiate exothermic and endothermic reactions
- handle the thermochemical equations
- calculate the heats of reaction, heats of formation and heats of combustion by the application of Hess's law
- calculate heats of solution and heats of neutralisation
- calculate the heats of reaction at different temperatures
- calculate heats of reaction from bond energies

2.2 INTRODUCTION

There are several reacitons which are accompained by the evolution of heat like the burning of wood, coal and kerosene, action of alkali metals on water, reaction between acids and bases. On the other hand there are also some reactions which tak eplace only when heat is continuously supplied to them as in the formation of nitric oxide from nitroten and oxygen, or carbondisulphide from carbon and sulphur. These reactions take place only in the electric furnace. Such heat changes follow the law of conservation of energy according to which the total energy of a system before a reaction must be equal to its energy after the reaction has taken place. Now, different substances possess different amounts of energy and it is unlikely that the energy content of the reactants be equal to the energy content of the products. This difference in energy is accounted for as the heat change accompanying the chemical reaction.

2.3 EXOTHERMIC AND ENDOTHERMIC REACTIONS

Consider a general of the type A + B = C + D

Let the internal energies of reactants be E_A, E_B products be E_C and E_D respectively. then if $E_{A'} + E_B > E_C + E_D$ to satisfy the first law of themodynamics some energy must appear along with the products so that $E_A + E_B = E_C + E_D + Q$. Here Q is the heat evolved in the reaction. From the above equations wemay write.

$$(E_c + E_D) - (E_A + E_B) = - Q \text{ or } \Delta E = - Q$$

ΔE (delta E) is the change in the itnernal energy in the reaction (Internal energy of the products minus Internal energy of the reactants). The negative sign for Q indicates that there is a decrease in the internal energy in the reaction. We may also write the reaction as A + B = C + D + Q.
Such a reaction which is accompained by the evolution of heat is called an exotherimic reaction. An example of such a reaction is the formation of copper sulphide from its elements.

$$Cu + S = CuS + 11{,}600 \text{ Calories}$$

The above reaction states that in the formation of copper sulphide from its elemtns, copper and sulphur 11,600 calories of heat is liberated. The energetics of the reaction may be written as

$$E_{cu} + E_s = E_{cus} + 11{,}600 \text{ cals.}$$

The internal energy of copper sulphide is less than the internal energy of copper and sulphur put together. This difference appearsas the heat of reaction.

$$E_{cus} - (E_{cu} + E_s = - 11{,}600 \text{ cals.}$$
$$\Delta E = - 11{,}600 \text{ cals}$$

By convention, the heat of reaction is shown separately from the reaction

$$Cu + S = Cu\,S, \ \Delta E = - 11{,}600 \text{ cals.}$$

Exothermic reactions are very common. Some examples are:

$$C + O_2 = CO_2, \ \Delta E = - 94{,}050 \text{ cals.}$$
$$K + \frac{1}{2}Cl_2 = KCl \ \ \Delta E = - 93{,}500 \text{ Cals.}$$
$$Ca\,Cl_2 + 6H_2O = Ca\,Cl_2 \cdot 6H_2O, \ \Delta E = - 22{,}500 \text{ Cals.}$$

In all the above reacitons, the internal energy of the products is less than that of the reactants. Now we will consider reactions in which the internal energy of the products is greater than that of the reactions.

If in the general reaction considered before $E_C + E_D > E_A + E_B$ then for the reaction to take place, heat must be continuously supplied so that energy balances according to the equation.

$$E_A + E_B + Q = E_c + E_D$$
$$\text{Then } (E_C + E_D) - (E_A + E_B) = Q \text{ or } \Delta E = Q$$

In this reaction Q the heat of reaction is positive because Δ E is positive. The internal energy of the products is greater than that of the reactants and to make the reaction go towards the right, heat must be continuously supplied. We say the reaction takes place with the absorption of heat. Reactions which take place with the absorption of heat are called endothermic reactions. A very good example is the formation of carbon disulphide from its elemtns. It is written

$$C + 2\,S + 30,600 \text{ calories} = CS_2$$

In this reaction $E_{CS_2} - (E_c + 2\,E_s) = 30,600$ calories

$$\Delta E = 30.600 \text{ calories}$$

So we write the formation of carbon disulphide reaction as

$$C + 2S = CS_2\,;\ \Delta E = 30,600 \text{ cals.}$$

Two more examples of endothermic reactions are

$$N_2 + O_2 = 2NO;\ \Delta E = 43,200 \text{ cals.}$$

$$2C + H_2 = C_2H_2;\ \Delta E = 54.190 \text{ cals.}$$

2.4 THERMOCHEMICAL EQUATIONS

Equations which also show the heat change accompanying chemical reactions are called thermochemical equations. To be complete in every respect they should also indicate the state of the substances taking part in the reaction. Whether they are solid, liquid or gas and if solid the allotropic modification if any. The equation should also indicate the temperature at which the measurements were carried out. Thus the formation of copper sulphide reaction is written as

The symbol (g) is written to indicate gaseous reactants and symbols (1) and (s) dfor liquids and solids respectively. Usually where there is no ambiguity regarding the state of the substance the symbol may be dropped. The temperature indicates the temperature at which reactants are taken and that at which products are obtained.

Again the amount of heat absorbed or evovled in a reaction depends upon the condition in which the experiment is performed' whether in a closed vessel under conditon of constant volume or in an open vessel at the constant pressureof the atmosphere.

We have seen in previous unit that the heat absorbed or liberated at constant volume is equal to Δ E and that at constant pressure is equal to Δ H the heat of reaction at constant pressure. The two are realted by the equation obtained from the first law.

$$\Delta H = \Delta E + P\,\Delta V$$

Here Δ V represents the difference between the volume of products and the volume of reactants. However if the reaction involves only solids and liquids, the hange in their volume as a result of reaction will be negligible. Hence E and H will be nearly equal. On the other hand if the reaction involves gaseous substances, either as reactants or as products, then the volume change will be significant, even in such cases we may neglect the volume change produced in solids and liquids. For example in the reaction

$$Zn = H_2SO_4\,(1) = Zn\,SO_4\,(aq) + H_2$$

Compared to the volume of hydrogen gas produced, the volume of H_2SO_4 used up or zine dissolved will benegligible. Hence V in the above reaction represents only the volume of gaseous proudcts - volume of gaseous reactants.

$$\Delta V = V_p\,(g) - V_r\,(g)$$

For gaseous reactants and products we may write the equation of state as

$$PV_{pr} = n_{pr}RT \text{ and } PV_{re} = n_{re}RT.$$

Where n_{pr} and n_{re} are the number of moles of gaseous products and number of moles of gaseous reactants respectively.

$$\text{Therefore } P\Delta V = P(V_{pr} - V_{re}) = (n_p - n_r)\ RT = \Delta n.\ RT.$$

$$\text{and therefore we get } \Delta H = \Delta E + \Delta nRT$$

This gives the relation between heat of reaction at constant pressure and that at constant volume. Δ n can easily be known from the thermochemical equation.

Examples

$$\text{i) } C(gr) + 2H_2(g) = CH_4\ (g)$$

$$\Delta n = 1\text{-}2 = -1.$$

$$\text{ii) } CH_4 + 2O_2 = CO_2 + 2H_2O\ (1)$$

$$\Delta n = 1\text{-}3 = -2.$$

It is customary to refer all the heats of reactions to constant pressure.
Example: Given that at 25° C. ΔE = 16,548 cals for the reation

$$H_2S\ (g) + I_2\ (s) = 2HI\ (g) + S\ (\text{rhombic})$$

Calculate the heat of reaction at constant pressure

$$\Delta H = \Delta\ E + \Delta n\ RT$$

$$\Delta\ E = 16.548 \text{ cals } n = 2{,}1 = 1,\ T = 298\text{ K. Substituting we get}$$

$$\Delta H = 16,548 + 1 \times 1.987 \times 298 = 17140 \text{ cals.}$$

2.5 HESS LAW OF CONSTANT HEAT SUMMATION

Internal energy E and enthalpy H of substances are functions of state which meansΔ E and Δ H for any change in system must depend upon the initial andfinal statesof the system and not on the manner in which the change has been brought about. These are the conclusions of the first law of thermodynamics. For reactions since Δ E andΔ H are the heats of reaction measured at constant volume or constant pressure, it follows that the heat of reaction must also depend upon the initial state (reactants) and final state (products) and not on the methodby which it has been carried out. The truth of this was realised from the beginning, and Hess, as the result of a number of experiments carried out by him, stated his findings in the form of law.This has come to be known as Hess law of constant heat summation. It may be stated as follows. The heat evolved or absorbed in a given reaction must always be constant and idnependent of the path by which it is carried out whether in one step or several steps. That this law directly follows from the law of conservation of energy can easily be seen. For suppose a reactant A could be converted into B into B in two ways(i) directly in one step when sppose Q calories of heat is liberated (ii) through an intermediate C in two steps when Q_1 +Q_2 calories of heat are liberated as shown below.

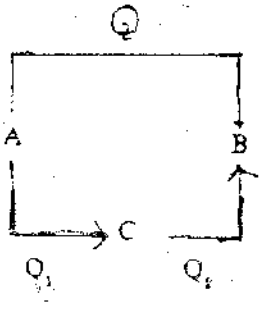

Fig: 2.1 Different Paths

Hess law requires that Q be equal to $Q_1 + Q_2$. If this is not so, the first law would be violated. Suppose $Q > (Q_1 + Q_2)$, then A could be converted into B by path I when Q calories of heat is liberated, and B is converted into A by the path II. The reverse reaction is endothermic reaction requiring absorption of heat $= Q_1 + Q_2$. Since Q calories of heat are liberated in path I and since $Q > Q_1 + Q_2$ only part of Q is needed for the reverse reaction. Hence in the cycle of reaction there is a net saving of Q - calories. This cycle may be repeated continuously to produce a large amount of heat. Since at the end of every cycle the reactant is produced, this amounts to producing energy from nothing. This is against the law of conservation of energy according to which energy can neither be created nor destroyed. The same conclusion can be arrived supposing $Q > Q_1 + Q_2$. Therefore $Q = Q_1 + Q_2$.

2.6 INDIRECT CALCULATION OF HEATS OF REACTIONS

A direct consequence of Hess law is that thermochemical equation can be added and subtracted just as algebraic equations. Taking advantage of this, we can combine thermochemical equations of those reactions whose enthalpy changes are known to give a required thermochemical equation of are action whose enthalpy change cannot be determined expermentally. There are a large number of reactions whose heat change cannot be measure either because the reaction does not take place to completion or more than one product results from the reaction. To such reactions Hess's law can applied for obtaining their H values.

For example, the enthalpy change of the following reaction cannot be determined experimentally. $C + {}^1/_2\, O_2 = CO$.

This is because the reaction does not stop with the formation of CO but if oxygen is present in CO_2 may be formed.

$C + O_2 = CO_2$

However carbon and carbon monoxide can be burnt separetaly in oxygen and the heat liberated in these reactions can be determined (see under heat of combustion). The necessary thermochemical equations are

$C + O_2 = CO_2$; $\Delta H = -\,94,050$ cals

$CO + {}^1/_2\, O_2 = CO_2$; $\Delta H = -67,900$ cals.

If we subtract the second equation from the first and rearrange we get $C + {}^1/_2\, O_2 = CO$. ΔH of this reaction is obtained by subtracting the ΔH of the second reaction from that of the first.

$-94,050 - (-67,900) = -26,150$ cals.

Hence we may write $C + {}^1/_2\, O_2 = CO$. $\Delta H = -\,26,150$ cals.

A second example is the reaction between carbon monoxide and steam. The heat change of the reaction

$CO + H_2O\,(g)$ -- $CO_2 + H_2$

cannot be determined experimentally as it does not take place to completion and only an equilibrium mixture containing all the four gases is obtained ΔH of this reaction can be obtained from the following thermochemical reaction

$CO + {}^1/_2 O_2 = CO_2$: $\Delta H = 67,900$ cals

$H_2 + {}^1/_2\, O_2 = H_2O\,(g)$ $\Delta H = -57,800$

The second equation may be rewritten as

$H_2O(g) = H_2 + {}^1/_2 O_2$; $\Delta H = +57800$ cals

adding. $CO + {}^1/_2 O_2 = CO_2$; $\Delta H = -67,900$ cals

we get $CO + H_2O\ (g) = CO_2 + H_2$; - 10,100 cals

More examples are given later.

The heat changes accompanying reactions are given different names depending upon the type of reaction.

2.7 HEAT OF FORMATION

The amount of heat absorbed or evolved in the formation of one mole of a compound from its elements is called the heat of formation of the compound.

C (graphite) + $O_2 = CO_2$; $\Delta H = -94,050$ cals.

C (graphite) + $2H_2 = CH_4$; $\Delta H = -17,890$ cals

The heat changes in these reactions are the heats of formation of the compounds formed in the respective reactions.

However consider the thermochemical equations

$2H_2 + O_2 = 2H_2O(1)$; = $\Delta H = -136,600$ cals.

and $H_2 + Cl_2 = 2HCl$; $\Delta H = -44,120$ cals.

In these equations the ΔH values do not give the heats of formation as in each case two moles of compound are formed. The correct equations would be

$H_2 + {}^1/_2 O_2 = H_2O(1)$; = $\Delta H = -68,300$ cals.

and ${}^1/_2 H_2 + {}^1/_2 Cl_2 = HCl$; $\Delta H = -22,060$ cals.

Check your progress -1

What is heat of reaction ?

If the elements and the compounds are in their standard states, the heats of formation are referred to as standard heat of formation. By standard state of a substance is meant its most stable form at that temperature usually 25°c. For example at liquid mercury, solid iodine and rhombic sulphur are the standard states for the elements. The standard heats of formation are referred to 25°C and are expressed as ΔH°_f

The standard heats of formation of some compounds are given below. Try to write their equations.

Compound	C (graphite) ΔH°_f cals
Nitric Oxide (NO)	21,600
Ammonia (NH_3)	-11,040
Hydrogen fluoride (HF)	-64,200
Hydrogen iodide (HI)	8,660
Methane (CH_4)	-17,890
Ethane (C_2H_6)	-20,230
Ethylene (C_2H_4)	12,500
Acetylene (C_2H_2)	54,190
Benzene (C_6H_6 (1)	19,820
Ethyl alcohol C_2H_5OH (1)	-66,300

Two types of compounds an be recognized from the above table. Those which have positive ΔH values. These are compounds in the formation of which heat is absorbed. They are called endothermic compounds. Those in the formation of which heat is liberated and have negative ΔH are called exothermic compounds. The enthalpies of exothermic compounds are less than the enthalpies of the elemtns from which they are formed. Likewise enthalpies of endothermic compounds are more than those of their consituent elements. Thus if we consider CH_4 $\Delta Hf = -17{,}900$ cals) and ethylene C_2H_4 $\Delta H = 12{,}500$ cals) We observe that in the that in the enthapy scale methane woould be low the level of the elements while ethylene would be above them. If the enthalpics of carbon and hydrocarbons would be above them. If the enthalpies of carbon and hydrogen are taken as zero, then the enthal[pies. it has been found convenient to take the enthalpies of all elements in their standard states as zero. With the help of this convention and making use of the standard enthalpics of formation, one may calculate ΔH° of any reaction. This would be given by the relation.

$$\Sigma \Delta H_f^\circ \text{ (Products) } - \Sigma\ \Delta\ H_f^\circ \text{ (rectants)}$$

Consider the reaction

$4\ NH_3 + 5O_2 = 4NO + 6H_2O$ (g)

ΔH° for this reaction would be

$6 \times \Delta H^\circ_f (H_2O (g)) + 4\ \Delta H^\circ_f (NO) - 4\ \Delta H^\circ_f (NH_3) - \Delta H^\circ_f (O_2)$

$6x(-57.800) + 4\ (+21600) - 4(-11.040) - 5xO$

$= -216, 240$ cals.

2.8 HEAT OF COMBUSTION

The heat of combustion of a compound is the amount of heat liberated when one mole of the compound is completely burnt in oxygen. Such values are imporant for fuels and foods because heats of combustion values are a measure of the energy that can be obtained from them. In the case of fuel and foods they are referred to as calorific values.

Organic compounds that contain only carbon, hydrogen and oxygen are oxidized to carbon dioxide and water on complete combustion reactions. For example when one mole of sucrose (cane sugar) is completely burnt in oxygen 1348900 calories of heat is libered. Since the products are only CO_2 and water, the thermochemical equation can easily be balanced.

$C_{12}\ H_{22}\ O_{11} + O_2\ 12CO_2 + 11H_2O$; $\Delta H = 1348.9$ K. cals.
Since the heats of combustion are very high, they are expressed in calories (K. calorie = 1000 calories)
A few more combustion reactions are
$C_2\ H_5\ OH\ (1)\ + 3O_2 = 2CO_2 + 3H_2O(1)$; $\Delta H = 326.7$ K. cals.
$C_6\ H_6\ (1) + 7^1/_2\ 6CO_2 + 3H_2O(1)$; $\Delta H = 780.98$ K. cals.

Determination of heat of combustion

To ensure complete combustion of the substance, it is burned in an excess of oxygen in a closed vessel. Since the volume remains constant, combustion is accompanied by large increasés in pressure. To withstand this large increase in pressure which is built up in a short internal of time, the vessel must be strongly built vessel. Vessel in which combustion reaction are carried out are called bombs. They are thick walled and made of acid resistant steel. One type of calorimeteris shown in the figure 2.2.

The bomb has tightly fitting screw cap which has a valve for admitting oxygen . Two metallic supports are connected to the lid. One of them contains a ring into which can be placed a small stainless steeel crucible. A thin wire is connected to the supports are connected to the supports and dips into the sample in the cruciable.

A known weight of the sample is placed in the crucible and the iron wire adjusted to immerse in it. The screw cap is tightly fitted and oxygen is admitted into the bomb up to a pressure of 20 to 25 atmospheres.

The bomb is immersed in a calorimeter containing a known weight of water. This whole arrangement is called a bomb calorimeter. The charge is ignited by passing an electric current through

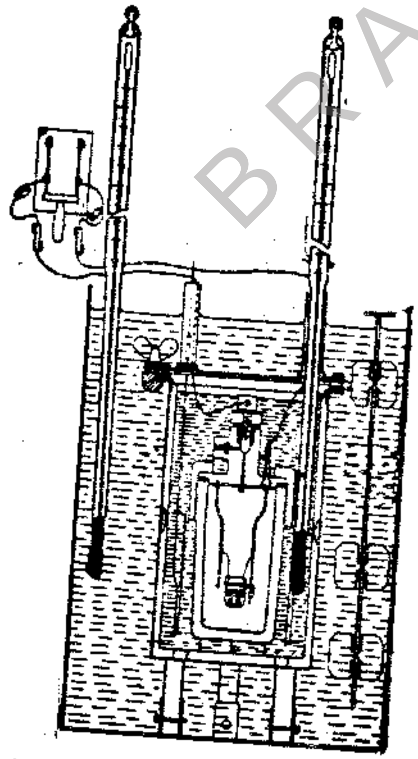

Fig 2.2 Bomb Calorimeter assembly.

thin iron wire. Combustion takes place and the heat that is liberated causes the temperture of water surrounding the bomb to rise. This rise in temperature t_2-t_1 is measured carefullly. W was the weight of the water taken, then the heat taken up by water is W (t_2-t_1)calories, assuming the specific heat of water to be one. If the mass of the bomb is m_1 and the specific heat of water material s_1, then m_1 s_1 (t_2-t_1) is the heat taken up by the bomb. In the same way the calorimeter also get heated and the heat absorbed by it is m_2 s_2 (t_2-t_1) Where m_2 & s_2 are the weight of the calorimeter and specific heat respectively. Thus when w gm of the substance is burnt the heat liberated causes the temperature of the bomb, water and the calorimeter to rise.

Therefore the heat of combustion for w gm of substance is

$$w(t_2-t_1) + m_1 s_1(-t_2-t_1) + m_2-s_2(t_2-t_1)$$
$$= (w + m_1 \ s_1 + m_2 s_2(t_2-t_1)$$
$$= C\,(t_2 - t_1)$$

where C is a constant equal to the heat capacity of calorimeter, water and the bomb. All the quantities m_1, m_2, s_1, s_2 can be determined separately. In the laboratory C is evaluated by making use of a compound with known heat of combustion. The standards that are commonly used are benzoic acid and napthalene. The heats of combustions are expressed per mole.

Example

The molar heat of combustion of benzoic acid ($C_6H_5CO_0H$) is 771.20 k. cals 0.61 g of benzoic acid on complete combustion in a bomb calorimeter produced a rise in temperature of 1.95°c. What is the total heat capacity of the calorimeter?

One mole, i.e. 122 g of benzoic acid on complete combustion produces 771.200 calories. Then

$$\text{produce } 771{,}200 \times \frac{0.61}{122} = 3856 \text{ cals.}$$

This heat increases the temperature of calorimeter and contents by 1.95°, Therefore C x 1.95 = 3856 calories where C is the total heat capacity of calorimeter.

$$\therefore C = \frac{3856}{1.95} = 1972 \text{ calories}$$

Heats of combustion of some organic compounds

Compound	Formula	Heat of combustion in k. cals/mole
Methane (g)	CH_4	212.8
Ethane (g)	C_2H_6	372.8
Propane (g)	C_3H_8	530.6
n-Butane (g)	C_4H_{10}	687.7
Ethylene (g)	C_2H_4	337.2
Acetylene (g)	C_2H_4	310.6
Benzene (l)	C_6H_6	781.2
Benzene (g)	C_6H_6	787.2
Methanol (l)	CH_3OH	173.6
Ethanol (l)	C_2H_5OH	426.8
Acetic acid (l)	CH_3COOH	209.4
Glucose (s)	$C_6H_{12}O_6$	6730
Sucrose (s)	$C_{12}H_{22}O$	1348.9
Napthalene (s)	$C_{10}H_8$	1.228
Benzoic acid (s)	C_6H_5COOH	771.4

Example

A 0.45 gm of sample of an organic compound burnt in the calorimeter in the above example causes the temperature to rise to 2.19°c what is the heat of combustion in calories per gm of the compound ?

Heat capacity of calorimeter = 1972 calories.
Heat liberated on burning 0.45 gm of compound = 1972x2.19 = 4318 cals.
Heat of combustion per gram = 4318/0.45 = 9595. 5 cals.

As indicated earlier, heat of combustion values are useful for fuel and foods. They are a measure of energy that can be obtained from them. Heat combustion values of some organic compounds are given in the above. table.

Heats of combustion values are important in another way. They can be used to determine the heats of formation of organic compounds. It is not possible to determine the heat of formation of compounds. It is not possible to determine the heat of formation of any organic compound in the laboratary but is heat of combustion can easily be determined. This value together with the heats of combustion of carbon and hydrogen can be used to estimate its heat of formation.

For example the heat of formation of ethyl alcohol cannot be determined as the reaction

$C\ (\text{graphite}) + \frac{1}{2} O_2 + 3\ H_2 = C_2H_5\ OH\ (l)$

cannot be realized experimentally

However if its heat of combustion is known as -326.7 k cals. This can be combined with the heat of combustion of graphite (-94.050; k cals) and hydrogen (-68.3 k cals) to give the following thermochemical equations.

(i) $C_2H_5\,OH(1) + 3O_2 = 2CO_2 + 3H(1)$; $\Delta H = -326.7$ kcals.

(ii) $C\ (\text{graphite}) + O_2 = CO_2$; $\Delta H = -94.05$ kcals

(iii) $H_2\ (g) + \frac{1}{2}O_2 = H_2O\ (1)$; $\Delta H = -68.3$ kcals.

These equations must be manipulated to get the reaction leading to the formation of ethyl alcohol from its elements.

Reversing (i) we get $2CO_2 + 3H_2O\,(1) = C_2H_5OH(1) + 3O_2$; $\Delta H = 326.7$

Multiplying (ii) by 2, $2\ C\ (gr) + 2O_2 = 2CO_2$: $\Delta H = -188.10$

Multiplying (iii) by 3, $3H_2\ (g) + 3/2\ O_2 = 3H_2O\ (1)$; $\Delta H = -204.9$

Adding the three $2\ C(gr) + 1/2O_2 + 3H_2 = C_2\,H_5\,OH\ (1)$; $\Delta H = 66.3$
we get the thermochemical equation for the formation of $C_2\,H_5\,OH$.

Example

Given the following heats of combustion

n-Butane ; $\Delta H = -687.9$ k cals.

C (gr) ; $\Delta H = 94.05$ K cals.

H_2 ; ΔH = - 68.3 k cals.

Calculate the heat of formation of n-butane at 25°C.

First we write the balanced thermochemical equations

(i) $C_4 H_{10}$ (g) + $6^1/_2 O_2$= 4 CO_2+ $5H_2 O$ (1) ΔH_1 = - 687.9 k cals.

(ii) C (gr) + $O_2 = CO_2$ ΔH_2 = -94.05 k cals.

(iii) H_2 + 1/2 $O_2 = H_2O$ ΔH_2 = -68.3 k.cals

The above three equations must suitably be manipulated to give the thermochemical equation for the formation of butane

4 C (gr) + 5 $H_2 = C_4 H_{10}$(g) ; ΔH = ?

This is done as follows.

Reverse equation (i) 4 CO_2 + $5H_2O$ (1) = $C_4 H_{10}$ + $6^1/_2$ O2 ; ΔH = 687.9

Multiply (ii) by 4, 4C(gr) + $4O_2$ = 4 CO_2; ΔH = - 376.20

Mulitply (iii) by 5, 5 H_2+ 5/2O_2= 5 H_2O ; ΔH= - 34.5

Simiplifying and adding 4 C(gr) + $5H_2 = C_4H_{10}$; ΔH =-29.8 K. cal.

2.9. HEAT CHANGES IN SOLUTION

It is known that the formation of a solution is accompanied by a heat change, that is, heat is absorbed or evolved . Thus when compounds such as sodium hydroxide or sulphuric acid is dissolved in water the resulting solution becomes warms, that is, heat is liberated, where as solution resulting from dissolving ammonium chloride or ammonium nitrate in water becomes cool and the solution has to absorb heat to reach the room temperature again. The heat change produced when a mole of solution is dissolved in solvent is called the heat of solution. The total heat change when one mole of a solute is dissolved in infinite quantity of solvent is called the integral heat of solution.

The integral heats of solution for various solution of H_2SO_4 of different molalities are given below.

Moles of water/moles of H_2So_4	6	10	25	200	α
Δ H/ m	-14.7	-16.2	17.5	- 18.13	- 23.0 k cals-1 mol)

If the heat changes are extrapolated to infinite dilution we get the itegral heat of dilution. Thus 23 k cals. is the total heat evolved when one mole of H_2SO_4 is dissolved in a very large quantity of water. This is a solution to which further addition of water produces no.thermal change and is referred to as the aqueous solution of $H_2 SO_4$ and is written H_2SO_4 (aq).

$H_2 SO_4$ (1) + aq = H_2SO_4 (aq); ΔH = 23.0 k. cals

When aqueous solutions of two salts are mixed, there will be no heat change produced provided no reaction takes place. Thus when a dilute solution of sodium chloride is mixed with a dilute solution of potassium nitrate no heat change is observed.

$$KNO_3\ (aq) + NaCl\ (aq) + Na\ NO_3\ (aq)\ \Delta H = O$$

This is because the same ions are present in the resulting solution. No reaction has taken place.

$$K^+ (aq) + NO_3 (aq) + Na^+ (aq) + Cl^- (aq)\ K^+ (aq) + Cl^{+}- (aq)\ Na^+ (aq) + NO3^- (aq)$$

If a chemical reaction takes place, then the heat of reaction is not zero.

$$Na\ Cl\ (aq) + Ag\ NO_3\ (aq) = Ag\ Cl \quad + Na\ NO_3\ (aq)\ \Delta H = O$$

It is seen that the net reaction $Ag+ (aq) + Cl- (aq) = Ag\ Cl$

2.10 HEAT OF NEUTRALIZATION OF ACIDS AND BASES

An important change takes place in solution when an acid is neutralized by a base. When a dilute solutiion of an acid is added to a dilute solution of a base, heat is liberated. The products of this reaction are salt and water. The heat liberated per mole of water formed is called the heat of neutralization. When dilute solution of strong acids (HCl or HNO·) are neutralzed by dilute solutions of strong bases (NaOH or KOH) the heat evolved per mole of water formed is nearly the same as may be seen from the examples given below.

$$KOH\ (aq) + HCl\ (aq) = KCl\ (aq) + H_2O\ (1)\ \Delta H = -13.695\ cal$$

$$KOH\ (aq) + HNO_3\ (aq) = KNO_3\ (aq) + H_2O\ (1)\ \Delta H = -13.670\ cal$$

$$Na\ OH\ (aq) + HCl\ (aq) = NaCl\ (aq) + H_2O\ (1)\ \Delta H = -13.680\ cal$$

$$LiOH\ (aq) + HCl\ (aq) = LiCl\ (aq) + H_2O\ (I)\ \Delta H = -13.700\ cal$$

This constancy in the value of heat of neutralization can easily be explained by the ionization theory. Strong acids, strong bases and their salts are completely ionized in dilute solutions. Hence the sodium ions, potassium ions, chloride ions and nitrate ions remain unchanged in the reaction.

For example the equation for the neutralization of HCl (aq) by NaOH (aq) the ionic reaction can be written as

$$Na^+ (aq) + OH^- (aq) + Cl^- (aq) = Na^+ (aq) + Cl\ (aq) + H_2O\ (I)$$

In this reaction Na^+ and $C1^-$ remain unchanged. The only chemical reaction taking place is therefore

$OH^- (aq) + H^+ (aq) = H_2O\ (I)$
and the ΔH of this reaction is - 13,610 cals

Thus we find the neutralization of any strong acid by any strong base in a dilute solution is brought about by the combination of hydrogen and hydroxyl ions to form water.

Hence the value of heat neutralization is constant $\Delta H = -\ 13.7$ k cal

However this constancy of heat of neutralization is not observed if the reaction involves a weak acid or a weak base as seen in the examples below

$Na\,OH_3\,(aq) + CH_3\;COOH\,(aq) = CH_3\,COO\,Na\,(aq) + H_2O; = \Delta H = -\,133{,}00$

$Na\,OH\,(aq) + HCN\,(aq)\;NaCN\,(aq) = H_2O\,(1)\;\Delta H = -\,2{,}900$

$NH_3 + H_2O + HCl\,(aq) = NH_4\,Cl\,(aq) + H_2O; = \Delta H = -\,12{,}400$

This means that in these reactions conbination between the hydrogen and hydroxyl ions does not take place to completion. This is so because a weak acid or a base is dissosiated to a very small extent in solution. There are very few hydrogen ions in aceticacid solution and very few hydroxide ions in ammonia solution. Neutralization involving weak acids and weak bases may be imagined to take place with neutral molecules.

$CH_3\,COOH\,(aq)\;OH^-\,(aq)\;\;CH\,COO^-\,(aq) + H_2O\,(1)$

$NH_3\,(aq) + HCl\,(aq)\;NH_4 + CL^-$

These reactions do not take place to completion, hence the heat evolved is less.

2.11. VARIATION OF HEAT OF REACTION WITH TEMPERATURE. THE KIRCHHOFFS, EQUATION

The heat of a reaction depends upon the temperature at which mesurements are made. It varies with temperature because the heat capacities of the reactants and products are not the same. However, for the applications of Hess' law, it is necessary to refer all ΔH values to the same temperature. For this reason we must know how the heat of a reaction varies with temperature. Such a relation was first obtained by Kirchoff. This can be understood from a simple cycle.

We represent the reactants by the symbol A and the products by B. Suppose the Δ H value for the reaction A - B is known at the temperature T_1, and it is required to find its value at T_2. We start with the reactants at the temperature T_1 and convert them into the products at the temperature T_2. This can be achieved by two paths as shown in the figure.

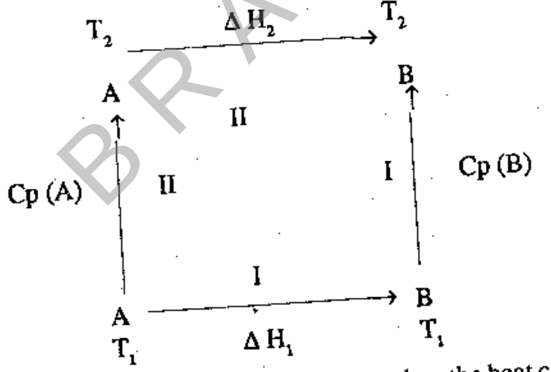

Fig. 2.3 Kirchhoff's Ideas.

Path I.

The reaction is allowed to take place at T_1 when the heat change ΔH_1 occurs. The products B at temperature T_1 are heated to T_2 when the heat absorbed is $C_p\,(B)\,(T_2 - T_1)$. Here $C_p\,(B)$ is the total heat capacity of the products.

Path II.

The reactants A at T_1 are heated to T_2 when the heat absorbed is $C_p\,(A)\,(T_2 - T_1)$. The reaction is allowed to take place at T_2, when we obtain the products B at T_2. The heat change in this reaction is ΔH_2 Since in both paths we started with the reactants A at the temperature T_1 and obtained the products B at the temperature T_2, the total heat change in both paths must be equal

i.e. $\Delta H_1 + C_p + (B)\,[T_2 - T_1) = C_p(A)\,(T_2 - T_1) + \;\Delta H_1$

from which we can obtain the relation

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = C_p(B) - C_p(A) = \Delta C_p$$

Where $\Delta C_p = \Sigma C_p$ (Products) - ΣC_p (reactants)

This equation is known as Kirchhoff's equation.

There is an alternate direct way of obtaining this equation.

For the reaction $A \rightarrow B$; $\Delta H = H_B - H_A$ for H_B is thge total enthalpy of the products and H_A total enthalpy of reactants

$$\therefore \Delta H = H_B - H_A \text{ Differentiating we get}$$

$$\frac{d(\Delta H)}{dT} = \frac{dH_B}{dT} - \frac{dH_A}{dT} : \text{By definition } \frac{dH_B}{dT} = C_p(B)$$

$$\text{and} \frac{dH_A}{dT} = C_p(A)$$

$$\text{Hence } \frac{d(\Delta H)}{dT} = C_p(B) - C_p(A) \text{ and } d(\Delta H) = C_p(B)\,dT - C_p(A)\,dT$$

Integrating between the limits T_1 and T_2 when ΔH values are

ΔH_1 and ΔH_2

$$\int_{\Delta H_1}^{\Delta H_2} d\Delta H = \int_{T_1}^{T_2} Cp(B)\,dT - \int_{T_1}^{T_2} Cp(A)\,dT$$

$$\Delta H_2 - \Delta H_1 = Cp(B)[T_2 - T_1] - Cp(A)[T_2 - T_1]$$

from which we obtain the same equation as before.

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = C_p(B) - C_p(A)$$

In the integration it has been assumed that the C_p values do not change with temperature.

Example

For the reaction $H_2(g) + {}^1/_2 O_2(g)$ $H_2O(g)$ $\Delta H = -57.8$ K Cals at 298 K

Calculate the value at 373 K.C_p (H_2) and C_p (O_2) are 6.5 cal degree mole^{-1} andfor H_2O $C_p(g)$ C_p is 7.5 cal degree^{-1} mole^{-1}.

We make use of the Kirchhoff's equation

$$\frac{\Delta H_{373} - \Delta H_{298}}{373 - 298} = C_p(H_2O) - [C_p(H_2) + \frac{1}{2} C_p(O_2)]$$

$$= 7.5 - (6.5 + \frac{1}{2} \times 6.5) = -2.25$$

$$\Delta H_{373} = \Delta H_{298} + 75 \times \Delta C_p$$

$$= -57{,}800 + (-2.25)\,75 = 57968 \text{ Cals.}$$

Check your Progress -2

Why the heat of reaction changes with the variation of temperature?

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2.12 CALCULATION OF HEATS OF REACTION FROM BOND ENERGIES

In this last section we will discuss an approximate method for calculating heat of reaction. This becomes necessary when Hess Law cannot be applied due to non availability of necessary thermochemical reactions. The method involves the use of bond energies. Bond energy is the energy required to break a bond and a separate the atoms. For example the ΔH of the reaction.

$A\text{-}B = A(g) + B\,(g)$

is the energy of the bond A--B

For diatomic molecules like N_2, NO, HCl and O_2, this quantity is merely the dissociation energy of the molecules and can be obtained from experiments. However for bonds of the type C-H, N-H, O-H etc only average values can be obtained. For example the bond energy for C-H cannot be determined directly. But consider the reaction;

$CH_4\,(g) = C(g) + 4H\,(g)$

Since this reaction involves the breaking of 4C - H bonds, one may suppose that one fourth the ΔH of this reaction gives the bond energy of a single C-H bond. This however gives only an average value because, with the removal of each H atom, the remaining C-H bonds become weaker. . Hence ΔH for the breaking of the first C-H bond in methane will be highest and that for removal of the last hpdrogen atom lowest.

The enthalpy change for the reaction
$CH_4 = C(g) + 4H\,(g)$
can be obtained as follows.

First the heat of formation of methane is calculated from the thermochemical equation involving combustion of methane, hydrogen and carbon.

$C\,(gr) + 2H_2\,(g) = CH_4\,(g)\,;\ \Delta H_1 = 17.89$ k cal.

This equation is reversed and combined with two equations

$CH_4\,(g) = C(gr) + 2H_2\,(g)\,;\ \Delta H = -17.89$ k. cal.

Dissociation of hydrogen $2H_2 = 4H$; $\Delta H = 208.36$ k. cals

Sublimation of graphite $C\,(gr) = C\,(g)$; $\Delta H = 171.7$ k. cals.

Adding $CH_4(g) = C(gr) + 4H\,(g)\,;\ \Delta H = 397.95$ k. cal.
This is the energy required to break 4 C-H bonds. Hence the bond energy for one C-H is one fourth this value, i.e. 99.49 k. cal. $mole^{-1}$.

In this way the values of the bond energies for a member of bonds have been obtained. Some of them are given in the table. The values in the table have been adjusted in such a way to be - applicable to largest number of compounds.

Bond energies in k. cal mole^{-1}.

H-N	104	N=N	225	C=C	145	C=O	173
H-F	135	N-H	92	C=C	198	C-Cl	76
H-Cl	102	O-H	109	C-H	98		
Cl-Cl	57	C-C	80	C-O	79		

Making use of these values the enthalpy change for a number of reactions involving these bonds can be calculated. In a chemicl reaction bonds are broken and new bonds are formed. Energy is absorbed in the breaking of a bond, and energy is released when a new bond is formed. The net heat change in a reaction is the algebraic sum of these However it should be remembered that this bond energy method can be applied only for gaseous reactions and only when covalent bonds are involved.

Example (i)

Using the values of bond energies given calculate ΔH for the following reaction

$CH_4 (g) + Cl_2(g) \quad CH_3 Cl (g) + HCl (g)$

In this reaction one C-H bond and one Cl -Cl bond are broken and one C-Cl bond and H-Cl bond are formed.

Energy required to break the bonds = 98+57 = 155 k. cals. mole^{-1}
Energy released in the formation of bonds = 76 + 102 = 178 k. cals. mole^{-1}
Net energy released = 178 - 155 =23k. cals. mole^{-1}
Therefore ΔH = -23 k.cals.

Example (ii)

Given the heat of formation of ethane as $\Delta H_f = -20.23$ k. cals. calculate the C-C bond energy.
$H_3 C - CH_3 \cdot \quad 2C (gr) + 3H_2 \ \Delta H = + 20.323$ k. cals.

combining this with

$2 C (gr) \quad - 2 C (g) \qquad \Delta H=2x171.7 = 343.4$ k. cal.

$3H_2 (g) \quad - 6H (g) \qquad \Delta H = 3 \times 104.18 = 312.54$ k. cal.

We have $H_3C - CH_3 \quad - 2C (g) + 6H (g) : \Delta H = 676.17$ k. cal.

This is the energy required to break 6 C-H bonds and one C-C bond. Since the energy required to break 6 C-H bonds is 6 X 98 = 588 k. cal, the energy required to break one C-C bond will be 676.17 - 588 k. cal mole-^{1}.

2.13 SUMMARY

Chemical reactions are usually accompanied by heat changes. Some are exothermic reactions and other are endo-thermic. Heat of a reaction is constant and it is independent of the path chosen, it may be carried out in one step or several steps. In the unit the thermochemical concepts heat of formation, heat of combustion, heat of solution and heat of neutralisation are briefly introduced. Heat of a reaction changes with the change of the temperature. Reactions between covalent substances proceed with the bond breakage of reactants and new bond formation. From the bond energies it is possible to calculate the heat of reaction.

2.14 MODEL EXAMINATION QUESTIONS.

I. Answer the following in 10 lines each

1. Obtain the relation between the heat of reaction at constant volume and that at constant pressure.

2. Suggest a method for estimation of the heat of conversion of graphite into diamond.
C (graphite) . - C (diamond)

3. Explain why the heat of neutralization of a weak acid by strong base is less than that of a strong acid by strong base.

4. Derive the Kirchhoff's equation.

II. Answer the following in 30 lines each

1. State and explain the Hess's Law of constant heat summation. Show how it is in agreement with the first law of thermodynamics. Mention two applications of the law.

2. What is meant by heat combustion of a compound ? Described the method by which heats of combustion are obtained. What is their importance for foods and fuels? Show how these values can be used to determine the heat of formation of organic compounds.

III. Solve the Problems

1. For the reaction between acetic acid and ethyl alcohol ΔH value at 25°C is 129 k. cal. Calculate the value of ΔE at the same temperature.

CH_3 COOH (1) + C_2H_5OH (1) = $CH_3COOC_2H_5$(1) + H_2O (g)

2. The combustion reaction of ethane is given below.
C_2H_6 (g) - $3^1/_2\ O_2$ (g) = $2CO_2$ (g) - $3H_2O(1)$
If the ΔH of this reaction at 25°C is 372.8 k. cal calculate the value of ΔE.

3. Write a balanced equation for the combustion of acetic acid. If the ΔH value for this reaction at 25°c is -207.9 k. cal. mole^{-1}. calculate the value of heat of formation of this compound. ΔH (formation) CO_2 = - 94.03 k. cal and ΔH (formation) $H_2O(1)$ = 68.3 k. cal.

4. The heat of formation of C_2H_5OH (1) is -66 k. cal. mole^{-1} while the heat of combustion of isomeric compound CH_3-O-CH_3 (g) is - 348 k. cal. mole^{-1}. Given the heat of formation of $H_2O(1)$ as -68 k. cal Mole^{-1} and heat of combustion of carbon to CO_2 (g) as -94k.cal. mole^{-1} (all data at 25°c). Calculate H_{298} K for the isomerization reaction.

C_2H_5 OH (1) = CH_3 -O- CH_3(g)

5. Calculate the heat of vaporisation of water at 12°c. The heat capacity of H_2O (1) may be taken as 1 cal gm^{-1} degree -I. C_p for water vapour as 0.45 cal. The heat of vaporisation at 100°C is 536 cal per gram.

6. For the reaction CO + $^1/_2\ O_2 = CO_2$ D H_{298} K = -676 k. cals. find its value at 323 K. The average values of C_p in this temperature range are CO 6.92, O_2 7.148 and CO_2 95 cals.

7. From the bond energy data given in this lesson, deduce ΔH_f for propane.

8. Using the date given in this lesson, estimate the heat of the following reaction assuming all

reactuants and products are in the gaseous state.

$$C_2H_4 + Cl_2 - C_2H_4Cl_2$$

2.15 MODEL ANSWERS TO CHECK YOUR PROGRESS.

1. Heat of a reaction is the amount of heat that is absorbed or evolved when the reactants completely change into the products indicated by the stoichimetric equation.

2. Heat of a reaction changes with the variation of the temperature due to the different heat capacities of reactants and products.

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UNIT -3 THE SECOND LAW OF THERMODYNAMICS

Contents

3.1 AIMS AND OBJECTIVES

In this unit you will learn about the second law of thermodynamics, its needs, its usefulness and the importance of the functions entrophy and free energy.

When you complete the reading and understanding of various aspects covered in this unit you must be able to:

- realise the limitation of the first law in its inability to predict whether a given process can take place spontaneously or not
- know that spontaneous process takes place in the direction in which equillibrium is reached. Spontaneous processes are irreversible. They cannot take place in the opposite direction without the expenditure of work.
- bear in your mind that, Heat cannot be completely converted into work without giving up some heat at lower temperature.
- define entrophy 'S' by the relation $dS = q/T$ for a reversible and $dS > q/T$ for an irreversible process.
- realise that for an isolated system $\Delta S = 0$ for equillibrium and $\Delta S > 0$ for spontaneous process.
- know that ΔG (Free energy change) combines the properties of ΔH and ΔS through the equation $\Delta G = \Delta H - T \Delta S$. A reaction will be spontaneous only when ΔG of the reaction is negative.

3.2 INTRODUCTION

The first law of thermodynamics is a statement of the equivalence of different forms of energy. While it tells us that in any process when energy of one kind disappears, an equivalent amount of energy of another kind makes its appearance, it does not give any information about the process itself. It cannot say whether the process is possible or not. For example, it cannot tell us whether a metal rod at uniform temperature can by itself become hot at one end and cold at the other. So long as the heat gained by one end is equal to the heat lost at the other, process in no way violates the first law. However, we know from our experience that such a process is never observed. Heat flows of its own accord (spontaneously) only from a region of higher temperature to one at a lower temperature. We can also, from our experience predict the course of many other processes. A solute diffuses from a concentrated solution into a dilute solution. These are spontaneous processes. All natural process are spontaneous as water running down a hill, decay of organic matter, demagnetization of magnets, disintegration of radioactive elements and so on.

3.3 SPONTANEOUS PROCESS

By observing the nature of these spontaneous processes we can arrive at some generalisations which have become statements of the second law of thermodynamics (i) **All spontaneous processes change in direction in which they attain a final state of 'rest' which we may call equillirium.** When two metal blocks at different temperatures are brought into contact, heat flows spontaneously from the block at higher temperature to that at the lower temperature until a uniform temperature is reached. We say there is **thermal equillibrium.** When two solutions of unequal concentration are carefully brought together the solute diffuses from the concentrated solution into the dilute solution until concentration is the same throughout. This is **diffusive equillibrium.** In the same way suppose as gas under high pressure is separated from one at low pressure by a partition. If the partition is removed the gas under higher pressure diffuses into the low pressure gas until the pressure is the same throughout. **This is called mechanical equillibrium.** These observations can be summarised as follows : **Every system left to itself changes slowly or rapidly in such a way as to approach a final state of rest called equillibrium.** This may be considered to be the origin of the second law of thermodynamics.

(ii) All spontaneous processes have one thing in common. They are unidirectional. They proceed in the direction in which equillibrium may be attained. They cannot take place in direction away from equillibrium without external aid. Work is necessary to carry water uphill. A gas that has expanded spontaneously into an evacuated vessel can be sent back by introducing a piston in the second vessel and compressing the gas, that is by doing work. The nonspontaneous process of transfer of heat from low temperature to a region at high temperature is carried out in the refrigerator, but this process is accompanied by a net input of work. These observations can be summarised into a statement of the second law of thermodynamics.

1. The spontaneous flow of heat is always unidirectional-from a body at higher temperature to one at lower temperature.

2. It is impossible to construct a machine which is able to convey heat by a cyclic process from a body at constant temperature to another at a higher temperature unless work is done on the machine by some outside agency.

Exceptions to this are observed at the microscopic level as for example in Brownian motion where one finds occassionally particles moving from lower concentration to higher concentration. But such violations are never observed at the macroscopic level.

3.3 CONVERSION OF HEAT INTO WORK

There is yet another limitation of the first law which gives rise to an additional statement of the second law. While the first law states that heat is completely converted into work it does not tell us the conditions under which this conversion can be achieved. While all other forms of energy can be completely converted into work. Heat is one form of energy for which there are restrictions to its being converted into workwork. This is because heat can be converted into work only through a working substance, say gas enclosed in a cylinder by a piston. By placing the cylinder in a heat reserviour the gas may absorb heat and do work by expansion against the piston. By expanding isothermally and reversibly the absorbed heat may be completely converted into work. Although complete conversion of heat into work has been achieved this, has resulted in a change in the state of the working substance (gas). It is now in an expanded state. To restore the gas its original state, it must be compressed. Work must be done, when heat is given out. To obtain work continuously from heat the gas must be brought back to its initial state after every expansion the working substance must operate in cycles. If the expanded gas is returned to its initial state by isothermal reversible compression the work done by the gas and heat liberated will be identical to the heat absorbed and work done by the gas in the expansion. At the end of the cycle, we are left with no heat absorbed and no work done. In order to retain some of the work done in the expansion, some heat must be rejected at lower temperature. This limitation is stated as another version of the second law of thermodynamics. It is not possible to convert heat into work by means of an isothermal cyclic process.

3.4. ENTROPY

Such definition of the second law as have been made above are not convenient of solving problems in chemistry. What is required is a criterion by which one may determine whether a particular chemical reaction can take place spontaneoulsy. The second law must provide a function which has the following characteristics.

1. It must be thermodynamic function of state
2. It must change in a definite way (say increase) in an irreversible process.
3. It must not change once equillbrium is reached.

A function satisfying these requirements has been 'devised'. It is called entrophy. It has the symbol S. For an infinitesimal change it is given by the heat absorbed (q) divided by temperature T.

$dS = q/T$ (for reversible process)

Check your progress -1.

What are spontaneous processes ?

Ifthe process takes place spontaneously then dS is greater than the heat absorbed (q) divided by temperature (T).

$dS > q/T$ (for irreversible process)

For non spontaneous processes the entrophy change is less than the heat absorbed (q) divided by temperature(T).

$dS < q/T$ (for non spontaneous process)

For an irreversible process the entropy change can be determined by carrying out the same process (same initial state to same final state) reversible and finding the heat absorbed. Hence dS for change is given by q_{rev} T where q_{rev} is the heat absorbed had the process taken place reversibly.

For a finite change the process is divided into a number of steps and the entropy change is the sum of the entropy changes in the individual steps.

$$\Delta S = \sum \frac{q_{rev}}{T}$$

Before proceeding further with this function, it should first be established that entropy is a thermodynamic function of state. This can be done through what is called the Carnot cycle.

3.6 THE CARNOT CYCLE

Carnot devised a cycle of operations for obtaining maximum work from a cycle of operations. In this cycle known as Carnot cycle a working substance undergoes a series of changes and is brought back to its initial state. Although any substance may be used as a working substance, we choose it as a gas enclosed in a cylinder. The four stages are (i) isothermal expansion (ii) adiabatic expansion (iii) isothermal compression (iv) adiabatic compression. Since the heat absorbed cannot be completely converted into work, part of it must be rejected at a lower temperature. Hence, two heat reservoirs must be provided one at a higher temperature. (T_2) called the source and another at a lower temperature (T_1) called the sink. In these reservoirs of constant temperatures isothermal processes can be carried out. For adiabatic process thermally insulated jackets are provided for the cylinder. The cycle of operation is represented on a pressure- volume diagram.

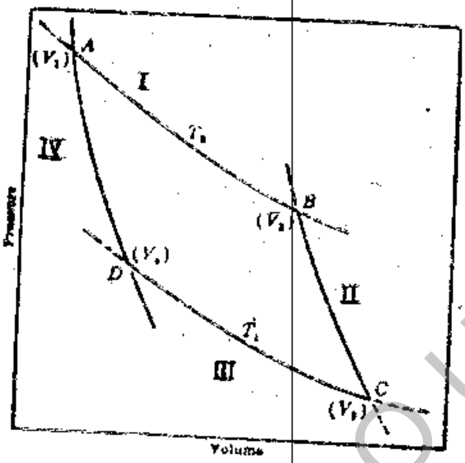

Fig: 3.1 The Carnot Cycle of operation

Stage I

Thecylinder containing one mole of a gas under a pressure P_1 and occupying V_1 is placed in the constant temperature bath at temperature T_2. The gas is allowed to expand reversibly until its final volume is V_2. In this isothermal reversible expansion the gas absorbs an amount of heat Q_2 which is equal to work done.

$$Q_2 = W_1 = R\, T_2 \ln \frac{V_2}{V_1}$$

The path is represented by AB in the diagram.

Stage II

The cylinder is removed from the reservoirs and placed in the non-conducting jacket. The pressure on the piston is adjusted so that the gas expands reversible until its volume increases to V_3 (point C). In this adiabatic expansion the temperature falls from T_2 to T_1. The work done by the gas W_2 is given by:

$$W_2 = - \Delta E = - C_v\ (T_1 - T_2).$$

This is represented by BC in the diagram

Stage III

The non conducting jacket is removed, and the cylinder is placed now in the hot reservoir at the lower temperature T_1. The gas is compressed reversibly until volume is reduced to V_4. In this isothermal compression, work W_3 is done on the gas and an equivalent amount of heat Q_1 given out.

$$Q_1 ,= W_1 = R\ T_1\ \text{In} \frac{V_4}{V_3}$$

This is the isothermal CD on the diagram.

Stage IV

Finally in the last stage, the cylinder is placed in the non-conducting jacket and compressed reversibly until the initial state is reached. Actually the final volume V_4 in stage III is adjusted in such a way that it falls on the adiabatic. In the adiabatic compression the temperature rises from T_1 to T_2. Work done in this compression W_4 is given by

$$W_4 = - \Delta E = - C_v\ (T_2 - T_1)$$

This is represented by PA in the diagram.

The total work performed in the complete cycle

$$= W_1 + W_2 + W_3 + W_4$$

$$= R\ T_2\ \text{In}\ V_2/V_1 - C_v\ (T_1 - T_2) + R\ T_1\ \text{In}\ V_4/V_3 - C_v\ (T_2 - T_1).$$

The second and the fourth terms cancel giving net work done as

$$= R\ T_2\ \text{In}\ V_2/V_1 + R\ T_1\ \text{In}\ V_4/V_3 \text{ or } R\ T_2\ \text{In} \quad \frac{V_2}{V_1} - RT\ \text{In} \frac{V_3}{4}$$

For any adiabatic reversible volume change we have relation.

$$\left(\frac{V_{\text{final}}}{V_{\text{initial}}}\right)^{\gamma 1} = \frac{T_{(\text{initial})}}{V_{(\text{final})}} \text{ (See Unit I)}$$

For the two adiabatic processes in stage II and III we can write

$$\left(\frac{V_3}{V_2}\right)^{\gamma-1} = \frac{T_2}{T_1} \text{ and } \left(\frac{V_1}{V_4}\right)^{\gamma-1} = \frac{T_1}{T_2}$$

From these we can get

$$\frac{V_3}{V_2} = \frac{V_4}{V_1} \text{ or } \frac{V_3}{V_4} = \frac{V_2}{V_1}$$

Substituting this relation in the expression for net work done we get

$$W = R\ T_2\ \text{In}\ V_2/V_1 - R\ T_1\ \text{In}\ V_2/V_1 = R\ \text{In}\ V_2/V_1\ (T_2 - T_1).$$

This is the net work obtained from the heat absorbed in the first stage

The heat absorbed is $Q_2 = W_1 = RT_2 \ln V_2/V_1$

The efficiency of the carnot cycle is therefore

$$\frac{W}{Q_2} = \frac{R \ln\frac{V_2}{V_1}(T_2-T_1)}{RT_2 \ln\frac{V_2}{V_1}} = \frac{T_2 - T_1}{T_2}$$

In this way we get the important result that the efficiency of a heat engine (mechanism for converting heat into work) operating in a carnot cycle depends only the temperatures between which it operates. It does not depend upon the nature of the working substance. This is the maximum efficiency possible because every stage is conducted reversibly.

For a given temperature T_2 of the source the efficiency can be increased by keeping the temperature of the sink as low as possible. If $T_1 = 0$ then $\frac{W}{Q} = \frac{T_2}{T_2} = 1.$ This means that in a cycle of operation heat can be completely converted into work. Since according to the second law heat cannot be completely converted into work in a cyclic process we arrive at the conclusion that we cannot have reservoir at absolute zero of temperature. Of course, it can also be shown, independent of the second law that the absolute zero is unattainable.

3.7 ENTROPY AS A THERMODYNAMIC FUNCTION OF STATE

After going through the carnot cycle, the working substance (gas) is brought back to its initial state, so that net change in its internal energy is zero. Then from the first law

$$\Delta E = Q_{total} - W_{total} = 0$$

$$\therefore \; W_{total} = Q_{total} = Q_1 + Q_2$$

$$\text{But} \; \frac{W_{total}}{Q_2} = \frac{T_2 - T_1}{T_2}$$

$$1 + \frac{Q_1}{Q_2} = 1 - \frac{T_1}{T_2}$$

$$\text{or} \quad \frac{Q_1}{Q_2} = -\frac{T_1}{T_2}$$

From which we can show that

$$\frac{Q_1}{T_1} = -\frac{Q_2}{T_2} \text{ or } \frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

Thus, we find that in the carnot cycle the sum of the Q/T terms is zero where Q is the heat absorbed at the temperature T. This must be true for any cyclic process. Because any such process can be divided into a large number of carnot cycles by drawing isothermals and adiabatics passing through it. The $\sum \frac{q}{T} = 0.$ Sum of the heat changes in every step, each term being divided by the appropriate temperature, will be zero, If the number of steps is very large the summation can be replaced by integuration and we may write $\int \frac{q}{T} = 0.$ q is the heat absorbed reversibly in each small step.

Since every step is carried out reversibly in each small step. Since every step is carried out reversibly

$q = q_{rev}$ and $dS = \frac{q_{rev}}{T}$ (by definition).

Hence, $$\oint \frac{q_{rev}}{T} = \oint dS = 0$$

The meaning of the expression is as follows : When a substance is carried through a number of processes but ultimately returned to its original state (cyclic process) the net change in entropy is zero.

This is exactly the condition to be satisfied by a thermodynamic function of a state. In a cyclic process there is no change in the value of a thermodynamic function of the state. This has been in the case of the internal energy of a system (see unit 1 under internal energy). Hence, entropy is also a thermodynamic function of state for which we may write

$$\Delta S = ? \int_{S_1}^{S_2} dS = S_2 - S_1.$$

3.8 ENTROPY AND THE SECOND LAW

We have defined entropy change as in a reversible process to be equal to q/T and for irreversible process dS > q/T. Since entrophy is a function of state we can write these conditions as $\Delta S = Q/T$ and $\Delta S > Q/T$.

Consider the changes taking place in a thermally isolated system. These are adiabatic changes. Heat can neither enter the system nor leave it $Q = 0$. Hence, the changes the condition for reversibility would be $T \Delta S = 0$; Since T can never become zero (absolute zero cannot be reached) $\Delta H = 0$ for reversible process in isolated systems. For irreversible process the condition becomes $\Delta S > 0$.

From these findings we can write these conclusions (i) Since every stage of a reversible process is an equillibrium stage, the condition for reversibility is also the condition for equillibrium. **Hence, for equillibrium $\Delta S = 0$.** (ii) Since all naturally occuring processes are irreversible, any process ocurring in nature is accompanied by an increase in entropy. Hence, we can state that **entropy of the universe (an isolated system)** is constantly increasing.

This had led **clausius** to state the second law in terms of entropy. This statement along with his statement of the first law are given below:

(i) Energy of the universe is constant
(ii) Entropy of the universe tends towards a maximum.

The meaning of the second statement can be appreciated better in terms of the molecular interpretation of entropy.

3.9 MOLECULAR INTERPRETATION OF ENTROPY

Thermodynamics is concerned with the observable or bulk properties of matter. It has nothing to do with structure of matter - the molecules and atoms the structure of these particles. However, we can get a better understanding of thermodynamic properties, if they can be correalated with the properties of individual molecules. Such a study is made in statistical thermodynamics. There, the internal energy of a gas is related to, and calculated from the kinetic and potential energies of the constituent molecules.

Entropy however is not related to any molecular property. It is regarded as a measure of the randomness in a system. By randomness we mean the number of ways the molecules can arrange themselves without any change in the observable properties of the system. The number of arrangements possible obviously depends upon the number of positions available into which they can move. The randomness in a liquid is greater than that in a solid because in a liquid the molecules have greater freedom to move about. The randomness in a gas is much more because in the absence of any significant attractive forces, the molecules can occupy any position in the vessel. Randomness is thus the disorder in the system because greater the number of positions the molecules can assume greater the disorder. Entropy is a measure of this disorder. In passing from ordered solid state to the highly disordered gaseous state the entropy should increase.

On the basis of this interpretation it is easy to show that any spontaneous process is accompanied by an increase in entropy. Consider the spontaneous expansion of a gas from a high pressure (small volume) region to a low pressure (large volume) region. In the larger volume the number of positions available for each molecule is more than in the smaller volume. Hence, the randomness has increased and so the entropy.

Similarly in the diffusion from a concentrated solution into a dilute solution the molecules move towards a more random distribution. In the spontaneous flow of heat from a hot body to cold one, there is a more random distributions of heat among molecules. Thus in all natural process whether it is evaporation of liquids or oxidation of organic matter (to give smaller molecules) the systems move towards a more disorder state (greater entropy).

3.10 FREE ENERGY AND FREE ENERGY CHANGE

The conditions $\Delta S = 0$ for equillbrium and $\Delta S > 0$ for spontaneous process apply for isolated systems. For non adiabtic systems these conditions apply for systems plus surroundings.

$$\Delta S_{systems} + \Delta S_{surroundings} = 0 \text{ and } \Delta S_{sys} + \Delta S_{sur} > 0.$$

We require a criterion that is appplicable to the system alone. This is provided by another thermodynamic property - introduced by Gibbs.

This is free energy with the symbol G. **Free energy is defined by the equation**

$$G = H - TS. \quad - \quad - \quad - \quad (1)$$

Since enthalpy and entropy are functions of state, free energy is also a function of state. Introducing the relation $H = E + PV$ into (1), we ahave

$$G = E + PV - TS \quad - \quad - \quad - \quad (2)$$

For a change of state from (1) to (2) the free energy change is given by

$$G_2 - G_1 = E_2 - E_1 + P_2 V_2 - P_1 V_1 - (T_2 S_2 - T_1 S_1) \quad - \quad - \quad - \quad (3)$$

At constant temperature and pressure this equation 3 becomes

$$G_2 - G_1 = E_2 - E_1 + P(V_2 - V_1) - T(S_2 - S_1) \quad - \quad - \quad - \quad (4)$$

$$\text{or } \Delta G = \Delta E + p \Delta V - T \Delta S \quad - \quad - \quad - \quad (5)$$

Now from the first law $\Delta E = Q - W$

$$= Q_{rev} - W_{max} \text{ (for a reversible process)} \quad - \quad - \quad - \quad (6)$$

Since $\Delta S = Q_{rev}/T$, $Q_{rev} = T\Delta S$ and $\Delta E = T\Delta S - W_{max}$, we have

$$\Delta G = T\Delta S - W_{max}, + P\Delta V - T\Delta S \qquad - \quad - \quad - \qquad (7)$$

$$= - W_{max} + P\Delta V$$

which we may write as

$$- \Delta G = W_{max} - P\Delta V. \qquad - \quad - \quad - \qquad (8)$$

This equation (8) helps us to understand the meaning of free energy change. When the temperature and pressure are constant the decrease in free energy is equal to the maximum work done in the process other than the pressure - volume - work, which is the work done in displacing the environment . This is called the maximum work or net useful work. For a chemical reaction this can be the electrical work that can be obtained from it. For example when zinc is added to a solution of copper sulphate, copper is precipitated and heat is liberated but no work is done. However, if the same reaction is carried out in the galvanic cell, useful electrical work can be obtained.

3.11 GAS A CRITERION FOR EQUILLIBRIUM AND SPONTANEOUS CHANGE

We start with the equation,

$$G = H - TS = E + PV - TS$$

Differentiating we get

$$dG = dE + PdV + VdP - TdS - SdT$$

$dE = q - W = q - PdV$, if only pressure-volume work is involved.
Substituting

$$dG = q - TdS.$$

$dS = q_{rev}/T$ or $TdS = q_{rev}$ where q_{rev} is the heat absorbed when the process is carried out reversibly.

Hence, $dG = q - q_{rev}$

Here q is the heat absorbed in the actual process and q_{rev} is the heat absorbed had the process taken place reversibly.

For a reversible process $q = q_{rev}$ and $dG = 0$

For an irreversible process $q < q_{rev}$ and $dG < 0$.

Since all spontaneous processes are irreversible, the free energy change should decrease in a spontaneous process and we may state that all natural processes proceed in the direction in which free energy decreases. When the free energy reaches a minimum, there is no further tendency to change, the system is at equillibrium and $dG = 0$. Since G is a function of state we can replace dG by ΔG and write

$\Delta G = 0$ for equilibrium

$\Delta G < 0$ for spontaneous change.

The appartus consists of a tube in which a porous plug divides a gas into two regions of different pressures P_1 and P_2 which are maintained constant by two movable pistons. The tube, the porous plug and the pistons are made of perfect thermal insulating material so that any process in the tube can be considered adiabatic. A gas of volume V at pressure P_2 is slowly forced through the barrier by the piston. As it posses through the porous barrier the gas expands against a constant pressure P_2 and fills the volume V_2 (figure 1.11). The work done on the gas is P_1V_1 and that done by the gas is P_2V_2. Net work done by the gas is $P_2V_2 - P_1V_1$.

As the process is adiabatic Q=0

$\Delta E = -W = -(P_2V_2 - P_1V_1) = 0$ for real or ideal gases?

$E_2 - E_1 = P_1V_1 - P_2V_2$

$E_2 + P_2V_2 = E_1 + P_1V_1$

or $\Delta H = 0$

The heat content of the gas is constant in this free expansion of a gas.

For real gases ΔE will not be zero in expansion and to compensate for this the temperature must change. Thermometers placed on either side of the porous barrier showed a difference $T_2 - T_1$. At ordinary temperature and pressure all gases except hydrogen and helium have been found to show a cooling effecting in such a free expansion.

This change in temperature in the adiabatic expansion of a gas through a porous plug (or throttle) is called Joule Thomson effect.

The change in temperature $T_2 - T_1$ depends upon change in pressure $P_2 - P_1$. The ratio $\frac{dT}{dP}$ called the Joule-Thomson coefficient and is a measure of deviation from ideal behaviou It is givne by the symbol m. Its value can be found by determining ΔT, ie, $T_2 - T_1$ for a series of values of ΔP, ie, $P_2 - P_1$.

and obtaining the limiting value of $\dfrac{T_2 - T}{P_2 - P_1}$ as $P_2 - P_1$ approaches zero.

In the expression $\Delta T/\Delta P$, ΔP is always negative since in the expansion of a gas $P_2 < P_1$. If m is positive then ΔT will also be negative and there should be cooling on expansion. If m is negative, then ΔT must be positive, resulting in a warming of the gas upon expansion. The temperature at which there is neither heating nor cooling in Joule Thomson expansion. $\mu = 0$ is called the inversion temperature of the gas. For most gases ordinary temperatures are already below their inversion temperatures, hence they show cooling in Joule- Thomson expansion. The inversion temperatures of hydrogen and helium are much lower than ordinary temperatures and hence they show warming in expansion. However, if they are cooled to temperatures below their iversion temperatures they would also show cooling in such expansion.

This cooling in Joule-Thomson effect is made use of in the liquefaction of gases. The gas cooled in the free expansion of a gas is used to precool the gas before expansion. By repeating the process a number of times, the gas finally liquefies on expansion.

1.17 SUMMARY

Zeroth and first law of thermodynamics are discussed in this unit. First law of thermodynamics states that energy can neither be created nor destroyed. This law is also called the law of conservation of energy. E is a state function whereas Q and W are not.

By applying the first law, relationships are derived between the observable properties of gases under isothermal and adiabatic conditions. Heat capacities of gases are expressed in thermodynamic equations. Thermodynamic criterian of a perfect gas is, its internal energy should not chnage with the change of volume at constant temperature. An attempt has been made in this the unit to study the behaviour of real gases by the application of Joule-Thomson experiment.

1.18 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines.

1. The equation Q= $\Delta E + P \ \Delta V$ represents the first law of ther modynamics. What form would it assumes under (a) constant volume (b) constant pressure (c) isothermal conditions (d) adiabatic conditions?

2. Define the term reversible process and give one example (other than expansion of gases).

3. Derive an expression for the work done in an isothermal reversible expansion of a gas

4. Explian why a gas becomes warmer in an adiabatic compression and cooler in adiabatic expansion.

5. Give the thermodynamics criterion of a perfect gas.

II Answer the following in 30 lines.

1. Give the different forms in which the first law of thermodynamics can be exressed. Explain their significance. Do you consider evolution of energy in nuclear fission a violation of the first law?

2. Describe the experiment for Joule-Thomson effect. Why do some gases show warming in Joule-Thomson expansion. Explain how cooling in Joule-Thomson effect useful in the liquefaction of gases.

III Solve the following Problems.

1. In the expansion of a gas against constant pressure of atmospheres, its volume increases by 5 litres. Calculate the work done in this process in the following units (i) litre atmospheres (ii) ergs (iii) calories.

2. When one mole of zinc is dissolved in dilute HCl at 25_{o}c, the hydrogen gas evolved pushes the atmosphere above it. Calculate the work done in this process.

3. Find the amount of heat necessary to heat 5g of Argon from 0° to 25°c at constant volume and at constant pressure (Molar heat capacity C_v of a gas = 3 cals/mole^{1}; degree)

4. One mole of an ideal gas (C_v = 5 cal mole^{-1} degree^{-1}) at S.T.P. is heated to twice its initial temperature. Calculate Δ E and Δ H in this process. (1365 cals, 1911 cals)

5. One mole ofan ideal gas expands reversibly at constant temperature 0^0 c from 2 atmosphere pressure to one atmosphere. Calculate W, Δ E and Q in this change.

6. Calculate the minimum work that must be done at 25^0 c Tt on 2 moles of CO to compress it from a volume of 20 litres to a volume 1.0 litre. (Hint: Minimum work is done in isothermal reversible compression).

Check your progress -2

What is the relation between free energy and spontaneous processes?

3.12 FREE ENERGY CHANGE OF CHEMICAL REACTIONS

The free energy change equation is written

$$\Delta G = \Delta H - T \Delta S$$

For a chemical reaction ΔH is the heat of reaction. It is negative for exothermic reactions and positive for endothermic reactions. ΔG and ΔS are the differences in the values of products and reactants. For a reaction to proceed spontaneously ΔG of the reaction must be negative. This is possible under three conditions.

ΔH is negative ΔS is positive

ΔH is negative ΔS is negative but $T\Delta S < \Delta H$.

ΔH is positive ΔS is positive but $T \Delta S > \Delta H$.

Entropy values do not varry significantly from molecule so that ΔS values are usually small. Hence, at ordinary temperatures $T \Delta S$ values can never be expected to be greater than ΔH values. Hence, for most reactions at ordinary temperatures the sign of ΔH alone decides the direction of the reaction. This means that a reaction is possible if it is exothermic. Examples of exothermic reaction with negative ΔG values are many,

$H_2 + {}^1/_2 O_2 = H_2O\,(1)\ \Delta H - 68.3$ k. cal, $\Delta G = 56.7$ k. cals.

$CCl_4\,(g) + 2H_2O\,(g) = CO_2\,(g) + 4HCl\,(g)$

$\Delta H = 41.2$ k. cals, $\Delta G = 61.2$ k. cals.

Endothermic reactions are not favoured at ordinary temperatures, but at high temperature the product $T \Delta S$ may exceed ΔH to make ΔG negative.
An example for the reaction

$Ca\,CO_3 + (S) \rightleftharpoons CaO(S) + CO_2(g)$

$\Delta H = 42.5$ k. cals, $\Delta S = 38.36$ Cals $= 0.0384$ k Cals.

At room temperature $T \Delta S = 298 \times 0.03841 = 11.4$ k, Cals

$\Delta G = \Delta H - T \Delta S = 42.5 - 11.4 = 31.1$ k. Cals.

BLOCK - 2

ELECTRO-CHEMISTRY

This Block deals with the interaction of electricity with matter. In the interaction electrical energy gets converted into chemical energy. Substances also produce electricity and undergo chemical changes. Here chemical energy gets converted into electrical energy. Substances which conduct electricity through them without undergoing any change are called electronic conductors (metals). If they Undergo chemical changes, they are called electrolytic conductors. These substances are electrolytes. They conduct elctricity by the migration of ions to electrodes. Therefore they function as conductors either in the molten state or in the aqueous solution where mobility is possible for ions.

electrolytic conductors or **electrolytes.** Example of the first type are solid and molten metals and certain solid salts (cupric sulphide and cadimum sulphide). Fused salts and solutions of acids, bases and salts are the examples of the second type. Current flow in electrolytic conductors is accompanie by chemical changes at the electrodes. These changes depend on the characteristics of chemical substances undergoing electrolysis and the electrodes.

4.3 THE PHENOMENON OF ELECTROLYSIS

When an electric current is passed through an electrolytic conductor, the transport of matter takes place. This can be illustrated by an example. If two plantinum wires attached to a source of EMF i.e. battery are immersed in a dilute solution of an acid in water, bubbles of hydrogen and oxygen are evolved at the platinum wires. Instead, if the platinum wires are placed in a solution of salt of copper or silver the corresponding metal is deposited at one of the wires instead of hydrogen. This phenomenon is referred to as electrolysis. This was first studied by M. Faraday in 1832-33. As per the nomenclature used by Faraday, the platinum wires are referred to as electrodes, the anode and cathode depending on the fact that current is brought into and out of the electrolytic solution at these electrodes. By convention, anode is the one attached to the positive pole of the battery and the cathode is that attached to the negative pole. During electrolysis of aqueous solutions of electrolytes. The hydrogen gas or as the metal case may be obtained at the cathode and oxygen gas in general appears at the anode, provided the electrode material is not attacked. It was assumed by Faraday that the flow of current through an electrolyte was associated with the movement of charged particles. Those carrying positve charge and moving towards the cathode are referred to as cations and those carrying negative charge and moving in the opposite direction towards anode are called anions. On reaching the electrodes, the ions are supposed to have their charges neutralised and deposited as neutral atoms or molecules.

4.5. FARADAY'S LAWS OF ELECTROLYSIS

The process of current passage through an electrolytec with all the accompanying chemical and migratory changes is called electrolysis the mechanism of electrolysis can be described as follows :

> Electrons enter and leave the solution through chemical changes at the electrodes and it is also known that the number of electrons that pass through the solution and leave it, is equal to the number that enter. Taking these facts into account 'Faraday has enunciated the laws of electrolysis which give the quantitative relatonships between the quantity of electricity passing through an electrolyte and the amount of chemical change occuring at the electrodes.

i) The amount of chemical decomposition produced by a current, that is the amopunt of any substance deposited or dissolved atain appropriate electrode is proportional to the quantity of electricity passing through the solution.

ii) The amounts of different substances deposited or dissolved by the same quantity of electricity are proportional to their chemical equivalent weights.

The first law is verified by allowing currents of different strength to pass different period of time through a given solution and determining the amount of material deposited at the cathode or dissolved from the anode. The quantity of electricity is equal to the product of the current strength and the time during which it is passed.

The second law is verified by allowing the same current to pass simultaneously through a series of solutions. The amounts ofchemical substance deposited at the cathodes or dissolved from anodes are proportional to the equivalent weights of the respective substances deposited or dissolved.

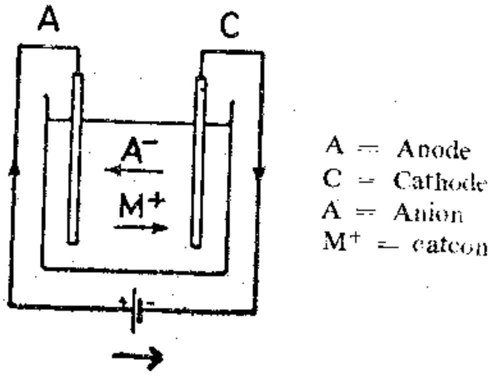

Fig. 4.1 Flow of current and electrons

4.6 ELECTROLYTIC CONDUCTANCE

T. Von Grotthuss made the first attempt to explain the principle of electrolysis. He suggested that molecules are oriented by the electric current in a way such that positive parts point towards the negative electrode and vice-versa. The electrodes then attract the ends of the chain thus, liberating the positive end of an end molecule at the negative electrode. Then a reorientation of the molecules takes place throughout the length of the chain. The process of splitting takes place once again with the liberation of the respective species at the electrodes. Objections were raised against this theory in view of the fact that, only small current strength is enough for the electrolysis whereas, large currents are needed to break a molecule into its component parts.

R. Clausius to overcome this, has suggested that the positive and negative parts of a molecule are not firmly held, and are capable of separating from each other for short intervals. These charged particles, (ions) are supposed to carry the current during the short period of their free existence, when these ions are removed at the electrodes. Fresh ions are obtained by the vigorous molecular vibration or molecular collisions. It was assumed by Clausius that only a small number of molecules are split into ions at any instant.

Van't Hoff observed large deviations in osmotic properties for electrolytic solutions. This led S. Arrhenius to propose a theory of electrolytic dissociations. He made the assumption that when an acid, base or salt is dissolved in water, a considerable portion of it dissociates spontaneously into postive and negative ions, that is

$$MA \rightleftharpoons M^+ + M^-$$

These ions are free to move independently, and are guided to the electrodes of opposite sign by the applied electric field. The proportion of molecules dissociating into ions was believed to vary with the concentration, and the degree of dissociation (i.e. the fraction of total molecules split up into ions) which was considered to approach unity at infinite dilution. In extremely dilute solutions, almost the whole of the acid, base or salt is disssociated into ions

Electrolytic solutions too, like metallic conductors, obey Ohm's law, except under abnormal condtions. If a potential difference E is applied to a conductor of resistance R, then by Ohm's law the current i which flows is

$$i = E/R \qquad (1)$$

From the above equation it can be said that the current flowing through a given conductor, under the influence of a constant electromotive force (E) is inversely prosortional to the resistance (R). The quantity $\left(\frac{1}{R}\right)$ is a measure of the conducting power and is called the couductance. It is expressed in rociprocal ohms ie.. ohm $^{-1}$, sometimes called 'mhos'. The resistance of any conductor varies direcly as its lenght (1 cm) and inversely as its area (a sq. cm): that is

$$R = \rho \frac{1}{a} \qquad (2)$$

Where ρ is a contant, the specific resistance or the resistivity, of the conducting material. Specific resistance, canthen, be defined as the resistance in ohms of specimen 1 cm in length and 1 sq cm in area of cross section. The specifif conductance, designated as k, of a given material is defined as the reciprocal of specific resistance i.e. 1/ ρ ohms^{-1} cm^{-1}.

$$R = \frac{1}{K} \times \frac{1}{a} \qquad (3)$$

$$k = \frac{1}{a\ .\ R} \qquad (4)$$

If the conductance of the solution is represented by C, then

$$C = \frac{1}{R} = \frac{ka}{1} \text{ ohms}^{-1} \qquad (5)$$

The conducting power of all the ions produced by 1 gram equivalent of an electrolyte at any particular concentration may be evaluated if it is imagined that two large parallel plates are set 1 cm apart and the whole of the solution containing 1 gram equivalent of the electrolyte is placed between them. The conductance of electolyte in the resulting system is called the equivalent of an electrolyte is dissolved in V c c of soultion, then the solution covers an area of V Sq.cm of the electrodes set 1 cm apart. It follows from equation 5 that

$$\lambda = \frac{k \times V}{l} \qquad \therefore a = v$$

$$l = 1$$

$$\text{or } \lambda = \frac{k \times 1000}{c} \qquad (6)$$

Where c is the concentration of the solution in equivalents per litre. The equivalent conducance is therefore defined as the product of specific conductance and the volume in c c containing one equivalent of the electrolyte. Molar conductance (μ) which is occasionally employed in conductance studies is defined similarly as the product of the specific conductance and the volume in cc containing 1 gram mole of the lectrolyte. For univanlent electrolytes λ and μ are identical, since the molecular weight and the equivalent weight are equal.

Check your progress - 1

What are electrolytes?

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4.7 MEASUREMENT OF ELECTROLYTIC CONDUCTANCE

In order to evaluate equivalent conductance, we have to make use of equation (6). Since this equation involves specific conductance (k), it is necessary to determine this. For each concentration of the solution, it is, therefore necessary to determine the specific conductance. Thedetermination of the specific conductance involves the measurement of resistance R and the ratio $\left(\frac{1}{a}\right)$ (equation 4)

The familiar wheatstone bridge is generally employed to measure the resisitance of the solution. Serious errors may however arise if a source of direct current is used in the determination because the liberation of gases during electrolysis at the electrodes increases the resistance of the solution. This is known as polarisation and opposes the passage of current. To overcome this onset of polarisation, an alternating current source is employed which reverses the current about thousand times per second, This results in the elimination of polarisation by the exact reversal of the reactions at the elctrodes. The balance point in the determination is therefore detected by the use of ear phones instead of a galvanometer used in the direct current experiments. Figure4.2 shows the arangement of the apparatus.

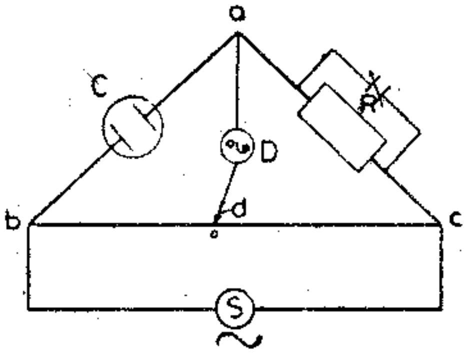

Fig: 4.2 Measurement of Resistance.

C is the conductivity cell containing the electrolyte and R is the variable standard resistance (a resistance box), S is the source of alternating currnet and D is the null detector. (ear-phones). The balancing point is obtained by moving the Jockey 'd' on the wire b c so that the sound in the ear phones at this point is minimum.The observation of mimimum sound in the ear phones is an indication of balance point. The resistance in the arms of the bridge are related by

$$\frac{C}{R} = \frac{bd}{dc} \qquad (7)$$

Originally, an induction coil was used by Kohlransch as a source of alternating current. But in recent years other alternate current sources are recommended. One among them is the electron tube oscillator.

Conductivity cells: Different types of cells are used for the measurement of resistance of electrolyte solutions. They normally have thick platinum electrodes coated with platimum black to reudce the effect of polarisation. The different types of cells are shown in Fig. 4. 3. The electrodes should be fixed firmly so that there is no variation in the distance between the electrodes during the course of the measurement.

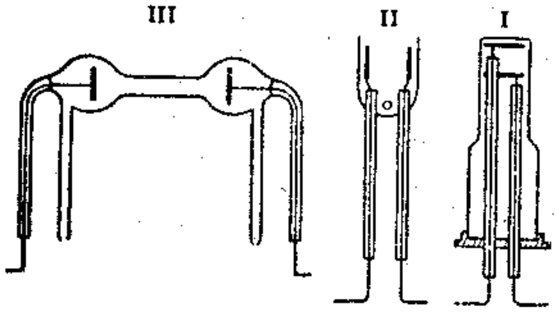

Fig. 4.3 Types of Conductance Cells

Specially pure water, called conductivity water should be used in all conductance measurements. This water is obtained by repeated distillation of deionized water containing a little alkaline KMn^0_4 in all glass apparatus. The water thus obtained, is stored in well steamed stoppered bottles. The specific conductance of conductivity water is of the order of 0.8 x 10^{-6} ohms cm $^{-16}$

4.8 CELL CONSTANT $\left(\frac{1}{a}\right)$

According to equation (4), the specific conductance (k) of an electrolyte solution is given by

$$k = \frac{1}{a \,.\, R}$$

It is seen from this equation that to calculate specific conductance trom the measured resistance (R), it is necessary to know the value of $\frac{1}{a}$ for the particular cell used in the determination. For a given cell '1' and 'a' are constant and the quantity 1/a is called the cell constant. '1' is the distasce between the two electrodes in the conductance cell and 'a' is the area of cross section of each electrode. To obtain the vaule of the cell consant, it is not necessary to determine '1' and'a' separately. The ratio is directly determined. For this a solution of known specific conductance is taken in the cell and its resistance R is measured. From the known specific conductance k and the resistances R measured, the cell constant $\left(\frac{1}{a}\right)$ is calculated from equation 4. For this purpose, potassium chloride solutins of various concentrations are made use of, since their specific conductances measured in cells of known dimensions are known accurately. A given solution of potassium chloride of specific conductance (k_o) is placed in the experimental cell and its resistance R_o is measured, then the cell constant $\left(\frac{1}{a}\right)$ is equal to $k_o R_o$. If R_o is the resistance of any other solutin in the same cell, its, specific conductance k is

$$k = \frac{1}{a} \,.\, \frac{1}{R} = \frac{K_o R_o}{R}$$

Check your progress - 2

What is cell constant?

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4.9 VARIATION OF EQUIVALENT CONDUCTANCE OF AN ELECTROLYTE WITH CONCENTRATION.

The specific conductance of a number of electrolytes is found to increase sharply with increase in concentration, while in some cases the increase in the specific conductance is gradual. In both cases, the increase in conductance can be related to the increase in th enumber of ions per unit volume of the soluton. In the former case, the increase in the number of ions is proportional to the concentration, but in the later it is not so due to partial ionisation.

A better insight into the behaviour of electroilytes was obtained by calculating the equivalent conductance (λ) of solutions of different concentrations making use of the equation (6). (Table 4.1 gives equivalent conductance of different electrolytes at 25° c.)

Table 4.1 Equivalent Conductance (25 C in ohms^{-1} cm^{2}

Conc. (N)	HC1	NaOH	KCl	NiSO$_4$	CH$_3$COOH
0.0005	422.7	246.0	147.8	118.7	--
0.001	421.4	245,.0	146.9	113,1	48.63
0.005	415.8	240.0	143.3	93.2	22.80
0.01	412.0	237.0	141.3	82.7	16,20
0.02	407.2	233.0	138.3	72.3	11.57
0.05	399.1	227.0	133,4	59.2	7.36
0.10	391.3	221.0	129.0	50.8	5.20

It is seen from the table that the equivalent conductance decreases with increase in concentration. It is observed that the change in equivalent conductance is not very large in the case of HC1)strong acid,) NaOH (strong base) and KC1 (salts). In the case of CH$_3$ COOH (weak acid), the equivalent conductance falls off rapidly as the ocnentration increased and further the conductance values are very low at about 0.1g equiv. per litre. The former type i.e. strong acids strong bases and many salts, are called **strong electrolytes** and the latter, mainly organic acids and bases, are known as **weak electrolytes.** It is also difficult to draw a sharp line between the two categories, since many substances show intermediate behaviour e.g. nickel sulphate. (NiSO$_4$)

The equivalent conductance of strong electrolytes approaches a limiting value with decrease in concentration. This limiting value is called the equivalent conductance at infinite dilution and is reprsented by and it is determined by the extrapolation method. Kohlrausch had shown that λ of strong electrolytes.

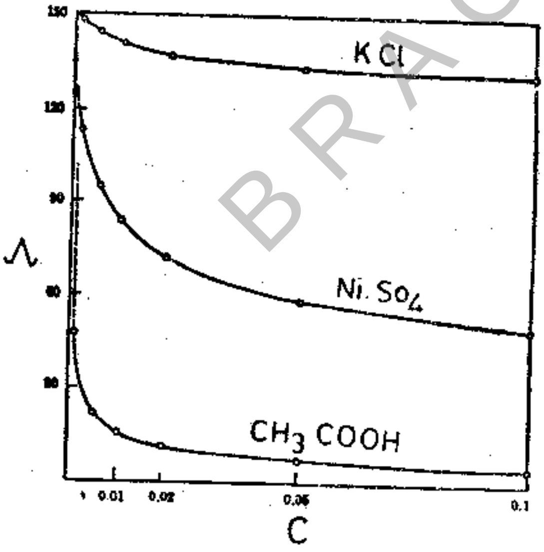

Fig: 4.4 Variation of equivalent conductance with concentration

varies linearly with concentration in dilute solutions and it can be represented by the equation.

$$\lambda = \lambda_o \quad \sqrt{C} \ - b \qquad (8)$$

Where b is a constant. In order to test the validity of the equation, plots are drawn between λ and $\sqrt{C}$. In the case of strong electrolytes like HCl and KCl, linear plots are obtained. From these linear plots, λ_o can be obtained by extrapolating the linear portion of the plots to $\sqrt{C} = O$. The intercept will be equal to . In an alternate method, the slope of the linear portion is calculated and λ_o solved by equation (8). This method can be adopted in the case of all strong elelctrolytes.

At the same time, this method cannot be used to evaluate in the case of weak electrolytes since the plots of λ Vs $\sqrt{C}$ for these do not approach linearity even in dilute solutions. They exhibit a very rapid increase in λ with decrease in concentration.

4.10 KOHLRAUSCH'S LAW OF INDEPENDENT MIGRATION OF IONS.

An alternate method is necessary to evaluate of weak electrolytes since it cannot be obtained by equation (8). λ_o for weak electrolytes is obtained by the application of Kohlrausch's lawof independent migration of ions.

Table 4.2: equivalent conductances at infinite dilution at 25°c.

Electrolyte	λ_o	Difference	Electrolyte	Differrence	λ_o
KCl	149.9		HCl	426.2	
LiBl	115.0	34.9	HNO_3	421.3	4.9
KNO_3	145.0		KCl	149.0	
$LiNO_3$	110.1	34.9	KNO_3	145.0	4.9
KOH	271.5		LiCl	115.0	
LiOH	236.7	34.8	$LiNO_3$	110.1	4.9

From the values of pairs of electrolytes given in table 4.2, it is noted that, irrespective of the nature of the common ion between potassium and lithium salts the difference between the equivalent conductances of these salts is the same and is equal to 34.9. Similar difference (4.9) is seen with respect to common cation and different anions given in the table. From this observation F. W. Kohlrausch,proposed tht each ion contributes a definite amount to the total conductance of the electrolyte, irrespective of the nature of the other ion. This is known as Kohlrausch's law of independent migration of ions. It is strictly true only at infinite dilution when there is no mutaul ionic interaction. The law may be expressed mathematically.

$$\lambda_o = \lambda_+ + \lambda_- \qquad (9)$$

Where λ_+ and λ_- are called the ion conductances at infinite dilution, of the cation and anion, respectively. They are the conductances contributed by each of the ions, independent of the other, to the total equivalent conductanc

In order to obtain the ion conductances let us consider another property of the ions, known as trasport number. Transport number of an ion is defined as the fraction of the total current carried by an ion. This number therefore represents as well the fraction of the total conductance due to the ion. Consequently λ_+ and λ_- are related to by the relations.

$$\lambda_+ = t^o + \lambda_o$$

$$\lambda_- = t^o + \lambda_o$$

t^o_+ and t^o_- being the transport numbers at infinite dilution obtained by extrapolation method. These equations permit us to calculate the ionic conductances from the trasport numbers and values of strong electrolytes. This calculation of ionic conducdances can be explained by the following example. Given that for hydrocholoric acid at 25°c is 426.16 and the transport number for hydrogen ion (t_+) is 0.819. We can calculate λ_{H+} and λ_{Cl}- as follows:

$$\lambda_{H+} = t_{H+} \;+\; \lambda_o = 0.821 \times 426.16 = 349.9$$

$$\lambda_{Ci=} = t_{Hu-} \;\lambda_o = 0.179 \times 426.16 = 76.3$$

In a similar way, the ionic conductances of other ions can be evaluated.

Since the ionic conductances at infinite dilution are available for a number of ions, it is possible to calculate the equivalent conductance at infinite dilution of a weak electrolyte using equation (9)

The equivalent conductance at infinite dilution of a weak acid can also be obtained in a different way. If we have to calculate the λ_o for acetic acid what we have to do is to determine for hydrochloric acid, sodium acetate and sodium chloride by the extrapolation method. This is possible since all the three are strong electrolytes. λ_o for acetic acid is thus obtained by adding λ_o (HC1) and λ_o (NaAc) and subtracting λ_o (NaC1) from the sum. Thus

$$\lambda_o \;(HC1) + (NaAC - \lambda_o \;(NaC1) = \lambda^+_H + \lambda_c + 1 - \lambda^+_{Na} + \lambda_{Ac-} - \lambda^+_{Na} = \lambda_{cl-}$$

$$= \lambda^+_H + \lambda_{Ac-}$$

$$= \lambda_o \;(HAC)$$

Worked examples

1. Specific conductance of a decinormal solution of potassium chloride at 18°c is 0.0112 ohm^{-1} cm^{1-} .The resistance of the solution was found to be55 ohms. What is the cell constant?

Resistance of the solution = 55 ohms

Specific conductance of KC1 solution k = 0.0112 ohm^{-1} cm^{-1}

$$k = \frac{1}{a} \times \frac{1}{R} \text{ where } \frac{1}{a} = \text{cell constant.}$$

Now, substituting the values of k and R given- We get 0.0112 =

$$\therefore \frac{1}{a} \quad (\text{cell constant}) = 0.0112 \times 55 = 0.616$$

2. The resistance of a 0.01 N electrolyte was found to be 210 ohms at 25°c. Calculate the equivalent conductance of the solution at 25°c, given that the cell constant is 0.88.a × 55

Resistance of the solution = 210 ohms

Cell constant = 0.88

Specific conductance $$k = \frac{1}{aR} \text{ where } \frac{1}{a} = \text{cell constant} = 0.88 \text{ and}$$

R = 210. ∴ Specific conductance of the solution $\frac{0.88}{210} = 4.19 \times 10^{-3}$.

Concentration of the solution = 0.01N

∴ Volume of the solution containing 1 gram equivalent of the electrolyte = 100,000 cc. (since $\frac{1}{100}$ gram equivalent is present in 1000 cc, the volume containing 1 gram equivalent is 100 x 1000 = 100,000). Equivalent conductance = k x V (V is the volume in cc containing 1 gram equvalent and k is the specific conductance)

$\therefore$ Equivalent conductance $= 4.19 \times 10^{-3} \times 100{,}000 \quad = 419\ \text{ohm}^{-1}\ \text{cm}^{+2}$

3. The equivalent conductances of sodiun acetate, hydrochloric acid and sodium chloride at infinite solution are 91.0, 426.16 and 126.45 $\text{ohm}^{-1}\ \text{cm}^{2}$ respectively at 25°c . Calculate the equivalent conductance of acetic acid at infinite dilution.

$$\lambda_0 = \text{CH3 COOH} = \lambda_o \text{H}_+ \; \lambda^\circ_{\text{CH3COO-}}$$

$$\lambda_o = \text{CH}_3\text{COONa} + \lambda_o \text{HCl} - \lambda^\circ \text{NaCl}$$

$$91.0 + 426.16 - 126\text{-}41 = 390.71 \ \text{ohm-1 cm2}$$

4.11 SUMMARY

Electrochemistry is the study of the interaction of electricity with the matter. Faraday's laws are the quantitative laws that relate the quantities of the substances that deposit and the amount of electricity passed through the solutions. Theory of electrolytic dissocation and electrolysis are explained in this unit. Substances which conduct electricity through them and undergo chemical changes are electrolytes. Those substances which dissociate more in water are called strong electrolytes. If their dissociation is less comparitively, they are called weak electrolytes.

For any type of electrolytes the specific conductainces decrease and equivalent conductances increase with dilution. It is possible to calculate values of strong clertrolytes by the graphical method. The values of weak electrolytes are calculated by the application of kohlrausch law.

4.12 MODEL EXAMINATION QUESTIONS

I **Answer each of the following in 10 lines.**

1. State Faraday's laws of electrolysis.
2. State and explain Kholrausch's law of independent mobility of ions.
3. Derive the relation between equivalent conductance.
4. How is cell constant of a conductance cell determined?
5. Discuss the applications of Kohlrausch's law.

II **Answer each of the following in 30 lines**

1. Explain the terms, conductance, specific conductance, cell constant, equivalent conductance and molar conductance. Derive the interrelationships between them.
2. Describe how, the equivalent conductance of ;an electrolyte is determined inthe laboratory.
3. Discuss the variation of equivalent conductance with concentration.

4.13 MODEL ANSWERS TOCHECK YOUR PROGRESS

1. Those substances which conduct electric current through them either in the molten state or in the form of aqueous solutions are called electrolytes.
2. The ratio between the distance (l) of the electrodes of a cell and the area (a) of cross section is called cell constant.

Auther: Dr. K. Lakshmi Narayana

UNIT - 5 GALVANIC CELLS AND ELECTRO MOTIVE FORCE (EMF)

Contents

5.1 AIMS AND OBJECTIVES

To know how chemical energy is converted into electrical energy in galvanic cells and to derive the relationship between the electromotive force and the extent of the chemical reaction and the thermodynamic functions.

Once you complete the study and understanding of various aspects of this unit, you must be able to:

- differentiate galvanic voltaic cells which consist two electrodes immersed in an electrolyte solution. Cells are classified as reversible and irreversible based on the nature of the cell reaction.
- explain the electromotive force (EMF) of cells and its measurement.
- relate electrical energy and free energy change of cell reaction
- account for the sign convention of electrode potentials.
- describe the utility of standard hydrogen electrode and subsidiary reference electrodes calomel and silver-silver chloride electrodes.

5.2 INTRODUCTION

In electrochemistry, we encounter two situations that involve electrochemical changes.

i) Situation where chemical changes are brought out a (passage of electric current). Such a process where chemical change is brought out by applied voltage is called electrolysis.

ii) Situations where chemical changes (EMF) help to produce electrical energy . Such changes occur in chemical cells.

In either of these situations, we require at least one electrolyte solution in which two metal rods are dipped. Chemical cells used to produce electrical energy are of two types a) Primary cells and b) Secondary cells.

a) **Primary cell:** A cell which produces electric energy (current) directly by a chemical reaction. Voltaic or galvanic cells are considered as primary cells.

b) **Seondary cell:** A cell whcih generates elecric energy (current) if a current is earlier passed through it for sometime from an external source of EMF. In the former process (the charging process) the elecrtic energy is converted into chemical energy chemical cells used to produce electrical energy and this chemical energy is converted in a latter process (discharging process) back into electrical energy. Thus it functions as a source of voltage in the latter process. Lead acumulators, and batterires are examples of secondary cells.

5.3 GALVANIC OR VOLTAIC CELLS (PRIMARY CLELS)

A galvanic or a voltaic cell consists essentially of two electrodes combined in such manner that when they are connected by a conducting material, for example, a metal wire, an electric current flows through it. Each electrode, in general, involves an electronic (metal rod) conductor and an electrolytic conductor in contact with each other. There exists a potential difference called electrode potential at the surface of separation between the metal and the solution. If there is no other potential difference in the cell, the electromotive force (EMF) of the cell is taken as equal to the algebric sum of the electorde potentials, due allowance being made with respect to the sign of each electrode potential. During the operation of a voltaic cell a chemical reaction takes place at each electrode, and it is free energy of this reaction that provides the electrical energy of the cell. In general there will be an overall chemical reaction when we take into consideration all the processes occuring in the cell. Such a cell is referred to as a chemical cell. In other type of cells the reaction occuring at one electrode is exactly reversed at the other, but there may be a net change of free energy because of a difference in concentration of one or other of the reactants concerned at the two electrodes. Such cells are called concentration cells. The electrical energy arises in these cases from the energy change accompanying the transfer of the same material from one concentration to another.

Check your progress - 1.

Differentiate a galvanic cell from an electrolytic cell.

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5.4 REVERSIBLE AND IRREVERSIBLE CELLS.

Cells may further be classified into i) reversible and ii) irreversible cells. The first category of cells where no net flow of current takes place unless the two electrodes are connected is called reversible cells. The extent of chemical reaction occurring in such cells is proportional to the quantity of electricity passing in accordance with the Faraday's laws. A reverssible cell shall satisfy the following conditions.

i) When the cell is connected to an external source of EMF, exactly equal to that of the cell, no chemical reaction should occur within the cell.

ii) If the driving force is decreased by an infinitesimally small amount, then the current should flow from the cell to the external source.

iii) When the driving force is increased by an infinitesimally small amount, the current should flow from the external source to the cell.

If chemical reaction takes place at either electrodes even when there is no net flow of current, they are cell called irreversible cells. The following are the example of the two categories of cells.

The first type of cell illustrated by the Daniel cell, is made up of a zinc electrode dipped in zinc sulphate solution and copper electrode dipped in copper sulphate solution. The two solutions are usually separated by means of a porous partition. Neither metal is attacked until the electrodes are connected and a current is allowed to flow. This cell is an example of the reversible cell.

The second type cell consists of zinc and copper electrodes dipped in dil. sulphuric acid. The zinc electrode reacts with the acid spontaneously even if there is no passage of current. This type of cells, where there is spontaneous reaction, are examples of the irreversible cells.

It is necessary to relate the electrical energy produced in a galvanic cell thermodynamically to the process occuring in the cell. This can be done only when the cell behaves as a rversible one.

The Daniel cell, mentioned above, satisfies these requirements and so it is a reversible cell. It may be noted that galvanic cells are excepted to behave reverscbly only when the currents passing through are infinitesimally small, so that the system is always virtually at equilibrium.

5.5 REVERSIBLE ELECTRODES

The electrodes of a reversible cell are called reversible electrodes. There are three main types of reversible electrodes.

i) The first type of reversible electrode consists of a metal or non-metal in contact with the solution of its ions. zinc in zinc sulphate solution, copper in copper sulphate solution. Hydrogen gas in contact with hydrogenions, oxygen gas in contact with hydroxyl ions, and chlorine gas in contact with chloride ions are some examples. In the case of non metal electrodes, platinum or any other unattackable metal is generally used for electrical contacts. In these cases, the metal comes rapidly into equilibrium with the gases.

The reaction taking place in the reversible electrodes of the first kind can be written in the following manner. If the electrode material is a metal (M), the reaction can be written as follows:

$$M = M^+ + e$$

Where M^+ is corresponding ion of the metal and e indicates an electron. In the case of non metal electrodes, the reactions may be represented by the following examples.

$$\frac{1}{2}O_2 + H_2 + 2e = 2OH^-$$

$$Cl_2 + 2e = 2Cl^-$$

In the case of hydrogen electrode the reaction is similar to a metal, metal ion electrode, since hydrogen gives a positive ion i.e.

$$\frac{1}{2}H_2 = H^+ + e$$

ii) Reversible electrodes of the sencond type involve a metal and a sparingly soluble salt of this metal in contact with a solution of a soluble salt of the same anion. An example of this kind is the silversilver choloride. Electrode in contact with a solution of a soluble chloride like KC1. The elelctrode reaction cna be written as

$$AgC1\ (S) + e = Ag\ (S)\ + C1^-$$

The above reation is virtually equivalent to the cell reaction of a chlorine gas electrode except that the silver

$$\frac{1}{2}C1_2 + e = C1^-$$

chloride can be regarded as the source of chlorine. In fact the silver-silver chloride electrode is thermodynamically equivalent to a chlorine electrode with chlorine at a pressure equivalent to the dissociation pressure of the silver chloride into silver and chlorine at the experimental temperature. The other examples of the second kind of reversible electrodes are:

i) $Hg, Hg_2C1_2(s)$, KC1 Solution

ii) $Ag, Ag\ Br\ (S)$ HBr Solution

The electrodes of this kind are of great value in electrochemistry because they permit the ready establishment of an electrode reversible with respect to anions like (chloride, bromide, sulphate and oxalate, which could not be obtained in a direct manner.

iii) The third type of reversible electrode electrode consists of an unattackable metal, e.g; platinum or gold, immersed in a solution containing both oxidised and reduced species of an oxidation-reduction system e.g.

Sn^{4+} and S^{2+}

Fe^{3+} and Fe^{2+}

$Fe\ (CN)_6^{3-}$ and $Fe\ (CN)_6^{4-}$

The unattackable metal serves as the conductor for making electrical contact. The oxidised and reduced states need not be ionic always. For example, in a system consisting of quinone and hydroquinone in presence of hydrogen ions quinone is the oxidised form, while hydroquinone is the reduced form. This also constitutes an electrode of the third type. These electrodes are known as oxidation-reduction electrodes. These electrodes are represented as

a) $Pt/Sn^{4+}, Sn^{2+}$

b) $Pt/Fe^{3+}, Fe^{2+}$

The electrode reactions are written as

$$Sn^{4+} + 2e = Sn^{2+}$$

$$Fe^{3+} + e = Fe^{2+}$$

In order that the electrode may behave reversibly, it is essential that the system contains both oxidised and reduced states.

Since a reversible electrode always involves an oxidised and reduced state using the terms oxidised and reduced in the broadest sense, all the reactions tking place at an electrode may be considered as an oxidation reduction reaction in the most general sense. So the reaction at any elelctrode may be written as general form, reduced form = oxidised form+ ne

Where n is the difference in the number of electrons of the oxidised and the reduced forms.

5.6 ELECTROMOTIVE FORCE (EMF) AND ITS MEASUREMENT

Electric current cannot flow from one point to another unless there is a potential difference between the two points. Hence the flow of electric from one electrode to another in a galvanic cell indicates that the two electrodes have different potentials. The difference of potential which causes the flow of current from one electrode to another in a galvanic cell indicates that the two electrodes have different potentials. The difference of potential which causes the flow of current from one electrode to another is called the electromotive force (EMF). As stated earlier, the EMF of a cell is equal to the algebraic sum of the two electrode potentials, due allowance being made to the sign of the electrode potential.

The EMF of a cell cannot be measured by directly connecting the cell terminals to a voltmeter. It is because during such a measurement some current is drawn from the cell and a chemical reaction occurs in the cell to some extent. This brings a change in the concentration of the electrolytes and hence in the potential. Because of the flow of current, a part of the EMF is used to overcome the internal resistance of the cell. Because of these two reasons, the EMF of the cell given by the voltmeter will not correctly represent its voltage.

To overcome this difficulty the **Poggendrpff compensatin method** is used. This method has got the advantage of measuring the EMF of the cell on "open circuit" i.e, when it is producing no current. As mentioned earlier, the cell can be expected to behave reversibly only when it is produceing an infinitesimally small current and hence use of an open circuit is ideal one for determining the EMF of a reversible cell.

The device used for the measurement of EMF of galvanic cells is called the potentiometer. The experimental set up is given in fig. 5.1. It consists of storage battery B of a constant EMF whihc is much larger than the EMF of the cell to be measured.

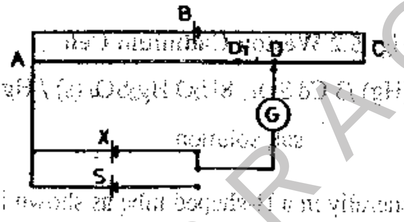

Fig: 5.1 Measurement of EMF

This is connected across the ends of a uniform conductor AC of high resistance. The cell X, whose EMF is being measured is connected through a galvanometer G to a sliding contact D which can be moved along AC. The position of D is adjusted until no current flows through the galvanometer, i.e., it gives no deflection. The potential fall between A and D due to the battery E is exactly compensated by the EMF of X, that is E_X. The cell X is replaced by a standard cell S of accurately known EMF (E_s). The sliding contact is readjusted until a point of balance (D_1) is reached. The fall of potential between A and D_1 is equal to E_s. Since conductor AB is supposed to be uniform, it follows that

$$\frac{E_X}{E_S} = \frac{AD}{AD_1}$$

$$E_X = E_S \times \frac{AD}{AD_1}$$

Since E_s is known, and AD and AD_1 can be measured, tho EMF (E_X) of the unknown cell can be evaluated.

In the simplest form of the potentiometer, AC is 1 meter long and the EMF of the Battery is 2 volts. Then the corresponding error in the evaluation of EMF is 0.001 volt.

5.7 STANDARD CELLS

The accuracy of the measurement of EMF depends on the accuracy of the standard cell used, The cell now widely used for the purpose is the Weston Standard cadmium cell. The characteristics of the cell are i) it is highly reproducible, ii) its EMF remains constant over long periods of time and iii) it has a small temperature coefficient. In order to retain constancy of EMF while in use, only very minute currents are drawn from the cell, as is actually done if the potentiometer is operated properly. One electrode of the cell is a 12.5 percent cadmium amalgam placed in a saturated solution of cadmium sulphate ($3CdSO_4 . 8H_2O$) and the other electrode consists of mercury and solid mercurous sulphate placed in the same cadmium sulphate solution, The cell is represented as follows:

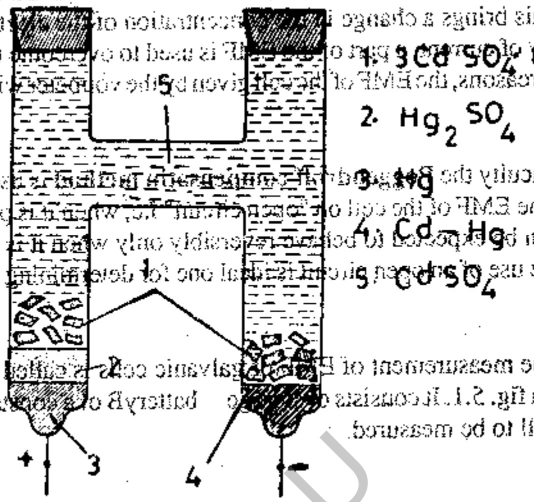

Fig: 5.2 Weston Cadmium Cell

$$12.5\%\ Cd(Hg) / 3\,CdSO_4,\ 8H_2O\ Hg_2SO_4 (s) / Hg$$

sat. solution

The Westorn cell is set up generally in a H-shaped tube as shown in Fig.5.2

The right hand limb contains cadmium amalgam and the left hand limb the mercury. The amalgam is covered with crystals of $3Cd\,SO_4\ 8H_2O$ and the mercury with mercurous sulphate and $3Cd\,SO_4\ 8H_2O$ crystals. The whole cell is filled with a saturated solution of cadmium sulphate. The EMF of the weston Cadmium cell is 1.018636 (international) absolute volts at 20°c and its temperature coefficient is 4×10^5 volt (The EMF decreases by this quantity for every degree rise of temperature). For ordinary purposes unsaturated Weston cell is used which makes use of a solution of cadmium sulphate saturated at 4°c and becomes unsaturated at normal temperature. The temperature coefficient is negligibly small and so its EMF can be taken as equal to 1.0186 volts.

5.8 FREE ENERGY CHANGE AND ELECTRICAL ENERGY

The second law of thermodynamics is applicable to reversible processes. Since the study here involves reversible cells, it is possible to apply thermodynamics to the results. If the EMF of a voltaic cell is E voltsand the process taking place in it is accompanied by the passage of n faradays, (nF coulombs) where F represents 96500 coulombs, the work done by the system in the cell is nFE volt-coulombs or Joules. If the cell is a reversible one, this work represents the maximum work, and it may be taken as equal to the change of free energy accompanying the cell reaction. Hence it follows that

$$\Delta G = -nFE \qquad (3)$$

Where ΔG is the increase in free energy for the process taking place in th ecell under consideration. According to the Gibbs-Helmholtz equation,

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_p \qquad (4)$$

Where ΔH is increase of heat content for the cell reaction. Introducing -nFE for ΔG in the eqation the result is

$$-nFE = \Delta H \quad -nFE\left(\frac{\partial E}{\partial T}\right)_p \qquad (5)$$

$$\Delta H = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_p \qquad (6)$$

$$= -nF\left[E - T\left(\frac{\partial E}{\partial T}\right)_p\right] \qquad (7)$$

It is seen from the equation that if the EM F. of the reversible cell E and its temperature coefficient, at $\partial E/\partial T$ constant pressure are known, it is possible to evaluate the heat change of the reaction occuring in the cell.

Further since $\Delta G = \Delta H - T\ \Delta S$ (from thermodynamics), the above measurements of E and dE can be used to calculate ΔS, the entropy change in the process. It can also be shown that

$$\Delta G = nF\left(\frac{\partial E}{\partial T}\right)_p$$

5.9 ELECTRODE POTENTIAL

Suppose the reaction occuring in a reversible cell is represented by the equation.

$$A + B \rightleftharpoons C + D$$

The decrease in free energy $= \Delta G$ accompanying the process is given by van't Hoff reaction isotherm.

$$-\Delta G = -\Delta G^0 - RT \text{ in } Qn \qquad (9)$$

Where $-\Delta G^0$ is the decrese in free energy accompanying the same process when all the reactants and the products are in their standardstates of unit activity and Qn stands for the reaction quotient of the acitvities of the products and the reaction. Substituting the value of Qn we have

$$-\Delta G = -\Delta G^0 - RT \ln \frac{a_C \times a_D}{a_A \times a_B} \qquad (10)$$

If E is the e.m.f. of the cell in volts and the cell reaction involves the passage of n Faradays, i.e, nF coulombs, the electrical work done by th ecell is nFE Volt coulombs, or joules. It is known that this elelctrical energy is equal to decrease in free energy. The above equation can be written as

$$nFE = \Delta G^0 - RT \ln \frac{a_C \times a_D}{a_A \times a_B} \qquad (11)$$

$$nFE = nFE - RT \ln \frac{a_C \times a_D}{a_A \times a_B} \qquad (12)$$

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_C \times a_D}{a_A \times a_B} \qquad (13)$$

Where E^0 is the EMF of the cell in which the activity or as an approximation the concentration of each reactant and each resultant of the cell reaction is equal to unity. E^0 is known as the standard EMF of the cell. The above equation is often referred as Nernst equation. Nernst equation can be written in the following form by replacing the activity terms by the concentration terms as an approximation.

$$E = E^0 - \frac{RT}{nF} \ln \frac{C_C \times C_D}{C_A \times C_B} \qquad (14)$$

This equation helps us to calculate the EMF of the cell when the concentratins of the reactants and products of the cell reaciton and E are known.

We know that the reversible cells are made up of two reversible electrodes.The over all cell reaction and in turn the EMF of the cell can be split up into two, one for each electrode. This can be explained by the following example,

The cell reaction for the cell

$H_2/HCl\ (c),\ AgCl\ (s)\ /Ag$

is $\frac{1}{2}H_2 + AgCl\ (s) = H^+ + Cl^- + Ag\ (s)$

for the passage of one faraday. Then Nernst equation takes the form

$$E = E^0 - \frac{RT}{F} \ln \frac{a_{H^+} \times a_{Cl^-} \times a_{Ag}}{a^{1/2}_{H_2} \times a_{AgCl}} \qquad (15)$$

We can write the individual electrode reactions as

1) $\frac{1}{2}H_2 = H^+ + e$

and 2) $AgCl\ (s) + e = Ag + Cl^-$

Based on these two reactions equation (15) can be aplit up as

$$E = \left[E_1^o - \frac{RT}{F} \ln \frac{a_{H^+}}{a^{\frac{1}{2}}_{H_2}}\right] + \left[E_2^o - \frac{RT}{F} \ln \frac{a_{Ag} \times a_{Cl^-}}{a_{AgCl}}\right] \qquad (16)$$

$$\therefore E_1 = E_1^o - \frac{RT}{F} \ln \frac{a_{H^+}}{a^{\frac{1}{2}}_{H_2}} \qquad (17)$$

$$E_2 = E_2^o - \frac{RT}{F} \ln \frac{a_{Ag} \times a_{Cl^-}}{A_{AgCl}} \qquad (18)$$

Where E_1 and E_2 are the single electrode potentials.

The standard state of hydrogen is the gas at 1 atmosphere pressure and the standard states of silver and silver chloride are the solids, it therefore follows that a_{H_2} and a_{AgCl} are unity, so equations 17 and 18 are written as

$$E_1 = E_{H_2/H^+} = E_1^o - \frac{RT}{F} \ln a_{H^+} \qquad (19)$$

$$E_2 = E_{Ag/AgCl} = E_2^o - \frac{RT}{F} \ln a_{Cl^-} \qquad (20)$$

Where E^o terms are the standard potentials of H_2/H^+ and $Ag/AgCl,\ Cl^-$ electrodes, It is seen, therefore, that in the cell under consideration the potential of each electrode depends only on the activity of one ionic species apart from the standard potential of the system.

A general expression for an electrode potential can be obtianed by writting the general elelctrode reaction as

$$\text{Reduced State} \rightleftharpoons \text{oxidised state} + ne$$

Where n is th enumber of electrons by which the reduced state and the oxidised state differt. The electrode potential is given by

$$E = Eo - \frac{RT}{nF} n \frac{[\text{Oxidised State}]}{[\text{Reduced State}]}$$

Where E° is the standard potential

Thus if the electrode is formed from a metal M of valency Z_+, revesible with repsect to M^{Z+} ions, the electrode reaction is written as

$$M = M^{Z+} + Ze$$

The equation for the potential is written as

$$E = E^\circ - \frac{RT}{Z^+F} In \frac{a_M^{Z+}}{a_M} \qquad (21)$$

Where a_M, a_M^{Z+} ar erespectively the activities of the solid metal M and M^{Z+}. The cations M^{Z+} M and M in solution are in equillibrium with each other. By convention the solid state of the metal is taken as the standard state (unit activity) for an electrode consisting of the pure metal, therefore, a_M may be replaced by unity. The equation (21) is then written as

$$E = E^\circ - \frac{RT}{Z^-F} In \frac{a_A}{a_A^{Z-}} \qquad (22)$$

Similarly for an electrode involving a non-metal A, reversible with its anions A^{Z-}, the electrode reaction is

$$A^{Z-} \rightleftharpoons A + Ze$$

The equation for the electrode potential is

$$E = E^\circ - \frac{RT}{ZF} In \frac{a_A^{Z-}}{a_A} \qquad (23)$$

As before, the actiivity a_A. of A is taken as unity. The equation for electrode potential is written as

$$E = E^\circ - \frac{RT}{ZF} \; In \; \frac{1}{a_A^{Z-}} \qquad (24)$$

Thus the magnitude of tendency of a substance to lose or gain electrons when it is in contact with its ions is expressed by the electrode potential. Since the tendency to lose electrons means the tendency to get oxidised, the potential is called oxidation potnetial. Similarly the tendency to gain electrons means the tendecy to get reduced, and hence the potential is called reduction potential. It may be noted, that the reduction potential is the reverse of the oxidation and vice versa.

Check your progress - 2

Why iron cannot precipitate zinc from the aqueous solution of a zinc salt?

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5.10 STANDARD HYDROGEN ELECTRODE

It is not possible to determine experimentally the potential of a single electrode, It is only the difference of potentials between two electrodes that we can measure by combining them to give a complete cell. By arbitrarily fixing the potential of one elctrode as zero, it is therefore possibleto assign numerical values to potentials of the each other electrode. Accordignly, the potential of a reversible hydrogen electrode in which the H gas at atmospheric pressure is bubbled through a solution of hydrogen ions at unit activity, has been fixed as zero. This electrode is known hydrogen electrode and is represented as

$$Pt, H_2 (1 \text{ atm}) / H^+ (a = 1)$$

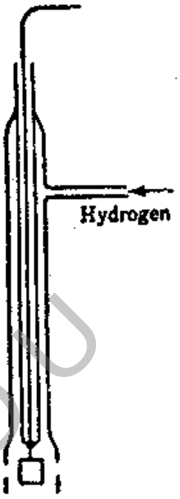

Fig: 5.3 Hydrogen Electrode

where Pt is Platinum used for getting the electrical contact. The potentials of all other single electrodes are generally expressed on this hydrogen scale. If it is required to find the electrode potential, of, say zinc electrode, in a solution of zinc sulphate (i.e, Zn/Zn^{++}) it is needed to combine it with a standard hydrogen electrode and construct the cell.

$$Zn/Zn^{++} \text{ solution} // H^+ (a = 1) / H_2 (1 \text{ atm.}) Pt$$

The EMF of this cell, determined potentiometrically, is equal to the potential of the Zinc electrode, since the potential of the standard hydrogen electrode is zero. In this cell, oxidation takes place at the zinc elecrode and reduction at the hydrogen electrode as shown below.

$$Zn (s) \rightleftharpoons Zn^{2+} + 2e$$

$$2H^+ + 2e \rightleftharpoons H_2 (g)$$

The net cell reaction is

$$Zn (s) + 2H^+ \rightleftharpoons Zn^{2+} + H_2 (g)$$

5.11 SIGN CONVENTION OF ELECTRODE POTENTIAL

According to one convention the electode potential is given a postive sign if the electrode reaction invovles oxidation when connected to the standard hydrogen electrode and a negative sign if the electrode reaction involves reduction reaction when connected to standard hydrogen elelctrode whose potential is arbitrarily taken as zero. This can be explained by the following examples.

i) When copper electrode is connected to the standard hydrogen electrode, reduction takes place at the copper electrode. The electrode reactions are:

At Hydrogen electrode $H^2 (g) \rightleftharpoons 2H^+ + 2e$ Oxidation
At Copper elelctrode $Cu^{++} + 2e \rightleftharpoons Cu$ reduction

Hence according to the above convention, the potential of copper eletrode is taken as negative.

However, if the zinc elelctrode is connected to the standard hydrogen electrode, oxidation takes place at the zinc eleltrode. The reactions that take place at the electrodes are:

At zinc electrodes $Zn (s) \rightleftharpoons Zn^{++} + 2e$.
at hydrogen electrode $2H^+ + 2e \rightleftharpoons H^2$ (g) 1 atm.

The potential of the zinc electrode is therefore taken as positive. The standard potential (E°) of any substance (electrode) is the potential of the electrode where the substance is in equillibrium with its ions in solution present at unit activity.

In a cell the electrode reactions are written as oxidation reations. The electrode with more postive potential is represented as left hand electrode and the one with negative (less positive) potnetial as the right hand electrode. The overall cell reaction is obtained by subtracting the right hand electrode reaction from that of the left hand electrode reaction. In a similar way the standard potential of the cell (E° cell) is given as the difference between the standard oxidation potentials of the right hand electrode and the left hand electrode.

$$Zn/Zn^{++} // Cu^{++} / Cu$$

$$E^\circ = E^\circ_{Zn/Zn++} - E^\circ_{cu^{++}/Cu}$$

5.12 SECONDARY REFERENCE ELECTRODES

The standard hydrogen electrodes as mentioned earlier is used as a reference electrode for determining the single electrode potentials. But it is not always convenient to set up this electrode on account of difficulties involved in maintaining the activity of hydrogen ions at unity and in keeping the pressure of the gas uniformly at one atmosphere. Hydrogen electrode also gets poisoned if there are traces of impurities in the gas. To overcome these difficulties, other electrodes, called secondary reference electrodes have been employed. Two such electrodes in common use are i) calomel electrode and ii) slver-silver chloride electrode.

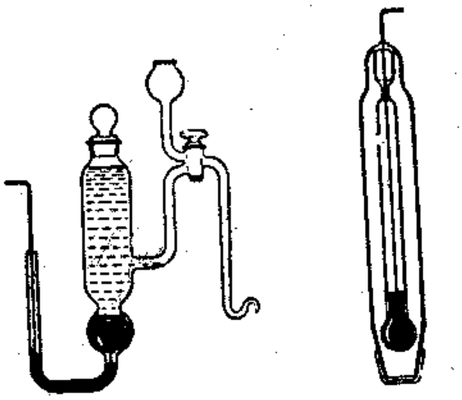

Fig: 5.4 Secondary Reference Electrodes (Calomel electrodes)

i) **Calomel Electrode:** This is the commonly used reference electrode. It consists of mercury, solid mercurous chloride, and a solution of potassium chloride of a definite concentration. The electrode reaction that takes place is

$$Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+} + 2Cl^-$$
$$Hg_2^{2+}\ 2e \rightleftharpoons 2Hg\,(l)$$
$$\overline{Hg_2Cl_2\,(s) + 2e \rightleftharpoons 2\,Hg + 2\,Cl}$$

The electrode is therefore treated as an electrode reversible with choride ions. The potential hence depends on the concentration of the chloride ions. The potential of this electrode therefore varies with the concentration of potassium chloride solution.

Three different concentrations of potassium chloride are generally employed in constructing the electrode. These are 0.1. N, . 0 N and a saturated solution. The following potentials are obtained for the three calomel electrodes on the hydrogen scale.

0.1 N KCl, Hg_2Cl_2 (s), Hg	- 0. 3338 V Vs SHE
1.0 N KCl, Hg_2Cl_2 (s), Hg	- 0. 2800 V Vs SHE
Saturated KCl, Hg_2Cl_2 (s), Hg	- 0.2415 V Vs SHE

ii) **Silver - Silver Chloride electrode.**

In recent years, the silver, silver chloride electrode has been extensively used as reference electrode for accurate work. It is normally obtained by the following method. A small sheet or short coil of platinum is first coated with silver by electrolysis of argentocyanide solution. This coated silver is partly converted into silver chloride by using it as an anode and electrolysis is carried out in a chloride solution. The electrode thus prepared is kept in a solution of KCl or HCl of unit activity. The elctrode is represented as $(a = 1)\ Cl^-\ AgCl\,(s), Ag$. It is an electode reversible with respect to chloride ion. The standard potential of this electrode is - 0.2224 V on the hydrogen scale.

Fig. 5.5 Silver - Silver Chloride Elecrode

Worked Problems

1) Write the electrode reactions and cell reaction for the Daniel cell $Zn/ZnSO_4$ $//CuSO_4/Cu$

Solution: Let us consider that the reactions at the electrodes as oxidation reactions, we first write the right hand electrode reaction and then the left hand electrode reaction.

$Cu \rightleftharpoons Cu^{++} + 2e$ ii) Right hand electrodes.

$Zn \rightleftharpoons Zn^{++} + 2e$ i) Left hand electrodes.

The over all cell reaction is obtained by substracting (ii) from (i)

$Zn - Cu \rightleftharpoons Zn^{++} - Cu^{++}$

The over all cell reaction is

$Zn + Cu^{++} \rightleftharpoons Zn^{++} + Cu$

2) Calculate the standard EMF of the cell,

$Cd\ (s) / Cd^{++} \rightleftharpoons Cu^{++} / Cu\ (s)$

given that $E^{\circ}_{cd/cd++} = + 0.40$ V and $E^{\circ}_{cu++/cu} = - 0.34$ V

Solution: Write the cell reaction. According to convention, the standard EMF of the cell is equal to the difference in the standard potentials of the left hand electrode and the standard potential of the right hand elelctrode.

$$E^{\circ}_{cell} = E^{\circ}_{left\ hand} - E^{\circ}_{right\ hand}$$

$$E^{\circ}_{cell} = 0.40 - (- 0.34) = 0.74\ V$$

3) Calculate the standard EMF standard free energy change and the equillibrium onstant for the folowing reaction that takes place in a cell at 25°c

$$\frac{1}{2} Cu\ (s) + \frac{1}{2} Cl_2\ (g) = \frac{1}{2} Cu^{++} + Cl^-$$

Solution: The overall cell reaction can be split up into two half cell reactions (both as reduction reactions)

(i) $\frac{1}{2} Cl_2 + e = Cl^-$

(ii) $\frac{1}{2} Cu^{++} + e = cu$

The reaction (i) is considered as the reaction at the right hand electrode and (ii) as the reation at the left hand electrode on the basis of their potentials.

The standard EMF of the cell is the difference in standard potentials of the left hand and right hand electrodes.

From tables it is known that $E^{\circ}_{Cl2\ Cl-} = - 1.36$ and $E^{\circ}_{cu++/cu} = - 0.34$

$$E_o = - 0.34 - (- 1.36)$$

$\therefore E^{\circ}$ for the given reaction is 1.02 V.

Standard free energy change is givneby the equation $G^\circ = \Delta$ $-nFE^\circ$

If n the number of electrons involved in the reaction and F° the standard EMF are known, ΔG° can be calculated since F is equal to 96500 coulombs. In this reaction n = 1 and $E^\circ = 1.02$ V and so

$\Delta G^\circ = -1 \times 96500 \times 1.02$

$\Delta G^\circ = -98430$ Joules.

The equillibrium constant for the reaction is calculated making use the thermodynamic relationship between standard free energy change and the equillibrium constant K

i.e. $-\Delta G^\circ = RT \ln K$.

Since we got the value of ΔG° it is possible for us now to calculate K for the reaction, making use of the equation.

$$-\Delta G^\circ = RT \ln K = n FE^\circ$$

$$\ln K = \frac{nFE^\circ}{RT}$$

$$\text{or } \log K = \frac{nFE^\circ}{2.303\ RT}$$

In this n=1, F=96500, $E^\circ = 1.02$, R= 8.314 Joules nd T=273 + 25 = 298°. by substituting these values in the above equation we get

$$\log K = \frac{1 \times 96500 \times 1.02}{2.303 \times 8.314 \times 298}$$

$$= 17.2507$$

$$\therefore K = 1.781 \times 10^{17}$$

Thus the equilibrium constant for the given reaction = 1.781×10^{17}

5.13 SUMMARY

Galvanic cell is a device of converting chemical energy into electrical energy. These cells are two types called reversible and irreversible. EMF of a cell can be measured by Poggendorfis compensation method. Weston cell is a standard cell which gives constant EMF if considerable quantity of electricity is not drawn out from it. If the signs are changed oxidation potentials become reduction potentials. In order to develop a scale the potential of standard hydrogen electrode is taken as zero. EMF of a cell is the sum of the oxidation potential of anode (left side electrode) and the reduction potential of cathode) (right side electrode).

5.14 MODEL EXAMINATION QUESTIONS

I Answer each of the following in 10 lines

1. Explain the meaning of a reversible electrode.
2. How are reversible elelctrodes classified?
3. Discuss the principal underlying the sign conventions of elelctrode potentials.
4. Explain the meaning and construction of a standard Cell.
5. Obtain the relation between the free energy change and the EMF of a galvanic Cell.
6. Describe hydrogen electrode and silver-silver chloride elelctrode.
7. Write the cell reaction for the Daniel Cell.
8. Write a brief account of the construction of Calomel elecrode.

II **Answer each of the following in 30 lines**

1 Give an account of the reversible electrodes, reference electrodes add sign convention of electrode potentials.
2. How is single electrode potential of an electrode determined?
3. Derive the relation between the equillibrim constant of the Cell reaction and the EMF of the Cell.

5.15 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Galvanic cell is a mechanical device to convert chemical energy into electrical energy where as electrolytic cell is a device of converting electrical energy into chemical energy.

2. It is because the oxidation potential of zinc is more than the oxidation potential of iron.

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UNIT - 6 THEORIES OF ELECTROLYTIC CONDUCTANCE

Contents

6.1 AIMS AND OBJECTIVES

The main aim of this unit is to explain you different theories of electrolytic conductance and get at the expressions for the variation of equivalent conducatnace of strong electrolytes. After an intensive study and understanding the various aspects of this unit, you must be able to:

- explain Arrehenius theory of electrolytic dissociation which proposes that weak electrolytes are incompletely ionised at moderate concentrations is called degreee of ionisation. It reaches a limiting value of one at infinite dilution.
- find out the Ostwald's dilution law is an outcome of the application of Arrehenius theory and law of mass action to ionisation of weak electrolytes in solutions.
- account for the strong electrolytes abnormal conductance behaviour. They show an increase in equivalent conducatance with dilution even though they are completely ionized at moderate concentrations.
- bear in mind that the conductance behaviour of strong electrolytes is explained satisfactorily by Debye, Hickel and Onsager in their Interionic attraction theory.

6.2 INTRODUCTION

The behaviour of electrolytes is obtained on the basis of the variation of electrolytic conductance of electrolytic solutions with concentration. These results explain the reasons for failure of Ostwald's dilution law in the case of some electrolytes called strong electrolyte. These facts helped to develope the modern theories of strong electrolytes.

6.3 ARREHENIUS THEORY OF ELECTROLYTE DISSOCIATION

We have seen in 4.5 that the electrical conductance of electrolytes is due to the presence of charged particles, i.e. ions, in solutins of electrolytes. Let us now consider here the impornat postulates of the Arrhenius theory of electrolytic dissociation and their limitations.

i. Eletrolytes in aqueous solution undergo spontaneous dissociation into postiive and negative ions. This phenomenon or dissociation is called inoization.

ii. The degree of ionization or dissociation (defined as the fraction of the total electrolyte dissociated) is appreciable even at moderate concentrations and it further increases with dilution until at infinite dilution it approaches unity.

iii. At moderate concentrations, an equillibrium exists between the ions and the undissociated electrolyte (MA)

$$MA \rightleftharpoons M^+ + A^-$$

Since equal number of positive and negative ions are present in solution, it will be electrically neutral. On the basis of the degree of dissociation, Arrhenious, classified eletrolytes as strong and weak. If the degree of dissociation is great even at moderate concentrations, the electrolyte is said to be strong If the degree of dissociatin is low under the same conditions, it is called a weak electrolyte.

Arrhenious theory explains the following experimental facts:

a. The electric current in electrolysis is carried by the ions in solution and the ions lose their charges when they reach the appropriate electrodes during electrolysis.

b. The degree of dissociation of an electrolyte increases with dilution. In other words, the equilibrium between undissociated electrolyte and its ions, shifts more and more towards right on dilution.

$$MA \rightleftharpoons M^+ + A^-$$

This explains why the equivalent conductance increases with dilution and ultimately acquires a limiting value at infinite dilution. The electrolyte is assumed to be completely dissociated if the degree of dissocaition is unity. Therefore, at any other concentration when the value of the equivalent conductance is the degree of dissocaition (α) is given by the expression.

$$\alpha = \frac{\lambda_c}{\lambda_o} \quad \frac{\text{Equivalent conduction at a given concentration}}{\text{Equivalent conduction at infintie dilution}} \qquad (1)$$

c. Arrhenius theory offered, for the first time, a plausible expplanation for the abnormal behaviour of electorlytes in aqueous solution. while studying colligative properties, Van't Hoff observed that these electrolytes gave abnormal values for osmotic pressure and other colligative properties. The molecular weights calculated were always higher than the theoretical values. In order to correct this, Van't Hoff introduced the factor "i" and it is given by the expression

$$i = \frac{\text{Observed colligative property}}{\text{Calculated colligative property}}$$

Arrhenius put forth the argument that since the colligative property is dependent on the number of particles, (molecules or ions,) ~~it~~ is evident that a binary electrolyte, which is capable of dissociation, into a cation and an anion produces depression in freezing point or elevation of boiling point twice as much as that calculated from the equation for a single molecule. This expalins the limiting value of 2 obtained for "i" factor of binary electrolytes. The value of "i" changes depending on the number of ions produced by the dissociation of the electrolyte. Thus in the case of electrolytes like $BaCl_2$, Na_2SO_4 where 3 ions are obtained, the "i" factor takes a limiting value of 3.

d. It explains the concept of Ionic reactions. When a solution of alkali metal chloride or hydrochloric acid is mixed with a solution of silver nitrate, a white precipitate of silver chloride is obtained. Ethyl chloride, on the other hand does not give any such precipitate with silver nitrate. Ferrocyanide ion in potassium ferrocyanide is formed by the combination of four cyanide ions with a molecule of ferrous cyanide. The solution of potassium ferrocyanide gives neither reactions of ferrous ion nor of cyanide ion. The above facts are explained on the basis of formation of free chloride ions in the case of alkalimetal chloride due to ionisation of alkali metal chloride or HCl and absence of free chloride ions in the case of ethyl chloride due to non-ionization of ethyl chloride and absence of free ferrous or cyanide ions in the case of potassium ferrocyanide since ferrocyanide ion does not ionise.

e. It is well known that solutions of electrolytes with a common ion show similar chemical properties. For example, solutions of acids show the acidic properties and solutions of bases show the alkaline prosperties. This is be cause acids ionise in solutions to give hydrogen ions and bases ionise to give hgydroxhye ions. This is the basis for the Arrhenius concept of acids and bases. Similarly, the solutions of salts, either having the common cations or common anions, will show the same properties of the same cations or same anions.

f. The heats of neutralisation of all strong acids and strong bases are about 13.7 Kcal. It is therefore concluded that all strong acids HX, and strong bases MOH are completely dissociated into ions the respective ions

$$\begin{aligned} HX &\rightleftharpoons H^+ + X^- \\ MOH &\rightleftharpoons M^+ + OH^- \end{aligned}$$

and the neutralisation of strong acid by a strong base involves the same chemical reaction. i.e, the combinatin of hydrogen ions with the hydroxyl ions, to form undissociated water.

$$H^+ + OH^- \rightleftharpoons H_2O$$

The heat evolved is therefore the same. If the dissociation of the acid or base is not complete, then heat evolved in the neutralisation of waek acid with a strong base' or the reaction of a weak base with a strong acid will be less than that in the case of a strong acid and strong base.

Check your progress - 1

What is the relationship between degree of dissociation and equivalent conductances?

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6.4 OSTWALD'S DILUTION LAW

Let us recall what we have studied in Block 5. unit 30 of II year under the application of 'law of mass action' to ionic equilibrium.

Consider an eletrolyte MA, C moles of which are dissoloved per litre of an aqueous solution . Let (α) be its degree of dissocation. Then.

$$\begin{array}{ccc} MA & = & M^+ + A^- \\ C(1-\alpha) & & C\alpha \quad C\alpha \end{array} \qquad (3)$$

The equilibrium concentration of the undissociated electrolyte will be C (1-α) and the ocncentration of the ions M^+ and A^- will each be equal to Cα. Applying the law of mass action to the above equillibrium, we have

$$K = \frac{C^2\alpha^2}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \qquad (4)$$

Here K is called the dissociation constant.

The Ostwald's dilution law is verified by conductances method by substiuting $\frac{\lambda_o}{\lambda_o}$ fo r α. the law was found to hold good in the case of weak electrolytes, such as acetic acid and ammonium hydroxide only.

The law failed to hold good in the case of sdtrong electrolytes, such as sodium chloride, hydrochloric acid or sodium hydroxide.

6.5 BEHAVIOUR OF STRONG ELECTROLYTES

Strong electrolytes do not obey Ostwald's dilution law. But equivalent conductances increased with increase in dilution. eventhough the values of degree of dissociation obtained in freezing point depression method and in condutance method were fairly equal for uni-univalent electrolytes (NaCl) they were not at all so for bi-univalnnt and bi-bivalent electrolytes (e.g. $BaCL_2$, $MgSO_4$) Strong electrolytes, like KCl and NaOH are found to be good conductors of electricity even in the molten state. It indicates that the ionisation takes place in these cases even in the molten state (absence of water). X- ray analysis of crystals of these salts has shown that the solids consist of ions held together by electrostatic attraction. When the solids are brought into solution the ions will become free to conduct electricity. Similarly when the solid are melted, the ions will become free to conduct electricity and there is no possibility of undissociated elelctrolyte being present in these cases. As already stated earlier Arrhenius had assumed that increase in equivalent conductance with increase in dilution is due to increase in the number of ions. This as seen above, is not correct in the case of strong electrolytes since the strong electrolytes are present completely in the form of ions even in the solid state.

6.6 THEORIES OF STRONG ELECTROLYTES

In order to explain this anomalous behaviour of strong electrolytes, namely, increase in equivalent conducatance with dilution even though the electrolytes are completely ionized at high concentrations, and even in the solid state, various views have been expressed by different workers.

Sutherland (1906) suggested that since the number of ions remains unaltered the increase in conductance is due to the increase in ionic mobilities. The ionic mobilities increase partly due to the weakening of the interionic forces. Every ion is surrounded by a large concentration of ions of opposite sign. But this was not developed further until J.C. Ghose (1918) revived it. According to him, all the ions are not free to move owing to the influence of opposite electric charges, and only the mobile ions affect the conductance of the solution. In this way α represents the proportion of active or mobile ions of the electrolyte. Hehas derived an experssion of the form given below to account for the behaviour of strong electrolytes.

$$3\sqrt{V} \log \alpha = K$$

This was obeyed by uni-univalent electrolytes. This theory of Ghosh was found not of much use to explain the behaviour of all strong electrolytes. This theory was however later developed by Debye and Huckel (1923) and then by Onsager (1926)

6.7 DEBYE-HUCKEL-ONSAGER THEORY OF STRONG ELECTROLYTES OR THE INTERIONIC ATTRACTION THEORY.

The conductance of a solution of an electrolyte depends on two factors. These are (i) the number of ions and (ii) their speeds in the solution. The change in equivalent conductance is generally ascribed to the change in the number of ions on dilution. This assumption implies that the speed of the ions does not vary appreciably with the ocncentration. This is true only in th ecase of weak electrolytes. It is certainly not true in the case of strong electolytes. This is supported by the fact that the transport number of an ion varies with cocentration implying variation of ionic speeds. It follows, therefore, that the dependence of the speeds of ions on the conceniration of the solution must be, atleast partly, responsible for the change in the equivalent conductance.

In the case of strong electrolytes, the view widely adopted is that they are completely ionised at all concentrations. This is supported by the X-ray analysis of crystals of the slats which indicates that these salts are completely in the ionic form and that the positive and negative ions one held by electrostatic and other forces. When the salt is brought into solution, these ions become free to move and conduct electricity,

The increase of equivalent conductance with dilution therefore cannot be ascribed to the increase in th enumber of ions on dilution. Theincrease in equivalent conductance must therefore be ascribed to increase in the speed of the ions with decrease in concentration. This is the basis of the interionic attraction theory of electrolytic conductance. The theory proposes that in concentrated solutions the ions come closer and the strong attraction between ions of opposite charge results in a decrease of the speeds. On dilution, the ions move far apart and exist little influence upon their speeds. This in turn results in the increase of speeds on dilution and consequent increase in the equivalent conductance.

Debye-Huckel and Onsager have derived a quantitative expression on the basis of these assumptions of the interionic attraction theory. The fundamental assumption is that every ion is associated with a cluster of ions of oppostie charge, as a result of the electrostatic attraction between postive and negative ions. Because of this, on average, ions of oppostie charge will be present in the neighbourhood of particular ion than the ions of the same charge. it means that every ion may be regarded as being surrounded by a centrally symmetric ionic atmosphere with the magnitude and sign of the charge of the being equal and opposite to that of the central ion respectively. When E.M.F. is applied to the electrolyte solution the central ion and the ionic atmosphere move in oppostie directions. As a result of this it may be supposed-that as central ion moves away from its position a new ionic atmosphere will be formed around the central at its new place, while the old ionic atmosphere decays or dies out. If this formation and decay take place simultaneously at the same rate the symmetry of the atmosphere is maintained. Sincethese do not take palce the atmosphere will be asymmetric. This results in the decrease of the speed of the central ion because of the greater influence of the asymmetric atmosphere on the ion. This effect on the speed of an ion is called asymmetry or relaxation effect.

Another factor which is responsible for the decrease in the speed of the ion is the tendency of the applied E.M.F. to move the oppositely charged ionic atmosphere, with its associated molecules of solvent or water, in a direction oppostie to that of the central ion. This is knwon as electrophoretic effect.

Check your progress - 2

Why the equivalent conductivities of strong electroglytes increase with dilution even through they undergo complete dissociation?

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Debye and Huckel thus attributed the increase in equivalent conductance with dilution, even thoght the number of ions is unaltered to the change in the speed of the ion. On the basis of this assumption Debye and Huckel derived an equation for the variation of equivalent conductance with concentration. This was modified by Onsager. The following is the final form of the equation for a uni-univalent electrolyte.

$$\lambda = \lambda_o - \left[\frac{82.4}{(DT)\frac{1}{2\eta}} + \frac{8.20 \times 10^5}{(DT)\,3/2}\right]\lambda_o \sqrt{C}$$

where D is the dielectric constant of the solvent is viscosity of the medium, T the absolute temperature, andC is concentration of the solution in moles per liter or gram equivalent per liter. The above equation, generally known as Debye, Huckel Onsager equation or simply Onsager equation, accounts for the falling off in the equivalent conductance from the limiting value with increasing concentration of the electrolyte. The first term in the brackets is due to the electrophoretic effect, while the second represents the asymmetry effect.

By writing A and B in place of the two quotients within the brackets of the equation, we have

$$\lambda = \lambda_o$$

Where A and B are ocnstants for a given solvent that depend only on the temperature. For water at 25°c, A is 60.20 and B is 0.229, So for aqueous solutions of strong uni:univalent electrolytes, the equation becomes

$$\lambda = \lambda_o$$

This means that the plot of the equivalent conductance against the square root of the concentration $\sqrt{C}$ should give a straight line of slope 60.2 + 0.229 . It has been observed so in the case of dilute solutions of uni-univalent electrolytes.

6.8 SUMMARY

Arrhenius theory of electrolytic dissociation explains the behaviour of weak electrolytes. Ostwalds dilution law is the result of the simultaneous application of law of mass action and Arrhenius theory to the dissociatin of weak electrolytes. The behaviour of strong electrolytes can be expalined by Debye Huckel theory.

6.9 MODEL EXAMINATION QUESTIONS

I **Answer each of the following in 10 lines.**

1. Give an account of Arrhenius theory of electrolytic dissociation.
2. What are the anomolies observed in the conductance behaviour of strong electrolytes.
3. Give the basic postulates of interionic attraction theory.

II **Answer each of the following in 30 lines**

1. Discuss critically the reasons for the failure of Arrhenius theory in the case of strong electrolytes.
2. Discuss Debye-Huckel theory of strong electrolytes.

6.10 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Degree of dissociation of a weak electrolyte is the ratio between its and λ_v and λ_v $\alpha = \frac{\lambda_v}{\lambda_o}$ values.

2. Equivalent conductivities due to the disappearance of the interionic attractions.

BLOCK - 3

CHEMICAL KINETICS

Chemical Kinetics deals with the velocity of reactions. By a study of the reaction rates, it is possible to propose reaction mechanisms.

There are some chemical reactions which come to a completion in a fraction of a second. Ionic reactions are of this type. They are very fast reactions. Some reactions are very slow like the rusting of iron. The measurment of the rates of the above two types of reactions is difficult and as such they are not studied in chemical kinetics. There are reactions called moderately slow reactions eg. esterification. Only such reactions are studied in chemical kinetics. We also study the reaction conditions that influence the reaction rates.

at temperatures that are easily accessible in the laboratory. The subject of chemical kinetics deals with the study of the rates at which reactions occur, and the influuence of conditions on these rates. The information is helpful to propose the mechanisms of the reactions.

7.3 RATE OF REACTION

The rate of a reaction, which may also be called its velocity or speed, may be expressed in terms of the concentration change of a reactant or of a resultant of the reaction with time. It is expressed as the rate of decrease of concentration of a reactant or as a rate of increase of concentration of a resultant of the reaction with time. Thus, if the substance chosen is a reactant and if it has a concentration 'c' at time 't', the rate is-$\frac{dc}{dt}$, the rate with respect to a resultant having a concentration 'x' at time 't' is $\frac{dx}{dt}$. Here dc, dx and dt refer to the small changes in concentration of the reactant, concentration of the resultant and in reaction time. According to this formulation the rate must have the units of concentration divided by time. The time is almost invariably expressed in seconds, while concentrations are frequently given as moles per litre or moles per cubic centimetre; in such a case the units for the rate are moles litre^{-1} sec^{-1} or moles cc^{-1}. The rate is expressed in atmospheres per second for a gaseous reaction where pressure units are used in place of concentration.

Since the rate of a chemical reaction depends upon the concentrations of the reactions, the rate of the process must fall off as the reaction proceeds, for the reactants are continuously consumed in the course of the reaction, that is, their concentrations are decreasing steadily. The reaction rate varies thus with time, somewhat in the manner shown Fig. 7.1. The process becomes slower and slower as the reactants are used up. The reaction never ceases, and therorctically, the rate-time curve should be asymptotic to the time axis.

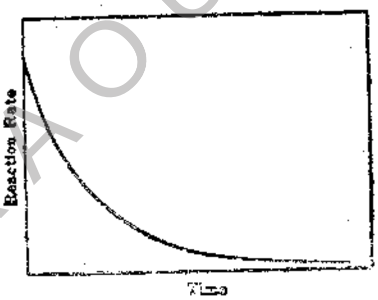

Fig: 7.1 Rate-time curve

7.4 CLASSIFICATIONS OF REACTIONS

From the stnadpoint of the quantitative consideration of reaction rates, reactions are classified by i) the order of the reaction and ii) molecularity of the reaction.

ORDER OF A REACTION

The order of a reaction is identical with the number of atoms or ions molecules whose concentrations determine the velocity or kinetics of the reaction. In order to understand the term, order of a reaction, let us consider the following reactions.

Equations i) $A \rightarrow$ Resultants

Rate $= k\,[A]^1$

ii) $2A \rightarrow$ Resultants

Rate $= k\,[A]^2$

iii) $A + B \rightarrow$ Resultlants

Rate $= k\,[A]^1\,[B]^1$

iv) $2A + B \rightarrow$ Resultants

Rate $= k\,[A]^2\,[B]^1$

or in general

v) $aA + bB + \rightarrow$ Resultants

Rate $= k\,[A]^a\,[B]^b$

It is seen from the above exmaples that the reaction rate depends upon the concentration and number of molecules or ions or atoms of reactants undergoing the chemical change. Thus,the order of a reaction may be defined as the sum of the powers to which the concentration terms are raised in order to express the rate of the reaction.

Thus, for the reaction (i) the order is 1, for(ii) and (iii) it is 2, for (iv) the order is 2+1 = 3, and for the general reaction (v) it is a+ b+ ---------

Check your progress - 1

What is order ?

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MOLECULARITY OF REACTION

The molecularity is given by the number of atoms or molecules taking part in the act leading to chemical reaction. thus, the reactions (i to iv) can be classified as unimolecular, bimolecular and termolecular provided these steps represent the (rate determing steps) acts leadingto chemical reactions.. These correspond to first, second and third order reactions too respectively. Althogh this equality of the reaction order and the molecularity is observed in many reactions, it does not hold in all cases. For example for the reactions.

$$CH_3CHO \rightarrow CH_4 + CO$$

$$3\,KClO \rightarrow KClO_3 + 2\,KCl$$

It is anticipated that the first reaction is of the first order and the second reaction is of the third order. Actually both reactions are found to be second order reactions. This is because the acts leading to chemical reactions are not represetned by the above equations. A distinction therefore must be made between the moleculraity and the order of a reaction. According to the former, reactions are unimolecular, bilolecular etc., depending on whether one, two or more molecules (or ions or atoms) are involved in the act***leading to the reaction** (rate detemining act). On the other hand, order of a reaction illustrates the dependence of the observed rate on the concentrations of the reactants.

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* Any reaction takes place in a sequence of steps. The solwest step in this sequence is called act leading to the reaction.

The reaction in presence of mineral acid
Ester + Water → Organic acid + Alcohol

is first order while it is a bimolecular reaction. This happens because one of the reactatns is in excess. In the above example water is in excess. Reactions having zero and fractional orders are known. The molecularity, on the other hand is always an integer and never zero.

7.5 REACTIONS OF THE FIRST ORDER

In a first order reaction, the rate is directly proportional to the concentration of one reactant. Let the first order reaction be written as follows.

A → Resultants

The rate is expressed mathematically by the equation

$$-\frac{dc}{dt} = kc \qquad (1)$$

Where c is the concentration of the reacting substance. This equation states that the rate of disappearance of the reactant at any instant is proportional to the first power of its concentration at that instant. If 'a' is the initial concentration of the reacting species and X is the decrease in concentration after a lapse of time 't', the concentration at time 't' will be (a-x). The reaction velocity is thereofore obtained by sucstituting (a-x) for c in (1) thus,

$$v = -\frac{d\,(a-x)}{dt} = k\ (a-x)$$

Rate or velocities can also be expressed in terms of the concentration of resultant (x) at time 't'.

Thus $$\frac{dx}{dt} = k\ (a-x) \qquad (2)$$

The quantity, $\frac{dx}{dt}$ is a measrue of the rate of increase of the resultant concentration with time and is called the reaction velocity. The proportionality constant k is called the specific reaction rate, or velocity constant or velocity coefficient.

In order to get the velocity constatn, equation (2) is rearranged and integrated.

$$\frac{dx}{(a-x).} = k.dt \qquad (3)$$

$$\int \frac{dx}{(a-x)} = \int k.dt \qquad (4)$$

$$-\ in\ (a-x) = kt + C$$

Where C is the constant of integration. In order to get the value of C, the condition that X=O, when t=O is made use of. Substituting that x = O, when t = O in equation (4), We have

$$-\ In\ a = C \qquad (5)$$

If this value of C is substituted in equation (4),we have

$$-\ In\ (a-x) = kt - 1n\ a \qquad (6)$$
$$kt = 1n\ (a-x)$$

$$kt = \ln \frac{a}{(a-x)}$$

$$k = \frac{1}{t} \ln \frac{a}{(a-x)} \qquad (7)$$

On converting the natural logarithm (1n) to the logarithm to base 10, we get

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)} \qquad (8)$$

This equation is known as the rate equation or expression for a reaction of the first order. The specific reaction rate (k) can be obtained by substituting the values of 'a', and (a-x) corresponding to different times 't' during the course of the reaction. The same equation may be written in the form

$$(a-x) = a\,e^{-kt} \text{ or } c_t = c_0\,e^{-kt} \qquad (9)$$

Where c_o is the initial concentration of the reactant and c_t is the concentration after time 't'. This shows that the concentration of the reactant falls exponentially, and theoretically the reaction is complete, (when $c_t = 0$) i.e, when 't' is infinite. In practice most reactions taking place at a reasonable rate are virtually complete within the limits of ordinary analytical detection, in the course of a short time.

Equation (8) may also be tested graphically. On rearranggement this equation becomes

$$\log (a-x) = \frac{-kt}{2.303} + \log a \qquad (10)$$

since for any one experiment 'a' is a constant, a plot of log (a-x) verses 't' should yield a straight line and the ordinate will be loga and the slope is -k/2.303. Consequently, when such a plot constructed from the experimental data is found to be linear, the reaction is taken as first order, and k can be calculated from the slope of the line.

$$k = -2.303 \text{ (slope)} \qquad (11)$$

The time necessary to decompose a definite fraction of the reactant, usually one half, can be determined for a number of different values of a. When one half of the reactant has undergone decompostion, (a-x) = a/2 and time (t1/2) necessary for this to occur is given by equation 12.

$$t = \frac{2.303}{k} \log \frac{a}{(a-x)}$$

For half change

$$t_{1/2} = \frac{2.303}{k} \log \frac{a}{a_{1/2}} = \frac{2.303}{k} \log 2$$

$$= 0.693/k \qquad (12)$$

This shows that t1/2 is independent of the initial concentration for first order reactions. The decay of a radioactive element is an example of a first order process, since the half life period of such an element is independent of the initial amount of the material.

7.6 EXAMPLES OF FIRST ORDER REACTION

Examples of first order gaseous reactions are: a) the thermal decompostion of nitrogen pentoxide, nitrous oxide, acetone, azo compounds, amines and b) isomerisation of d-pinene to dipentene.

The kinetics of gaseous reactions are most conveniently studied by observing the pressure of the gas at knwon intevals of time, provided the reaction is accompained by a change in the number of molecules. The decompostion of nitrogen pentoxide can be represented by the following equation.

$$N_2O_5 \rightarrow N_2O_4 + \frac{1}{2} O_2$$

It was shown, by measuring the partial pressure of oxygen at regular intevals of time, that the above reaction follows the first order equation.

There are many reactions in solution which are kinetically of the first order. They are a) decompostion of H_2O_2, b) conversion of N-chloroacetanilide into p-chloro acetanilide, c) decomposition of ammonium nitrate and d) hydrolysis of benzene diazonium chloride. The hydrolysis of an ester in the presence f an acid and the hydeolysis of sucrose in presence of an acid (inversion of sucrose) into glucose and fructore follow th efirst order even though these are bimorecular

Ester + Water → Organic acid + alcohol

Surcrose + water → Glucose + Fructose

Let us consider the hydrolysis of an ester, e.g. methyl acetate, in the presence of an acid. The reaction can be written as

$$\underset{\text{Ester}}{CH_3COO\,CH_3} + H_2O \rightarrow \underset{\text{Acid}}{CH_3COOH} + \underset{\text{Alcohol}}{CH_3OH}$$

The reaction is too slow in the absence of acid but the rate is measurable in the presence of a small amount of mineral acid, acting as a catalyst. It does not appear in the equation for the reaction. Further, the water is present in such large excess that the concentration of this is virtually constant. The kinetics of the reaction is then detemrined solely by the concentration changes of the ester. Hence the proces is of first order and equation (8) should be applicable. This has been verified experimentally.

In order to verify this, the disappearance of the ester is followed by withdrawing portions of the reaction mixture from time to time and titrating with alkali. The volume of titrant (alkali) required at any time is equivalent to the sum of the mineral acid used as a catalyst, (which remains constant throughout) and of acetic acid produced in the hydrolytic reaction. The titre value at the commencement of the reaction T_0, is equivalent to the amount of mineral acid caalyst only, and the titre value $T\alpha$ at the end of the reaction is equal to the sum of acid catalyst and all the acetic acid resulted from complete hydrolysis of ester, hence $T\alpha - T_0$ is measure of 'a', the initial ester concentration. Similarly $T\alpha - T_t$ wereT is the titre value at time t, gives the quantity (a-x) of ester remaining at that time. It follows, therefore, for this first order process.

$$k = \frac{2.303}{t} \log \frac{T\alpha - T_0}{T\alpha - T_t} \tag{13}$$

the specific rate can be evaluated from equation

7.7 SECOND ORDER REACTIONS

A second order reaction can be represened as

$$A + B \longrightarrow \text{Resultants; rate} = \frac{dx}{dt} = k\ [A]^1\ [B]^1$$

Two cases may arise for second order reaction. One, where the initial concentrations of the two reactants are equal, and two where the initial concentrations are different.

Ist case

$A + B \rightarrow$ Resultants Initial (Reactants different)
a a O
$2A \rightarrow$ Resultants Initial
a O

It may be considered that the initial concentrations of each of two molecules is a and x is the amount of each reactant decomposed after time interval 't'. Then the concentration of each reactant after time 't' will be equal to (a-x). The rate of the reaction will be represented by

(14)

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

$$\frac{dx}{(a-x)^2} = k.\ dt \qquad (14)$$

Integration of equation (14) gives

$$\frac{1}{(a-x)} = k\,t + C \qquad (15)$$

Where C is the integration constant. The value of C can be obtained by putting the condition that $X = O$. When $t = O$

$$\therefore \frac{1}{a} = C \qquad (16$$

The value of C is then substituted in equation (15). Then we have

$$\frac{1}{(a-x)}\ k\,t + \frac{1}{a}$$

$$k\,t = \frac{1}{(a-x)} - \frac{1}{a} \quad = \frac{x}{(a-x)\,a}$$

$$k = \frac{X}{at\,(a-x)} \text{ or } \frac{1}{at}\ \frac{x}{(a-x)} \qquad (17)$$

Equation (17) represents the expression for the velocity constant k of a second order reaction when the concentrations of the two reactants are equal or when two molecules of the same reactant decompose.

2nd case

Let two molecules A and B react with initial concentrations a and b. At time t, it may be assumed that the quantity x of each molecule has reacted. The concentrations of A and B after time t will then be equal to (a-x) and (b-x).

$A + B \rightarrow$	Resultants	
a b	O	initially
(a-x) (b-x)	x	after time 't'

The rate of the reaction is given by

$$\frac{dx}{dt} = (a-x)\ (b-x) \qquad (18)$$

$$\text{or } \frac{dx}{(a-x)\ (b-x)} = k.dt$$

on separation of variables it follows that

$$\frac{1}{(a-b)} \left[\frac{1}{(b-x)} - \frac{1}{(a-x)}\right] dx = k\ dt \qquad (19)$$

on integration we get

$$\frac{1}{(a-b)}\ [-\ln (b-x) + \ln (a-x)] = k\,t + C$$

when t=O, x = O, then (20)

$$C = \frac{1}{a-b} \ln \frac{a}{b} \qquad (21)$$

Putting the value of C in (20) we get

$$\frac{1}{(a-b)} \left[\ln \frac{(a-X)}{b-X}\right] = k\,t + \frac{1}{a-b} \ln \frac{a}{b} \qquad (22)$$

Changing the natural logarithms to the base 10 and rearranging equation takes the form

$$K = \frac{2.303}{t\,(a-b)}\left[\log \frac{b\,(a-x)}{a\,(b-x)}\right] \tag{23}$$

This is the equation for all second order order reactions where the initial concentration, of the reactansts are different.

Examination of equations 17 and 23 suggests that the value of the second order specific reaction rate is dependent on the units employed to express concentrations unlike the first order reacation. It can be seen that there is one more concentration term in the denominator than in the numerator, therefore the specific rate is expressed in conc^{-1} time^{-1} units. A common form is (mole/litre)$^{-1}$ sec^{-1} or litre mole^{-1} sec^{-1}, the concentration being in moles per litre and the time in seconds.

The time taken for the initial concentration of the reactants to be reduced by a definite fraction may be readily calculated. The time t1/2 required to reduce the concentration to one half of its initial value in equation (17), is given by substituting a1/2 for X in equation (17)

$$t_{\frac{1}{2}} = \frac{1}{k.a} \quad \text{or} \quad t_{\frac{1}{2}} \; \alpha \frac{1}{a} \tag{24}$$

The half time is inversely proportional to the initial concentration of the reactants. The same relation applies for the completion of any other fraction of the reaction. Equation 12 and 24 make possible to distinguish in a simple manner the first order and second order reactions especially when only one reacting substance is involved.

Usually the equations 17, 23 and 24 are used to show whether a particular reaction is second order or not. Apart from this procedure, graphical analysis can also be used to establish whether a particular reaction is second order or not. For this purpose equation (17) is written in the form

$$t = \frac{1}{k\,(a-x)} - \frac{1}{k-a} \tag{25}$$

The plot of t against $\frac{1}{(a-x)}$ gives a linear plot, the slope being

7.8 EXAMPLES OF SECOND ORDER REACTIONS

There are not many gaseous reactions that are definitely of second order. But mention may be made of the following: i) thermal decomposition of nitrogen dioxide, chlorine monoxide and ozone. ii) combination of ethylene and hydrogen and iii) thermal decompostion of acetaldehyde over a certain range of temperature and pressure. Even though . the reactions follow second order rate, there are some complications in many of the above mentioned examples.

There are, however, a large number of processes taking place in solution that are kinetically of second order. One of the most familiar of these is the alkaline hydrolysis, or saponificaiton, of an ester:

Ester + alkali → acid + alcohol

This reaction differs from the acid hydrolysis, since none of the reactants in this need be present in excess. The course of the reaction can be followed by removing definite quantities of the reacting system from time to time and running it into excess of standard acid. The unreacted acid is then titrated with standard alkali. The concentration of unchanged hydroxide in the reaction mixture can be determined from this titre value.

Other second order reactions taking place in solution are the interaction of alkyl halides wih tertiary amines and of alkyl iodides with sodium phenoxide.

Check your progress - 2

Why a second order reaction becomes first order when one reactant is taken in encess?

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7.9 THIRD ORDER REACTIONS

A third order reaction may be defined as that in which the rate is determined by the concentration of three molecules of the reactants. There are three different types of third order reactions.

(i) The three reactants are same and have equal initial concentrations.

$$3A \rightarrow \text{Resultants}$$

(ii) The three reactants are different and have different concentrations.

$$A + A + C \rightarrow \text{Resultants}$$

and (iii) Two of the reactants are same and have equal concentration and the third is different and has different concentration too.

$$2A + B \rightarrow \text{Resultants} \quad \text{or } 2B + A \rightarrow \text{Resultants}$$

The first type is the simplest, where all the three reactants are the same and have equal concentration.

$$3A \rightarrow \text{Resultants}$$

Let the initial concentration of A, be 'a' moles and 'x' be the number of moles of A decomposed at time t, then there will be (a-x) moles of A after time t. The rate of the reaction is given by

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

$$\frac{dx}{(a-x)^3} = k\,dt \qquad (26)$$

on integration, we get

$$\frac{1}{2(a-x)^2} = kt + C \qquad (27)$$

Where C is the integration constant, when $t = 0$, $x = 0$

$$\frac{1}{2a^2} = C \qquad (28)$$

substituting the value of C in equation (27), we have

$$\frac{1}{2\,(a-x)^2} = kt + \frac{1}{2a^2}$$

$$kt = \frac{1}{2(a-x)^2} - \frac{1}{2a^2}$$

$$k = \frac{1}{2t}\left[\frac{1}{(a-x)^2 - a^2}\right] \qquad (29)$$

7.10 EXAMPLES OF THIRD ORDER REACTIONS

The reaction of nitric oxide with chlorine, or bromine, or oxygen or hydrogen is an example of third order reaction. Two molecules of nitric oxide will react with each molecule of the other reactant.

$$2\,NO + Br_2 \rightarrow 2\,NO\,Br \qquad (30)$$

$$2\,NO + Cl_2 \rightarrow 2\,NO\,Cl \qquad (31)$$

$$2\,NO + O_2 \rightarrow 2\,NO_2$$

It is observed that 2 molecules of nitric oxide will first form an associated moelcule $(NO)_2$ and this was supposed to combine with the other reactant. then the reaction may become a bimolecular process, but still kinetically it is a third order reaction.

Reactions in solution which are third order are the oxidatin of ferrous sulphate in water and the reaction between iodide and ferric ions in aqueous solution.

7.11 DETERMINATION OF ORDER OF REACTION

There are four different methods avialable for the determination of the order of reaction.

(i) Integration method.
(ii) Half-time method (Time to complete difinite fraction of the reaction)
(iii) van't Hoff's differential method.
(iv) Ostwald's isolation method.

7.11.1 Integration method

This method involves the determination of the concentration of reactants at various intervals of time and substitution of these results in the equations for the first, second and third order. The equation which gives the most constant values for the specific reaction rate suggests the order of the reaction.

For example if in an experiment the results satisfy the first order rate expression rather than the second order rate expression, the order is decided as first order (See Problems 1 and 3)

7.11.2 Half-time method

It is seen from rate expressions presented earlier that the time taken to complete one-half of the reaction, provided the reactants are all at the same initial concentration is independent of initial concentration for a reaction of first order. Inthe case of a second order reaction, it is inversely proportional to the initial concentration, while it is inversely proportional to the square of the initial concentration for a third order reaction, provided reactants have the same initial concentration. These facts may be generalised and written as

$$t_{1/2}\, \alpha \frac{1}{a^{n-1}} \qquad (32)$$

Where t1/2 is time required for half change, 'a' is the initial concentration and 'n' is the order of the reaction. If in two different experiments the initial concentrations are a_1 and a_2 and the corresponding half times are $t^1 1/2$ an d $t^2 1/2$ these are realted as

$$\frac{t^1\frac{1}{2}}{t^2\frac{1}{2}} = \left(\frac{a_2}{a_1}\right)^{n-1} \qquad (33)$$

Therefore 'n' can be evaluated directly from equation (33) (see problems 6 and 8)

3.14 MODEL EXAMINATION QUESTIONS

I. Answer the following in 10 lines each

1. In which of the following pairs would you expect the difference in entropy to be least ?

   (i) Solid iodine and iodine vapour (ii) Solid glass and molten glass (iii) Ice and water.

2. Show that free energy decreases in a reversible process.

3. Under what conditions can an endothermic reaction proceed spontaneously ?

II. Answer the following in 30 lines each

1. Give the different statements of the second law of thermodynamics and explain each one of them.

2. Dertive an expression for the maximum efficiency of a heat engine.

III. Solve the following problems

1. A heat engine operates between the temperature 120°C and 30°C. Find the maximum efficiency of this engine.

2. A steam engine operates between the temperatures 140°C and 40°C. What is the minimum amount of heat that should be withdrawn from the hot reservoir to obtain 250 calories of work?

3. A refrigerator (reverse of a carnot cycle) transfers heat from 0° C (inside the refrigerator) to 25° C (room). Find the work that must be done to freeze 1 Kg of water. (Hint : Amount of heat to be withdrawn is 1000 g x 80 Cal gm^{-1})

3.15 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Those processes which proceed at their own accord without the interference of man are called spontaneous processes. ex :- Diffusion of a gas from a region of higher pressure to a region of lower pressure.

2. Those processes which proceed with free energy decrease are called spontaneous processes.

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UNIT - 4 ELECTROLYTIC CONDUCTANCE

Contents

4.1 AIMS AND OBJECTIVES

To discuss electrical properties of solutions of electrolytes and to elucidate the relation between chemical action and current passing through such systems. Once the reading and understanding of the matter presented in this unit is over, must be able to:

- explain electrolysis and Faraday's laws of electrolysis.
- give the relation between resistance, specific resistance and cell constant.
- know the experimental details of measurement of resistance.
- explain the variation of equivalent conductivity with dilution
- appreciate the calculation of λ o of weak electrolytes by the application of Kohlrasch's law.

4.2 INTRODUCTION

What are electrolytic conductors and how many types are there? Electrolytic conductors are called electrolytes. Faraday's Laws describe quantitative aspects of electrolysis. The variation of equivalent conductance with concentration differentiates strong electrolytes from weak electrolytes.

4.3 ELECTROLYTIC CONDUCTION

The passage of electricity through a conductor depends on the nature of the conductor. The mechanism is not the same in all conductors. In certain cases it involves the flow of electrons from a point of higher negative potential to one of lower. It means that the passage of electricity in such cases is accompanied by the direct migration of electrons through the conductors. Such type of conductors are known as **electronic conductors.** On the other hand, in certain other cases the passages of electricity leads to the transfer of matter by the migration of ions. Such type of conductors are referred to as

electrolytic conductors or electrolytes. Example of the first type are solid and molten metals and certain solid salts (cupric sulphide and cadimum sulphide). Fused salts and solutions of acids, bases and salts are the examples of the second type. Current flow in electrolytic conductors is accompanie by chemical changes at the electrodes. These changes depend on the characteristics of chemical substances undergoing electrolysis and the electrodes.

4.3 THE PHENOMENON OF ELECTROLYSIS

When an electric current is passed through an electrolytic conductor, the transport of matter takes place. This can be illustrated by an example. If two plantinum wires attached to a source of EMF i.e. battery are immersed in a dilute solution of an acid in water, bubbles of hydrogen and oxygen are evolved at the platinum wires. Instead, if the platinum wires are placed in a solution of salt of copper or silver the corresponding metal is deposited at one of the wires instead of hydrogen. This phenomenon is referred to as electrolysis. This was first studied by M. Faraday in 1832-33. As per the nomenclature used by Faraday, the platinum wires are referred to as electrodes, the anode and cathode depending on the fact that current is brought into and out of the electrolytic solution at these electrodes. By convention, anode is the one attached to the positive pole of the battery and the cathode is that attached to the negative pole. During electrolysis of aqueous solutions of electrolytes. The hydrogen gas or as the metal case may be obtained at the cathode and oxygen gas in general appears at the anode, provided the electrode material is not attacked. It was assumed by Faraday that the flow of current through an electrolyte was associated with the movement of charged particles. Those carrying positve charge and moving towards the cathode are referred to as cations and those carrying negative charge and moving in the opposite direction towards anode are called anions. On reaching the electrodes, the ions are supposed to have their charges neutralised and deposited as neutral atoms or molecules.

4.5. FARADAY'S LAWS OF ELECTROLYSIS

The process of current passage through an electrolytec with all the accompanying chemical and migratory changes is called electrolysis the mechanism of electrolysis can be described as follows :

Electrons enter and leave the solution through chemical changes at the electrodes and it is also known that the number of electrons that pass through the solution and leave it, is equal to the number that enter. Taking these facts into account Faraday has enunciated the laws of electrolysis which give the quantitative relatonships between the quantity of electricity passing through an electrolyte and the amount of chemical change occuring at the electrodes.

i) The amount of chemical decomposition produced by a current, that is the amopunt of any substance deposited or dissolved atain appropriate electrode is proportional to the quantity of electricity passing through the solution.

ii) The amounts of different substances deposited or dissolved by the same quantity of electricity are proportional to their chemical equivalent weights.

The first law is verified by allowing currents of different strength to pass different period of time through a given solution and determining the amount of material deposited at the cathode or dissolved from the anode. The quantity of electricity is equal to the product of the current strength and the time during which it is passed.

The second law is verified by allowing the same current to pass simultaneously through a series of solutions. The amounts ofchemical substance deposited at the cathodes or dissolved from anodes are proportional to the equivalent weights of the respective substances deposited or dissolved.

7.11.3 Van't Hoff Differential Method.

This method, suggested by Van't Hoff, is based on the fact that the rate of a reaction of nth order is proportional to the nth power of the initial concentration.

$$-\frac{dc}{dt} = kc^n \tag{34}$$

c being the initial concentration and n is the order.

For two different concentrations and , c_1 and c_2 the rate expressions are

$$-\frac{dc}{dt} = kc_1^n, \ -\frac{dc_2}{dt} = kc_2^n \tag{35}$$

Hence

$$\frac{-\frac{dc_1}{dt}}{-\frac{dc_2}{dt}} = \left(\frac{c_1}{c_2}\right)^n \tag{36}$$

on taking logarithms and rearranging, we have

$$n = \frac{\log\left(\frac{-dc_1}{dt}\right) - \log\left(\frac{-dc_2}{dt}\right)}{\log c_1 - \log c_2} \tag{37}$$

By carrying the experiment with different initial concentrations c_1 and c_2 the order of the reaction 'n' can be calculated by making use of equation (37),

7.11.4 Ostwald's Isolation method

The method finds its use if two or more than two reactants are involved in a reaction. The method is based on the principle that all the reactants except one are taken in excess, and the order is determined by any method described earlier. The order thus determined corresponds to the reactant taken not in excess. Since it was used by W. Ostwald for the first time, the method is called Ostwald isolation method. If a reaction involves A, B, andC and if the rate is controlled by the concentration of a moles of A, b moles of B and c moles of C, the total order is equal to a+b+c. If in an experiment the concentrations of B and C are in ecxcess, the order 'a' determined by any one of the above methods will be with respect to A. Similarly the process is repeated with excess of C ard A and A and B respectively and the orders 'b' and 'c' are obtained. The orders correspond to B and C respectively. The total order of the reaction is a + b + c. The isolation method gives satisfactory results in the case of reactions involving two reactants. But it may give misleading results in other cases.

Problems

1. A certain amount of methyl acetate was hydrolysed in the presence of an excess of 0.05 N HCl at c. When 25 ml aliquotes of reaction mixture were removed and titrated with NaOH solution, the volumes V of alkali required for neutralisation after time 't' were as follows:

t (min)	0	21	75	119	α
V (ml)	24.4	25.8	29.3	31.7	47.2

show that the reaction is a first order reaction.

Solution:

The first order equation $k = \frac{2.303}{t} \log \frac{a}{(a-x)}$

will take the form $$k = \frac{2.303}{t} \log \frac{V\alpha - V_o}{V\alpha - V_t}$$

Where

V_o = Volume of alkali required for neutralisation of HCl.

$V\ \alpha$ = Volume of alkali required for the neutralisation of HCl and acetic acid obtained from the complete hydrolysis of methyl acetate.

Vt = Volume of alkali required for the neutralisation of HCl and acetic acid obtained from the hydrolysis of methyl acetate at time t.

$$V\alpha - V_o = 47.2 - 24.4 = 22.8$$

At t = 21

$$V\alpha - Vt = 47.2 - 25.8 = 21.4$$

$$k_1 = \frac{2.303}{21 \times 60} \log \frac{22.8}{21.4}$$

$$= 5.60 \times 10^{-5} \text{ sec}^{-5}$$

At t = 75

$$V\alpha - Vt = 47.2 - 29.3 = 17.9$$

$$k = \frac{2.303}{75 \times 60} \log \frac{22.8}{17.9} = 5.6 \times 10^{-5} t \text{ sec}^{-1}$$

At t = 119

$$V\alpha - Vt = 47.2 - 31.7 = 15.5$$

$$k_1 = \frac{2.303}{119 \times 60} \log \frac{22.8}{15.5}$$

$$k_1 = 5.6 \times 10^{-15} \text{ sec}^{-1}$$

Since the value of k is same for different times, the acid hydrolysis of methyl acetate is a first order reaction.

2. From the following data show that the decomposition of hydrogen peroxide is a first order reaction.

Time (minute)	0	10	20
y (in ml)	22.8	13.8	8.28

y is the volume in ml of standard potassium permanganate required for a definite volume of hydrogen peroxide for the first order reaction.

$$k = \frac{2.303}{t} \log \frac{a}{(a - x)}$$

$$a = 22.8$$

Time (t)	(a-x)	k	
10	9.0	9.2×10^{-2}	min^{-1}
20	13.52	9.20×10^{-2}	min^{-1}

Since k is almost the same, the above reaction is a first order reaction.

3. One gram mole of ethyl acetate was hydrolysed by NaOH of equal concentration. The volume of acid used to titrate alkali at various time intervals is

t (minutes)	0	4	6	10	15	20
Volume of acid used (in ml)	8.04	5.30	4.58	3.50	2.74	2.20

Show that the reaction is of second order.

Solution

The second order rate expression for the reaction involving same initial concentration of reactant is

$$k = \frac{1}{at}\frac{x}{(a-x)}$$

Here a = 8.04   x = a - (a-x)

Volume of acid at any time will give (a-x).

Time	(a-x)	x	k
4	5.30	2.74	1.60×10^{-2}
6	4.58	3.46	1.62×10^{-2}
10	3.50	4.54	1.65×10^{-2}
15	2.74	5.30	1.61×10^{-2}
20	2.20	5.84	1.60×10^{-2}

The value of k is fairly constant and so the reaction is of second order.

4) Hinshelwood studied the thermal decomposition of acetaldehyde at 5.18°c, The following results are obtained.

t Seconds)	42	73	105	190	242
x (mm ot Hg)	34	54	74	114	134

Show that the reaction is of second order if the initial pressure is 363 mm of Hg.

If P_i is the initial pressure, the rate expression for the decompostion of acetaldehyde is

$$k = \frac{1}{P_i t}\frac{x}{(P_i - X)}$$

Here P_i = 363 mm.

t	x	k
42	34	6.79×10^{-6}
73	54	6.60×10^{-6}
105	74	6.71×10^{-6}
190	114	6.64×10^{-6}
242	134	6.66×10^{-6}

The constancy in the values of 'k' indicates that the reaction is of second order.

5) Halflife for disintegration of Radium is 1590 years. Calculate the rate constant in s^{-1} and also how many years will be taken for the disintegration of 80% Radium?

$$t\frac{1}{2} = \frac{0.69}{k} \text{ ie } K = \frac{0.69}{t_{1/2}} = \frac{0.69}{5.014 \times 10^{10}}$$

$$= 1.376 \times 10^{-11} \text{ sec-1}$$

UNIT - 8 THEORIES OF REACTION RATES

Contents

8.1 AIMS AND OBJECTIVES

To discuss the influence of temperature on the reaction rate and to explain the meaning of 'energy of activation'. To give an account of the 'simple collision theory' and the 'absolute rate theory' of reaction rates.

After the thorough study and understanding of this unit you must able to:

- expalin the effect of temperature on the reaction rate in terms of arrhenius equation.
- find out that the energy of activation is the difference in potential energy between the reactants (initial state) and the activated state or the transition state.
- realise that according to the simple collision theory, (a) collisions of the molecules possessing a certain minimum amount of energy (activation energy) only result in reaction (b) the specific reaction rate is equal to the product of the collision number and the Boltzmann factor $e^{-E/RT}$T.
- appreciate the absolute rate theory which says that two or more reactant molecules possessing the necessary energy, come together to form the transition state complex which subsequently decomposes under favourable conditions to give products.

8.2 INTRODUCTION

Increase of temperature increases the rates of most of the reactions. An attempt is made in this unit to explain as to why the rates of reactions increase with the increase of temperaure. Temperature has two fold effect on reaction rates. Temperature rise not only increase the frequency of molecular collisions but also the fraction of reacting molecules that contain the minimum amount of energy to react called activation energy. Therefore rate increases.

8.3 EFFECT OF TEMPERATURE ON REACTION RATE

The rate of a reaction increases with increase in temperature markedly. The increase is generally expressed in terms of specific rate or rate constant (k). The increase in rate constant of a homogenous processes is two-fold or three-fold for every 10° rise in temperature. The only known exception to the generally of this statement is the reaction $2\,NO + O_2 \rightarrow 2\,NO_2$ which exhibits a small negative temperature effect. The increase in the rate of a reaction with temperature is generally denoted as temperature coefficient.

$k_{t+10} + / k_t = 2$ to 3 where k is the specific rate at t° c and k_{t+10} is at a temperature (t+10)°c. This is only an approximate method for predicting the effect of temperature on a reaction rate. This increase of 200-300% in specific rate by a 10° rise in tmeperature is surprising since the increase in the number of oollisions of reacting molecules increases by 2% for the same 10° rise in temperature.

8.4 THE ARRHENIUS EQUATION

A quite satisfactory explanaiton for this effect of temperature was given by S. Arrhenius. He based his explanation on the Van't, Hoff equation (equation 1) which describes the variation of equillibrium constant (Kc) with temperature.

$$\frac{d\ln Kc}{dT} = \frac{\Delta E}{RT^2} \qquad (1)$$

Since K_c is equal to K_f / K_b where K_f and K_b are the specific reaction rates of the forward and backward reactaions of the equilibrium processes, it follows that

$$\frac{d\ln\ kf}{dT} - \frac{d\ln\ kb}{dT} = \frac{\Delta E}{RT^2} \qquad (2)$$

Equation (2) may be split into two simple equations (3 & 4)

$$\frac{d\ln\ kf}{dT} = \frac{E_1}{RT^2} + A \qquad (3)$$

$$\frac{d\ln\ kb}{dT} = \frac{E_2}{RT^2} + A \qquad (4)$$

Where $E_1 - E_2$ is equal to Δ E and 'A' is a constant. It was found experimentally that the temperature variation of the specific rate is best expressed if A is assumed to be zero. Thus equations (3) and (4) are written as

$$\frac{d\ln\ kf}{dT} = \frac{E_1}{RT^2} \qquad (5)$$

$$\frac{d\ln\ kb}{dT} = \frac{E_2}{RT^2} \qquad (6)$$

Since wer are interested only in a reaction taking place only in one direction, the equation (5) can be taken to express the variation of the specific rate with temperature. This expression on integration gives

$$\ln kf = -\frac{E_1}{RT} + \text{Constant or } \log k_f = -\frac{E_1}{2.303RT} + \text{constant}$$

or in general

$$\log k = -\frac{E}{2.303\ RT} + \text{Constant} \qquad (7)$$

Equation (5) or integrated form (7) is referred to as Arrhenius equation. 'E' in these equations is known as the energy of activation.

To test the validity of the arrhenius equation we resort to equation (7). According to equation (7) a plot of log k against 1/T should be a straight line with slope equal to $-\frac{E}{2.303\ R}$ and the intercept is equal t° C. It is possible to calculate E, the energy of activation from the slope of the straight line. The relationship has been found to hold good in a large number of reaction.

Where 'σ' is the molecular collision diameter and 'M' the gram molecular weight. Substitution in (11) gives

$$k = 4\sigma^2 \left(\pi RT/M \right)^{\frac{1}{2}} e^{-E/RT} \quad (13)$$

$$= Z e^{-E/RT}$$

the quantity $Z = k = 4\sigma^2 \left(\pi RT/M \right)^{\frac{1}{2}}$ which is equivalent to the frequency factor 'A' in equation (8), is being called the collision number. It is the number of collision per second when there is only one molecule of the reactant per ml.

$$\sigma^2 \left[8\pi RT \left(M_1 + M_2 \right) M_1 M_2 \right]^{\frac{1}{2}} \quad (14)$$

When the bimlecular reaction involves two different molecular species, the collisions number 'Z' assuming one molecule of each kind per ml, is equal to $\sigma^2 \left[8\pi RT \left(M_1 + M_2 \right) M_1 M_2 \right]^{\frac{1}{2}}$ where 'σ is the mean of the molecular collision diameters of the two reactants, and M_1 and M_2 are their molecular weights.

The collision theory has been tested with the reactions (i) decompostion of hydrogen iodide or (ii) the reaction between hydrogen and iodine to give hydrogen iodide. It has been shown that there is good agreement between the expermental and calculated values.

The collision theory is expected to be applicable to a number of reactions. But it failed conspicuously in many cases. It was observed that the theory does not give values agreeable with experimental values. The experimental specific rate is much less that expected from the theoritical considerations. the discrepencies observed are of the order of 10^{-5} to 10^{-8}. In order to account for the discrepencies equation (14) is modified empirically to take form

$$k = PZ.\ e^{-E/RT} \quad (15)$$

Where 'P' the probalility factor or steric factor, makes allowance for the effect causing deviations from the expected behaviour from equation (14). The value of P variesfrom unity to about 10^{-8} based on the nature of the rection.

Check your progress-2

What is collision number?

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8.7 THEORY OF ABSOLUTE REACTION RATES

Polanyi and others suggested an alternative point of view, which provides a complete interpretation of the significance of the frequency factor in the reaction rate equation. This point of view has accounted for the failure of the simple collision theory. The calculation of the rate, as per this theory, involves only such basic fundamental physical properties as dimensions, vibrational frequencies, masss etc. This treatment is therefore referred to as the theory of absolute reaction rates or transition state theory. This theory is based on the fact that when two or more molecules possessing the necessary amount of energy, come together and form the transition state complex which decomposes generally into resultants.

Let us consider a reaction involving the reacting substances A and B etc which form the transition state complex X which gives the resultants.

$A\,B + \rightleftharpoons X \rightarrow$ Resultants

The rate of the reactions is equal to the product of the concentration of the transition state complex at the top of the energy barrier multiplied by the frequency with which it crosses the barrier. If δ represents the reaction coordinate, at the top of the barrier and $\overline{V}$ is the mean velocity of the transition state compelxes in the same coordinate, the frequency of crossing the barrier is given by $\overline{V}\,\delta$. If the number of activated complexes per unit volume lying in the length σ is C_x then it follows that

$$\text{Rate of reaction} = C_x\,\overline{V}/\delta \qquad (16)$$

The transition state complex differs from normal molecules in the respect, that one of its vibrational degrees of freedom is replaced by translational degree of motion in the reaction coordinate. The complex can, therefore, be treated as normal molecule/with one very stiff vibrational mode. Separating this vibrational mode out and taking its limiting value the rate of reaction is represented by equation 17.

$$\text{Rate of reaction} = C\neq\ (kT/h)) \qquad (17)$$

It follows, therefore, that the effective rate of crossing the energy barrier by the transition state complex is equal to kT/h which is a universal frequency, haivng the dimensions of time^{-1}. Its value is dependent only on the temperaure and is independent of the nature of the reactants and the type of reaction.

If the specific reaction rate of a a bimolecular reaction is represented by k_r, the reaction rate can be expressed in the familiar manner as

$$\text{Rate of reaction} = k_r\,C_A\,C_B \qquad (18)$$

Hence from equantions 17 and 18 we have

$$k_r = \frac{kT}{h}\,\frac{C\neq}{C_A\,C_B} = \frac{kT}{h}\,K\neq \qquad (19)$$

Where $K\neq$ represents the equillibrium constant of the reaction $A + B \rightleftharpoons X$ which is supposed to exist between the reactants and the transition complex.

8.8 SUMMARY

An ettempt is made in the unit to explain the effect of temperature on reaction rates. Molecules are supposed to possess a minimum amount of energy to participate in fruitful collisions called activation energy. Temperature rise not only increases the collision number but also the number of molecules possessing activation energy. Molecules of the reactions with the activation energy come closer and form the transition state or complex which decomposes finally into the products.

8.9 MODEL EXAMINATION QUESTIONS

I Answer each of the following in 10 lines

1. Explain in brief the effect of temperature on the rate of reaction.
2. Give the important postulates of transition state theory.
3. Write and explain absolute rate equation.

II Answer each of the follwoing in 30 lines

1. Discuss the simple collision theory of reaction rates.
2. Expalin clearly the absolute rate theory or transition state theory of reaction rates.

8.10 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. The minimum amount of energy that the molecules are expected to possess in order to participate in fruitful collisions leading to chemical reaction is called the energy of activation.

2. The number of collisions that the molecules make in a homogeneous reaction mixture of 1cc per second is called collision number.

Author: K. Lakshminarayana

BLOCK 4

SURFACE CHEMISTRY

Surface chemistry deals with the interactions of the surfaces of different substances with others. A liquid wets a solid surface if the contact angle is less than 90°. Liquid surface always remains in tension to undergo contraction. Therefore, liquids form spherical drops which possess the least surface area. Surfaces of solids remain unsaturated and enable them to adsorb gases. A colloidforms if a substance insoluble in the other, is dispersed uniformly in the latter. We come across many colloids inour daily life. They are milk, blue ink, fog, mist, soap foam etc.

UNIT - 9 PROPERTIES OF INTERFACES

Contents

9.1 AIMS AND OBJECTIVES

The main aim of the this unit is to explain you the properties of interfaces and to illustrate the same with suitable examples.

Once you complete the study and understanding the contents of this unit, you are supposed to:

- realise that the surface tension of a liquid is due to the tendency of the surface of the liquid to contract.
- be convinced that liquid wets the surface with which it is in contact if the contac gle is less than 90°, and does not wet if the ocntact angle is between 90° and 180°.
- explain that the rise in the level of a liquid in a capillary tube is due to the surface tension of the liquid
- know that the surface tension can be measured by the drop-weight and capillary rise methods.
- find out that the surface tension and adsorption are related to each other.

9.2 INTRODUCTION

The molecules of a liquid are similar to each other and the force of attraction between such moelcules of a liquid is called **cohesion**. On the other hand, the molecules of one liquid will be different from those of another liquid or solid and the force of attraction between such dissimilar molecules is known as **adhesion**. The spherical shape of free drops fo liquids illustrates the forces of cohesion while the sticking together of wet pieces f paper and cloth illustrates the forces of adhesion. Both forces are of the Van der Waals type which may be very intense at short range, but decrease rapidly as the distance increases.

We all observe that rain drops are spherical and that mercury forms nearly spherical drops on a piece of glass. In both these instances, the liquid assumes the shape of least surface, (surface has least surface for a given weight) which minimises their enrgies. Let us see how this happens.

9.3 SURFACE AND INTEFACIAL TENSIONS

Le t us consider two different molecules of a liquid, A and B , one in the interior of the liquid and the other at the surface as represented in Fig. 9.1. The arrows represent the forces attracting the molecules towards their neighbours. The molecule A, which is in the interior of the liquid, will be attracted equally from all sides whereas, the moelcule B, which is at the surface, will be attracted more by the many molecules in the body or bulk of the liquid than by the few in the vapour above the surface. As a result of this pull the surface of a liquid always tends to contract to the smallest possible area. It is because of this reason, that drops of liquids and bubbles of gases in liquids become spherical, the surface being the minimum for the particular volume. In order to extend the surface area, work has to be done to bring the molecules in the interior of the liquid to the surface against the attractive forces drawing them inside. The work required to extend the surface area by 1 sq. cm. is known as the surface energy. Since attainment of equillibrium is always accompanied by a decrease in the freee energy, the tendency of a liquid to contract may be regarded as a consequence of its possession of free energy.

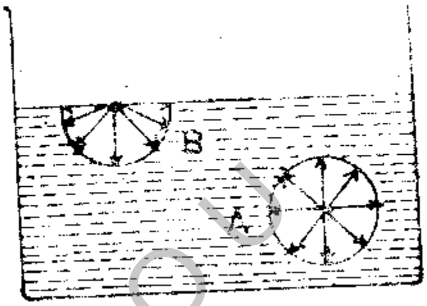


Fig: 9.1 - Liquid molecules in the interior and at the surface of a liquid

Due to the tendency of the surface to contract, the surface behaves as if it were in a state of strain or tension and this is knwon as the surface tension, which is the same at all points and in all directions on the surface of the liquid. The surface tension is usually repreented by the symbol, γ and can be defined as the force in dynes acting at right angles to a line of 1 cm length at any point on the surface.

We have already seen that the surface energy is the work required to increase the area of the surface by 1 sq. cm i.e. ergs cm^{-2}. Hence from the definition of surface tension,it follows that the surface free energy is equal to the surface tension multiplied by 1 cm, dynes cm^{-1}. In other words, the surface tension and surface free energy are identical with each other because 1 dyne = 1 erg cm^{-1}. .

The surface tension of a liquid is dependent on the nature of the liquid and gas with which the liquid is in contact. Usually, surface tensions are measured (and recorded) when the liquid is in contact with air saturated with its vapour. It can therefore be seen that some what different values will be obtained in the absence of air or in the presence of othe gases. The surface tension of mercury is particularly sensitive to such variations.

In the case of mixtures of two immiscible or partially miscible liquids, the work required to enlarge the surface of separation between the two liquids, is known as interfacial surface energy, and is generally expressed in terms of the interfacial tension in dynes cm^{-1} . The interfacial tension of such/mixture is usually less than the higher value of the two surface tensions.

The interfacial tensions at the liquid - solid interfaces are beyond your scope.

9.4 CONTACT ANGLE AND WETTING

Let us suppose that a liquid rests on a solid surface and attains equillibrium. The gas which is usually in contact with the solid and liquid is air. If θ is the angle of contact (Fig.9.2), measured in the liquid at equillibrium, the forces acting at the interfaces must balance. As assuming that these forces can be represented by the surface tensions at the respective interfaces, it follows that

$$\gamma_{gs} = \gamma_{ls} + \gamma_{gl}\cos\theta \qquad (9.1)$$

Where γ_{gs}, γ_{ls}, and γ_{gl}, are the surface tensions at the gas-solid. liquid-solid and gas - liquid interfaces respectively. from equation (9.1) it is evident that the contact angle, θ is governed by the values of the three surface tensions, γ_{gs}, γ_{ls}, and γ_{gl}. However, the possibility of the contact angle being greater than or less than 90°, is governed by the magnitudes of γ_{gs} and γ_{ls}. Thus, if γ_{gs} is greater than γ_{ls} then cos θ is postiitive and θ will be less than 90°. On the other hand, if γ_{gs}, is less than γ_{ls}, then cos θ will be negative and θ must lie between 90° and 180°. In the case of wateron glass, θ is less than 90°, whereas in the case of mercury on glass or water on paraffin, θ lies between 90° and 180°. In the former case, i.e. when θ is less than , the liquid is said to wet the solid, whereas in the latter case, i.e. when θ lies between 90° and 180° the liquid is said not to wet the solid.*

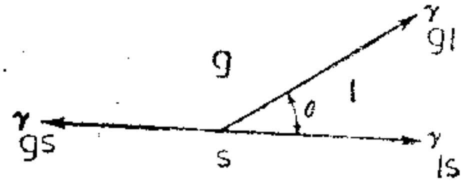
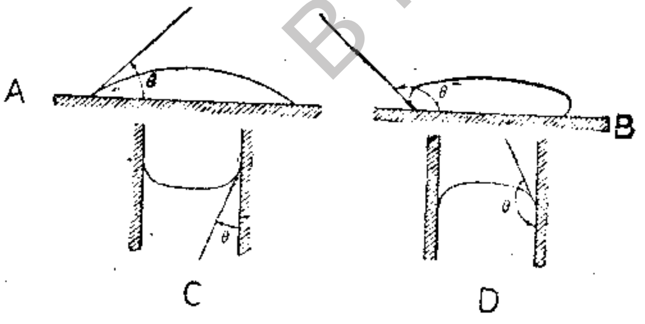


Fig 9.2 Gas liquid - solid interface

The effects of contact angle and wetting on a plane surface and in a tube, involving the two types of behaviour mentined above, are depicted in Fig. 9.3, where A and B are plane surfaces and C and D are tubes. It is seen that the surface or meniscus of a liquid in a tube is not flat but curved. The mensicus of the liquid is concave upward with liquids wetting the surface of the tube, whereas it is convex upward with liquids which do not wet the surface of the tube. We are all familiar with water (c) add mercury (D) in glass tubes exhibiting these two phenomena.



9.3 contact angle and wetting

c = liquid wetting the surface of the tube-D = liquid not wetting the surface of the tube.

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*Strictly speaking, complete wetting implies a contact angle to 0° and absolutely no wetting, an angle of 180°. But conventionally it is said that wetting occurs if θ < 90° and no wetting if θ > 90°.

Check your progress-1

When does a liquid wet a solid surface?

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9.5 CAPILLARY RISE

In view of the curved nature of the surface of a liquid, there will be a difference of pressure on the two sides and the magnitude of this difference is dependent onthe radius of curvature. If the liquid is in a capillary tube, since the radius of curvature of the capillary tube will be small, the difference in pressure will be large.

Let us suppose that a capillary tube is immersed in a liquidcontained in a large vessel and that the meniscus of the liquid in the capillary tube is concave upward, i.e, the liquid wets the surface of the capillary tube. If 'a' is the radius of curvatue of the meniscus, and is the surface tension of the liquid, then the pressure immediately below the meniscus, i.e, on the convex side, will be less by $2\gamma/a$ than at the same level outside the capillary tube. Because of this pressure differnece, the meniscus of the liquid will be forced up the capillary tube. If h is the height in cm by which the meniscus rises in the capillary tube at equilibrium, the pressures at the two points will be the same and the hydrostatic pressure of the column of the liquid of h cm will be equal to the difference in pressures under the curved meniscus and at the flat surface, the latter being $2\gamma/a$. If ρ^1 and ρ are the densities of the liquid and surrounding gas, i.e. air or

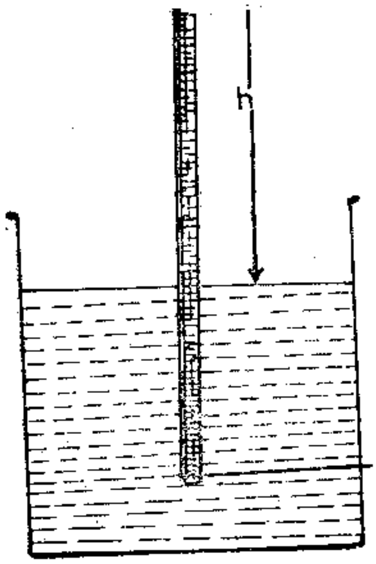

Fig. 9.4 capillary rise

liquid vapour respectively, the hydrostatic pressure of the column of the liquid of h cm is euqal to hg $(\rho - \rho^1)$, or

$$\frac{2\gamma}{a} = hg\,(\rho - \rho)$$

since $\rho >>> \rho$, ρ can be neglected (9.2)

$$\frac{2\gamma}{a} = hg\,\rho$$

$$\text{or } \gamma = \frac{1}{2}\,hg\,\rho\,a \qquad (9.3)$$

Generally, $a = r/\cos\theta$, so that

$$\gamma = \frac{1}{2}\,\frac{hg\rho r}{\cos\theta} \qquad (9.4)$$

If the angle of contact between the liquid and glass is zero, in a capillary tube, the radius of curvature of the meniscus 'a' will be equal to the radius of the cpaillary tube, *r*, so that

$$\gamma = \frac{1}{2}\,hg\,\rho\,r \qquad (9.5)$$

Liquid like mercury, which do not wet glass, form surfaces which are convex upward and the pressure just under the meniscus will be greater than that at the plane surface. Consequently, when a glass tube is placed inside mercury, the level ofmercury in the capillary tube will be below that of the surrounding liquid. In other words, there will be a fall in the level of mercury in the capillary tube. Under these conditions, the 'h' in equation (9.3) represents the fall in the mercury level in the capillary tube.

We thus see that the rise or fall in the level of a liquid in a capillary tube is dependent upon the surface tension of the liquid an dth ephenomena associated with surface twnsion are therefore considered under the general title of **capillary action** or **capillarity**, irrespective of the involvement of capillary tubes.

9.6 DETERMINATION OF SURFACE TENSION

a) Capillary rise method

The surface tension of a liquid can be determined by the capillary rise method in which the rise in the level of the liquid in a capillary tube, placed in the liquid, is measured. If this rise is 'h', 'r' is the radius of the tube, and ρis the density of the liquid, the surface tension, γ, can be calculated utilising equation (9.5). The results are satisfactory for approximate work, but for precision work, a number of corrections have to be made.

b) Drop-weight method

The surface tension of a liquid can be determined by the drop weight method also. The principle of this method is that the weight of a drop falling from a tube is governed by the radius of the tube, r, and the surface tension of the liquid,γ. According to Harkins and Brown (1919); the apparent mass, m, of a liquid falling from a tube is given by

$$mg = 2\pi r\gamma\phi \qquad (9.6)$$

where ϕ is a correction factor dependent upon r/v^3, v being the volume of the drop. The values of for different liquieds are tabulated by Harkins and Brown. The apparent mass, m, in equation (9.6) is given by

$$m = \frac{m_o(\rho - \rho)}{\rho} \qquad (9.7)$$

where m is the mass of the drop in vaccum andρ are ρ^1 the densities of the liquid and surrounding medium, i.e, air, respectively.

where τ is the surface concentration per unit area of the interface, c is the bulk concentration, γ is the surface tension, R is the molar gas constant and T is the absolute temperature. From equation (9.12) it is evident that if $d\gamma/dc$., i.e, the change in interfacial tension with concentration, is negative then τ is positive, or in other words, the concentration of the substance at the surface will be higher than that in the bulk.

Check your progress -2

Why do solids adsorb gases?

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9.9 INTERFACIAL TENSION AND ADSORPTION BY SOLIDS FROM SOLUTION

It is well known that charcoal removes coloring matter from solutions and that finely-divided powders take up dyestuffs and other substances from solutions and this is another aspect of adsorption. Here it may be assumed that the surface acts in the same manner as in the adsorption of gases by virture of molecular attraction or alternatively, it may provide an inteface of large area where a solute, which is capable of decreasing the interfacial tension, may accumulate. The information available for the tensions at the solid liquid interfaces is very little and although there is no theoretical justification, it can be assumed that the tensions for solid - liquid interfaces run parallel to the air - liquid interfaces since the experimental evidence seems to support the validity of this parallelism. For example, charcoal adsorbs dyestuffs more readily from aqueous solutions than from alcoholic solutions. In fact, the dyestuff adsorbed by charcoal from aqueous solution can be readily extracted by alcohol. The air - liquid interfacial tension of water is highehr than that of alcohol, and hence the decrease in surface tension of the aqueous solution with increasing concentration of the dyestuff will be higher than that for the alcoholic solution. Therefore, in accordance with the Gibbs adsorption equation. (equation 9.12), the adsorption of the dyestuff at the air-liquid interface will be greater in aqueous than in alcoholic solutions. The same result is observed at the solid-liquid interfaces also.

The parallelism mentioned above, however, breaks down sometimes. For example, although amyl alcohol lowers the surface tension of water more than phenol, charcoal adsorbs phenol more readily from aqueous solution than amyl alcohol.

Many of the substances are adsorbed from their aqueous solutions because of the high surface tension of water. Very few cases of negative adsorption from aqueous solutions by solids like powdered silica and charcoal, occur with electrolytes and as has already been mentioned, there will be an increase in the surface tension at the air-liquid interface. The Gibbs adsorption equation cannot explain this adsorption of electrolytes and one of the reasons attributed for this failure of adsorption is that the Gibbs equation does not take the electrostatic forces into consideration.

9.10 SUMMARY

Cohesion and adesion are the attractive forces between identical and different molecules respectively. In liquids the molecules of the bulk attract the molecules present at the surface due to which they exhibit the characteristic property surface tension. A liquid wets a surface if the contact angle is less than 90. Surface tension can be determined by eithre capillary rise method or drop weight method. The surface of a solid remains unsaturated and this tendency is responsible for their adsorption of gases.

9.11 MODEL EXAMINATION QUESTIONS

I **Answer the following in 10 lines**

1. Explain the difference between cohesion and adhesion, with suitable examples.
2. Why does a tension exist at the surface of a liquid?
3. Describe the effects of contact angle and wetting on a plane surface and in a tube.
4. Derive the equation for the surface tension of a liquid by the method of capillary rise.
5. Explain how surface tension and adsorption are related to each other.

II **Answer the following in 30 lines.**

1. Write an account of the origin of contact angle and the phenomenon of wetting.
2. Describe the method of determination of the interfacial tension at the interface of two immiscible or partially miscible liquids.

9.12 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. A liquid wets a solid surface if the contact angle is less than 90°.
2. Surfaces of the solids remain unsaturated. Therefore they adsorb gases and undergo free energy decrease.

Author: Prof. N. Venkateswar Rao

UNIT - 10 COLLOIDAL SOLUTIONS

Contents

10.1 AIMS AND OBJECTIVES

To explain you the term colloidal state and describe the methods of preparation, properties and uses of colloidal solutions.

After the thorough study and undertanding of the contents of this unit you are expected to:

- findout that colloidal solution consists of very fine (1 to 100 n m i.e, 1 x 10 to 1 x 10 cm diameter) particles of substance, dispersed in a medium in which it is immscibel.
- know that colloids are prepased by different methods and they exhibit typical optical and electrical properties.
- state the applications of colloids in chemical analysis, medicine and industry.

9.2 INTRODUCTION

A colloidal solution may be defined as a heterogeneous mixture, consisting of a dispersed distributed in a continuous phas or **dispersion medium**. Colloidal matircals like purple of Cassius, alchemical potable gold and colloidal clay used in making pottery and Chinaware, have been known for centuries. It was, however, in 1861 that Thomas Graham, studied the diffusion of solutes in solutios, and divided solutes into two types, namely, crystalloids and colloids. But, since almost any substance, may be prepared in the colloidal condition, crystalloids and colloids ar e no longer regarded as different from each other.

The dispersed phase and dispersion medium of a colloidal system may be in any of the three states of matter, namely, solid, liquid and gas, and the names of the colloidal systems based on these combinations are given in Table 10.1.

Table 10.1: Classification of Colloidal systems

Dispersed phase	Dispersion medium	Name of colloidal system	Examples
1	2	3	4
Solid	Solid	Solid sol	Gold in ruby glass,
	Liquid	Sol	AsH_2SH_3 or S in H_2O,
	Gas	Solid aerosol	Smoke, NH_4Cl fumes
liquid	Solid	Solid emulsion or gel	Milky quartz; opal
	Liquid	Emulsion	Milk; oil in H_2O
	Gas	Liquid aerosol	Fog, mist
Gas	Solid	Solid foam	Pumice stone
	Liquid	Foam	Soap foam; whipped egg white
	Gas	---	Unknown

Of the eight types of colloidal systems mentioned in Table 10.1., although sols, emulsions, gels and foams are of particular importance, we shall consider here sols, emulsions and gels.

10.3 SOLS

Colloidal solutions are generaly referrned to as 'Sols'

Sols may be classified according to the liquid which acts as the dispersion medium. Thus, if water is the dispersion the sol is called a hydrosol, and if the dispersion medium is alcohol, the sol is called an alcosal, etc. The hydrosols can be further divided into hydophinic sols (solvent - loving) and hydrophobic sols (solvent-hating). Sols of hydrous oxides like Fe_2O_3, SnO_2, starch, and protein etc are examples of hydrophilic sols while sols of metals, sulphides, Ag Cl, etc. are examples of hydophobic sols. Lyophilic (solvent-loving) and lyophobic (solvent-hating) are more general terms. Sols which on addition of electrolytes to them, permit the separation of dispersed phase as a precipitate are referrned to as hydrophobic sols. The phenomenon of such precipitation is called co-agulation . Thhose sols whihc do not permit this under normal conditions are called hydrophilic sols.

10.4 PREPARATION OF SOLS

Hydrophilic sols of organic substances like gum arabic, gelatin, starch, etc can be prepared by dissolving them in water.

Hydrophobic sols can be prepared by only **condensation** and **dispersion methods**. Sols are coagulated by addition of electrolytes and hence it is necessary that all vessels used should be thoroughly clean and that all the materials used should be pure. The cleaning of the vessels is best achieved by steaming them out.

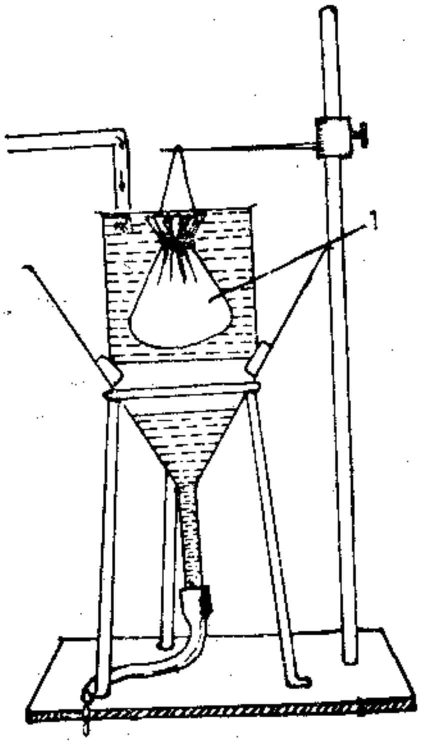

Fig 10.2 Dialysis of colloidal solution

membranes, in place of parchement paper. Dialysis is generally slow at room temparature and can be hastened by warming the solution.

Electro Dialysis: Electrodialysis, which involves the passage of current through a colloidal membrane, hastnes the process still further. The apparatus consists of a vessel which the sol is enclosed between two colloidal membranes, M_1 and M_2; (Fig. 10.3).

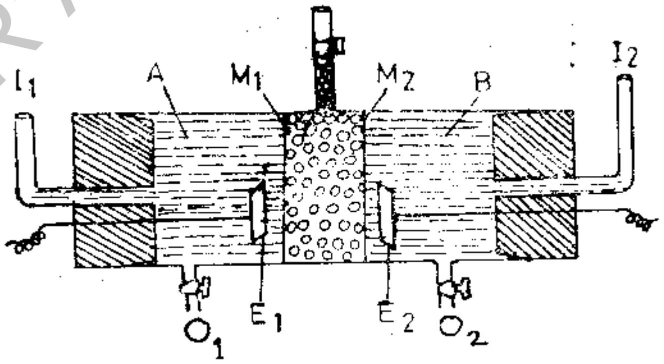

Fig: 10.3 Electro-dialysis

Two electrodes E_1 and E_2 are placed near the membranes and water is contained in the end compartments A and B. When emf is applied between the electrodes, ions of the electrolyte pass into the water through the collidal membrane. Fresh water is added through the inlet tubes I_1 and I_2 and dilute electrolyte is removed through the outlets, O_1 and O_2

Ultra Filtration: Purificaiton of colloids can also be achieved by the process of ultrafiltration, which is similar to that of filtration of an ordinary precipitate, except that a membrane, through which electrolytes, but not the colloid, passes, is used as the filtering, medium. Filter paper impregnated with collodion, unglazed porcelain, finely sintered glass, etc. can be used as suitbale filtering media. Ultrafiltration proceeds very slowly and hence pressure or suction is used to speed up the process.

10.6 OPTICAL PROPERTIES OF SOLS

Sols possess characteristic optical properties. A strong beam of light when passed through a sol, is made visible by the light scattered by the particles of the sol. This phenomenon, which was first noticed by Michael faraday (1857) was studied in detail by John Tyndall (1869) and is known as the Tyndall Effect. The intensity of the scattered lgith depends upon the wavelendgth of the light, the refrcactive index of the particles relative to the medium and their number and size. According to Lord Rayleigh (1875) the light scattered by a particle of radius 'r' which is small when compared to the wavelength of the light, is given by the equation.

$$I = \frac{498 I_0 (m-1)2r^6}{\lambda^7_{4R^2}} \qquad (10.1)$$

Where I and I_0 are the intensities of the illuminating and scattered beams at a distance, R, and 'm' is the refractive index of the particle relative to the medium. Since blue light, which is of shorter wavelength than the red light, is scattered more than the red, the dispersed particles in the atmosphere scatter the blue light more and transmit the red light better. This phenomenon of multiple scattering accounts for the blue colour of the sky and the red colour of the sun near the horizon.

Since the sizes of molecules of the solutions are too small (when compared to those of sols) to cause appreciable scattering of light, the formation of a Tyndall beam distainguishes a sol from a true solution. Further, the intensity of the Tyndall beam increases with increasing size of the particles of a sol. There is a marked difference in the Tyndall beams of lyophilic and lyphobic sols. The lyophilic sols adsorb the liquid molecules very strongly and the resulting micelle largely consists of the dispersing liquid. The refractive index of the micelle will almost be the same as that of the solvent and hence the light scattering will not be appreciable.

The particles of a sol cannot be seen by microscope, but can be seen in the ultramicroscope (Fig. 10. 4) in which the Tyndall beam passing through the sol is viewed with a microscope at right angles to the beam. Individual particles of the sol appear as bright spots of light against a dark background.

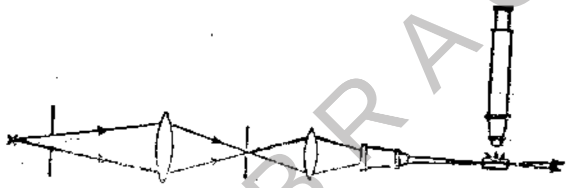

Fig: 10.4 Schematic representation of ultramicroscope

If, in an experiment, 'n' is the number of particles observed in a field or view of volume 'v' 'b'is the weight of the substance in grams per ml (determined by evaporation and weighing), and 'ρ is the density of the dry substance, then, the mean radius 'r' of the particles is given by equation (10.2)

$$r = 3\sqrt{\left(\frac{3bv}{4\pi n\rho}\right)} \qquad (10.2)$$

Equation (10.3) is based on two assumptions, namely, that the particles are spherical, and that the density of the substance in the sol is the same as that of the dry substance.

The limit of visibility of the particles of a sol in the ultramicroscope is governed by the optical nature of the particles of the sol as well as that of the dispersion medium. Sols of metals can be detected down to diameters of 6 x 10^{-7} cm, while particles of organic sols can be seen down to 4 x 10^{-7} cm only.

Particles which cannot be seen even with the ultramicroscope are known as amicrons.

10.7 ELECTRICAL PROPERTIES OF SOLS

When current is passed through a sol, the colloidal particles move towards the cathode if they carry a positive charge, and towards the anode if they carry a negative charge. This movement of colloidal particles towards an electrode is knwon as electrophoresis. Experiments carried out with different types of sols have indicated that sols of metals, metallic sulphides and organic substances like gum arabic, etc. are negatively charged, while sols of metallic hydroxides and oxides and basic dyestuffs are positively charged.

The origin of the charge (positive or nagative) of a colloidal particles is ascribed to the adsorption of positive or negative ions, present in the dispersion medium, by the colloidal particles. It has been shown by Hardy that the sign of the charge on sol could be varied by placing the sol in an environment of ions of an opposite sign to that which it has. Thus, mastic has almost no charge when it is suspended in water, but becomes positively charged when placed in an acid solution, and negatively charged when placed in an alkaline solution.

Check your progress - 1

What is electrophoresis?

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10.8 KINETIC PROPERTIES OF SOLS

Brownian movement is an important kinetic property of colloids. Robert Brown (1827) a botanist, observed that pollen grains, when suspended in water, move ceaselessly. When colloidal particles also under the ultramicroscope, it was found that the colloidal particles also move ceaselessly in a zig-zag manner. It was also shown that the motion of the colloidal particles was almost independent of their nature but is dependent on their sizes. The movement was more rapid, the smaller the particle and the lesser the viscosity of the solution.

In view of the haphazard movement of a colloidal particle, although it is difficult to make an accurate observation on the motion, the probable displacement of a particle after a given time, can be calculated (Fig. 10.5)

If Δ is the displacement of a colloidal particle along the x-axis in a given time 't' , it is given by

$$\Delta = \sqrt{\left(\frac{RT}{N}\left(\frac{t}{3Phr}\right)\right)}$$

where R is the molar gas constant, T is the absolute temperature, N is the Avogadro number, 't' is the time, 'n' is tjhe viscosity coefficient and 'r' is the diameter of the colloidal particle

Perrin and others have calculated the Avogadro number utilising equation (10.3)

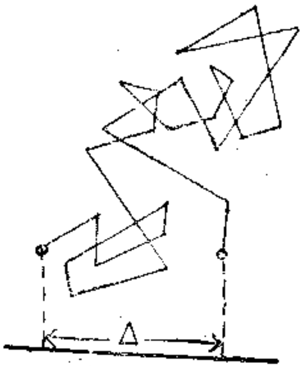

Fig. 10.5 Brownian Movement

10.9 COAGULATION OF SOLS BY ELECTROLYTES

Addition of an electrolyte to a sol often results in precipitation. You have already learnt that the origin of charge on a colloidal particle is due to the adsorption of ions by the colloidal particle. Therefore, it follows that removal of the charge on the colloidal particle by the addition of an electrolyte having an oppositely charged ion, should result in the precipitation of the colloid. Further, the efficacy of the electrolyte should depend upon the valency of the oppositely charged ion.

Hardy and Schultz have investigated these aspects in detail and have enunciated a law, known after their names, which states that the coagulating effect of an ion depends upon its valency. This is evident from the data given in Table 10.2.

Table 10.2 Coagulation of As_2S_3 Sol (1.85 g litre^{-1})

salts of Univalent cations	Coagulation value	salts of Bivalent cations	Coagulation value	salts of Trivalent cations	Coagulation value
NaCl	51	$MgSO_4$	0.81	Al_3Cl_3	0.093
LiCl	58	$MgCl_2$	0.72	$Al(N_3)$	0.095
KCl	49	$BaCl_2$	0.69	$Al_2(SO_4)_3$	0.096
KNO_3	50	$ZnCl_2$	0.68	$Ce(NO)_3$	0.080
Average	52		0.72		0.091

Arsenic sulphide sol is negatively charged and hence, the coagulation values (millimoles of electrolytes per litre of sol) of the ions are in the order univalent > bivalent > trivalent, which is in agreement with the Hardy Schultz law.

10.10 PROPERTIES OF COLLOIDS

You have seen that hydrophobic sols are precipitated by the addition of electrolytes. Bu this precipitation can be prevented by the addition of suitable agents called protective agents. Substances capable of forming hydrophilic colloids (Agar, gelatin) generally act as protective agents. The sol can be evaporated to dryness and can be regenerated by dissolving the substance obtained evaporation. Thus the behaviour of the sol is changed from an irreversible one to that of a reversible one.

Zsigmondy introduced the concept of gold number, to measure the relative protecting powers of organic colloids. The gold number defined as the quantity, in mg, of the added hydrophilic colloid which can protect 10 ml of a standard red gold sol (0.0053 to 0.0058 per cent) from coagulation by the rapid addition of 1 ml of a 10 per cent solution of sodium chloride. The gold sol has to be prepared in accordance with prescribed procedure.

The gold number is not a very accurate measure but has always a range of values as can be seen from the results in Table 10.3

Table 10.3 Gold numbers

Protective agent	Gold number
Gelatin	0.005 - 0.01
Albumen	0.1 - 0.2
Guma Arabic	0.15 - 0.25
Detrin	6-25
Potato starch	20-25

Protective action of colloids is a very important phenomenon and enables preservation of colloids. Making use of this phenomenon, Carey Lee prepared metal sols of high concentrations, of as high as 99 percent, by reducing silver nitrate solution with a mixture of ferrous sulphate and sodium citrate, the organic matter acting as a protective colloid for the silver. Such sols are used in medicine, in the form of ointments or intravenous injections. In the preparation of ice cream, gelatin is added as a protective colloid, to give a smooth appearence to the ice cream. If the gelatin is not added, small gritty crystals of ice and lactose would separate.

Check your progress - 2

What is gold number?

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10. 11 EMULSIONS

An emulsion is a colloidal dispersion of one liquid in another, the liquid acting as the dispersion medium being present in excess. Thus an emulsion of nitrobenzene in water can be obtained by shaking little nitrobenzene with excess of water, and an emulsion of water in nitrobenzene is obtained by shaking a little water with excess of nitrobenzene.

The emulsions mentioned above are respectively called oil in water (Nitro benzene in water) and water in oil (water in nitro benzene) types of emulsions. Emulsions are not generally stable since the drop lets of the dispersed phase coalesce forming a second continuous dispersion medium. But the presence of some substances called emulsifying agents-stabilises the emulsions. An emulsifying agent forms a film at the oil-water interface and prevents the coalescence of the droplets. This stabilises the emulsion. Soaps, gelatin and other hydrophilic sols are useful as emulsifying agents.

Stable emulsions can be broken, or deemulsified, by the addition of a reagent which attacks the emulsifying agent and destroys the interfacial film between the colloid droplet and the dispersion medium.

Thsu addition of an acid to an emulsion stabilized by soap, converts the soap into the corresponding fatty acid, which has no emulsifying action and thus allows the droplets to coalesce.

The droplets in an emulsion behave like colloidal particles in that they are electrically charged (usually negative) and migrate in an electric field. Addition of a salt containing a divalent, or trivalent cation, results in the 'salting out' of the colloidal droplets. Heating, cooling vibration and centrifugation also causes coalescence of the colliodal droplets and separation of the two liquid phases.

Many ointments and other pharmaceutical preparations are emulsions. Milk also is an emulsion of butter fat in water, the hydrophilic sol case in acting as the emulsifying agent.

10.12 GELS

A gel is a semirigid mass of a lyophilic sol, in which the dispersion medium is completely adsorbed by the sol particles and producing a spongy structure of micelles. By suitable choice of conditions, almost all lyophilic sols can be converted into gels. Since the gel possesses a completely continuous structure, it follows that the micelles built up must be intricately interwoven.

Gels of a large number of inorganic and organic substances, such as the hydrous oxides of iron, aluminium, silicic acid, many kinds of soaps, gelatin, starch, etc, can be prepared. Calcium acetate alcohol (obtained by the addition of ethanol to a solution of a calcium acetate in water) forms a gel called "solid alcohol", on standing.

Gels can be subdivided into two kinds namely, elastic and non-elastic. Gels of gelatin, agar, etc.are of the elastic type while silica gel is of the elastic type. A completely dehydrated elastic gel can be regenerated by the addition of water whereas such a gelation does not take place in the case of elastic gel. The difference in this hydration behaviour is attributed to the difference in the structures of the dried gels.

When water is added to dehydrated elastic gels, the latter adsorb water, sometimes in large volumes, leading to swelling of the gels. Both elastic and nonelastic gels, shrink in volume on standing, with an attendant exudation of the solvent. this phenomenon is knwon as syneresis. Again, some gels, particularly those of gelatin and hydrous oxides, liquefy and form a sol on shaking, and the sol reverts to a gel on standing, i.e, the sol-gel transformation occurs reversibly. This phenomenon is called thixotropy.

10.13 APPLICATIONS OF COLLOIDS

Colloids find applications in qualitative and quantitative chemical analysis and in industry also. It is always essential that organic matter should be removed before starting in a qualitative analysis, one of the reasons being that the organic matter may form protective colloid resulting in an incomplete precipitation of the cations in different groups.

One of the chief sources of error in gravimetric analysis is adsorption, which depends upon the particle size. The adsorption is greater the smaller the particle. This error due to adsorption can be eliminated by carrying out the precipitation at elevated temperatures and also by employing fairly concentrated solutions of the reagents.

Colloids find graeat application in industry particularly in adsorption. Silica gel is very effective in the adsorption of gases and is used in large quantities for this purpose. Many of the impurities in sewage are colloidal in nature and hence the treatment of sewage is also a collidal problem. Colloid science plays an important role in the study of soils, tanning, cooking and paint industries as well as several biological processes.

10.14 SUMMARY

A colloid is a heterogeneous mixture of a dispersion phase distributed uniformly in a dispersion medium. In the unit classification of colloids which based on the physical states of dispersion phase and medium and different methods of preparation of colloids are presented. Electrophoresis, tyndal effect and Brownian movement are the typical properties of colloids electrolytes can coagulate hydrophobic colloids . Hydrophilic colloids protect the hydrophobic colloids from coagulation by the addition of electtrolytes. colloidshave many applications.

10.15 MODEL EXAMINATION QUESTIONS

I Answer the following in 10 lines

1. Describe the preparation of a colloid by the Bredig's arc method.
2. Explain the origin of charge on a colloidal particle.
3. What is ultramicroscope and how is it useful in studying colloids?
4. State and explain Hardy-Schultz law with suitable examples.
5. Explain the protective action of colloids with suitable examples.

II Answer the following in 30 lines.

1. Describe the Brownian movement of colloidal particles and expalin application.
2. Give an account of the different methods of purification of colloids.

10.16 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. On passing electricity through a sol, the colloidal particles move towards anode or cathode based on their charge. This movement of colloidal particles to cathode or anode is called electrophorisis.
2. Gold number is the minimum dry weight of a hydrophilic colloid which is to be added to 10 ml of a standard gold solution to prevent coagulation by the addition of 1 ml of 10% NaCl solution .

Author : Prof. N. venkateshwara Rao

BLOCK 5

PHASE RULE

The study of homogeneous equilibria is the slope of chemical equilibrium. Heterogeneous equilibria are studied in phase rule. Phase rule is a mathematical expression, $F = C - P + 2$. This rule enables us to forecast the changes that take place in heterogeneous equilibria under different experimental conditions.

if the temperature is fixed, the vapour pressure is fixed, and vice versa. We can therefore say that such a system has only one degree freedom.

Consider now a system consisting of gaseous phase only. It is well known that in the case of gases, pressure, volume, and temperature are related by means of one equation or another. Out of these three quantities, it is just sufficient if any two are fixed, because the third quantity is automatically fixed. In other words, any two of these three quantities completely define the system and the two quantities can be varied without altering the number of phases present. That is, the number of degrees of freedom of the system is 2.

Check your progress -1

What do you mean by a univariant system?

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Components

The number of components may be defined as the smallest number of independently variable constituents by means of which the composition of each phase of the system can he expressed in the form of a chemical equation.

To illustrate the definition, let us consider the system consisting of sulphur and its allotropes, liquid sulphur, and sulphur vapour. In this system the composition of each phase can be expressed in terms of only one constituent, namely sulphur. The system is thus a one component system.

The equilibrium $CaCO_3 \rightleftharpoons CaO + CO_2$

contains three different molecular species, namely, $CaCO_3 \rightleftharpoons CaO$ and CO_2 the first two being solids and the last one, a gas. The composition of each phase can be expressed in terms of two components. For example, if CaO and CO_2 are chosen as the oenstituents then the compositions of the three phases can be expressed as :-

$$CaCO_3 = CaO + CO_2$$

$$CaO = CaO + 0\,CO_2$$

$$CO_2 = CO_2 + 0\,CaO$$

On the other hand, if $CaCO_3$ and CO_2 are chosen as the two constituents, then,

$$CaCO_3 = CaCO_3 + 0CO_2$$

$$CaO = CaCO_3 - CO_2$$

$$CO_2 = 0\,CaCO_3 + CO_2$$

Thus in this system the smallest number of constituents that fixed the composition of each face is two, or this is a two-component system.

Phases

A phase may be defined as a part of the system which is homogeneous through out and can be separated from other homogeneous parts of the system by a boundary.

Considering the equilibrium mentioned above,

$$CaCO_3 \rightleftharpoons CaO + CO_2$$

We can see that there are three phases in this system, namely, $CaCO_3$, CaO and CO_2 the first two being solids, and the third one, a gas.

In this system under consideration consists of a mixture of liquids, the number of phases depends upon the miscibility or othewise of the liquids. If the liquids are miscible with each other, the number of phases is only one. On the other hand, if the liquids are partially miscible depending upon the concentrations, the number of phases may be one or more. However, if the liquids are immiscible, each liquid will constitute a separate phase.

In the case of a system of a mixture of gases, the number of phases will be only one. Since gases are always completely miscible, no matter how many different molecular species make it up.

11.4 APPLICATION OF PHASE RULE TO SINGLE-COMPENT SYSTEM

Water Vapour - Water - ice equilibrium

The number of components in this system is only 1, but the number of phases may be varying. Thus, if we consider an equilibrium of phases may be varying. Thus, if we consider an equilibrium in which all the three phases, i.e. ice, water and vapour, are present, then according to the phase rule, the number of degrees of freedom

$$F = 1 - 3 + 2 = 0$$

That is, the system has no degree of freedom and such systems in which F = O are called "non-variant', or 'invariant" systems. For a system to have no degreee of freedom (F =O), means that none of the variables, pressure, temperature and concentration, can be altered without the disappearance of the phases, from the system. The three phases can therefore exist, only under one condition of temperature and pressure, their values being 0.00075° C and 4 mm respectively.

Considering the existence of only two phases, ice-water, water-water vapour, ice - water vapour, i.e, P =2, it follows that

$$F = 1 - 2 + 2 = 1$$

This means that such 2-phase systems are univariant, and one of the degrees of freedom, say temperature, can be varied without altering the number of phases.

These facts are borne out by experiment and Fig. 11.1 represents the variation of vapour pressures of ice, water and water vapour with temperature.

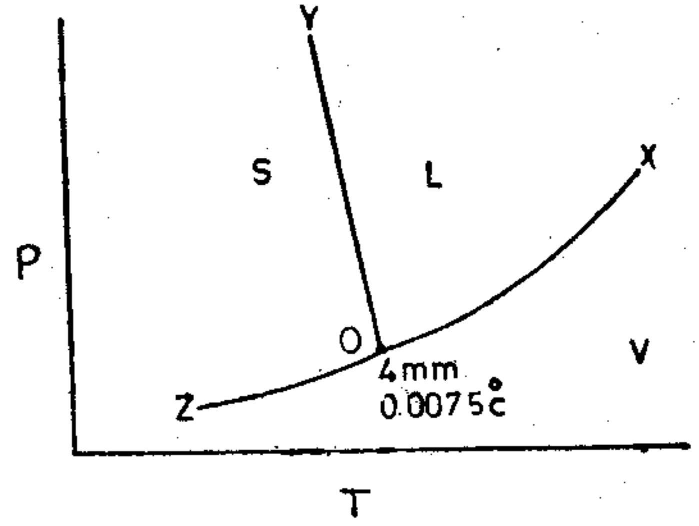

Fig: 11.1 P-T diagram for water

In the Fig. 11.1 OX, OY and OZ represent the vapour pressure curves of the equilibria, water-water vapour, ice-water, and ice and water-vapour respectively. The three curves meet at a point O; which is called the triple point (0.0075 C and 4 mm), where ice, water and water vapour can co-exist. It is represented only by a point which indicates that the three phases can exist only under one set of conditions, as envisaged by the phase rule. Once the conditions are altered, one phase disappears, and this disappearance depends upon the direction in which the conditions are altered.

Along the lines OX, OY and OZ, two phases exist and in any of the areas bounded by two lines, one phase exists, i.e, ice, water and water vapour exist in the areas ZOY, YOX, and XOZ respectively. If it were possible to have water represented by the point P, (firgure 11.2) it would be metastable and would soon turn into vapour. Similarly, water may be supercooled to 'X' but the supercooled water will be in a metastable state. It can therefore be concluded that in diagrams of this kind-a point, a line and an area represent the existence of an invariant, univariant and bivariant systems respectively.

From a careful exmaination of the curves in Fig. 11.1 it is seen that the curve OX ends abruptly at a point which corresponds to the critical temperature (374°C) and critical pressure (218.5 atm) of water, beyond which, the water and water vapour phases cannot be dstinguished from each other. Similarly, the curve OZ ends abruptly at O° K and zero pressure.

In the case of the curve OY, however, no limit can be fixed, at least in principle, although it leads to a region where at least six polymorphic forms of ice exist. Further the sloping of the curve OY indicates that melting of ice is always accompanied by a decrease in volume, as predicted by the Le Chatlier principle according to which increase of pressure at a constant temperature will result in a decrease in volume. If the pressure on the system is increased at the point A, at a constant temperature, the system will be represented by B, i.e, wate ris formed and the change is accompanied by a decrease in volume. Similarly, freezing of water will be accompanied by an increase in volume (dotted line AC in the figure).

The diagram shown in Fig. 11.1 is only an approximate one and a more accurate one, in the neighbourhood of the triple point is shown in Fig. 11.2.

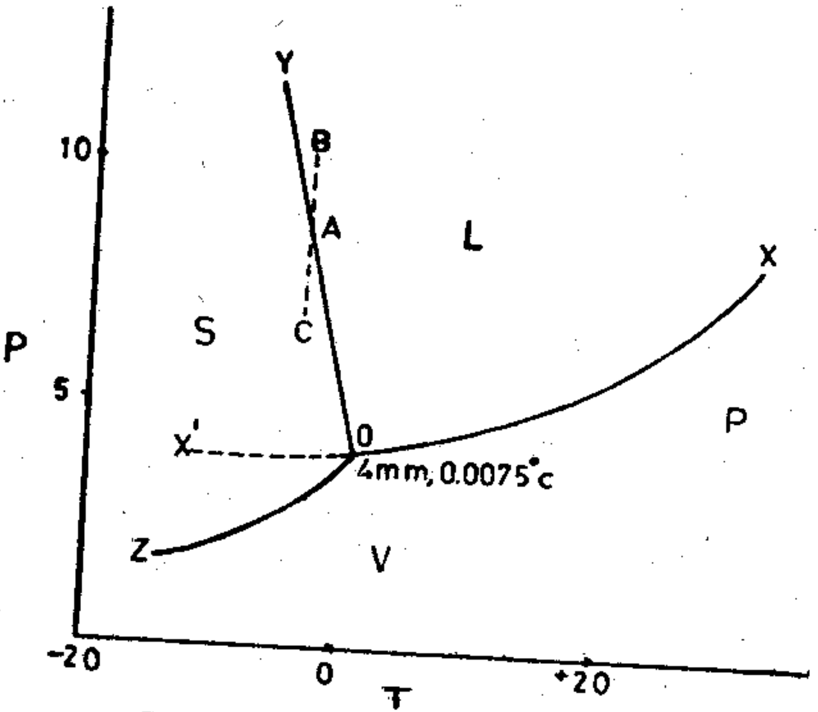

Fig: 11.2 Triple point of water (enlarged scale)

Check your progress - 2

What is triple point?

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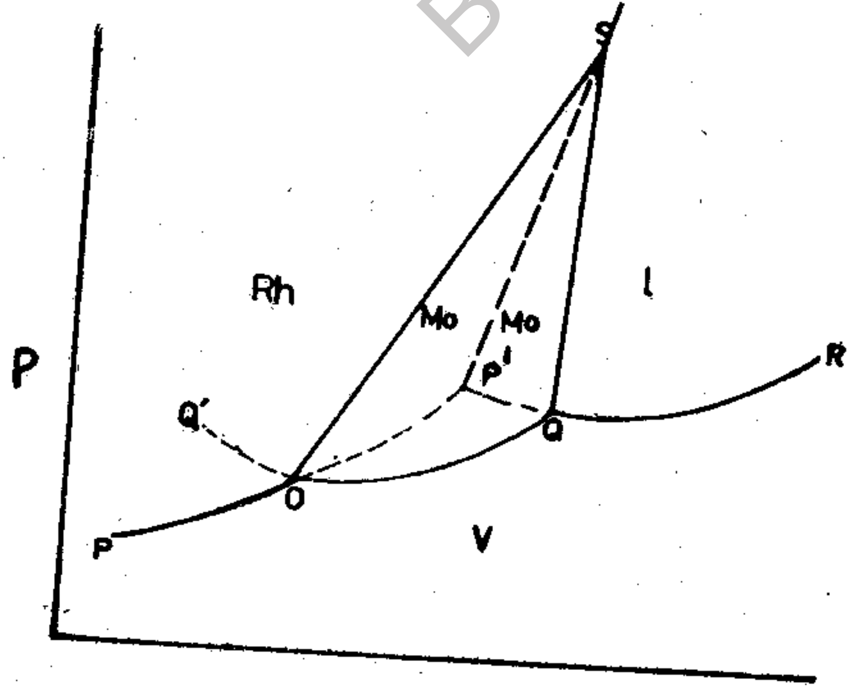
The Sulphur System

Sulphur exists in several allotripic forms some of them being stable while the others are metastable. The stable forms are: rhombic, monoclinic (both are solids), liquid sulphur and sulphur vapour. The vapour pressure-temperature curves for these different forms are given in Fig 11.3



Let us now try to calculate the degrees of freedom for the existence in equilibrium of the different forms of sulphur - rhombic, monoclinic, liquid and vapour. If all the four phases were to exist in equilibrium i.e, p= 4, the number of degrees of freedom would be

$$F = 1 - 4 + 2 = -1$$

which means that it is not possible for all the phases to co-exist in equilibrium. On the other hand, for the existence of any three phases in equilibrium, i.e, p = 3, then

$$F = 1 - 3 + 2 = 0$$

That is , a system consisting of any three phases is invariant, just as in the case of the water system. Such a system is represented by a point and variation in the temperature or pressure will result in the disappearance of one of these three phases.

Considering the equilibrium between any two phases, i.e, P = 2,it can be seen that these systems are univariant and one of the factors can be altered without disappearance of the phase. If P = 1, that is for any single phase, F = 2 or the system is bivariant, and the two factors can be altered without any disappearance in the phase.

From the analogy with the water system, it follows from what has been mentioned above, that three phases can exist at a point, two phases pressure-temperature curves for the different forms of sulphur are given approximately in Table 11.3. OP, OQ, and QR are vapour pressure curves of rhombic, monoclinic and liquid sulphur respectively. OS represents the equilibrium between the rhombic and monoclinic forms of sulphur and is obtained from the effect of pressure on the transition point. QS represents the equilibrium between monoclinic and liquid sulphur. The sloping of the line OS to the right indicates that when monoclinic sulphur is converted into rhombic sulphur, there is an increase in volume, in accordance with the Le chatlier principle (just as in the formation of ice from water). Similarly, the sloping of the curve QS slightly to the right shows that there is a decrease in volume when liquid sulphur is converted into the monoclinic form.

An examination of the Fig. 11.3 indicates the existence of three triple points, O, Q, and S for the sulphur system, the points corresponding to the equilibria :- rhombic, monoclinic - vapour, monoclinic, liquid - vapour and rhombic-monoclinic - liquid , the point S existing under the conditions 151° C and 1288 atm.

Liquid sulphur can be supercooled to the point P and it is also possible to superheat rhombic sulphur along O P. The point P is thus another tribple point, but is a metastable one and is not frequently attained.

11.5 SUMMARY

Phase rule is a mathematical expression, F = C - P + 2. The terms involved in phase rule components (C) degrees of freedom (F) and phases (p) are explained. This unit is restricted to the application of phase rule to one component systems i.e., water and sulphur. In the phase diagrams of one component systems areas represent bivariant systems, lines represent univariant systems and point represents an invariant system.

11.6 MODEL EXAMINATION QUESTIONS

I Answer the following in 10 lines

1. From the vapour pressure-temperature curves of the water system, explain how a point, a line and an area represent the equilibria between 3 phases, 2 phases and single phase respectively.

2. From the vapour pressure temperature curve of the sulphur system, show that the triple point between rhombic, monoclinic and liquid forms of sulphur, is a metastable one.

3. From the vapour pressure-temperature curves of water system, show that there is an increase in volume when water is converted into ice.

II Answer the following in 30 lines

1. State the phase rule and explain the terms involved, with suitable examples.

2. Discuss the application of phase rule to the water or sulphur system.

11.7 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. In the phase diagram of a one component system, the stage where only one parameter among temperature and pressure can be varied without the disappearance of one phase among the two is called a univariant system. Lines represent univariant systems.

2. In the phase diagram the point where three lines join is called triple point. The system at this point is invariant.

UNIT - 12 PHASE EQUILIBRIUM - TWO COMPONENT SYSTEM

Contents

12.1 AIMS AND OBJECTIVES

To Discuss the application of phase rule to two component systems.

Once you completely study and understand the contents of this unit, you must be able to apply the phase rule to:

- Metallic alloys and salt hydrates
- Solutions of gases in gases
- Solutions of gases in liquids - Henry's law
- Solutions of gases in solids
- Solutions of liquids in liquids

12..2 METALLIC ALLOYS AND SALT HYDRATES

Let us discuss the application of phase rule to a system of two solid metallic components, say an alloy of zinc and cadmium. Since there will not be any noticeable change in the volume of a solid by the application of pressure, pressure will not have any effect on this equilibrium. Hence it is sufficient to consider the effects of only temperature and composition on this euqilibrium.

Since the vapour pressures of solids are small and the experiments are usually carried out at atmospheric pressure, the phase rule can be written in a 'reduced' form as

$$F = C - P + 1 \qquad (12.1)$$

where F represents the number of degrees of freedom which the system possesses in addition to the pressure.

Fig: 12.1 represents the phase equilibrium diagram of alloys such as those of zinc-cadmium, where there is no miscibility of the components in the solid state and also no compound formation. AB represents the freezing point curve of znc to which cadmium is added in successive small quantities and similarly B represents the freezing point curve or cadmium to whihc zinc is added in successive small amounts. At the point B, solid zinc and solid cadmium will be in equilibrium with the fused mass and udner these conditions, the number of phases is 3 and the number of components is 2. Hence from the "reduced" phase rule, it follows that $F = 2 - 3 + 1 = 0$. That is, the equilibrium at B is invariant. Along the line AB, solid zinc will be in equilibrium with the melt, or $C = 2$, $P = 2$ and so $F = 1$, which means that the equilibrium is univariant along AB. The same argument is applicable to the line CB also.

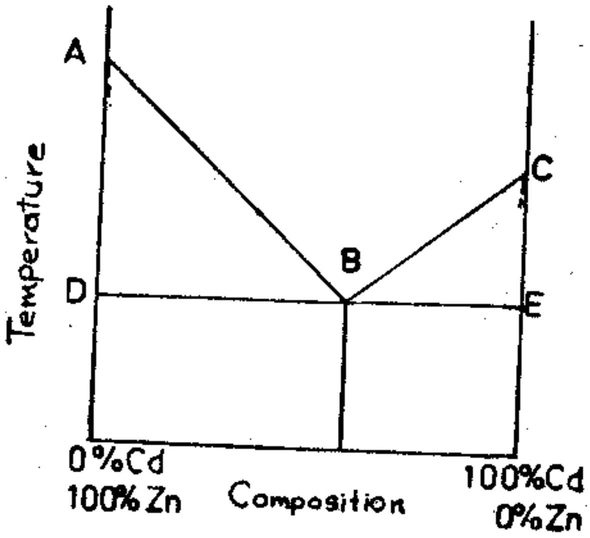


Fig: 12.1 phase Equilibruim diagram of Zn - cd alloys

The point B is known as the eutectic point and represents the compositions of the two metals when a melt containing these two metals is cooled. From the figure, it is also seen that below the dotted lines, each metal solidifies along with the eutectic.

The curve AB and CB represent a univariant system which means that pure zinc and pure cadmium can be in equilibrium with a continuous range of liquid compositions along AB and CB, i.e, fixing the composition of the solid phase does not fix the composition of the co-existing liquid phase.

The curve given in Fig. 12.1 is not quite accurate and the strictly accurate diagram is given in Fig. 12.2. where the dotted lines represent the composition of the solid phase in equilibrium with the liquid.

If the two substances form a solid solution, there can be only two phases, namely, the liquid and solid solution and hence from the "reduced" phase rule, it follows that F=1, ie., there can be no eutectic point. Such a type of equilibrium is shown in Fig. 12.3 where the curves A X B and A Y B represent the equilibria between the liquid and mixure of-mixed crystals and liquid and between the mixture of mixed crystals and liquid and solid (C+L) respectively. Further, these also represent the melting point and freezing point curves.

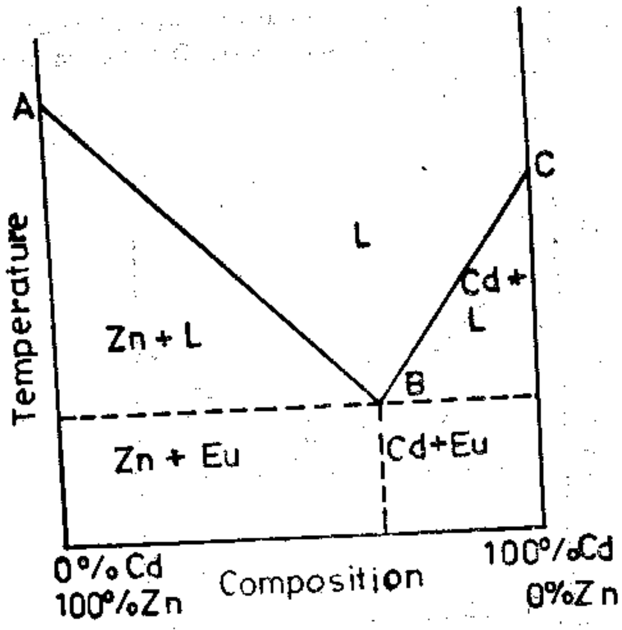


Fig. 12.2 More accurate phase equilibrium diagram of an alloy

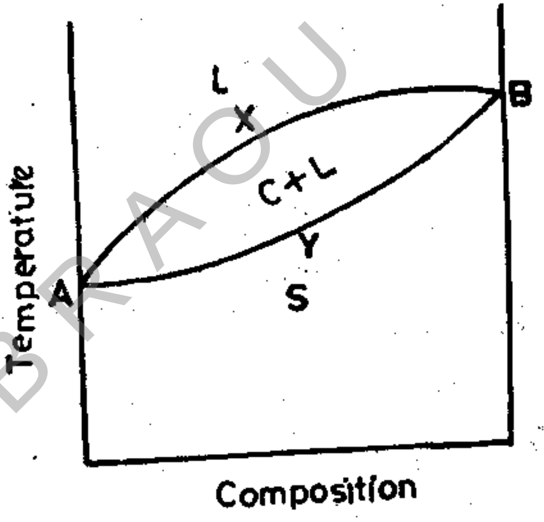


Fig. 12.3 Phase equilibrium diagram fo binary system of solid solutions

Check your progress-1

What do you mean by eutectic mixture?

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Till now, we have considered cases involving formation of an eutectic and solid solution. In addition to these, sometimes there may be the formation of one or more chemical compounds, for example, a system consisting of Mg and Sn in which the compound Mg_2Sn is formed. The temperature-composition curve of this system is given in Fig. 12.4.

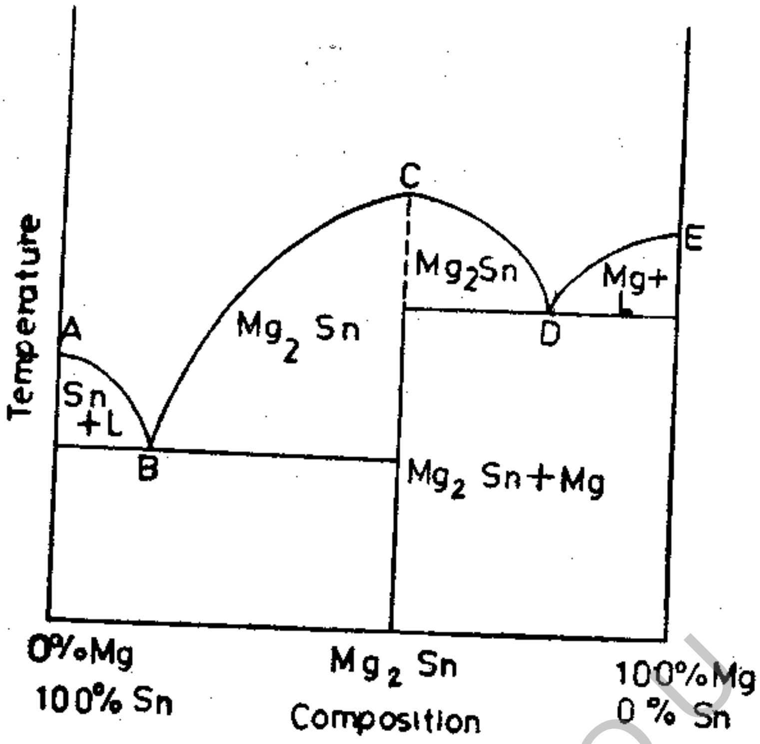

Fig. 12.4 Phase Equilibrium Diagram of a system involving compound formation

The point B and D correspond to the eutectics at which each of the three phases, Sn Mg_2Sn and liquid and Mg, Mg_2Sn and liquid are present. Along the curves AB and DE, pure tin and pure Mg respectively will be deposited while the pure compound Mg_2Sn will be deposited along BC and CD.

The point C is at the maximum of the curve BCD and represents the composition of the pure compound. Addition of Sn or Mg to the compound will result in a lowering of the melting point of the pure compound and the behaviour is represented by the curves CB and CD.

The existence of a hump in the freezing point-composition curve indicates the existence of a compound and the number of humps indicates the number of such compounds formed.

The phase rule can be applied to salt hydrates also. If $CuSO_4 \cdot 5H_2O$ and $CuSO_4 . 3H_2O$ are taken in the two limbs of a tensimeter (appratus used for measuring vapour pressures), the vapour pressure of the mixture remains constant as long as the pentahydrate is present, but it falls down suddenly when the pentahydrate is completely converted into the trihydrate, and thereafter it again remains constant, till the trihydrate is completely converted into the monohydrate and the behaviour repeats itself till the salt completely becomes anhydrous. These facts are represented in Fig. 12.5 and can be very easily explained on the basis of phase rule. For the pentahydrate-trihydrate equilibrium, the number of phases is three (two solids and the water vapour), and the number of components is 2. Hence from the phase rule, it follows that

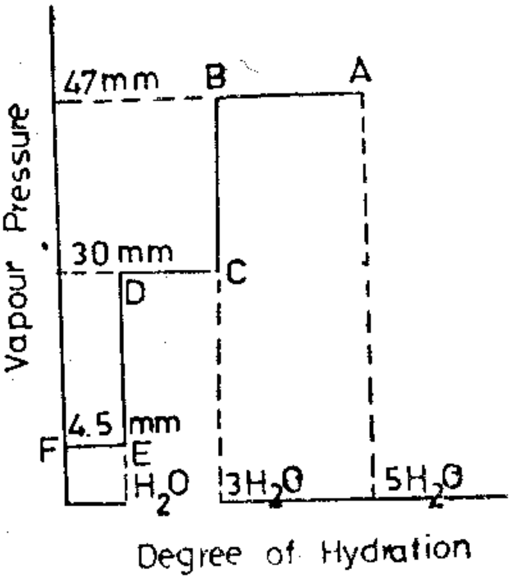

Fig. 12.5 Phase equilibrium Diagram of salt hydrate

F=2-3+2 = 1 or the system is univeriant. But since the temperature is already fixed (constant,) the system must beinvariant. That this is so is shown by the fact that the vapour pressure remains constant as long as the penta-and trihydrates are present in the equilibrium (curve AB). When the pentahydrate is completely converted into the trihydrate, there is a sudden fall in the trihydrate-monohydrate and monohydrate-anhydrous salt equilibria also (curves CD and EF).

12.3 SOLUTIONS OF GASES IN GASES

All gases which do not combine chemically mix in all proportions. Hence in the case of a solution of one gas in another, the number of phases is one and the number of components is 2. Hence according to the phase rule, the number of degrees of freedom will be, F = 2 - 1 + 2 = 3 which means that all the three quantities, temperature, pressure and concentration, can be varied over a limited range without the risk of the appearance of any new phase. It should, however, be borne in mind that if the variations are large, the possibility of formation of a new phase cannot be ruled out.

12.4 SOLUTIONS OF GASES IN LIQUIDS-HENRY'S LAW

In the case of a solution of a gas in a liquid, the number of phases is two, gas and solution, and the number of components also is two, namely, gas and liquid. Hence, according to the phase rule, F = 2 - 2 + 2 = 2 or the system is bivariant. That is, if the temperature is fixed, the gas pressure and concentration of the solution can be varied. On the other hand, if the composition is fixed, the gas pressure and temperature may be varied.

12.5 SLUTIONS OF GASES IN SOLIDS

The case of solutions of gases in solids can be considered in four different ways. Firstly, a perfectly homogeneous true solution, in which there is no alteration in the composition or constitution of the gas may be formed when a gas dissolves in a solid.

Secondly, two or more solid solutions, which may or may not be miscible with each other, may be formed. In the third case, there may be formation of a chemical compound between the gas and the solid. Lastly, the gas may be adsorbed by the solid.

In the first case, i.e, the one involving the formation of a true solution, the number of phases is two and the number of components also is two and hence the number of degrees of freedom will also be two, just as in the case of solutions of gases in liquids. If the temperature is kept constant the pressure and composition of solution can be altered, but one will depend upon the other.

In the case of a gas dissolving in solid to form solid solution, the number of phases would be three, solid, solid solution and gas, and the number of components is two, gas and solid. Hence the number of degrees of freedom $F= 2 - 3 + 2= 1$, or the system, is univariant. If the temperature is fixed, the pressure and compositions of the phases are also automatically fixed.

If the number of solid solutions formed is two, then the total number of phases would be 4 and from the phase rule equation, it follows that $F=0$, or the system is invariant. If a graph is drawn between the pressure of the gas and its concentration (the amount of the gaseous component in the system) at a constant temperature, it has been found to be of the form shown in Fig. 12.6

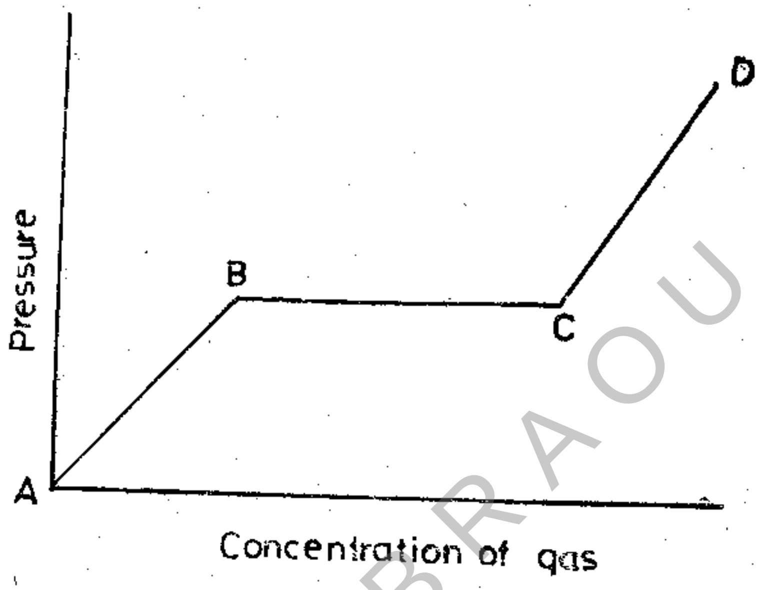

Fig. 12.6 Phase equilibrium diagram of system with two solid solutions

The portion AB of the curve in Fig. 12.6 represents the formation of the first solid solution. The number of phases is two, (solid and gas) and since the number of components is also two, the number of degrees of freedom is two. At constant temperature, the number of degrees of freedom becomes one. Hence at each concentration, there is a definite pressure along the line AB. At B, the formation of the new solid solution begins and, since the number of phases and components are three and two respectively, the number of degrees of freedom will be one an d at constant temperature, the degrees of freedom will be zero. that is why, the part BC of the curve is a straight line parellel to the X - axis. As the concentration of the gas is increased, the first solid solution gradually disappears and will be converted into the second solid solution, and then there are only two phases again and the curve would be of the form CD.

12.6 SOLUTIONS OF LIQUIDS IN LIQUIDS

Solutions of liquids are of 3 types, namely, (1) Completely miscible liquids, e.g, ethanol and wter, (2) partially miscible liquids, e.g. ether and water, and (3) practically inmiscible liquids, e.g. nitrobenzene and water. The liquids are not absolutely immiscible, but under ordinary concentration ranges, two liquid phases will always be present.

12.6.1 Completely miscible liquids

In this system, there will be two components and two phases, and according to the phase rule, the system should be bivariant. Hence at constant temperature, the pressure and composition must vary together. Thus, at a given temperature, the mixture of a given composition will have a fixed and definite vapour pressure.

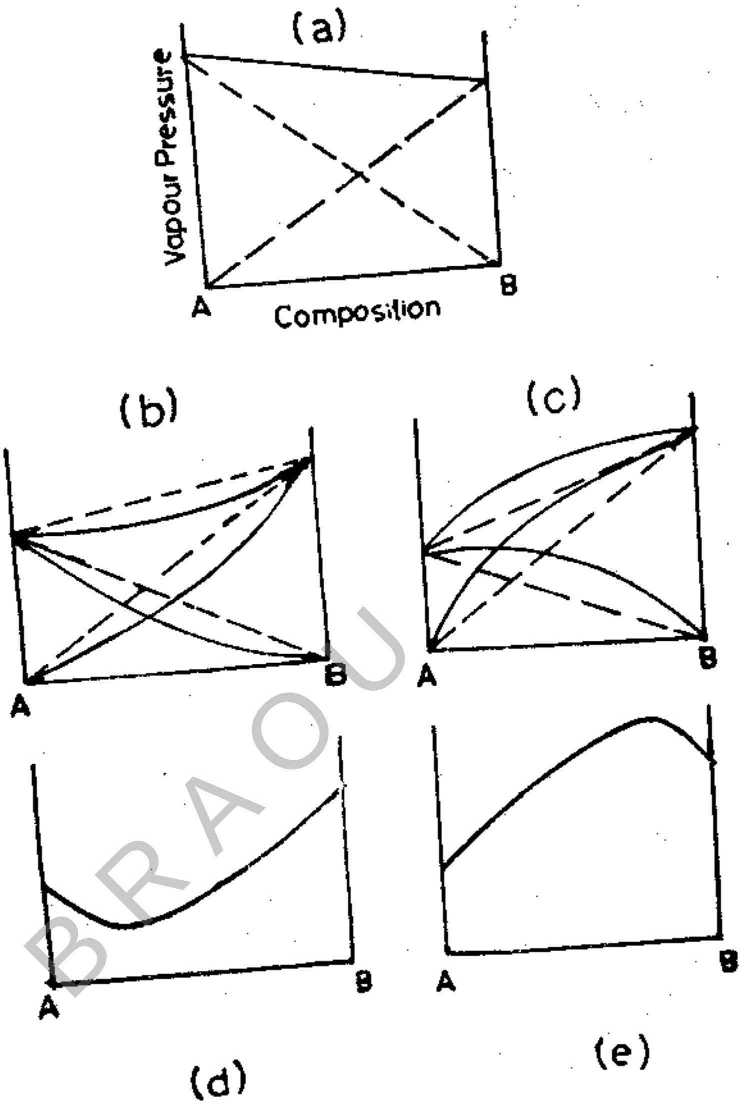

Fig. 12.7 liquids in liquids

The curves in Fig. 12.7 represent the variation of vapour pressures of completely miscible liquids with compostion, the composition being expressed as mole-fraction.

In the first case, Fig. 12.7 (a) the partial vapour pressure curves of both the liquids as well as the total vapour pressure of the mixture are straight lines. Such a situation obtains only in the case of ideal solutions, i.e, when Raoult's law is obeyed and is exhibited by pairs of closely related liquids like benzene + toluene, water + heavy water, etc. or intersection of the two partial pressure lines in Fig. 12.7 (a). The vapour at the point contains each of the two liquids in the proportion of its partial pressure, and will therfore be equimolar, although the liquid contains an excess of liquid B. This principle is known as Konowaloff's Rule is always obeyed and can be stated as the vapour over a binary liquid always contains an excess of that component whose addition to the liquid would raise the total vapour pressure. If the

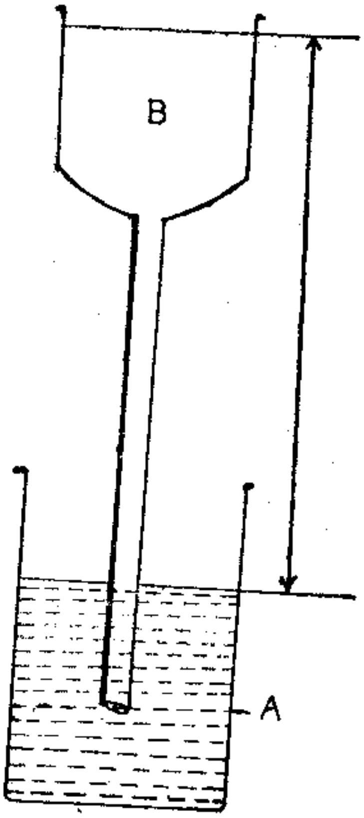

Fig. 9.5 (b) Interfacial Tension

the drops. The number of drops produced by a definite volume of the liquid is counted and its apparent mass, m, is calculated utilising equation (9.7)

$$m = \frac{m_o(\rho - \rho)}{\rho} \qquad (9.7)$$

Where ρ is the density of the drop-forming liquid, and 'ρ'' is that of the other liquid, and $m_o = v.\ \rho$, v being the volume of one drop. From a knowledge of m, the interfacial tension can be calculated employing equation (9.6)

9.8 INTERFACIAL TENSION AND ADSORPTION

We have seen that the surface of a liquid is in a state of tension. Similarly, the surface of a solid also will have a residual field of force or unsaturation which results in a tendency of the free energy of the surface to decrease. This tendency is responsible for the phenomenon of **adsorption which strictly refers to the existence of a higher conentration of the substance at the surface of a liquid or solid phase than is present in the bulk.** The component with the lower surface tension will tend to increase its concentration on the surface, because this will reduce the free energy of the surface. It may therefore be stated that if a solute lowers the tension at any interface, there will be a higher concentration of the solute at the interface than in the bulk of the solution. Such substances are said to be surface active.

On the other hand, with substances which increase the surface tension, at the interface, the concentration of the substance at the surface will be less than that in the bulk of the solution and this type of behaviour, which is known as negative adsorption, is exhibited by electrolytes.

The relationship between adsorption and surface tension is given by the Gibbs adsorption which may be represented as

$$\tau = -\frac{c}{RT}\frac{d\gamma}{dc} \qquad (9.12)$$

where τ is the surface concentration per unit area of the interface, c is the bulk concentration, γ is the surface tension, R is the molar gas constant and T is the absolute temperature. From equation (9.12) it is evident that if $d\gamma/dc$., i.e, the change in interfacial tension with concentration, is negative then τ is positive, or in other words, the concentration of the substance at the surface will be higher than that in the bulk.

Check your progress -2

Why do solids adsorb gases?

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9.9 INTERFACIAL TENSION AND ADSORPTION BY SOLIDS FROM SOLUTION

It is well known that charcoal removes coloring matter from solutions and that finely-divided powders take up dyestuffs and other substances from solutions and this is another aspect of adsorption. Here it may be assumed that the surface acts in the same manner as in the adsorption of gases by virture of molecular attraction or alternatively, it may provide an inteface of large area where a solute, which is capable of decreasing the interfacial tension, may accumulate. The information available for the tensions at the solid liquid interfaces is very little and although there is no theoretical justification, it can be assumed that the tensions for solid - liquid interfaces run parallel to the air - liquid interfaces since the experimental evidence seems to support the validity of this parallelism. For example, charcoal adsorbs dyestuffs more readily from aqueous solutions than from alcoholic solutions. In fact, the dyestuff adsorbed by charcoal from aqueous solution can be readily extracted by alcohol. The air - liquid interfacial tension of water is highehr than that of alcohol, and hence the decrease in surface tension of the aqueous solution with increasing concentration of the dyestuff will be higher than that for the alcoholic solution. Therefore, in accordance with the Gibbs adsorption equation, (equation 9.12), the adsorption of the dyestuff at the air-liquid interface will be greater in aqueous than in alcoholic solutions. The same result is observed at the solid-liquid interfaces also.

The parallelism mentioned above, however, breaks down sometimes. For example, although amyl alcohol lowers the surface tension of water more than phenol, charcoal adsorbs phenol more readily from aqueous solution than amyl alcohol.

Many of the substances are adsorbed from their aqueous solutions because of the high surface tension of water. Very few cases of negative adsorption from aqueous solutions by solids like powdered silica and charcoal, occur with electrolytes and as has already been mentioned, there will be an increase in the surface tension at the air-liquid interface. The Gibbs adsorption equation cannot explain this adsorption of electrolytes and one of the reasons attributed for this failure of adsorption is that the Gibbs equation does not take the electrostatic forces into consideration.

9.10 SUMMARY

Cohesion and adesion are the attractive forces between identical and different molecules respectively. In liquids the molecules of the bulk attract the molecules present at the surface due to which they exhibit the characteristic property surface tension. A liquid wets a surface if the contact angle is less than 90. Surface tension can be determined by eithre capillary rise method or drop weight method. The surface of a solid remains unsaturated and this tendency is responsible for their adsorption of gases.

UNIT - 11

PHASE EQUILIBRIUM - SINGLE COMPONENT SYSTEM

Contents

11.1 AIMS AND OBJECTIVES

To describe the phenomenon of heterogeneous equilibrium and discuss quantitatively the effect of parameters such as temperature, pressure, concentration and compostion on the equilibrium

Once you study and understand the contents of this unit you must:

- realise the importance of the statement ot phase Rule $F = C - P + 2$
- be able to describe the terms involved, namely degrees of freedom, components, and phases.
- be in a postiion to apply phase Rule to single component systems, lke water and sulphur.

11.2 INTRODUCTION

The phase rule derived by Gibbs, provides a convenient method for the treatment of heterogeneous equilibria i.e, equilibria in which reactions occur in more than one phase. The rule enables one to forecast the behaviour of heterogeneous systems under various experimental conditions. It has been derived from thermodynamics and does not involve any assumptions about the nature of matter. Thus, it is independent of any hypothesis concerning the nature of matter and coordinates a number of phenomena under one law. The rule applies only when equilibrium is attained. Each of the phases is supposed to be present in large quantities and the equilibrium is not disturbed by the addition of a little more of the reactants or products.

11.3 THE TERMS INVOLVED

The phase rule is stated in words but can be stated only mathematically, as where F, C and P are

$$F = C - P + 2 \qquad (11.1)$$

respectiely the number of degrees of freedom, components and phases and are explained as follows.

Degrees of freedom

The number of degrees of freedom is the number of the factors, pressure, temperature, and concentration of the system, which can be varied wihtout altering number of phases present in the system, which can be varied without altering the number of phases in the system.

Let us suppose that there is a system consisting of water in contact with its vapour. It is a fact that the vapour pressure of water is dependent only on the temperature and not on the mass of the water. Hence, if the temperature is fixed, the vapour pressure is fixed, and vice versa. We can therefore say that such a system has only one degree freedom.

Consider now a system consisting of gaseous phase only. It is well known that in the case of gases, pressure, volume, and temperature are related by means of one equation or another. Out of these three quantities, it is just sufficient if any two are fixed, because the third quantity is automatically fixed. In other words, any two of these three quantities completely define the system and the two quantities can be varied without altering the number of phases present. That is, the number of degrees of freedom of the system is 2.

Check your progress -1

What do you mean by a univariant system?

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Components

The number of components may be defined as the smallest number of independently variable constituents by means of which the composition of each phase of the system can be expressed in the form of a chemical equation.

To illustrate the definition, let us consider the system consisting of sulphur and its allotropes, liquid sulphur, and sulphur vapour. In this system the composition of each phase can be expressed in terms of only one constituent, namely sulphur. The system is thus a one component system.

The equilibrium $CaCO_3 \rightleftharpoons CaO + CO_2$

contains three different molecular species, namely, $CaCO_3 \rightleftharpoons CaO$ and CO_2 the first two being solids and the last one, a gas. The composition of each phase can be expressed in terms of two components. For example, if CaO and CO_2 are chosen as the ocnstituents then the compositions of the three phases can be expressed as :-

$$CaCO_3 = CaO + CO_2$$

$$CaO = CaO + 0\,CO_2$$

$$CO_2 = CO_2 + 0\,CaO$$

On the other hand, if $CaCO_3$ and CO_2 are chosen as the two constituents, then,

$$CaCO_3 = CaCO_3 + 0CO_2$$

$$CaO = CaCO_3 - CO_2$$

$$CO_2 = 0\;CaCO_3 + CO_2$$

Thus in this system the smallest number of constituents that fixed the composition of each face is two, or this is a two-component system.

Phases

A phase may be defined as a part of the system which is homogeneous through out and can be separated from other homogeneous parts of the system by a boundary.

vapour at point of intersection is removed and condensed in a separate vessel, the condensate will contain a larger proportion of the more volatile component than did the original liquid and the residual liquid will contain a larger proportion of the less volatile component than did the original liquid. This process of vapourisation and condensation (distillation) can be utilised to separate the two components and this is what happens in fractional distillation.

Fig. 12.7 (a) represents ideal behaviour which is generally rare for liquids, since there will be always be deviations from Raoult's law. These deviations are indicated in (b) and (c). At high concentrations, the partial pressures always start by obeying Raoult's law and the broken line follows the dotted line at first. But as the concentration of the second component increases, the pressure may deviate by dropping below the ideal line as in (b), or may rise above that, as in (c),. The situations represented in (b) and (c) are known as negative and positive deviations respectively.

From (b) and (c), it can be seen that the total vapour pressure has no maximum or minimum, because the departure from Raou't's law (or ideal behaviour) is not excessive. In such cases also, the two components can be separated by fractional distillation.

Sometimes, however, the total vapour pressure curve will have a minimum or maximum as shown in (d) and (e). This behaviour is exhibited by mixtures of hydrogen chloride-water and water-ethanol. Hydrochloric acid forms a constant boiling mixture containing 20.24% HCl which distils unchanged at 110ºC. This is a case of negative deviation from Raoult's law.

Mixtures of water and ethanol exhibit positive deviations from raoult's law and a constant boiling mixture containing 89% mole of alocohol boils at 78.15ºC

Check your progress-2

What do you mean by a constant boiling liquid mixture?

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12.6.2 Partially miscible liquids

A mixture of ether and water may be taken as an example of this class. The curve in Fig. 12.8 represents the variation of vapour pressure with composition.

When a small quantity of ether is added to water, the ether dissolves forming a true solution and the total vapour preassure of the mixture increases along the line AB. According to the Phase rule, the system is bivariant along AB, because there are two components, ether and water, and two phases, ether in water and vapour.

BLOCK - 6

CRYSTAL STRUCTURE

The fundamental properties of crystals are their symmetry in the external appearance and the orderly arrangement of atoms or ions or molecules. External symmetry of crystals is the result of the orderly arrangement of constituent particles. The symmetric external shape of a crystal is achieved by the repetition of the same basic units three-dimentionally. A crystal possesses aset of faces that join to form definite angles. Another important property of crystals is their tendency to break along their natural axes when force is applied. Amorphous solids break irregularly. Only one substance may exist in more than one crystalline form under different conditions. This phenomenon is called ploymorphism. Polymorphism of elements is allotrophy.

UNIT - 13 X - RAYS AND CRYSTALLOGRAPHY

Contents

13.1 AIMS AND OBJECTIVES

To describe the internal structure of crystals and to explain you how X-rays can be used to arrive at the type of arrangement of atoms (or ions) in a crystal.

Once you thoroughly study and understand the contents of this unit, you must be able to:

- realise that there are two aspects of crystal structure (i) dealing with the external symmetry and shape and (ii) internal arrangement of atoms, molecules or ions.
- to describe the external symmetry concerned with the outward arrangement of faces and the symmetry of the crystal as a whole
- find out that based on the external symmetry crystals are divided into seven systems. The seven crystal systems give rise to fourteen lattices. The crystal lattices differ from one another in their interplanar spacings.
- internal arrangement of atoms in a crystal is desbribed in terms of its space lattice which is a three dimensional arrangements of points in space.
- to know that by X-ray diffraction analysis of crystals, interplanar spacings can be determiend and such measurements help us in ariving at the type of lattice to which the crystal belongs.

13.2 INTRODUCTION

When we look at any crystalline solid what impresses us most is its outward geometric form, the symmetry in its extenal appearance. A definite set of faces meeting at definite angles. This symmetry can be easily recognized in naturally occurring mineral as for example in quartz crystals. However, if the solid occurs as powder or lumps the symmetry can be noticed only when the individual particles are observed under a microscope. Metals occur in polycrystalline condition. The crystalline nature is observed only by etching the surface, when a large number of tightly packed crystals in all possible orientations could be noticed. This external symmetry of crystals is however due to the regularity in its internal structure. The units of a crystal be the atoms, molecules or ions must be arranged in a regular order. The external shape of the crystal may be assumed to be obtained by the repetition in three dimensions, of a basic pattern containing atoms or ions. It is this intenal regularity of structure that is the more important and essential characteristic of the crystalline state and not the external geometry or form. However, since the latter is a direct result of the former, we can always get some hint as to the nature of the internal structure from observing the extenal form. Hence it is useful to consider some aspects of the outward spatial arrangement of the crystal faces that is the external symmetry of the crystal.

13.3 GEOMETRIC CRYSTALLOGRAPHY

The external surface of a crystal is made up of well defined faces which interest at constant angles. These angles are called interfacial angles and can be measured by a goniometer. It has been found that no matter how the faces developed, the angle between the correspnding faces remians constant for any crystal of a given substance. Again crystals of different substances exhbit different symmetries, but the crystals of the same substance possess the same symmetry. This is expressed in terms of elements of symmetry. They are axes of symmetry, plans of symmetry and centre of symmetry.

Axes of Symmetry

A crystal is said to possess an axis of symmetry, if when rotated about an imaginary line passing through the centre of the crystal, presents the same appearance more than once. The symmetry axis is said to be two fold, three fold or four fold depending upon whether it is brought into self coincidence twice three four times during a complete rotation, etc. For example, for a cube a line passing through the centres of opposite faces is an axis of four fold symmetry because the faces coincide one another, for every turn through 90°; 360/90=4 times in one complete rotation. The axis is represented by the symbol C_4. An axis of three fold symmetry (C_3) is the one passing through the opposite corners of the cube and an axis of two fold symmetry (C_2) is the one passing through the mid points of opposite edges. These are shown in the figure 13.1.

Planes of Symmetry

A Plane of symmetry is an imaginary plane which divides the crystal into two halves such that one half is a mirror image of the other. A cube can have two types of plane sof symmetry - rectanglular plane of symmetry parallel to the faces or diagonal plane of symmetry passing diagonally through the cube. These are shown in the figure 13.2. (b).

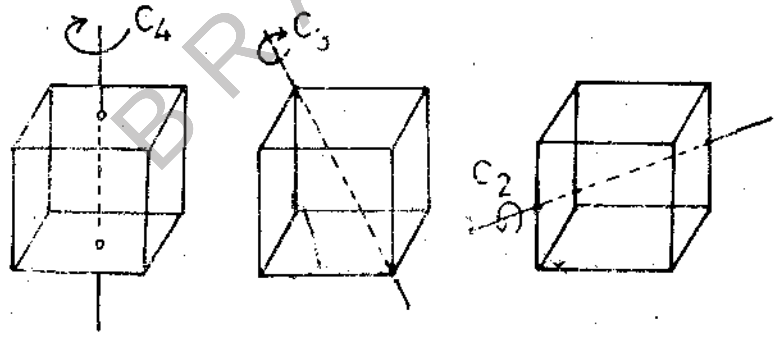

Fig 13.1 Axes of Symetry in a cube

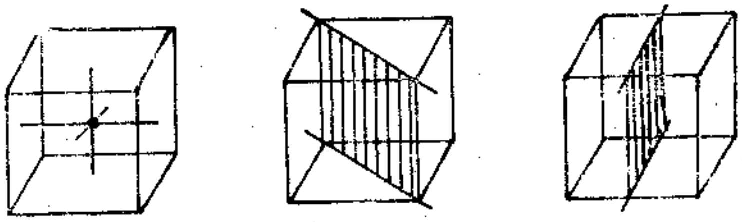

Fig. 13.2 (a) Centre of Symmetry in a Cube
(b) Planes of Symmetry in a Cube

Centre of Symmetry

A crystal is said to possess a centre of symmetry if any line drawn through it will intersect the surface of the crystal at equal distances on eitherside (fig. 13.2 a)

A crystal may have more than one axis of symmetry of any kind and more than one plane of symmetry of a given kind. But of course only one centre of symmetry.

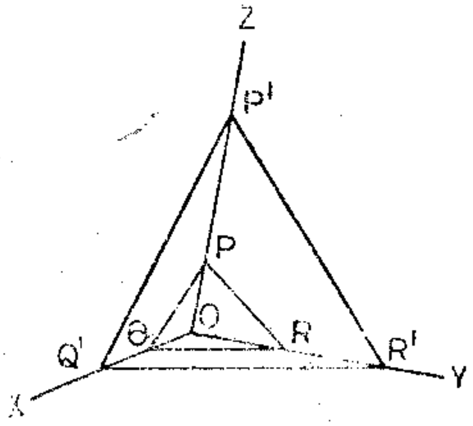

Fig. 13.3

In the external form of a crystal only those faces are possible and have physical existence which bear a simple relation to one another. This relationship can be obtained as follows. First three axes are chosen in a crystal and a standard plane $P^1 Q^1 R^1$ is chosen which is not parallel to any of these axes at distances a , b and c from the origin. These are the fundamental characteristics of the crystal. Let the intercepts made by any other plane P'Q'R' be OP', OQ' and OR'. For this plane to occur as a face, these intercepts must be related to the intercepts made by the standard plane OPQR in a simple manner. The relationship is given as OP':OQ':OR' = a/h:b/k:c/l where h,k & l must be small whole numbers like 0, 1,2,3, & 4. It very rarely exceeds four. The plane is called an hkl plane. hkl are called Miller indices of the plane.

For any crystal a set of axes can be constructed such that all naturally occurring planes have reciprocal intercepts that are proportional to small numbers. This is called the law of rational indices and can be applied to classify the planes. Consider a unit cell of a crystal. Let the three edges of the crystal form the axes which intersect at one point. The standard plane has to be chosen such that it is not paaralle1 to any of these axes. The plane ABC satisfies this condition. The intercepts made by this plane on the three axes are a,b & c which turn out to be the length of the sides of the cell. We can now find the **miller indices** of other faces. Consider top face CDEF. This does not cut the X and Y axes as it is parallel to them. It meets them only at infinity. It intercepts the Z axis at the same distances as the standard plane.

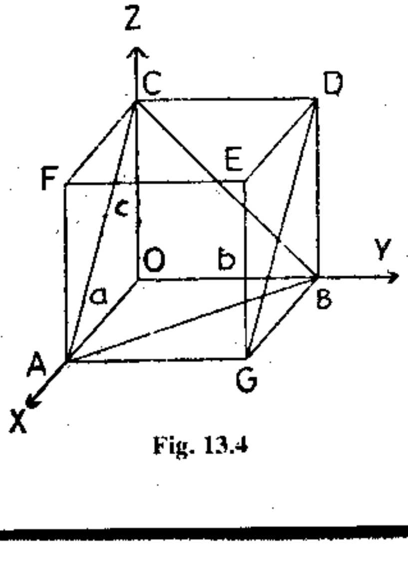

Fig. 13.4

The intercepts made by the top face on the three axes may be written.

$$a\ x\ \alpha : b\ x\ \alpha : c\ x\ 1$$

This can be written as a/0:b/0:c/1. The Miller indices of the plane are therefore 001. It is called a 001 plane. Similarly the side plane DEGB intercepts the Y axis but is parallel to the X & Z axes its intercepts are therefore $a\ x\ \alpha : b\ x\ 1 : c\ x\ \alpha$ which may be written as a/0:b/1:c/0. The Miller indices are 010. Miller indices are therefore the reciprocals of the intercepts in terms of the standard plane. In a similar way the indices for AGEF will be 100.

Example

A crystal plane intercepts the three crystallographic axes at the following mutiples of unit distance 3/2, 2, 1. What are the Miller indices of the plane?

We have seen that Miller indices are reciprocal of the intercepts. Hence they are 2/3, 1/2, 1 which in integral numbers become (436).

TABLE - 13.1

System	Axes	Angles	Essential	Example.
1. Cubic	a = b=c	$\alpha = \beta = \gamma = 90^0$	Four three fold axes	NaCl, KCl, NaF, Mgo diamond, CaF_2, pb, Hg, Au. TiO_2, SnO_2, Sn
2. Te'ragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^0$	Three two Fold exes	KNO_3, Rhombic sulphur, $PbCO_3$,
3. Ortho rhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^0$	One two fold axes	KNO, Rhombic sulphur, $PbCO_3$
4.Monoclinic	$a \neq b \neq c$	$\alpha = \beta = 90^0 \neq \gamma$	One two fold axis and one plane	MOnoclinic sulphur, Borax
5. Triclinic	$a \neq b \neq c$	$\alpha = \beta \neq \gamma \neq 90^0$	No axes, no planes	$CuSO_4$, $5H_2O$. $K_2 Cr_2 O_2$
6. Hexagonal	$a \neq b \neq c$ $\gamma = 120^0$	$\alpha = \beta \neq \gamma \neq 90^0$	One six fold axis	HgS, ice, graphite
7 Rhombo-hedral or Trigonal	a = b=c	$\alpha = \beta = \gamma \neq 90^0$	One thre fold axis	Silica, Magnesite, Calcite, $NaNO_3$

13.3 ISOMORPHISM AND POLYMORPHISM

In the above Table-13.1 we may notice that crystals of several compounds may belong to the same system. For example NaF, KCl and MgO have the same symmetry as sodium chloride. Different compounds which crystallize with the same structure are said to be isomorphous. The property is called isomorphism. Again the same compound may under different conditions crystallize with a different structure. Thus calcium carbonate crystallizes at low temperature in the rhombohedral form which is called calcite, but when it crystallizes at high temperature an orthorhombic structure results. This form is metastable and is called aragonite. The existence of the same substance in more than one crysalline form is known as polymorphism. Polymorphism occurring in elements is referred to as allotropy. Examples are carbon (diamond and graphite) and sulphur (Rhombic and monoclinic.)

Check your progress - 1

What is polymorphism?

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13.4 INTERNAL STRUCTURE OF CRYSTALS (SPACE LATTICE)

It has been stated in the introduction that the external shape of the crystal is reflection of its internal structure. This fact can be easily established. Suppose a small crystal of any salt like copper sulphate is suspended in its remain the same. Again when a large crystal is pounded into a powder any small grain observed under the microscope, it will be found to retain the shape of the original crystal. These facts suggest that the constituents of a crystal-atoms, molecules or ions are arranged in a repetitive pattern. That is, there must be an ultimate basic group of atoms called the unit cell which has a shape related to the original crystal. The repetition of this cell in three dimensions gives the whole crystal. Thus the cubic crystal may be visualized as built from the repetition of a small cube parallel to itself in three dimensions gives the whole crystal. Thus the cubic crystal may be visualized as built from the repetition of a small cube parallel to itself in three dimensions. The atoms are placed at the corners of the cube. By repetition of this basic group of atoms (cubic network of atoms) in three dimensions, we get what is known as the space lattie of the crystal. The space lattice is defined as a regular distribution of points in space.

To understand how this is obtained, consider a simple lattice in one dimension. This is merely an arrangement of points along a line so that they are regularly spaced.

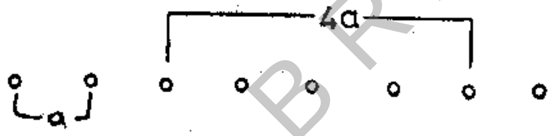


Fig. 13.5 One dimensional lattice

The lattice is obtained by the movement of a single point along a fixed direction in fixed increments. The fixed increment is called a primitive vector. The distance between any two points in the lattice can be expressed in terms of this primitive vector.

By moving a point in two directions by fixed increments we get a two dimensional lattice. In the lattice given below the primitive vectors are equal. The paralellogram constructed on these primitive vectors as sides is called the unit cell. Here the unit cell is a square. By repeating this sqaure parallel to

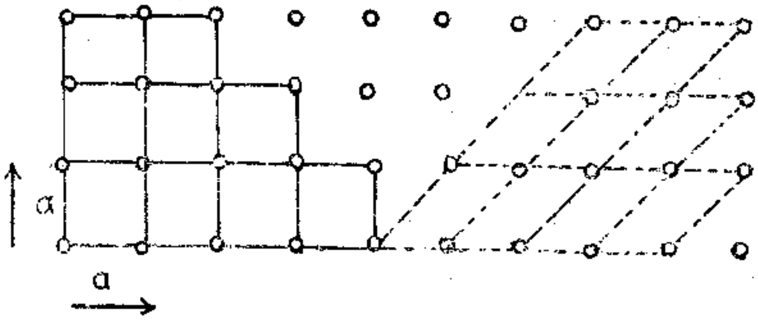


Fig. 13.6 Two dimentsional lattic

itself we obtain a two dimensional lattice. Here the two directions in which the point is moved are perpendicular to each other and the increments are equal. The result is a square lattice. This may not be so. We could have chosen a different unit cell and by the movement of this cell, a different space lattice would have resulted as shown by the dotted lines in the figure.

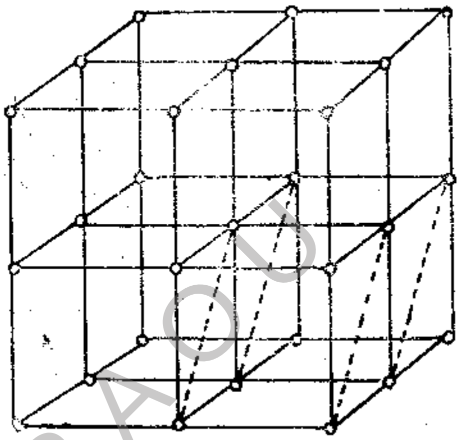


Fig. 13.7 Three dimensional (space) lattice

We may now extend these ideas into the third dimension. Through each point of the two dimensional lattice we have a parallell row of points in some third direction not in the same plane as the two dimensional lattice. Thus for example in the square lattice if we draw through each point a row of points in a third direction perpendicular to the square we get a cubic lattice as shown above. Here the three vectors are equal and the directions perpendicular to each other. The figure constructed on these three vectors as sides is a cube. The cubic lattics is thus obtained, by moving a single point by equal increments, along three directions perpendicular to each other. By choosing the vectors in a different way a different space lattice would have resulted (see the dotted lines).

From purely symmetry consideration, Bravais was able to show that only fourteen kinds of space lattices are possible. this means that there are only fourteen differnet ways of arranging points in three dimensional space. We find that the seven crystal systems have given rise to fourteen latiices. These are shown in the figure 13.8. The smallest portion of the crystal lattice which contains a representative portion of a crystal is called a unit cell. The unit cell repeated in three dimension will reproduce the crystal.

Our interest is primarily in the cubic lattices. There are three types of cubic latiices possible. The simple cubic lattice contains eight points at the corners of the cubes. The second is the face centered cubic lattice which contains an additional lattice point in the centre of each face of the unit cell. The third is the body centered cubic lattice which contains a lattice point in the centre of the unit cell of the simple cubic system. It must be borne in mind that the points represent the lattice, the lines are drawn only for clarity.

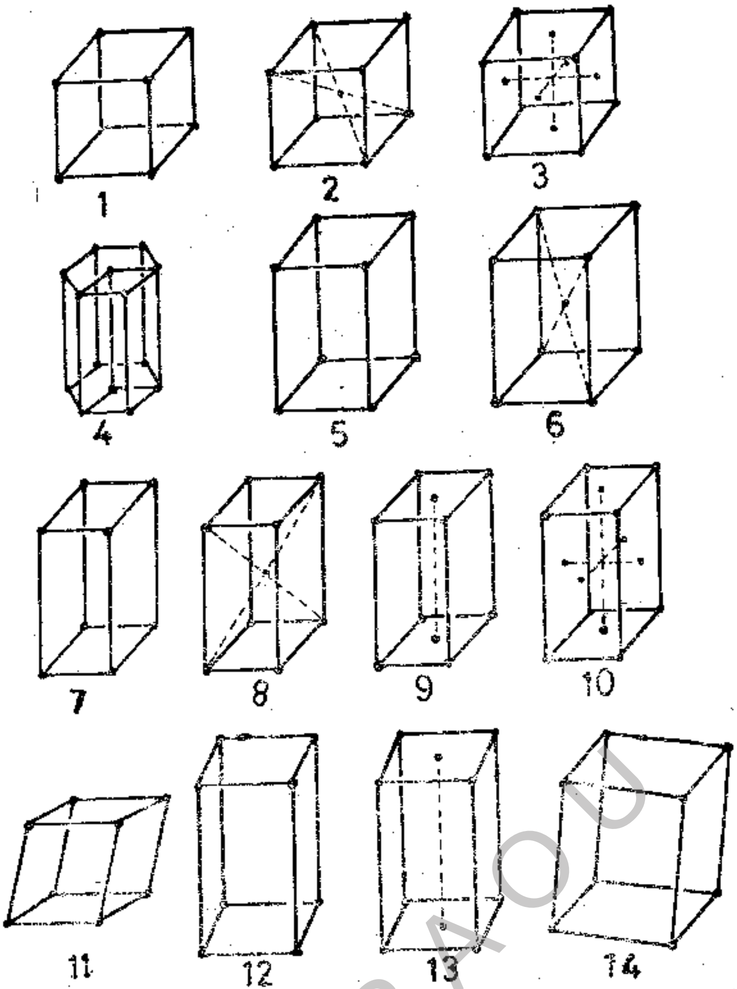


Fig. 13.8 The fourteen Bravais latices

1) Simple cube 2) body-centred cube 3) face-centred cube 4) hexagonal 5) simple tetragonal prism 6) body-centred tetragonal 7) rectanglular (orthorhombic) 8) body-centred rectangular 9) base-centred rectangular (10) face centred rectangular 11) rhombohedron 12) simple monoclinic 13) base-centred monoclinic 14) triclinic.

Check your progress - 2

What is unit cell?

....

....

....

....

Lattice planes

These are planes which divide the crystal into layers and pass through lattice points. Only those planes will have physical reality which are densely populated. The planes are described by numbers, the miller indices. Any set of parallel planes will have the same Miller indices. A simple method of obtaining the Miller indices of a set of planes is to count the number of planes crossed between one lattice point and the next along the direction of an axis. The description of Miller indices is clearly seen in the two dimentional lattice below. We have seen before that for any plane parallel to an aixs, the intercept on that axis will be at infinity and hence the Miller index (the reciprocal of intercept) for such planes will be zero for that axis. Since all the planes are perpendicular to the plane containing the lattice points they are parallel to the Z axis hence for all sets of planes the Miller index for the Z axis will be zero. Keeping this in mind it is easy to follow the allotment of Miller indices for the planes shown below.For example the 100 planes are parallel to the Y and Z axes. Along the Z axis one plane has to be crossed in going from one lattice point to the next. For the 210 planes on the right it is seen that while along the X direction two planes have to be crosse, along the Y direction one plane has to be crossed in going from one lattice point to the next.

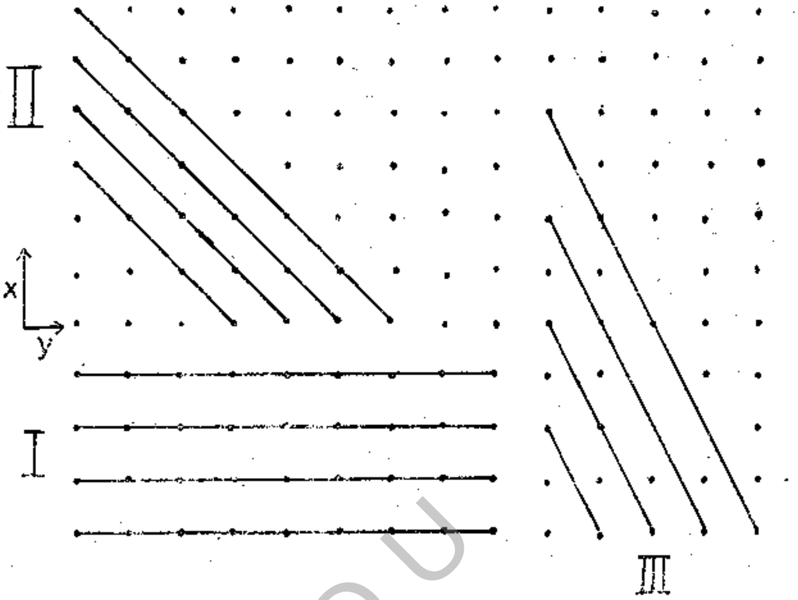


Fig. 13.9 Latiice planes in a two dimensional lattice
I = 100 planes, II = 110 planes, III = 210 planes.

For cubic crystals three sets of planes are important. (i) Planes parallel to a face (ii) planes perpendicular to the diagonal of a face (iii) planes perpendicular to the cube diagonal or body diagonal. These are shown below for the simple cubic system. Let us take the axes as X, Yand Z represented in the figure.

For the planes parellel to the face, we find that along the axis one plane should be crossed in going from one lattice point the next. Along the Y and Z axes no planes need be crossed. This is because the planes are chosen parallel to the Y and Z axes. Hence the Miller indices are 100. Such planes are called

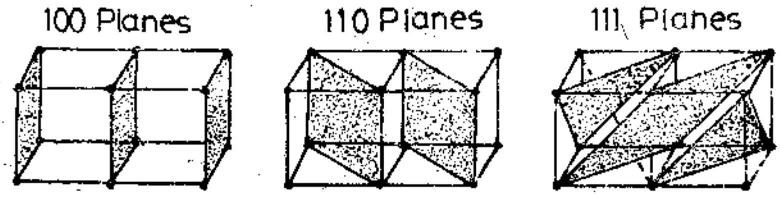


Fig. 13.10 Planes in the simple cubic lattice

100 planes. For planes perpendicular to the face diagonal, it is seen that they are parallel to the Z axis.In going from one lattice point to another along the X axis or the Y axis one plane has to be corssed. Hence indices are 110 and the planes are called 110 planes. Similarly one can see that the Miller indices of planes perpendicular to the body diagonal are 111 as one plane has to be crossed in every direction (X, Yand Z) in going from one lattice point to the next.

In the same manner we can select such planes for the face centred and body centred cubic systems and assign Miller indices to them. They are given below. For the face centred cubic system the planes parallel to a face are the 200 planes, planes perpendicular to the face diagonal are the 220 planes and planes perpendicular to the body diagonal are the 111 planes. For the body centred cubic system, these are 200, 110 and 220 planes. The distance between two successive planes (interplanar spacing) is given by the relationship.

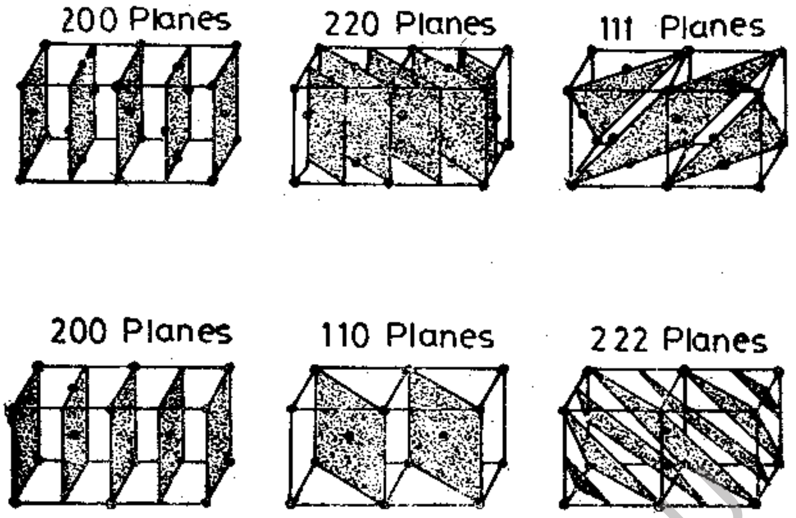


Fig. 13.11 planes in the face centered and body centred cubic lattices

$$d_{hkl} = \frac{a}{\sqrt{\left(h^2 + k^2 + l^2\right)}}$$

Where hkl are the Miller indices of the plane and 'a' is the length of the unit cell.

Thus for 100 planes $d_{100} = \frac{a}{\sqrt{\left(1^2 + 0^2 + 0^2\right)}} = a$

similarly $d_{110} = \frac{a}{\sqrt{\left(1^2 + 1^2 + 0^2\right)}} = \frac{a}{\sqrt{2}}$ and $d_{111} = \frac{a}{\sqrt{3}}$ and so on

We are interested in the ratio of the interplanar spacings for the different sets of places in each type of cubic crystal.

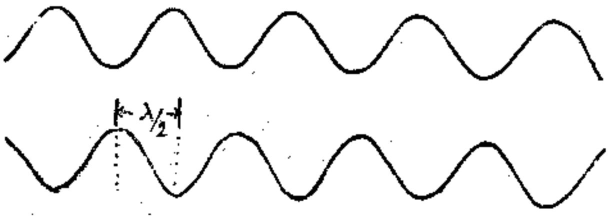


Fig. 13.15 Annulling of wave trains

Therefore, the condition for reinforcement or constructive interference is that the path difference between two rays scattered from adjacent planes must be an integral multiple of the wavelength. This fact is used to derive the Bragg's equation.

Let the two rays be AOB and RPQ. Drop perpendiculars to QP and PR from O. Then the path dfference between the two rays AOB and is RPQ - AOB = CP + PD. From simple geometry it can be shown that the angles COP and POD are also equal to O.

Then $CP = OP \ \text{Sin} \ \theta$ and $PD = OP \ \text{Sin} \ \theta$
or $CP + PD = 2 \ OP \ \text{Sin} \ \theta$

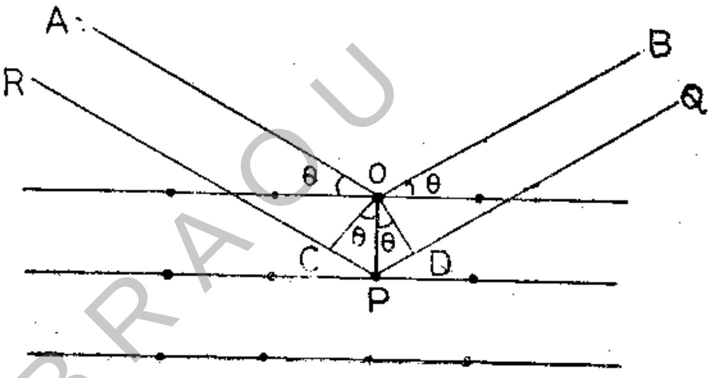


Fig. 13.16 Reflection of X -rays

But OP is the distance 'd' between two planes, so path difference can be written as 2d Sin θ. We have seen that for constructive interference path diffirence must be equal to n λ where 'n' is an integer.

$$\text{Hence } 2d \ \text{Sin} \ \theta = n \lambda$$

n λ can have the values of 1,2,3,.....is also called the order of the spectrum. This is called the bragg's equation.

Hence, when a beam of X-rays is directed on any face of a crystal, reflection will occur only when the X-ray beam is incident at an angle θ which satisfies the above equation. If the wavelength of the X-rays is known 'd' the interplanar spacing can be calculated from the above equation. A crystal can be cut in such a way that the 100-type planes, 110-type planes or 111-type planes face the X-rays beam. Then finding the value of θ at which reflection occurs, the value of 'd' for such planes can be calculated.

13.8 EXPERIMENTAL PROCEDURE

A monochromatic beam of X-rays (obtained from an X-ray tube with molybdenum or copper as anticathode) collimated by two slits falls on a known face of a crystal mounted on a spectrometer table. The radiation reflected from the crystal enters an ionization chamber. This consists of a gas like methyl bromide or sulphur dioxide between two plates that are highly charged. When X-rays enter the chamber, they ionize the molecules-the molecules lose electrons and form positive ions. The ions move towards the charged plates resulting in the flow of current between the plates. This is shown in the electrometer.

Now a current will flow and the electrometer will show deflection only when the X-rays are reflected from the crystal face into the ionization chamber. This happens only when the glancing angle θ satisfies the Brgg's equation $n\ \lambda\ = 2d\ \mathrm{Sin}\ \theta$ or $\mathrm{Sin}\ = n\ \lambda/2d$. If θ does not satisfy this equation then there will be no ioniztion current. The crystal and the ionization chamber can be rotated through measured angles on the spectrometer table. In the experiment the crystal is slowly rotated starting from the angle zero, the ionization chamber is rotated through an angle $2\ \theta$. No current will be shown by the electrometer until the angle θ satisfied the Bragg's equation $\mathrm{Sin}\ \theta = \lambda/2d$ when suddenly a large ionization current is registered by the electrometer. If the angle θ is increased further there is no reflection of the X-rays by the crystal planes, hence the current drops to zero, the current increasing again when the vlaue of θ satisfies the equation $\mathrm{Sin}\ \theta = 2\ \lambda/2d$. This happens again when $\mathrm{Sin}\ \theta = 3\ \lambda/2d$. However as n increases the intensity of the current falls off. Thus when the ionization current I is plotted agianst θ the following type of curve is obtained (fig. 13.18). Thus peaks will be obtained for certain settings of the crystal that is only for certain angles of θ. $\mathrm{Sin}\ \theta_1 = \lambda/2d$,

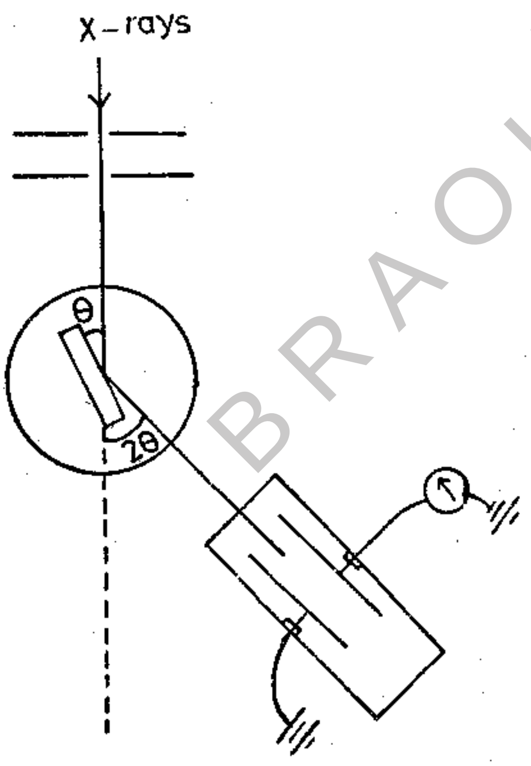


Fig: 13.17 Bragg's Spectrometer (Schematic)

$\mathrm{Sin}\ \theta_2 = \frac{2\lambda}{2d}$ and $\mathrm{Sin}\ \theta_3 = 3\lambda/2d$. For all other angles the ionization current is more or less zero as there is noreflection of X-rays for those angles which do not satisfy Bragg's equation.

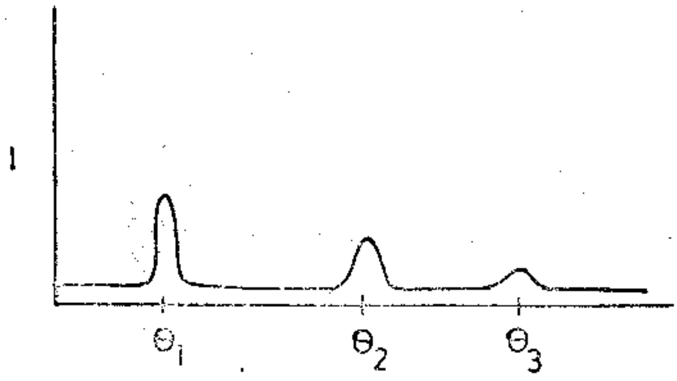


Fig. 13.18 Plot of ionization current Vs angle of diffraction (θ)

This procedure is repeated for all planes possible for the crystal and the angles at which coherent scattering takes place is determined for planes. The crystal is mounted in such a way as to present the particular aset of planes to the X-ray beam.

13.9 APPLICATION TO THE STRUCTURE OF SODIUM CHLORIDE

In a particular experiment the first order (n=1) reflections from different planes were found to occur at angles given below:

Planes	θ_1	**Sin θ_1**
Planes parallel to faces 100	5.90	0.103
Planes perpendicular to face diagonal 110	8.4	0.146
Planes perpendicular to body diagonal 110	5.2	0.0906

For the first order reflection $d = \lambda\ /2 \text{ Sin } \theta$
For the three sets of planes

$$d_{100} : d_{110} : d_{111} = \lambda/2 \times 0.103 : 1/0.146 ; \lambda/2 \times 0.0906$$

Since λ is the same for all the three planes

$$d_{100} : d_{110} : d_{111} = 1/0.103 : 1/0.146 : 1/0.0906 = 1 : 0.705 : 1.14$$

Through the equation $d = a/\sqrt{(h^2 + k^2 + 1^2)}$ where a is the length of the unit cell we have already established the following ratios for the simple cubic, face centred and body centred cubic lattices.

System	$\mathbf{d_{100}}$	$\mathbf{d_{110}}$	$\mathbf{d_{111}}$
Simple cubic	1	0.707	0.577
Face centred	1	0.707	1.154
Body centred	1	1.414	0.577

Comparing the experimentally obtained ratio with the above ratios it can be concluded that in the sodium chloride crystal, the constituent ions must be arranged in a face centred cubic lattice.

Relative position of Sodium and Chloride ions

The problem of finding the relative position of sodium and chloride ions can be solved by considering the intensities of the reflection maxima for the different crystal planes of sodium chloride.

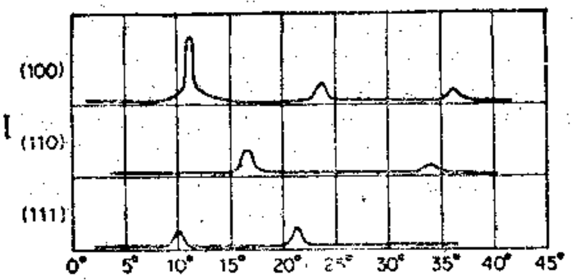


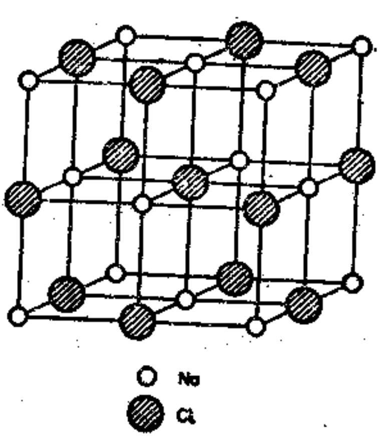
Fig. 13.19 I Vs θ for different planes of NaCl

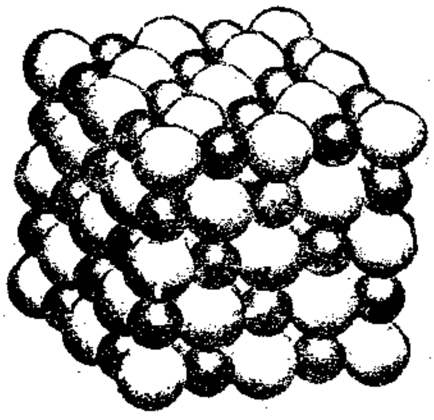
The intensity of scattered beam depends upon two factors, (i) the mass of the atom. Since scattering of X rays involves their interaction with the electrons in the atom, the intensity of the scattered beam depends upon the number of electrons in the atom and hence indirectly on the mass of the atom. The larger the mass, the more intense would be the diffracted beam (ii) on the order of diffraction - the intensity regularly falls off with increase in the order.

Let us apply these considerations to the above results for the 100 and 110 planes we find the normal decrease of intensity expected with the order of the spectrum. This means that different 100 type planes or differnet 110 type planes have the same scattering power leading us to conclude that such planes contain equal number of sodium ions and chloride ions. For the 111-type planes however there is an alternation of intensities, while the 2nd and fourth peaks are normal the first and third peaks are unusually small. This means that the planes alternate in their scattering power leading us to conclude that the 111 type planes are composed alternatively of sodium ions and chloride ions. These results are completely incorporated to give the following structure for sodium chloride.

The shaded circles represent chloride ions and the blank ones sodium ions. Though these are represented as small circles for purposes of clarity, in the crystal however the ions are quite close and almost touching each other as the figure on the side shows.

The above is a part of the lattice for sodium chloride. It may be imagined to have been obtained by the interpenetration of two face centred cubic lattices, one composed entirely of sodium ions and the other only of chloride ions. This can be visualised by supposing first that the blank circles to be absent. This gives a face centred cubic lattice consisting of only sodium ions. Into this imagine that a face centred cubic lattice consisting only of chloride ions (blank circles) penetrates halfway one from either side.





13.13 MODEL ANSWERS TO CHECK YOUR PROGRESS.

1. Existance of the same substance in more than one crystalline form under different conditions is to called ploymorphism eg. α - chromium and β - chormium.

2. The smallest portion of the crystal lattice which repeats three dimensionally forming the crytsal is called unit cell.

Author : Prof. J. Joga Rao

BLOCK - 7

D - BLOCK ELEMENTS

Those elements which possess unpaired electrons in the d-subshell eithre in the elemental state or combined state are called d-block elements, Their general outer electronic configuration is $(n-1)\,d^{1-10}\,ns^{12}$. The involvement of both s and d-subshell electrons enable them to exhibit variable oxidation states. Maximum oxidation state exhibited is + 8. They were found to form coloured and paramagnetic substances that contain unpaired electrons in the d-subshell. Other characteristic properties of these elements being their ability to form complexes and to exhibit catalytic property. All the transition elements are metals.

14.3 SOME PHYSICAL CHARACTERISTICS

In transition elements the differentiating electron enters the (n-1) d orbital in presence of ns. These elements are therefore expected to have many physical and chemical properties in common. The elements of the group having (n-1) d^{10} ns^2 electronic configuration show some differences from the remainder of elements. All the trasition elements are metals, and the number of electrons in the outermost shell is small, being equal to 1 or 2 . They are hard, malleable and ductile and good conductors of heat and electricity. They possess all the three types of structures namely face centred cubic (FCC), hexagonal close packing (HCP), and body centred cubic (BCC).

The transition elements having partially filled (n-1) dorbitals have very high melting and boiling points as compared to those of 's' and 'p' block elements. Zn, Cd and Hg having completely filled orbitals possess relatively low melting and boiling points. Although melting and boiling show no definite trends in the three transition series, the metals having the highest melting and boiling points are towards the middle of the each transition series.

The atomic (covalent) radii for the elements of the transition series are given in Table 14.1

Covalent radii (A°) of transition elements

Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
1.74	1.44	1.32	1.22	1.17	1.17	1.17	1.16	1.15	1.17	1.25	1.25
Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In
1.91	1.91	1.62	1.45	1.34	--	1.24	1.25	1.28	1.34	1.4	1.5
Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tp
1.98	1.69	1.44	1.34	1.30	1.28	1.26	1.26	1.29	1.34	1.44	1.55

It can be seen from the table that these values first decrease from Sc to V but later remains close to one another from Cr to Cu. This is due to the fact that an increase in the effective nuclear charge tends to attract the electron cloud, decreasing the radius from Sc to V. Addition of electrons to 3(n-1) d orbitals reverses the effect by screening the outer 4s electrons from the nuclear attraction resulting not much alteration in the covalent radius from Cr to Cu. In the first group the atomic radii show expected increase in size Sc-Y-La but in the subsequent groups is an increase in the radius of 0.1 to 0.2 A° between the first and the 2nd transition series and remains constant in the third transition series. This is known as the lanthanide contraction. The effect of the Lanthanide contraction begins to die out towards the right of the 'd' block elements and hence the radii increases.

The first ionization energies (potentials) of transition elements (Table 14.2) lie between the values of those of 's' and 'p' block elements. The addition of the idfferentiating electron to the (n-1) d level in transition elements provides a screening effect schielding the outer ns electrons from the nuclear attraction. Thus the effects of the effective nuclear charge and schielding due to the expansion of (n-1) d orbital oppose each other. On account of these counter effects the inoization energies (potentials) increase rather slowly along a period. The first ionisation energies (potential) of Zn is considerably high because of the completely filled 'd' and 's' orbitals which provides extra stability to the atom. The second ionization energis (potentials) seem to increase with increase in atomic number. These values of Cr and Cu are higher than those for their neighbours. This is due to the fact that the electronic configurations of Cr^{+3} and Cu^{+2} ions have extra stability having $3d^5$ and $3d^{10}$ configurations.

Table 14.2 First Ionization energies K J mole^{-1}

Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
590	631	656	630	652	717	762	758	736	745	906	579
Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In
549	616	674	664	685	703	711	720	804	731	876	558
Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl
503	541	760	760	770	759	840	900	870	889	1007	589

The transition elements are characterised by the formation o.

i) Compounds containing the metals in different variable oxidation states.

ii) Paramagnetic compounds

iii) coloured compounds

iv) complex compounds and

v) alloys

vi) The metals and their compounds in different oxidation states exhibit catalytic activity.

14.4 OXIDATION STATES

The chemistry of the transition elements is charactarised by the phenomenon of variable oxidation states. This is due to the presence of valence electrons in two different sets of orbitals of almost similar energy, the five degenerate (n-1)d orbitals and one ns atomic orbital. In simple compounds it can be said that the two electorns in the ns orbital of the transition metal atom are generally used giving a minimum of oxidation stateII, while the electrons in the (n-1) d orbitals may or may not be used for the purpose. For example, manganese atom which has the ground state electon configuration (Ar)3d^5 4s^2 exhibits oxidation states of II, III, IV, V, VI and VII. In the oxidation state II, the five 3d electrons are not used for bonding purposes and manganese atom is said to possess 3d non-bonding electrons. Similarly

Mn (III) has 3d^4 non-bonding electrons
Mn (IV) has 3d^2 non-bonding electrons
Mn (V) has 3d^2 non-bonding electrons
Mn (VI) has 3d^1 non-bonding electrons

Mn having 3d^0 non-bonding electrons in oxidation state VII belongs to the VII group of the periodic table. The different oxidation states observed in case of Mn are not stable. The relative stability of the oxidation states depends on the reduction potential.

The stable oxidation states of the transition elements are summarised in the Table 14.3

Table 14.3 Stable oxidation states of the transition elements

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
								1+	
--	2+	2+	2+	2+	2+	2+	2+	2+	2+
3+	3+	3+	3+	3+	3+	3+	3+	3+	3+
--	4+	4+	4+	4+	4+	4+	4+	3+	--
--	--	5+	5+	5+	5+	5+	--	--	--
--	--	--	6+	6+	6+	--	--	--	--
--	--	--	--	7+	--	--	--	--	--

Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
							1+		
--	--	2+	2+	2+	2+	2+	2+	2+	2+
3+	3+	3+	3+	3+	3+	3+	3+	3+	3+
--	4+	4+	4+	4+	4+	4+	4+	--	--
--	--	5+	5+	5+	5+	--	--	--	--
--	--	--	6+	6+	6+	6+	--	--	--
--	--	--	--	7+	7+	--	--	--	--
--	--	--	--	--	8+	--	--	--	--

La	Hg	Ta	W	Re	Os	Ir	Pt	Au	Hg
--	--	--	--	1+	1+	--	--	1+	1+
--	--	2+	2+	2+	2+	2+	2+	2+	2+
3+	3+	3+	3+	3+	3+	3+	3+	3+	3+
--	4+	3+	4+	4+	4+	4+	4+	--	--
--	--	5+	5+	5+	5+	5+	5+	--	--
--	--	--	6+	6+	6+	6+	6+	--	--
--	--	--	--	7+	--	--	--	--	--
--	--	--	--	--	8+	--	--	--	--

Copper, silver and gold exhibit an oxidation state of 1 + since this gives a very stable d non-bonding configuration. The greater stability of Ag (1) in solution and solid state as compared to Cu(1) and Au(1) is due to the energies required to promote an electron from the (n-1) d group of orbitals to the ns orbital. [$(n-1)d^{10}$ ns^{o} to $(n-1)$ $d^{9}ns^{1}$] .

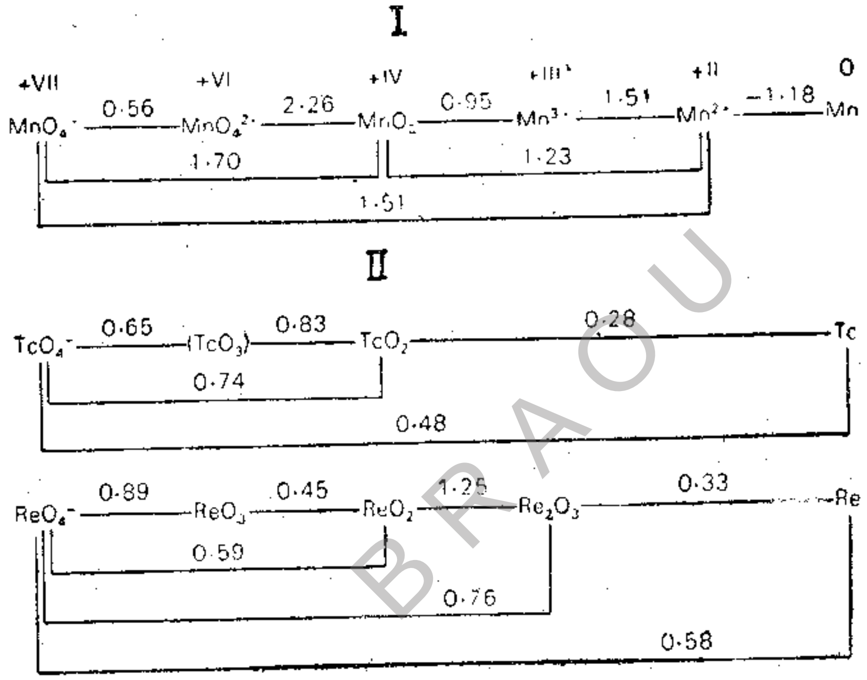
Cu (1) -- 62.73 K. cal

Ag (1) -- 112.32K.cal

Au (1) -- 43. 13 K.cal

Hg (1) with $5d^{10}$ $4s^{1}$ non-bonding configuration exists as the diatomic Hg^{2+} cation in which both the electrons in the 6s orbital are being used for bonding purposes (in forming Mercury-mercury covalent bond.) Theother electron is used in the ionization. The uni-negative oxidation states given for Ti and Re in the table are due to the stabilization of - 1 oxidation state by means of complexation.

The stability of the higher oxidation state increases down a transition sub-group. This general phenomenon observed for groups 4-8 can be explained on the basis of reduction potentials.



I Acid solutions ——— **II Basic solutions**

Check your progress - 1

How transition elements exhibit variable oxidation states?

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14.5 MAGNETIC PROPERTIES

The transition metal atom (or ions in different oxidation states) possess unpaired electrons. The atoms or ions which possess unpaired electrons are paramagnetic (attracted into a magnetic field) in nature where as those containing paired electrons (doubly occupied orbitals) are diamagnetic (repelled by a magnetic field). The paramagnetic moment 'μ' of a compound with 'n' unpaired electrons is given by the equation

$$\mu = \sqrt{n}\,[n + 2]\ \text{B.M}$$

(B.M. -- Bohr Magnetons) (1)

Where 'n' is the number of unpaired electrons. The values thus obtained for transition metal ions become equal to the values calculated by using the spin-only expression.

$$\mu = [4S\,(S + 1)]$$

S = Total spin of the electrons (2)

The detailed theory of magnetic behaviour indicates that the paramagnetism of a transition metal ion should be related to the total angular momentum of the unpaired electrons, rather than to just their number. The total angular momentum of an electron is the sum of two contributions: i) due to spinand ii) due to orbital motion. The spin angular momentum is uneffected by the environment of the electron, and so the contribution to the magnetic moment of the spins of the unpaired electrons cannot be effected by the nature of the bonding of the metal ion. The orbital angular momentum is effected by the environment of the electron and natureof bonding contributes to the deviation in the magnetic moment. Quenching or non-quenching of the orbital contribution depends on the field (of the ligands) present around the central metal ion. In a tetrahedral field quenching occurs for the metal ions with d^1, d^2 d^6 and d^7 configurtions but orbital contribution occurs for d^3, d^4 d^8 and d^9 configurations.

Table 14.4 Magnetic properties of the first transition series

Metal ion	Number of unpaired electrons	Magneticmoment(μ) calculated	Magnetic moment determined
Tr^{3+} V^{4+}	1	1.73	1.7 - 1.8
V^{3+} Cr^{4+}	2	2.83	2.8 - 3.1
Cr^{3+} Mn^{4+}	3	3.87	2.8 - 3.9
Cr^{2+} Mn^{3+}	4	4.90	4.8 - 4.9
Mn^{2+} Fe^{3+}	5	5.82	5.7- 6.0
Co^{2+}	3	3.87	4.3 - 5.2
Ni^{2+}	2	2.83	2.9 - 3.9
Cu^{2+}	1	1.73	1.9 - 2.1

Inspection of the table 14.4 indicates the deviations occur in the case of elements with high atomic number, particularly Cobalt (II) and Nickle (II) .This is due to the orbital contributin to the magnetic moment. In such cases the magnetic moment is calculated using the equation.

$\mu = g \sqrt{S (S + 1) + L (L+1)}$ B. M.

Where L = total angular moment

S= total spin of the electrons

g=gyroscopic constant (g=200)

14.6 COLOURED COMPOUNDS

The cation and the anions and oxy-anions of the representative elements ('s' and 'p' block elements except inert gases), are colourless. But the hydrated transition metal ions such as Cu^{2+}, Mn^{2+}, Cr^{3+} and the oxy-anions of the metals such as CrO_4^{2-} (yellow), $Cr_2O_7^{3-}$ (orange)and MnO_4^- (purple) are generally coloured. The colours of some of the hydrated cations containing (n-1) d^n electrons and n-number of unpaired electrons are given in table 14.5.

Table 14.5 Colours of hydrated cations

Hydrated cations	Electronic configuration	Number of unpaired electrons	Colour
Sc^{3+}, Ti^{4+}, Zn^{2+}	$3d^0$, $3d^{10}$	0	Colourless
Tl^{3+}	$3d^1$	1	purple
V^{4+}	$3d^1$	1	blue
Cu^{2+}	$3d^1$	1	blue
V^{3+}	$3d^9$	2	green
Ni^{2+}	$3d^2$	2	green
Cr^{3+}	$3d^8$	3	dark green
Co^{2+}	$3d^3$	3	pink
V^{2+}	$3d^7$	3	violet
Mn^{3+}	$3d^3$	4	violet
Cr^{2+}	$3d^4$	4	blue
Fe^{2+}	$3d^6$	4	pale green
Co^{2+}	3d	4	violet
Mn^{2+}	$3d^5$	5	faintly pink or buff

From the table it is inferred that the ions such as Sc^{3+}, Ti^{4+} which do not contain unpaired d-electrons and the ions such as Ag+, Zn^{2+}, Cu^{2+} which contain d^{10} configuration (paired electrons) are colourless. The other metal ions containing partially filled 'd' orbitals are coloured. The observed colour in case of transitionmetal ions can be explained with the help of Crystal Field Theory (CFT) described in unit 15. The octahedral field set up by the aquo molecular species splits the five degenerate 'd'orbitals into two energy states with a difference of Δ (Δ = crystal field stabilization energy).

An increase in the magnitude of Δ , changes the colour of the complex from violet to red. The observed colour not only depends on the number of ligands. In order to see the effect of the field strength of the ligands on the colour of the complex consider the octahedral complexes of Co^{2+} prepared with different ligands such as H_2O, NH_3, and CN^-. On the basis of the spectro chemical series the field strength set up by the ligands is CH> NH_3> H_2O). The wave length of the colour absorbed by these ions is in the reverse order (CN< NH_3 < H_2O. Consequently the colour of the light absorbed by the complex shifts from violet to red and the colour of the transmitted light (colour of the complex) shifts from yellow-green blue green. The colour of a complex is taken to be the colour of the light transmitted by the complex or the ocmplementary colour of the light absorbed by the complex.

Table 14.6 Colours of complex ions

Complex ion	Colour of the absorbed light	Colour of the complex (or colour of the transmitted light)
$[Co(H_2O)_6]^{3+}$	Orange	Greenish blue
$[Co(NH_3O)_6]^{3+}$	Greenish blue	Orange
$[Co(CN)_6]^{3+}$	Violet	Yellowish green

The colour of the complex depends not only on the number of unpaired electrons, strength of the field set up by the ligands around the metal ion but also on the coordination number and geometry of the complex. The metal ion having the same number of unpaired electrons may form complexes with the same ligand with different geometries. In such cases the value of Δ changes with the geometry of the complex. This in turn changes the colour of the complex. If the value of Δ is small, the metal ion absorbs in the infrared region and if Δ is large the metal ion absorbs in Ultraviolet region. In both cases the colour of the complex is colourless.

Check your progress - 2

What type of transition metal ions exhibit colour?

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14.7 COMPLEX COMPOUNDS

The transition metal ions in different oxidation states show a great tendency to form stable complexes with ligands such as NH_3, H_2O, CN^-, Cl^-, OH^-, etc. This tendency of formation of complexes can be ascribed to the following reasons.

1. The metal ions have relatively small size in higher oxidation state.

2. The small size of the transition metal ions and the availability of vacant (n-1) d orbitals make the metal ion accept easily the lone pair of electrons from the donar atoms of the ligand.

3. Metals of first transition series generally form complex compounds with coordination numbers 2,4 and 6 where as metals of 2nd and 3rd transition series form complexes with coordination numbers 7,8 and 9.

4. The metals of the first transition series form stable complexes with ligands containing N and O as donar atoms while the metals of the second and third transition series form stable complexes with ligands containing, P, As and S as donor atoms.

14. 8 COMPOUNDS WITH CATALYTIC PROPERTIES

The transitiion metals and their metal ions having high surface area and vacant orbitals possess catalytic properties. Some of the examples are (i) Vanadium is used as V_2O_5 or as ammonium metavandate in the manufacture of sulphuric acid by contact process. (ii) Finely divided Nickle is used in the hydrogenation of oils, conversion of the mixture of CO and H_2O into a mixture of CO_2 and H_2. (iii) Spongy Platinum is used in the conversion of SO_2 to SO_3 by air and oxidation of ammonia to nitric oxide. (iv) Iron is used as catalyst in the manufacture of ammonia by the Haber's process. Mo is used as promoter in some reactions.

14.9 FORMATION OF ALLOYS

Transition metals such as Mo, W and Cu, Ni having nearly the same atomic radii, crystal structure, minimum difference in electronegativity and same number of valence electrons form true solid soluitions. Elements such as H,B,C and N combines with transition metals to form non-stoichiometric interstitial compounds.

14.10 SUMMARY

d-Block elements are transition elements. The general physical propoerties of the elements like ionisation potentials, melting points and boiling points are described in this unit. Their outer electronic configurations vary from $(n-1)d^1 nS^{1-2}$ to $(n-1)d^{10} ns^{1-2}$. The characteristic properties of transition elements a) variable oxidation states b) paramagnetic character c) colour d) their tendency to form complexes e) catalytic property and f) alloys are described. All the transition elements are metals.

14.11 MODEL EXAMINATION QUESTIONS

I Answer the following in 10 lines each.

1. Explain why copper is a proper reducing agent than its neighbours
2. Illustrate the influence of the lanthanide contraction on the properties of transition metal elements.

II Answer the following in 30 lines each.

1. Discuss why the reduction potential for manganous ion is more negative than for chromous and ferrous ions.
2. explain the variable oxidation states and magnetic properties of transition metal on the basis of electronic configuration.
3. a) Expalin the trends in ionic radii and ionization potentials in the 1st series of transition elements.

   b) What are the common characteristics of transition elements?

14.12. MODEL ANSWERS TO CHECK YOUR PROGRESS.

1. They are able to exhibit variable oxidation states due to the involvement of both S and d-subshell electrons:
2. Transition metal ions which possess unpaired electrons in the d-subshell were found to exhibit colour.

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UNIT - 15 TRANSITION METAL COMPLEXES

Contents

15.1 AIMS AND OBJECTIVES

To explain you the principles underlying the formation of complex compounds.

After complete study and understanding of this unit, you must be able to:

- give the definitions of the terms commonly used in the coordination chemistry
- apply the rules pertaining to the nomenclature of coordination compounds (IUPAC) giving suitable examples.
- explain the theories of metal-ligand bond of isomerism of complex compounds
- describe the concept of stability constants and the factors affecting the stability constants
- give the applications of co-ordination compounds in analytical chemistry

15.2 INTRODUCTION

a) Double salt: When solutions of two salts are mixed in stoichiometric ratio and allowed to evaportate we get a crystalline solid named as double salt. The double salt dissociates into ions in water and these ions respond to qualitative tests.

Example:

$$K_2SO_4 + Al_2(SO_4,)_3 \xrightarrow[\text{-lization}]{\text{crysta}} K_2SO_4\,Al_2(SO_4)_3\,24H_2O \quad \text{(Crystalline Solid)}$$

$$\downarrow H_2O$$

$$2K^+ + 2\,Al^{3+} + 3SO_4^{2-}$$

b) Co-ordination compound: The compound is generally prepared by methods similar to those adopted for the preparation of a double salt. The compound does dissociate in water to give the constituent ions. But the ions do not respond to the tests answered in the ions present in the starting compounds.

Example: $Fe(CN)_6 + 4\,KCN \longrightarrow K_4Fe(CN)_6$ (Co-ordination compound)

$$\downarrow H_2O$$

$$4K^+ + [Fe(CN)_6]^4$$

The Co-ordination compound may be neutral like Ni $(DMG)_2$ (DMG: Dimethyl glyoxime) or ionic like $K_4Fe(CN)_6$, $(CO(NH_3)_6]Cl_3$.

In other words the co-ordination compound (neutral/ionic) may be defined as a compound formed by the chemical combination of a metal ion, in an oxidation state (O, n) and ligands, (DMG or NH_3 or CN)

a) **Ligand:** The ligand may be neutral molecule such as NH_3, Ethylenediamine (En), or Pyridine (Py) or anionic such as CN^-, OH^-, F^-, or cationic such as NH_2. NH_3^+ capable of donating an electron pair (A base).

b) **Co-ordination number:** The number of mono dentate ligands bound to the central metal ion inside the ocordinatin sphere to give a regular geometry0-lincar, trigonal planar, tetrahedral, a square planar, trigonal bipyramidal or octahedral-to the complex species.

c) **Chelate:** A chelate is a complex species formed between a metal ion and a bidentate ligand in which the points of attachments of more electrons and examples, the ligand to the metal in are more than one forming a ring structure (chelate from the Greek meaning 'claw').

d) **Classification of ligands:** On the basis of the donor atoms present in the ligand the ligands are classified into two groups.

i) Monodentate. ii) Polydentate.

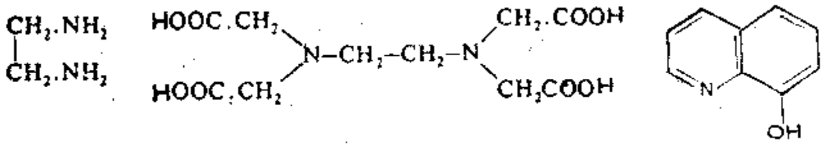
i) Monodentate ligands are those ligands containing one or more donor atoms, but donates only one lone pair of electrons to the central metal ion forming the complex.

Example:

OH	F	NH_2
Hydroxo	Fluoro	Amido

ii) Polydentate ligands are those ligands in which the numnbr of donor atoms and number of lone pairs of electrons donated are more than one. The points of attachments between the central metal ion and the ligand are therefore more than one.

Example:



1 2 3

Fig. 15.1 1. Ethylene Diamine 2. EDTA 3. 8-0H quinoline

d) **Bridging liquid:** A monodentate ligand having more than one lone pair of electrons on a donor atom may simultaneously donate its lone pairs to two different metal ions. Such a ligand is called a Bridging ligand and the resulting complex is ;known as Bridged complex.

15. 3 NOMENCLATURE OF CO-ORDINATION COMPOUNDS

The first comprehensive system of nomenclature was suggested by Alfred Werner. Subsequently this has been modified by the inorganic nomenclature comiittee of International Union of Pure and Applied Chemists (IUPAC). The modified form of nomenclature, approved by IUPAC is given below.

1. The neutral complexes (non-ionic) are given a one word name whereas the ioniccomplexes are named in the usual fashion by using two word name. The cation is named first and the anion is named later.

Tetra carbonyl Nickel (o)	(neutral)
Dichloro diamine platinum (II)	(neutral)
Hexamine cobalt (III) chloride	(cationic)
Potassium hexacyano ferrate (II)	(anionic)

The anionic complexes end with characteristic ending '-ate' the cationic and neutral complexes have no characteristic endings.

2. Names, order and the number of ligands present in the co- ordination sphere are described as stated below.

i) Neutral ligands are named as such (except NH_3 and H_3^2O, in which cases they are named as (amine' and 'aquo' respectively).

$H_2NCH_2CH_2NH_2$	ethylene diamine.
$(C_6H5)_3P$	triphenyl phosphine

ii) Negative ligands end in '-O' and positive ligands end with '-ium'.

Cl^-	Chloro		
CN^-	Cyano	$NH_2.NH^+_3$	Hydrazinium
CH_3COO^-	Acetate		

iii) The naming order of the ligands in a complex is negative, neutral and positive, each one separated by 'hyphen'.

iv) The number of ligands present in the complex is indicated by the prefixes di, tri, tetra etc., in the case of simple ligands such as bromo, nitro, oxalato. Prefixes like bis, tris and tetrakis etc., are used in the case of complex names (chiefly with ligands containing mono, di, tri, etc., in the ligand name itself, such as ethylene diamine and triphenyl phosphine).

3. The oxidation state of the central metal ion is designated by a Roman numeral in parenthesis at the end of the name of the complex species. For a negative oxidation state a minus sign is used before the Roman numeral and 'O' is used for zero oxidation state.

4. The ligands that bridge two centres of coordination are preceeded by the greek letter 'μ' which is repeated before the name of each different kind of bridging group.

5. Wherever necessary, the point of attachment of the ligand is designated by placing the symbol (in italics) of the elements attached after the name of the group, with separation by hyphen.

6. Illustration of the rules mentioned

i)	$[Co(NH_3)]\,Cl_3$	Hexamine cobalt (III) chloride
ii)	$[Co(en_3)]\,Cl_3$	Tris ethylendeidamine cobalt (iii) chloride
iii)	$K_4\,[Fe(CN)_6]$	Pottassium hexacyano ferrate (ii)

(iv)

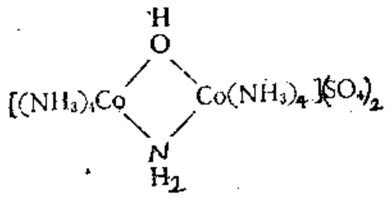


Fig. 15.2 μ - amido μ - hydroxo octaamine cobalt (iii) sulphate

15.4 THEORIES OF CO-ORDINATE (METAL-LIGAND) BOND

It is difficult to state exactly when the first metal complex was discovered. The earliest one on record is prussianblue, KCN, Fe (CN)$_2$, Fe (CN)$_3$. 'artists color' which was prepared by Diesbach in the beginning of the eighteenth century. The real beginning of the coordination chemistry has started with the preparation of hexamine cobalt (III) chloride by Tassaert in the year 1798. The compound CoCl$_3$ 6NH$_3$ with unique properties stimulated considerable interest in research on similar systems. Tassaert's experimental observations could not be explained on the basis of the chemical theory available at that time. It was necessary to understand how COCl$_3$ and NH$_3$, each being a stable compound of presumably saturated valence, could combine to make yet another stable compound. The answer for this was not found for 100 years. During that time many such compounds were prepared. To explain the observed properties several theories were proposed. As they were inadequate to explain the experimental data they were discarded.

The preparation of metal complexes generally involves the reaction between a metal salt and neutral ligards like NH$_3$ or anions like CN$^-$, NO$_2^-$, NCS$^-$ and Cl$^-$.

The complexes prepared by the interaction of CoCl$_3$ with ammonia exhibited a spectrum of colours and deffered in their chemical reactivity. The compounds along with their colours and names are given in table 15.1 The compounds are named on the basis of colour.

Table 15.1 Colours , names and formula of cobalt- ammonia complexes:

S.No	Complex	Colour	Name	Number of Cl ions precipitated	Present Formula
1.	Co Cl$_3$. 6NH$_3$	Yellow	Luteo cobalti chloride	3	[Co (NH$_3$)$_6$]Cl$_3$
2.	Co Cl$_3$. 5NH$_3$	Purple	Purpureo cobalti chloride	2	[Co (NH$_3$)$_5$Cl]Cl$_2$
3.	Co Cl$_3$. 4NH$_3$	green	Praseo cobalti chloride	1	trans [CO (NH$_3$)$_4$ Cl$_2$] Cl
4.	Co Cl$_3$. 4NH$_3$.	Violet	Violeo cobalti chloride	1	cis [CO (NH$_3$)$_4$ Cl$_2$] Cl
5.	Co Cl$_3$. 3NH$_3$		No ppt		

The addition of a solution of silver nitrate to a freshly prepared solution of CoCl$_3$, 6 NH$_3$ results in the immediate precipitaion of all the three chloride ions. The same experiment with CoCl$_3$. 5NH$_3$ is found to cause instant precipitation of only two chloride ions, the third chloride precipitates slowly on prolonged heating. The results of such studies are incorporated in the table. The compounds 3 and 4 having the same chemical composition $CoCl_3$ $4NH_3$ are different not only in colour but also in their physical and chemical properties. It was necessary to account for all these experimental facts with a suitable theory. Several hypothesis and theories were proposed. One amongst them is Bloomstrand-Jorgensen chain theory.

Bloomstrand - Jorgensen chain theory

The concept of the tetra valency of carbon and the formation of carbon-carbon chains in carbon compounds made a marked influence on the thinking of inorganic chemists. Mention may be made at this point about Bloomstrand, Professor of chemistry at the University of Lund, in Sweeden and his student Jorgensen, who proposed the chain theory to expalin the existence of metal complexes.

It was felt that the elements (metal ions) had only one type of valence and there could be only three bonds to cobalt in its complexes. Therefore a chain structure (I) was proposed to account for the additional six ammonia molecules in $CoCl_3$. $6NH_3$. The three chlorides are separated by some distance from cobalt and were therefore believed to precipitate readily as silver chloride on the addition of Ag^+. The theory represnted $CoCl_3$. $5NH_3$ as II. In this structure one chloride ion is directly attached to the cobalt and it was presumed that this is the one that does not ionize and does not precipitate instantly as silver chloride. Structure III, given for $CoCl_3$. $4NH_3$ accounts for the experimental results and showed that two chloride ions are held more firmly than the third. The next member of this series $CoCl_3$. $3NH_3$ was represented by IV. From this structure one would predict that the chlorides would behave as they do in $CoCl\ 4NH_3$. Professor Jorgensen, a very able experimentalist did not succeed in preparing the cobalt compound but made instead the analogous iridium complex $IrCl_3$. $3NH_3$. A solution of this compound did not give a precipitate upon addition of silver nitrate indicating that their chain theory is not correct. After the failure of the chain theory more convincing theory was proposed by A, Wernerin the year 1893.

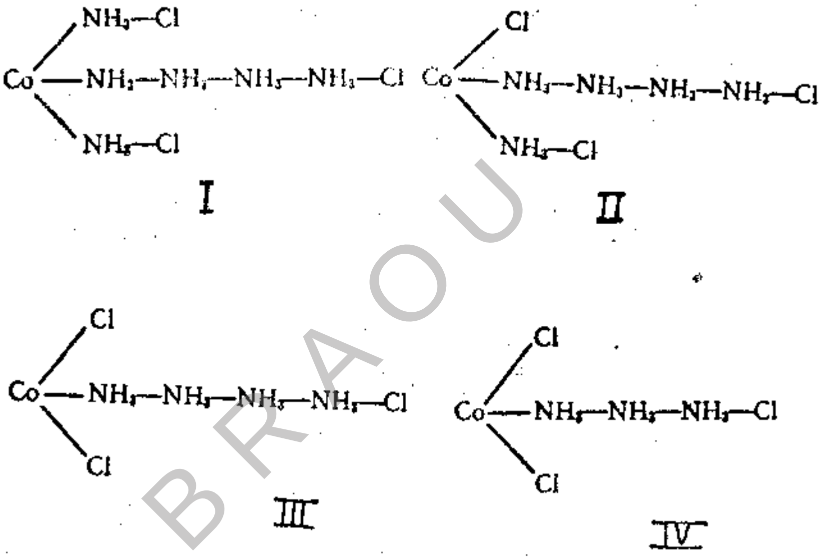


Fig. 15.3

Werner's coordination theory

Alfred Werner, at the age of only 26, proposed what is now commonly known as Werner's co-ordination theory. His theory has been a guiding principle in inorganic chemistry and in the concept of valence. The fundamental postulates of this theory are summarised as follows:

1. Most metals/ions exhibit two types of valence.

a) Primary valence or ionic valence.
b) Secondary valence or non-ionic valence
(In modern terminology (a) corresponds to oxidation state and (b) to coordination number.

2. Every metal/ion tends to satisfy both the primary and secondary valences.

3. The secondary valence is directed towards fixed positions in space around the central metal ion.

In the light of the above postulates the experimental facts described earlier, may now be properly explained. According to the theory, the first member of the series $CoCl_3$. $6NH_3$ is designated as V and formulated as $(Co(NH_3)_6\ Cl_3$ The primary valence or oxidation state of cobalt is 3. The three chloride ions saturate the primary valence of cobalt and are represented by solid lines. The secondary valence is six, and is satisfied by six ammonia molecules. The ammonia molecules are directly attached to the central metal ion and are said to be in the coordination sphere, represented by dotted lines.

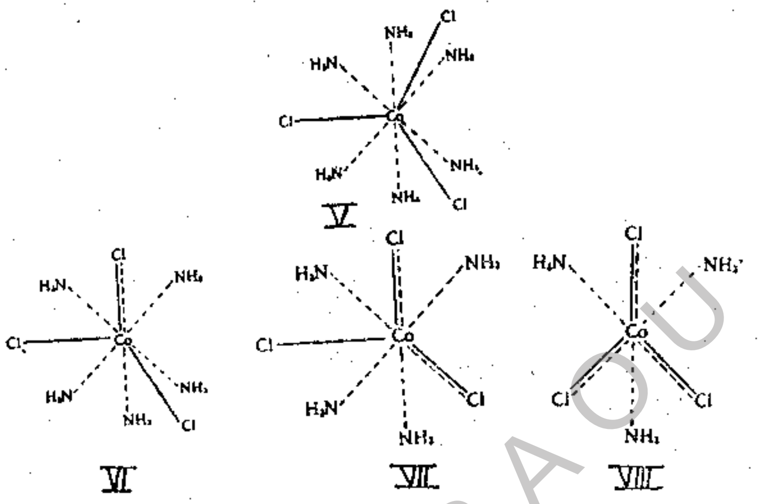


Fig. 15.4

The chloride ions in the compound (V) are not firmly bound. A solution of the complex conducts current equivalent to four ions and the three chloride ions arreadily precipitated by Ag^+ as silver chloride. Returning now to the theory, one finds that Werner represented $CoCl_3$. $5NH_3$ as VI. He did this in accordance with postulate 2 which states that both the primary and secondary valence tend to be satisfied. In $CoCl._3$. $5NH_3$ there are only five ammonia molecules to satisfy the secondary valence. Therefore one chloride ion must serve the dual function of satisfying both the primary and secondary valence. Werner represented the bond between such a ligand and the central metal ion by a combined solid line.

Such a chloride ion is not readily precipitated by the addition of Ag^+. The complex cation $(Co\ (NH_3\ ))_5\ Cl)^{2+}$ carries 2 + charge. The compound is now formulated as $(Co\ (NH_3\ )_5\ Cl)\ Cl_2$. Extension of this theory to the next member of the series $Co\ Cl_3$. $4NH_3$, required formula VII. In this two chloride ions satisfy both the primary and secondary valence. Hence they are firmly held in the coordination sphere. In solution the compound therefore dissociates into two ions C; and $[Co\ (NH_3\ )_4\ Cl_2\ ]Cl$. The weight of the precipitate of AgCl corresponds to only one chloride ion.

A very significant point arises with the next member of the series $CoCl_3$ $3NH_3$ (VIII). Werner's theory requires that it should be represented as VIII and formulated as $[Co\ (NH_3\ )_3\ Cl_3\ ]$. The Werner theory predicted that the complex would not yield Cl^- ion in solution. In contrast the chain theory predicted that the compound would dissociate to give one chloride ion. Postulate 3 of Werner's theory deals specially with the stereo chemistry of metal complexes. Co-ordination theory corrctly explains many of the structural features of co-ordination compounds.

Although the theory explains satisfactorily all the experimental observations it is not able to expalin the concept of secondary valnece, in the light of the electronic theory of valence.

Check your progress - 1

Why the chloride ions do not get precipitated on treating a solution of [(Co $(NH_3)_3$ Cl_3] with $AgNO_3$ solution?

Sidgwick's electronic Interpretation

Until the advent of electronic theory of valence, Werner's theory was regarded as satisfactory one. After the advent of electronic theory of valence by Lewis, it was considered necessary to make some modificatins to it. Sidgwick has introduced a new concept called 'coordinate bond' (sometimes called the semipolar bond or dative bond). According to Sidgwick's concept the molecules or ions attached to the central metal ion donate atleast one lone pair of electrons (donor) to the metal ion, which accepts the electron pair (acceptor). The bond established between the metal and ligand is termed as Co-ordinate covalent bond or Dative bond or Semipolar bond.

Once formed, this bond is not different from covalent bond. The only difference lies in the mode of its formation. The bond formed is usually represented as M ← L. On the basis of Sidgwick's concept the structure of the complex ion (Co $(NH_3)_6$ Cl^{3+} is represented as

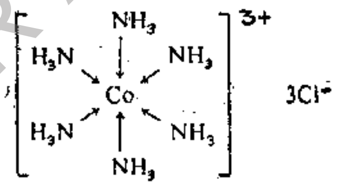


Fig. 15.5 Structural representation of (Co $(NH_3)_6$ Cl_3

In the formation of six coordinate covalent bonds, in all twelve electrons are donated to the central metal ion Co^{3+} by six ammonia molecules. On the basis of this Sidgwick suggested that after the ligands have donated a certain number of electrons to the central metal ion through bonding the total number of electrons present around the atom/ion becomes equivalent to the next this is inert gas configuration called EAN (Effective Atomic Number). For example: The EAN of (Co $(NH_3)_6$$Cl^{3+}$ an be calculated as follows:

1. Number of electrons present in cobalt (At.No 27) atom is 27.
2. Number of electrons present in Co^{3+} is (27-3) = 24.
3. Number of electrons donated by ~~6 ligands~~ = 2 x 6 = 12.

Total number of electrons present around the central metal ion in the complex species is 24+12 = 36. This is called EAN and it confers stability on the complex species.

Though in many cases the EAN is the same as the atomic number of next inert gas, yet it is not always true. For example in $[Ni(CN)_4]^{2-}$ EAN is 34.

1. Number of electrons present in Nickel (AT No. 28) is 28.
2. Number of electrons present in Ni (28-2) = 26
3. Number of electrons donated by 4 ligands 2 x 4 = 8.

Total number of electrons around Ni^{2+} is 34.

Check your progress -2

What is EAN?

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Metals having more than one coordination number do not attain the inert gas configuration (EAN) This raises doubts regarding the concept of stability in the light of EAN. To account for this stability several modern theories have been prooposed by

1. Linus Pauling (Valence Bond theory) 2. Bethe and VanVleck (Crystal Field Theory) and 3. Van Vleck (Molecular Orbital Theory)

The elementary treatment of the first two theories is given below.

Valence Bond Theory (VBT)

The next major step in the development of coordination compounds was due to Linus Pauling of California University of Technology, who applied the valence bond approximation to complexes in 1913. His valence bond theory is based upon electronic structure of the ground state of the central metal ion. Pauling's bonding picture involves the following assumptions.

1. The central metal atom or ion will make available vacant orbitals equal in number to its coordination number for accepting lone pairs of electrons for the formation of covalent bonds with ligands.

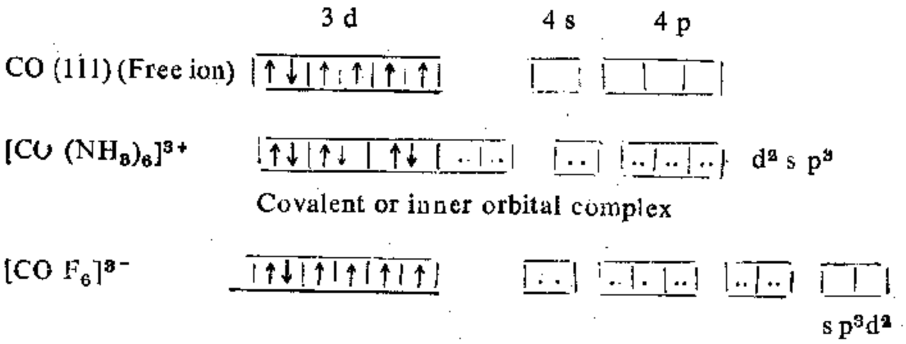
2. These vacant atomic orbitals undergo hybridisations to give an equal number of hybridised orbitals with a fixed orientation in space.

3. A 'σ'bond is formed by the overlap of empty hybridised orbitals of metal ion with the filled orbital of the ligand.

In octahedral or six coordinated complexes, the six hybrid orbitals are identical except that they are pointed along the six directions in space given by a set of cartesian axes. The six atomic orbitals used are the s, P_x, P_y, P_z, $d_{x^2-y^2}$ and d_{z^2}. For maximum stability, the 'd' orbitals used ar of the next lower princial quantum number than the s and p. Each hybrid orbital accepts a pair of electrons from a ligand.

In other words a set of six valence bonds are formed by the overlap of six hybridised orbitals of metal ion with the filled orbitals of the ligands. These bonds are of σ type, the electron density of the bond being symmetrical about the bond axis. It has been postulated by Pauling that, if a ligand has, 'd' electrons, Π bonding from the metal to the ligand, will occur. This will strengthen the metal ligand bond (making it a double bond) and help to reduce the negative charge formed on the central atom by the addition of electrons from ligands.

In order to account for the different magnetic properties of a given metal ion in various complexes, pauling postulated that a covalent bond forms when the ligand is of a highly electron donating type such as CN^-, whereas it is not so with a highly electro-negative ligand like F^-. Thus a distinction between covalent and ionic complexes was drawn and their magnetic moments were observed. Based upon these observations the nature of complex was determined. Thus the magnetic moment is taken as a criteria to decide the type of bond. To explain this, the electronic configuration of some complexes of Co(III) are furnished here.



ionic or outer orbital complex

The hexamine cobalt (III) ion being diamagnetic, was considered as a covalent complex, the hexafluoro complex shows paramagnetism consistent with its four unpaired electrons as an ionic complex. Tauble uses the terms 'Inner orbital' and 'Outer orbital' to distinguish between these two kinds of complexes respectively.

Although provides a satisfactory pictorial representation of coordination compounds based on the concept of oribtal hybridization it is limited only to qualitative explanations.

The major drawbacks of the valence bond theory are it is
i) not able to lend support to spectroscopic intepretaiton.
ii) not able to account for or predict in detail the magnetic properties.
iii) not able to account for the splitting of the 'd' orbital energy levels.

These lapses are to a large extent covered by electrostatic crystal field theory, ligand field theory and molecular orbital theory.

Electrostatic Crystal Field theroy

The crystal field theory, a refined form of electrostatic theory, developed by Bethe, Van Vleck calculate magnetic susceptibilities of certain complex compounds. In the theory the ligands are treated as negative point charges which set up an electrostatic field around the metal ion. The effect of the field on the central metal ion is then investigated.

In a gaseous transitional metal atom or ion, the five 'd' orbitals are degenerate, that is they have the same energy. These five 'd' orbitals are designated as d_{z^2}, $d_{x^2-y^2}$, d_{xy}, d_{xz}, d_{yz} ion is exposed to a negative electrostatic field, the energy of the system (Ion and the field) is increased. If the field is spherical in shape, the only effect is an increase in the energy of the system, but if the field is non-spherical, then the interaction has directional properties. The imposition of a field of point charges which has the shape of a regular octahedron increases the energy and removes the degeneracy of the set of 'd' orbitals. If the octahedral field is imposed along the positive and negative directions of the original cartesian co-ordinate system, the interaction with the field is maximum and their energy is increased. In d_{xy} d_{xz} and d_{yz} orbitals lie between the point charges, hence their interaction is minimum. Since the choice of x, y and z axes is orbitrary, the orbitals d_{xy} d_{xz} and d_{yz} are degenerate and higher in enrgy. The orbitals are also degenerate but lower in energy. The orbitals are also degenerate but lower in energy. The two sets of orbitals are conveniently labelled by the group theoretical representations as e_g for the doubly degenerate set and t_{2g} for the three fold degenerate set. The amount of splitting between e_g and t_{2g} orbitals is generally denoted by Δ or 10 Dq. The magnitude of splitting obviously depends on the central ion and ligands involved. Using an analogous line of reasonging, the splitting patterns of the d orbitals of a central ion in complexes having different geometries are shown below.

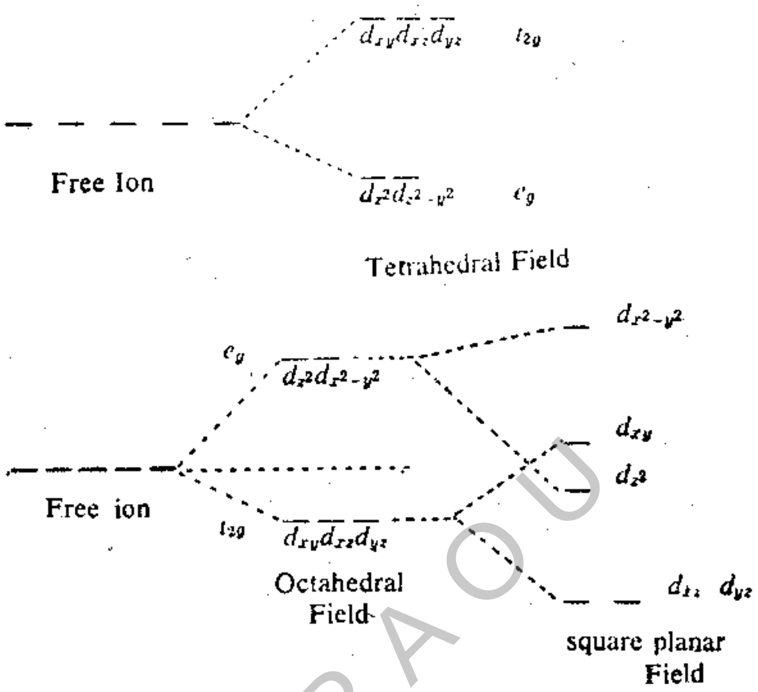


Fig. 15.6 'd' orbital splitting

15.5 ISOMERISM IN CO-ORDINATION COMPOUNDS

The compounds which have the same molecular formulae but have different structural arrangement of their atoms are called isomers and the phenomenon is knwon as isomerism. Co-ordination compounds similar to organic compounds, exhibit two main types of isomerism, namely structural isomerism and stereo isomerism.

Structural isomerism:

This isomerism arised because of the difference in structures of co-ordination compounds. The following are the different types of structural isomers.

i) **Linkage isomerism:** It deals with the ligands that are capable of forming co-ordinate bond though one type of donor atom in one situation and though a different atom in another situation. This type of isomerism is termed as linkage isomerism. The first example of this type of isomerism was provided by Jorgenson. His method of preparation was as follows.

$$[CO(NH_3)_5Cl]Cl_2 \xrightarrow{NH_3} \xrightarrow{HCl} \xrightarrow{NaNO_2} \text{solution}$$

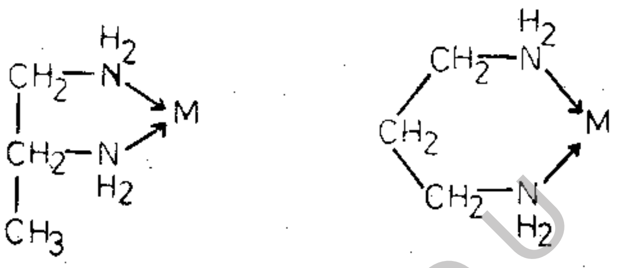
$$\text{Solution A} \xrightarrow[\text{in cold}]{\text{Let stand}} [(NH_3)_5\,Co\,ONO]\,Cl_2\ \text{(Red) Solution B}$$

$$\text{Solution B} \xrightarrow[\text{+ Conc. HCl}]{\text{Heat}} \xrightarrow{\text{cool}} [(NH_3)_5\,CO\,NO_2]\,Cl_2\ \text{Yellow}$$

Jorgenson and Werner agreed that the difference between the two isomers lies in the linkage of NO group to the cobalt. The N-bonded ("nitro") structure was assigned to the yellow isomer and the O-bonded ("nitrito") sturcture to the red isomer on the basis of the colour of the similar compounds.

ii) **Ligand isomerism:** since many ligands are organic compounds and the latter have a large number of possibilities for isomerism, the resulting complexes can show isomerism on this account. Examples of isomeric ligands are 1,2 - diamino propane ("propylene diamine" pn) and 1,3 diamino propane (trimethylenediamine" tn).

Structures:



1 2

Fig. 15.7

1. 1,2 diamino propane 2. 1,3 diamino propane

iii) **Ionization isomerism**: The compounds $[Co(NH_3)_5\,Br]^{2+}\,SO_4^{2-}$ and$[Co(NH_3)_5\,Br]^{2+}\,SO_4^{2-}$ Br dissolve in water to yield different ions and thus react differently to various reagents.

Example:

Compound	Ba^{2+}	Ag^+
$[Co(NH_3)_5\,Br]^{2+}\,SO_4$ $[Co(NH_3)_5\,Br]^{2+}\,SO_4]\,Br$	white ppt ($BaSO_4$) no ppt	no ppt light yellow ppt (AgBr)

v) **Solvate or Hydrate isomerism:** This is a special case of the interchange of ligands involving neutral water or solvent molecules. The best known examples are isomers of hydrate chromic chloride. These differ in their reactions.

1. $[Cr\ (H_2O)_6]\,Cl_3 \xrightarrow{\text{dehydration}} [Cr\ (H_2O)_6]\,Cl_3$ (no change in weight)
2. $[Cr\ (H_2O)_5\,Cl_2\,]\,Cl_2O \xrightarrow{\text{dehydration}} [Cr\ (H_2O)_5\,Cl]\,Cl_2$ (loss in weight)
3. $[Cr\ (H_2O)_4\,Cl_2\,]\,Cl2H_2O \xrightarrow{\text{dehydration}} [Cr\ (H_2O)_4\,Cl_2\,]\,Cl$ (greater loss in weight)

v) Co-ordination - isomerism: Salts that contain complex cations and anions exhibit isomerism through the interchange of ligands between cation and anion. For example, both hexamine cobalt (III) hexacyano chromate (III), (CO $(NH_3)_6$) [Cr $(CN_6]$ and its isomer hexamino chromium (III), hexacyano cobaltate (III) (Cr $(NH_3)_6$) [CO $(CN_6]$ are known, Another example that differs in colour is (Cu $(NH_3)_4$) [$(PtCl_4]$ Violet and $(CuCl_4)$ [(Pt $(NH_3)_4$] (green).

A special case of coordination isomerism has some times been given the name 'polymerization isomerism' since the various isomers differ in formulae weight from one another. However, it is unfortunate to use this term since polymerization is normally used to refer to the reaction in which a monomeric unit builds a larger structure consisting of a great number of repeating units. The isomers in question are represented by compounds such as.

1. $[Pt \{NH_3)_4] [Pt Cl_4]$

2 $[Co \{NH_3)_4] (NO_2)_2] [Co (NH_3)_2 (NO_2)_4]$

3. $[Co \{NH_3)_5 NO_2] [Co (NH_3)_2 (NO_2)_4]_2$

4. $[Co \{NH_3)_6] [(Co (NH_3)_2 (NO_2)_4]_3$

5. $[Co \{NH_3)_5 (NO_2]_3 [(Co (NO_2)_6]_2$

2,3,4,5 have the same empirical formula $[Co \{NH_3) (NO_2)]$ but have molecular formulae with weights, 2,3,4 and 5 times the weight of the empirical formulae.

Stereoisomerism: When two compounds containing the same ligands coordinated to the central metal ion with difference in spacial arrangement are said to be stereoisomers and the phenomenon is knwon as stereoisomerism. This is of two types (i) geometrical or cis-trans isomerism and (ii) optical isomerism.

Geometrical isomerism or Cis-trans isomerism: Geometrical isomers have the same molecular formulae but differ in chemical and physical properties because of the difference in special arrangement of ligands around the central metal ion. The common geometrical isomers are observed in complexes with coordination numbers 4 can be conveniently divided into tetrahedral and square planar forms, although intermediate and distorted structures are known.

Geometrical isomers are generally named by the use of the terms 'cis' to designate (90° apart) positions nad 'trans' for (180° apart) positions. Optical isomers 'dextro' or 'laevo' rotatory are designated by (+) and (-) or by d and l respectively.

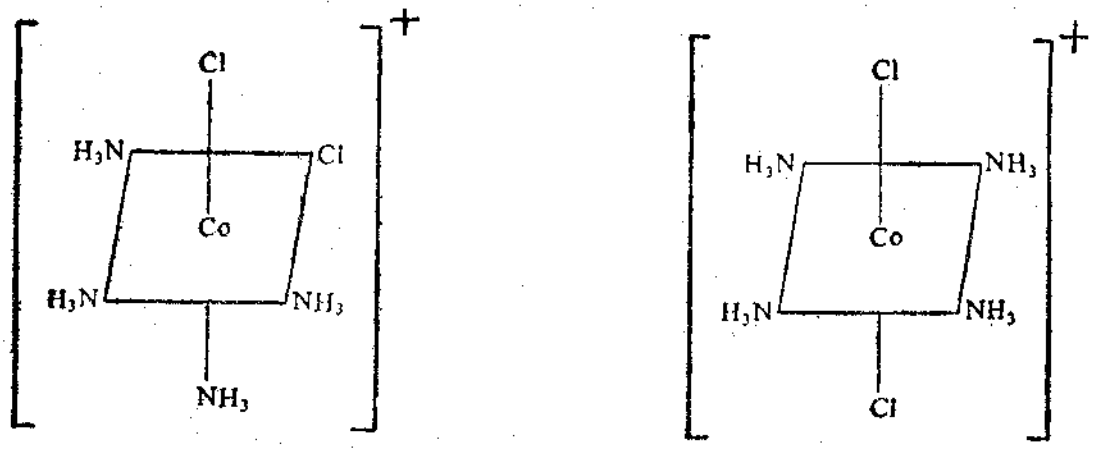


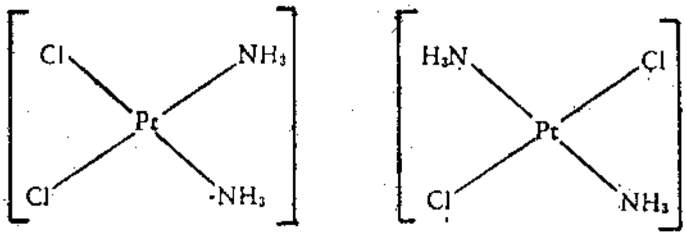
Fig. 15.8 **Cis** dichlorotetra amine cobalt (iii) **trans** dichloro tetramine cobalt (iii)

Squareplanar Complexes: Only square planar complexes with differnet molecular formulae are known to exist as cis-trans isomers. However, the compounds having the molecular formulae $(MA_2L_2)^{n+}$, $(MA_4 L)^{n+}$ $(MA_4 L_3)^n$ do not show geometrical isomerism.Th e complex with molecular formula only exhibits geometrical isomerism.

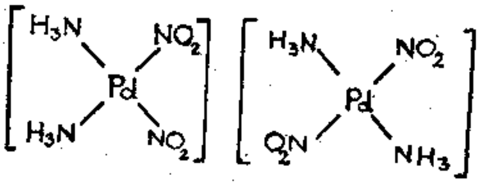
As examples of this type of complexes we have,

1. $[Pt \{NH_3)_2] (NO_2)_2]$ $[Pd (NH_3)_2 (NO_2)_2]$

Both these complexes have cis-trans isomers. The four bonds in both the compleces are coplanar with the central metal ion.



cis trans



cis *trans*

Fig. 15.10

2. Complexes with the molecular formula (MALXY) where A,L,X,Y are mono dentate ligands.

Complexes of this type exist in the isomeric forms,

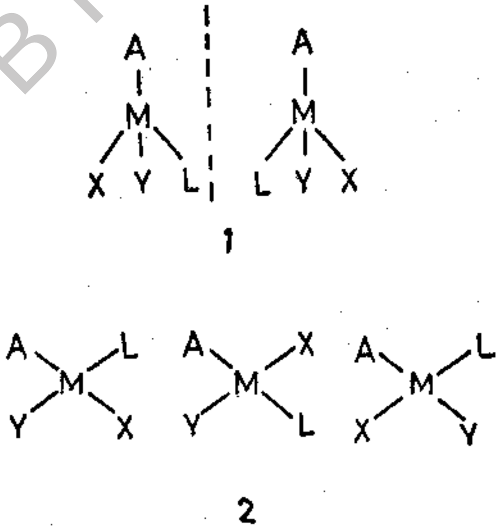
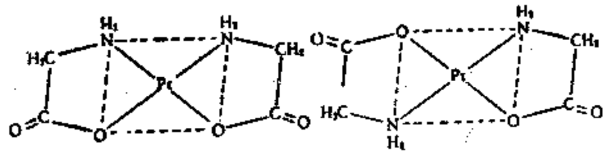


Fig. 15.10 1. Tetrahedral complexes 2. square-planar complexes

3. Complexes containing unsymmetrical bidentate ligand like glycyine give two geometrical isomers.



1 2

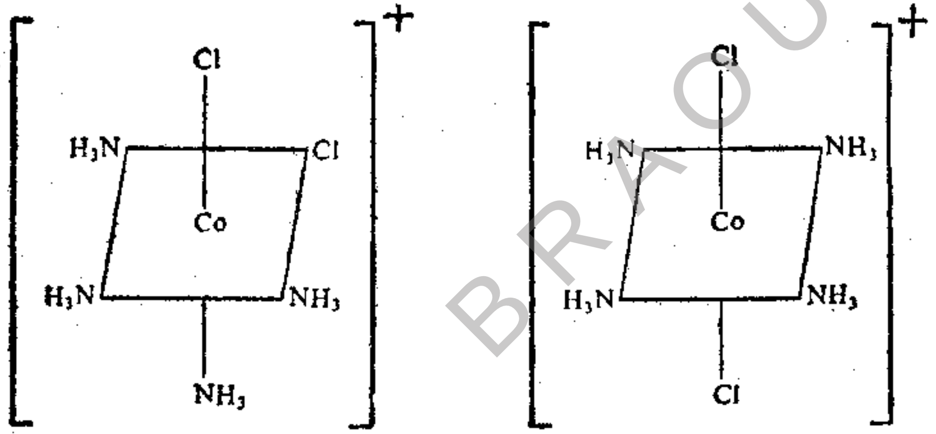
Fig. 15.11 1.Cis ; 2. Trans

complexes containing symmetrical bidentate ligands such as ethylene diamine do not exhibit cis-trans isomerism.

Octahedral complexes

Geometrical isomerism in octahedral complexes is closely related to that in square planar complexes. Amongst them most familiar ones are the violet (cis) and green (trans) forms of the dichlorotetraamine cobalt (III) and chromium (III) cations which have the structures.

In these complexes the like groups occupy corners of one of octa hedral faces (cis form) or they do not (trans form). Unsymmetryical bidentate ligands give rise to geometrical isomers in much, the same way as was described earlier for square planar complexes.



cis Fig. 15.13 trans

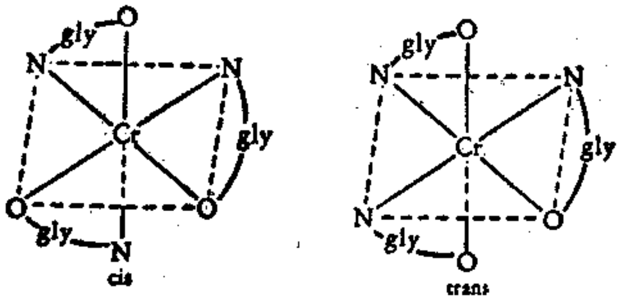


Fig. 15.12

15.6 STABILITY OF COMPLEX IONS

Metal ions, because of the charge and the size, do not exist freely in solutions. They are alw associated with the counter ions or other components of the solutions. In nearly all the cases the do property of the solvent itself is considerable. The metal ions are present as well defined stable spec called 'solvo complexes'. If the solvent is water, these are called 'aquo complexes' $[Cu\,(H_2O)_4]^{2+}$. If solution contains a more reactive ligand than the water the stepwise substitution of the water molecu by this ligand takes place.

For example:

when ammonia is added to a solution of Cu salt, there will be a rapid replacement of water molecu co-ordinated to the metal ion by molecules of ammonia giving rise to a final product $[Cu\,(NH_3)_4]^{2+}$ This can be represented by the equations,

$$[Cu\,(H_2O)_4]^{2+} + NH_3 \xrightleftharpoons{k_1} [Cu\,(NH_3)\,(H_2O)_3]^{2+}$$

$$[Cu\,(H_2O)_3]^{2+}\,(NH_3)]^{2+} + NH_3 \xrightleftharpoons{k_2} [Cu\,(NH_3)_2\,(H_2O)_2]^{2+}$$

$$[Cu\,(H_2O)_2]^{2+}\,(NH_3)_2 + NH_3 \xrightleftharpoons{k_3} [Cu\,(NH_3)_3\,(H_2O)_2]^{2+}$$

$$[Cu\,(H_2O)\,(NH_3) + NH_3 \xrightleftharpoons{k_4} [Cu\,(NH_3)\,(NH_3O)_4]^{2+}$$

According to law of mass action, 'the equilibrium constants' or otherwise called the 'stepwi formation constants' $K_1, K_2 \ldots\ldots K_4$ etc., for different steps can be written as,

$$K_1 = \frac{[Cu\,(NH_3)\,(H_2O)_3]^{2+}}{[Cu\,(H_2O)_4]^{2+}\ NH_3}$$

$$K_2 = \frac{[Cu\,(NH_3)_2\,(H_2O)_2]^{2+}}{[Cu\,(H_2O)_3]\ (NH_3)]^{2+} + NH_3}$$

$$K_3 = \frac{[Cu\,(NH_3)_3\,(H_2O)_2]^{2+}}{[Cu\,(H_2O)_2\ (NH_3)_2 + NH_3}$$

$$K_4 = \frac{[Cu\,(NH_3))_4]^{2+}}{[Cu\,(NH_3)_3\ (H_2O)]^{2+}\ [NH_3]}$$

The equilibrium constants characterise the stability of the complexes in solution and are usual called 'stability constants'. Sometimes the reciprocal values of these constants named as 'instabili constants' are also used. Another symbol β is used to represetn the overall formtaion of the complex. t overall formation constant β is the product of step wise formation constants. For example

$\beta_4 = K_1.\,K_2.\,K_3.\,K_4$

or $\beta_n = K_1\ \ K_2\ \ K_3\ \ K_n$

The numerical value of a stability constant describes the relative concentrations of different speci at equilibrium. Large stability constants indicate the at the concentration of complex is much greater th the concentrations of the components of which it is made. Then we say that a complex is stable.

15.7 FACTORS EFFECTING THE STABILITY CONSTANT

The factors effecting the stability of a complex in solution are :

12. 7 SUMMARY

In this unit we have discussed the following

a) **Alloys and salt hydrates:-** When metals form alloys, it can result in eutectic mixtures or inter-metallic compound to solid solutions.

b) **Solutions of gases in gases:-** Gases which do not react chemically mix in all proportions. They possess one phase and two components.

c) **Solutions of gases in liquids:-** These solutions are controlled by Henry's law. It states that the quantity of a gas that dissolves in a fixed quantity of a liquid is directly porportional to the pressure that it causes on the liquid with which it is in equilibrium.

d) **Solutions of gases in solids:-** Gases interact with solids in four ways i)a homogeneous true solution may formii)it may result in two or more solid solutions iii) a chemical compound may form and iv) gas may be adsorbed on the solid.

e) **Solutions of liquids in liquids:-** These are three types i) completely miscible liquids ii) partially liquids miscible. iii) practically immiscible liquids.

12.8 MODEL EXAMINATION QUESTIONS

I. Answer the following in 30 lines.

1) Explain the Phase rule diagram of an alloy.
2) Discuss the application of Phase rule to salt hydrates.
3) Discuss the application of Phase rule to a solutions of gases in solids resulting in the formation of chemical compound.
4) Explain the negative and positive deviations from Raoult's law involving solutions of liquids.
5) By means of Phase rule, show how a mixture of ethanol and water cannot be completely separated into the individual components.

II. Answer the following in 30 lines.

1) Discuss the application of Phase rule to solutions of liquids in liquids.
2) Discuss the application of Phase rule to solutions of solids in solids.

12.9 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Eutectic mixture is the mixuture of a fixed composition of two substances whose melting point is lower over tthe melting points of the individual constituents or any other mixture of them.

2. A mixture of two liquids is called a constant boiling liquid mixture if both the liquids undergo codistillation at a fixed temperature and the composition of the distillate is the same as the original liquid mixture.

   eg. H_2O, ethanol and H_2O + HCl.

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10^{-8} cm; a crystal can be used as a three dimensional grating. This was confirmed by his pupils Friedrich and Knippling. They passed a beam of X-rays through a single crystal and received it on a photographic plate. On developing the plate they found that a regular pattern of several spots was obtianed, clearly establishing that X-rays have been diffracted on passing through a crystal.

13.7 BRAGG'S EQUATION

Bragg suggested that a crystal could be used as a reflection grating. When a beam of X-rays falls on the face of a crystal at a certain angle they would be reflected due to scattering by the atoms of the crystal.

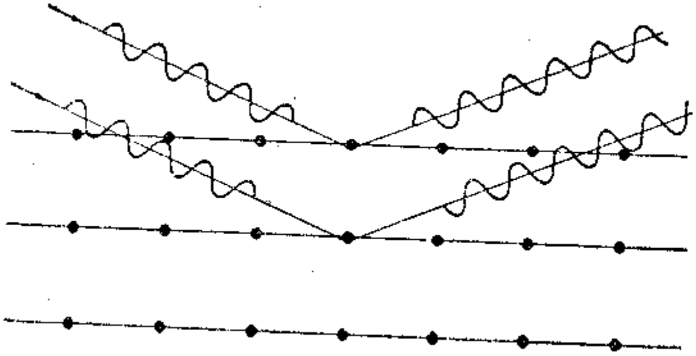

Fig. 13.13 Scattering of X-rays from parallel planes

If the crystal is cut in such a way that a set of planes face the beam, the X-rays would be scattered by the atoms of the different planes in such a way as to give the impression that the X-rays have been reflected from the face of the crystal.

Let us consider a beam of X-rays incident on a crystla making an angleθ with the plane of the crystal. This is called glancing angle. Part of the beam is scattered by the atoms of the first plane as shown in the figure, part enters the first plane and is scattered by the atoms of the second plane. Since the spacings between the planes is of the same order as the wave length of the X-rays , the X-rays reflected from the second plane may reinforce or destroy the beam reflected from the first plane (a phenomenon called interference). The condition for reinforcement can be worked out as follows. Two wave trains reinforce each other when the crest of one meets the crest of another or the trough of one meets with throught of another.

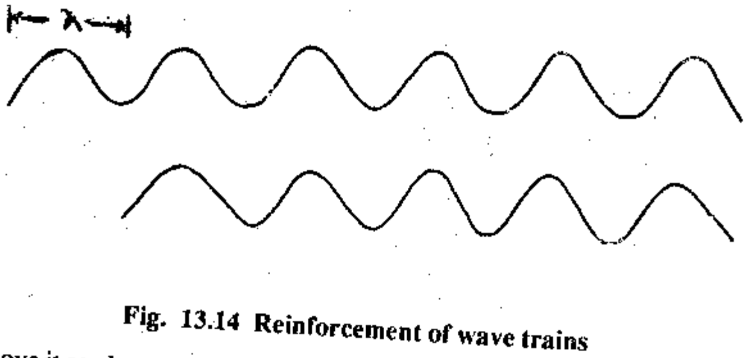

Fig. 13.14 Reinforcement of wave trains

From the figure above it can be seen that this can happen if one of the wave trains is one, two, three or an integral number of wavelengths behind the first. If it is half a wavelength behind or an integral number of half wavelengths behind, the crest of one will meet with the trough of another as seen below and there will be what is called destructive interference.

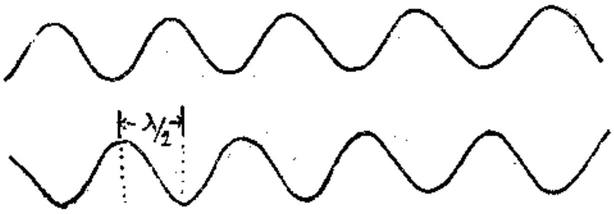

Fig. 13.15 Annulling of wave trains

Therefore, the condition for reinforcement or constructive interference is that the path difference between two rays scattered from adjacent planes must be an integral multiple of the wavelength. This fact is used to derive the Bragg's equation.

Let the two rays be AOB and RPQ. Drop perpendiculars to QP and PR from O. Then the path dfference between the two rays AOB and is RPQ - AOB = CP + PD. From simple geometry it can be shown that the angles COP and POD are also equal to O.

Then CP = OP Sin θ and PD = OP Sin θ
or CP + PD = 2 OP Sin θ

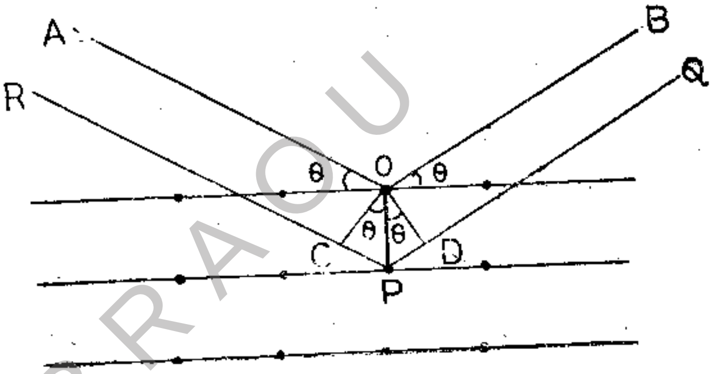

Fig. 13.16 Reflection of X -rays

But OP is the distance 'd' between two planes, so path difference can be written as 2d Sin θ. We have seen that for constructive interference path diffirence must be equal to n λ where 'n' is an integer.

Hence 2d Sin θ = n λ

n λ can have the values of 1,2,3,.....is also called the order of the spectrum. This is called the bragg's equation.

Hence, when a beam of X-rays is directed on any face of a crystal, reflection will occur only when the X-ray beam is incident at an angle θ which satisfies the above equation. If the wavelength of the X-rays is known 'd' the interplanar spacing can be calculated from the above equation. A crystal can be cut in such a way that the 100-type planes, 110-type planes or 111-type planes face the X-rays beam. Then finding the value of θ at which reflection occurs, the value of 'd' for such planes can be calculated.

For the planes prallel to the face d_{100} has been found experimentally. It is 2.81 / x 10^{-8} cm. Hence for the planes perpendicular to the face diagonal, $d_{110} = 0.707 \times 2.817 \times 10^{-8}$ cm.

13.11 SUMMARY

Orderly arrangement of ions or atoms or molecules leads to the formation of crystals. A particular type of crystal irrespective of the constituent particles possesses the same arrangement of particles. Crystals exhibit different symmetry elements. Space lattice is the regular distribution of points (particles) in space. Smallest unit of the crystal lattice whose three dimensional repetition produces a crystal is called unit cell.In crystals there are some planes which divide them into layers called lattice planes. These planes are indicated by Miller indices. The structures of crystals are determined by their diffraction of x-rays.

13.12 MODEL EXAMINATION QUESTIONS

I **Answer the following in 10 lines.**

1. Draw neat diagrams of unit cells having simple cubic, face centred cubic and body centred cubic lattices. Why are the planes parallel to the face called 200 planes in the face centred cubic cell?
2. Obtain the ratio of the three interplanar spacings for the face centred cubic lattice.
3. Derive Bragg's equation.
4. A metal crystalllises in the body centred cubic lattice. Calculate the effective number of atoms per unit cell.

II **Answer the following in 30 lines**

1. Describe in detail Bragg's method of arriving at the crystal structure of sodium chloride.

III **Problems**

1. For a cubic crystal having the simple cubic lattice, the spacing between the 100 planes is 3.42 A, Find the spacings between 110 planes(2. 418 A).

2. The first order reflection of a beam of X rays from a crystal occurs at 14.7. At what angles does the third order reflection take place?

3. An element crystallises in the cubic system. Using X rays of wavelength 1.54 A the first order reflections from 100, 110and 111 type planes were found to occur at angles 13°, 18.4° and 22.8° respectively. Find whether the unit cell is simple, face centred or body centered.

4. Tungsten (at Wt = 183.9) forms body centred cubic crystals. From the fact that the density of tungsten is 19.3 g per cc. Calculate.

   a) the length of the side of the unit cell and

   b) d_{200} d_{110} and d_{222} (a = 3.63A)

5. Cesium chloride has a body centred cubic lattice. Using X rays of wavelength 0.6 A the first order reflection from 110 type panes were found to occur at 4.88 A. Calculate the length of the unit cell (5A)

6. Nickel crystallises in the face centred structure with $a_o = 3.52$ A. Calculate the interplanar spacing for the 100, 110, and 111 type lines.

13.13 MODEL ANSWERS TO CHECK YOUR PROGRESS.

1. Existance of the same substance in more than one crystalline form under different conditions is to called ploymorphism eg. α - chromium and β - chormium.

2. The smallest portion of the crystal lattice which repeats three dimensionally forming the crytsal is called unit cell.

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UNIT - 14 STUDY OF 'd' BLOCKELEMENTS (Transition elements)

Contents

14.1 AIMS AND OBJECTIVES

To describe the physical and chemical properties of elements and to relate them to electronic configuration of the metals

After the thorough study and comprehension of the transition elements you must be able to know that:

- their general outer electronic configuration is (n-1) d^{1-10} ns^{1-2}
- all the transition elemetns are metals with high melting and boiling points.
- they exhibit variable oxidation states and form coloured and paramagnetic salts.
- they form complexes, alloys and exhibit catalytic property.

14 .2 INTRODUCTION

The elements lying between 's' block and 'p' block elements of the long form of the Periodic table are collectively known as transition elements. These elements either in their atomic state or in any of their common oxidation state have prtiallyfilled (n-1) d orbitals. In the elemental state they possess the electronic configuration (n-1) d^1 ns^2 to (n-1) d^{1-10} ns^2. It is for this reason they are named as 'd' block elements.

Position of 'd' block elements

There are four series of 'd' block elements corresponding to the 3d, 4d, 5d and 6d orbitals. They are

ist series	--	21^{Sc}	to	30^{Zn}	--	3d series
2nd series	--	39^{Y}	to	48^{Cd}	--	4d series
3rd series	--	57^{La}	to	72^{Hf} to 80^{Hg}	--	5d series
4th series	--	89^{Ac}-104^{Ku}		and105^{Ha}	--	6d series

The elements in the 6d series are incomplete and the missing elements are yet to be synthesized.

14.3 SOME PHYSICAL CHARACTERISTICS

In transition elements the differentiating electron enters the (n-1) d orbital in presence of ns. These elements are therefore expected to have many physical and chemical properties in common. The elements of the group having (n-1) d^{10} ns^2 electronic configuration show some differences from the remainder of elements. All the trasition elements are metals, and the number of electrons in the outermost shell is small, being equal to 1 or 2. They are hard, malleable and ductile and good conductors of heat and electricity. They possess all the three types of structures namely face centred cubic (FCC), hexagonal close packing (HCP), and body centred cubic (BCC).

The transition elements having partially filled (n-1) dorbitals have very high melting and boiling points as compared to those of 's' and 'p' block elements. Zn, Cd and Hg having completely filled orbitals possess relatively low melting and boiling points. Although melting and boiling show no definite trends in the three transition series, the metals having the highest melting and boiling points are towards the middle of the each transition series.

The atomic (covalent) radii for the elements of the transition series are given in Table 14.1

Covalent radii (A°) of transition elements

Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
1.74	1.44	1.32	1.22	1.17	1.17	1.17	1.16	1.15	1.17	1.25	1.25
Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In
1.91	1.91	1.62	1.45	1.34	--	1.24	1.25	1.28	1.34	1.4	1.5
Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tp
1.98	1.69	1.44	1.34	1.30	1.28	1.26	1.26	1.29	1.34	1.44	1.55

It can be seen from the table that these values first decrease from Sc to V but later remains close to one another from Cr to Cu. This is due to the fact that an increase in the effective nuclear charge tends to attract the electron cloud, decreasing the radius from Sc to V. Addition of electrons to 3(n-1) d orbitals reverses the effect by screening the outer 4s electrons from the nuclear attraction resulting not much alteration in the covalent radius from Cr to Cu. In the first group the atomic radii show expected increase in size Sc-Y-La but in the subsequent groups is an increase in the radius of 0.1 to 0.2 A° between the first and the 2nd transition series and remains constant in the third transition series. This is known as the lanthanide contraction. The effect of the Lanthanide contraction begins to die out towards the right of the 'd' block elements and hence the radii increases.

The first ionization energies (potentials) of transition elements (Table 14.2) lie between the values of those of 's' and 'p' block elements. The addition of the idfferentiating electron to the (n-1) d level in transition elements provides a screening effect schielding the outer ns electrons from the nuclear attraction. Thus the effects of the effective nuclear charge and schielding due to the expansion of (n-1) d orbital oppose each other. On account of these counter effects the inoization energies (potentials) increase rather slowly along a period. The first ionisation energies (potential) of Zn is considerably high because of the completely filled 'd' and 's' orbitals which provides extra stability to the atom. The second ionization energis (potentials) seem to increase with increase in atomic number. These values of Cr and Cu are higher than those for their neighbours. This is due to the fact that the electronic configurations of Cr^{+3} and Cu^{+2} ions have extra stability having $3d^5$ and $3d^{10}$ configurations.

Temperature
Nature of the medium
Properties of the metal ions
Properties of the ligand.

Effect of temperature: In general the formation of complex is favoured by negative enthalpy and itive entropy change. The relative importance of these effects is found to be dependent on variations he ligand as well as the central metal ions.

Nature of the medium: The effect of dielectric constant on the stability of the complex in solution f two types. One is the medium in which the complex is present and the other is due to the interaction ween the metal and the ligand. the later effect is much smaller when compared to the first one and its ct value is usually not available. It has been observed by many that in semiaqueous media thereis a ar relationship between the mole fraction of the non aqueous solvent of the medium.

Properties of the metal ions: A number of attempts have been made to ascertain the effect of the tral metal ion on the stability of the metal complex. On the basis of the observations made it is found t the most stable complexes are formed with cations of comparatively small size and high nuclear or ichcarge. Ions with these properties will naturally have the greatest attractive power for the electrons he ligand. The quantity defined to measure this attractive power is the ionic potential ϕ.

$$\phi = \frac{\text{Cation charge}}{\text{Cation radius in A}^{o}}$$

values of ϕ for different cations with relative complexing ability are given in the table.

Ions	Ionic potential	Relative complexing ability
K^+	0.75	Forms few complexes
Hg^{2+}	1.8	Forms many complexes
Cd^{2+}	2.1	Forms many complexes
Zn^{2+}	2.7	Forms many complexes
Co^{2+}	2.8	Forms many complexes
Ni^{2+}	2.9	Forms many complexes
Fe^{3+}	4.7	Always complexed
Cr^{3+}	4.7	Always complexed
Co^{3+}	4.8	Always complexed
Pt^{4+}	6.2	Always complexed

It is usually true that if ϕ is greater than 2, the possibility for complex formtion is good. In-riminate use of the ionic potential to predict stability of complex can lead to discrepancies. The lability of unfilled 'd' orbitals into which the electrons donated by the ligand can enter, leads to the nation of greater number of complexes with greater stability. On the basis of study of the stability stant's of the different metals with ligands containing oxygen, nitrogen the metal ions are grouped into e categories.

Metal ions that form most stable complexes with oxygen containing ligands

$Ba^{2.}$ Ca^{2+}, Mg^{2+}, Be^{3+}, Al^{3+} , Ga^{3+}, In^{3+}, Tl^{3+}, Ti^{4+} , Zr^{4+}, Th^{4+}, Ge^{4+}, Sn^{4+}, Mo^{4+}, U^{4+}, U^{6+}, Fe^{3+}ano

Metal ions hsowing equal affinity for oxygen and nitrogen containing ligands.

Be^{2+}, Cr^{3}, Fe^{2+}, Pt^{2+} and Pt^{4+}

c) Metal ions that form most stable complexes with nitrogen containing ligands.

Cu^+, Cu^{2+}, Au^+, Cd^{2+}, Hg^{2+}, Co^{3+} and Ni^{2+}

The compelx forming abilities of the bivalent transition metal ions are frequently characterised by a stability order. Irving and Williams comparing ionic radii and second ionization potential of the metal ions rationalised such an order $Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} \quad Cu^{2+} > Zn^{2+}$ which is valid for nitrogen and oxygen donar ligands, irrespective of the nature of the ligand.

4. **Properties of the ligand:** Although the large numner of ligands are known, the donor atoms that undergo combinations with the metal ions are restricted to the strongly non metallic elements like N, O, S and halide ions. The radius of the donor atoms and the charge or the dipole moment of the ligand influence the stability of complexes. In the halide series the order of the stability is $F^- > Cl^- > Br^- > I^-$.. For a charged ligand it is observed that the greater the charge, the strongest is the bond.

$$PO_4^{3-} > SO_4^{2-} > ClO_4^-$$

For the neutral molecules the dipolemoment is the important factor. Other factors being equal the ligands with largest permanent dipole moment will give the most stable complexes. This is nicely illustrated in the substituted ammonia series.

$$NH_3 > R\text{-}NH_2 > R_2\,NH > R_3\,N$$

Where R is an alkyl group.

Complexes formed with poly dentate ligands like ethylenediamine, salicylaldehyde and oxine are more stable when compared to the mono dentate ligands forming five and six membered rings. This effect is termed as chelate effect. Introduction of the bulky group into the ligand molecules decreases the stability of the chelate because of steric hinderance.

15.8 USE OF COMPLEX COMPOUNDS IN ANALYTICAL CHEMISTRY

The following complex formation reactions are well known in analytical chemistry.

1. **In qualitative analysis**

a) Formation of nitroso complex (brown ring) is used in the identification or confirmation of nitrate (NO_3^-) or nitrite (NO_2^-) ion

b) Formation of $(Ag\,(NH_3)_2\,)^+$ ion in the confirmation of chloride ions.

c) Formation of $[Fe\,(CNS)_6\,]^{3-}$ion (red coloured solution) is used in the confirmation of Fe^{3+} ion

d) Formation of $(Co\,(\alpha$ - nitro β- naphthol$)_3\,^{3+}$ (red coloured solution is used in the identification f Co^{2+}

e) CN^- ion is used in the detection of C^{2+}d in presence of Cu^{2+} ions.

2. **In quantitative analysis**

f) Al^{3+} is preicipitated by 8- OH quinoline $(oxinate)_3^{\,]}$ quantitatively as $[(Al\,(oxine)_3]$ complex from the solution at 4 and is estimated gravimetrically.

g) Dimethylglyoxime (DMG) is used in the precipitation of Ni from aqueous solutiosn as $[Ni\,(DMG)_2]$ complex at 8. The precipitation is quantitative, hence it is used in the gravimetric estimation of Ni^{2+}.

h) CNS^- ions are used in the spectrophotemetric determination of Fe^{3+} ion $[Fe\,(CNS)_6]^{3+}$.

15.9 SUMMARY

Double salts and coordination complexes are additive compounds. They differ in the properties of the constituent ions. Jorgensens theory and Werner's theory are the classical theories of coordination complexes. Sidgwick's electronic interpretation of complexes tries to expalin the tendency of transition metals to form coordination compounds. Valence bond theory and crystal field theory explain the structures, magnetic properties and colour phenomenon of complex compounds. A good number of complexes exhibit different types of isomerism. Complexes differ in their stability. A number of complexes are formed in qualitiative analysis. These reactions usually involve precipitaiton (white or coloured) colouration, dissolution of precipitates etc.

15.10 MODEL EXAMINATION QUESTIONS

I Answer the following in 10 lines

1. What are co-ordination compounds? In what way they are different from double salts?
2. What are the postulates of Werner's Co-ordination theory?
3. Mention the advantages of valence Bond theory over EAN rule.
4. (Co $(NH_3)_6$] Cl_3 is diamagnetic where as $[CoF_6)]^{-3}$ is paramagnetic, explain.

II Answer the following in 30 lines

1. Explain the structural isomerism in co-ordination compounds.
2. What are the defects in the valence bond theory?
3. What is Pauling's contribution to co-ordination compounds?
4. What are the applications of co-ordination compounds in analytical chemistry?

15.11 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Ions present in the coordination sphere do not get precipitated on treatment with a precipitating agent.

2. The total number of electrons present in the central metal atom or ion of the complex including those donated by the ligands is called its EAN.

Author:Prof. P. Lingaiah

UNIT - 16 METALLIC BOND

Contents

16.1 AIMS AND OBJECTIVES

To explain the metallic properties like malleability, ductility and high electrical and thermal conductivity in terms of metallic bond.

After the detailed study and understanding of the contents you should be able to:

- realise that the metals possess three different types of lattices. These are face centered cubic (FCC), hexagonal close packing (HCP) and body centered cubic (BCC).packing
- find out that allotropes are the different modifications of a metal which differ in the lattice structures.
- extend valence bond theory and molecular orbital theory to metals which explain the matallic character satisfactorly.

16.2 INTRODUCTION

Many metals are quite hard. Therefore they should possess considerably strong attractive forces between their atoms. But they cannot have conventional ionic or covalent bonds due to the non-availability of so many electrons to form bonds with eight or twelve surrounding atoms. Therefore it is proposed that metals possess special attractive forces between their atoms called metallic bond.

16.3 GENERAL CHARACTERISTICS OF METALS

Metals are characterised by the properties like high electrical and thermal conductivity, metallic luster, malleability (ability to be rolled into sheets) and ductility (ability to be drawn into wires). The properties are linked to the type of bonding present in the solids. X-ray diffraction studies show that metals form srystals in which the atoms are arranged in one of the three different lattice geometries. These are knwon as face centered cubic (FCC), the hexagonal close packing (HCP) and body centered cubic (BCC). In the first two structures each atom is surrounded by twelve atoms. Six atoms in the same plane and three atoms each above and below as shown in figures 16.1 and 16.2.

Check your progress - 1

what are the characteristic properties of metals?

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In the body centered cubic structure a single atom is sand-wiched between two layers of four atoms as shown in figure 16.3.

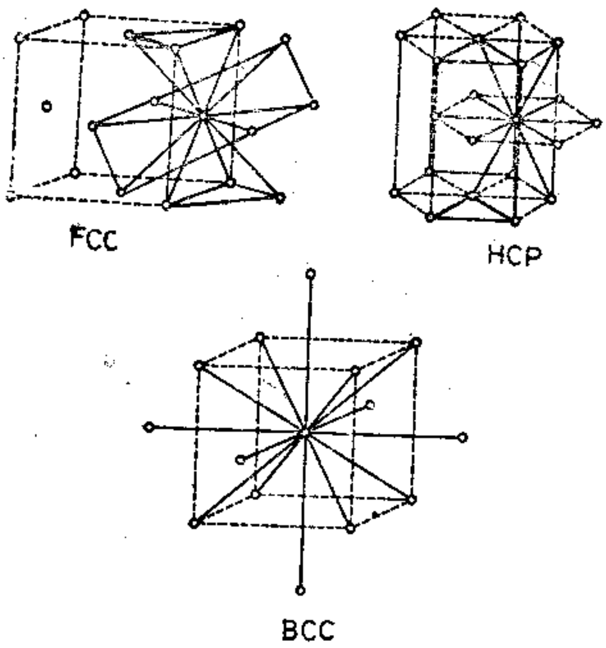

Fig. 16.1 Face centred cubic lattice (FCC) Hexagonal close packing (HCP) Body centred cubic lattice (BOC)

The crystal structure: types of some of the metals are given in the table 16.1

Table 16.1 Crystal struture types of some metals

Li BCC		Be HCP								
Na BCC		Mg HCP		Al FCC						
K BCC	Ca FCC HCC	Si FCC HCP	Ti HCP BCC	V BCC	Cr BCC	Fe BCC FCC	CO HCP FCC	Ni FCC	Cu FCC	Zn HCP
Rb BCC	Sr FCC HCP BCC	V HCP	Zr HCP BCC	Nb BCC	Mo BCC	Ru HCP	Rh FCC	Pd FCC	Ag FCC	Cd HCP
Cs BCC	Ba BCC	La HCP FCC	Hf HCP BCC	Ta BCC	W BCC	Os HCP	Ir FCC	Pt FCC	Au FCC	

The metals like iron and hafnium exists in more than one crystalline forms. Such modifications are named as 'allotropes'.

The deformation properties of metals, such as ductility and malleability are directly linked to their crystal structure. Thus, when a metal is subjected to a stress, such as hammering or the rolling operation it deforms by planes of atoms gliding past each other. The planes of atoms are known as glide or slip planes.

Since these atoms are closest together (unlike the lattice diagrams shown earlier) they will have the greatest cohesive forces and therfore will exert the greatest resistance to deformation. The greater the number of glide planes in a given structure, the more directions there will be in which the crystal can yield under a stress and therefore the more ductile or less brittle it will be. The other properties like high electrical and thermal conductivity can be explained in terms of bonding in metals ('Metallic bonding'). Two main theories are available to explain the bonding in metals, one being the 'Valence bond theory' and the other 'Molecular orbital approach'.

Check your progress -2

Why the metals of FCC crystalline structure are more malleable and ductile over other types of metals?

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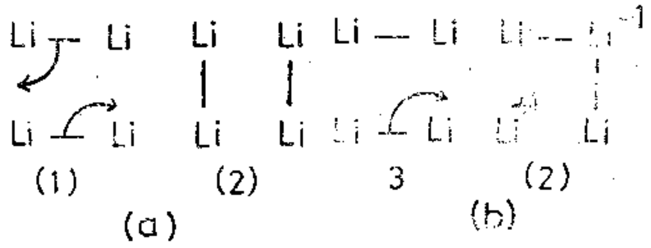
16.4 VALENCE BOND THEORY OF THE METALLIC BOND

The Valence bond approach of metals, due mainly to Pauling, is simpler than the molecular orbital approach. This approach uses the principle of electron pairing to form covalent bonds between atoms in the metal similar to simple molecules such as H_2, Cl_2, O_2. However, one important difference lies between metals and these molecules. In metals, there are not enough number of electrons between the nearest neighbour atoms to form a complete set of electron pair bonds or in other words the metallic structure is said to be electron deficient.

As an example a unit cell of the body-centered cubic crystal of lithium is considered. In this structure a lithium atom in the body of the unit cell is surrounded by eight nearest neighbours at the corners of the cell and by six more next nearest neighbours at the centres of the six surrounding cells. Thus, the central lithium atom could form covalent bonds wiith fourteen other lithium atoms in a crystal. Each of the lithium atom has only one '2s' electron available to form a covalent bond. A total of 28 electrons are required for the formation of 14 localised electron pair bonds (covalent bonds). But only 15 electrons are available, from this one draws the conclusion that 14 localised - electron pair bonds are not formed in metals. It means the bonds in metals are highly delocalised. This is similar to the conjugate double bonds in benzene in which the bonds are resonating. A schematic representation of the resonating structure in the case of lithium atoms are shown in figure 16.2.



Synchornons resonance resulting in non-ionic resonance forms

Pivotal resonance resulting in ionic resonance forms

fig. 16.2 Resonating Structures in Lithium

For simplicity only four atoms are shown, but of-course, this situation can be continued throughout the three dimensional structure. The resonance occurs through the shifting of electrons as shown by the arrows in structure (1) of figure (a) to give new bonds between atoms, as shown in structure (2). An important feature of this type of resonance in metals should be noted. since only one 2s electron is available in each atom for bonding, no one atom can form two bonds simultaneously. Thus when one of the two bonds in structure (a) shifts the other also must shift at the same time, so that the resonance switch must be synchronous for all bonds in the crystal. It is known that the more the number of the resonance structures, the more is number of the resonance structures, the more is the stability of the speices. Resonance leading to the ionic structure is illustrated in figure (b) in which the shifting of bonds are not synchronous. This leaves the lower left hand atom with a + 1 charge and the upper right hand atom - 1 charge (structure2). Resonance of this type can be considered to occur by the lower bond in structure - 1 pivoting about the atom on the lower-right hand side, and hence is known as pivotal resonance. The additional one electron on the right hand side of the lithium atom is accommodated in the next higher energy empty 2 p orbital, which is named as metallic orbital. The energy required for promotion of an electron to a 2p orbital in lithium is only 1.84 e.v. which is equal to the difference in ionization potentials of the 2S and 2P orbitals. This in-put of energy is more than that available from the resonance stabilization (energy acquired from the large number of ionic resonating structures). This becomes possible through the use of metallic orbitals. The presence of these metallic orbitals in metals allow for the enhanced electron mobility as a result they will have high electrical conductivity.

The availability of both s and p orbitals in many metals led pauling to conclude that the sp hybridization is also possible in metals like Be. These permit greater overlap of orbitals forming stronger bonds. Because of this, the alkaline earth metals are known to be hard having higher melting points as compared to the alkali metals which are soft and have low melting points. This trend in properties continues upto the III group of the periodic table through the transition metals. This trend in properties is due to the availability of larger number of atomic orbitals of similar energy, to form hybridized orbitals required for the formation of strong bonds. Thus, Pauling has assigned a valence, called metallic valence to each metallic elements. The metallic valence parallel the properties of the metal crystal such as density and hardness. Eventhough the Pauling valence bond treatment is useful in explaining the metallic properties through the formation of bonds between the metal atoms, yet it is qualitative one.

16.5 MOLECULAR ORBITAL APPROACH OR BOND THEORY OF SOLIDS

To explain the metallic properties, molecular orbital concept was used by Elock in 1928. In solids one deals with infinite number of atoms instead of small number of atoms as in descrete molecules. In this theory starting from 'N' number of atomic orbitals present in the metals an equivalent number of molecular orbitals are constructed. The total number of quantum states with a particular quantum number does not change. Even when the atoms come together, to form a crystal. Thus in a lithium crystal with 'N' number of atoms, each atomic orbital having two possible spin states + 1/2 and - 1/2 will have 2N quantum states. This large number of states leads to very closely spaced energy levels, which constitute an energy band in the crystal. This is illustrated in Fig. 16.3.

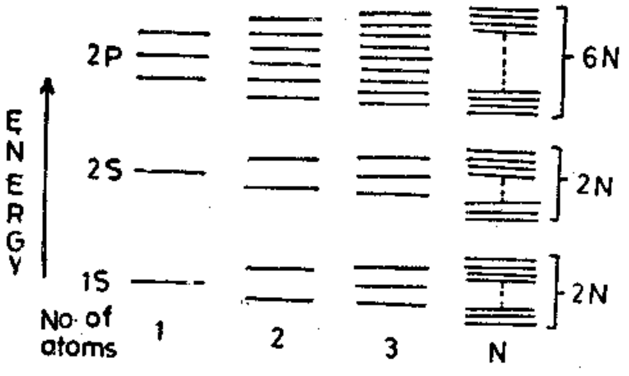


Fig. 16.3 Energy bands in metals

When a second atom is brought up to the first atom, the energy level in each state is split to give two molecular orbitals, one higher and one lower in energy than the original atomic orbital as shown in the diagram. When a third atom is added three different energy levels are formed from each atomic energy levels by the combination of the atomic orbitals of three atoms. This process continues till it reaches the value of N, in which a band of N number of closely spaced energy levels is formed. It should be recalled that each level in the band formed from the s atomic orbitals can accommodate two electrons with spins paired, and eahc energy level in the band formed from the three p atomic orbitals can accommodate six electrons with spins paired. Thus, a band formed from Ns states will have 2-N energy levels. A band formed from N,p states will hav e6-N energy levels and a band from N, d states will have 10-N energy levels. When the number of atoms in a system becomes equal to 10, the spacing between the levels in a band will be the order of 10 e.v.

The separation between energy bands depends on the energy difference between the pure atomic orbitals and on the distance between adjacent atoms in the solid. If the individual atomic energy levels are widely separated or if the distnace between the individual atoms is large the individual energy bands will be separated without any overlap. In a system in which the difference in energies of atomic orbitals is less and the distance between the individual atoms is small, we get an overlap of energy bands. This is illustrated in figure 16.4 in which potential enrgy is plotted against 'r', the internuclear distance for a system in which four atoms are used. At the extreme right of the diagram, the bands formed at the distance r are shown indicating the bands which are allowed forbidden.

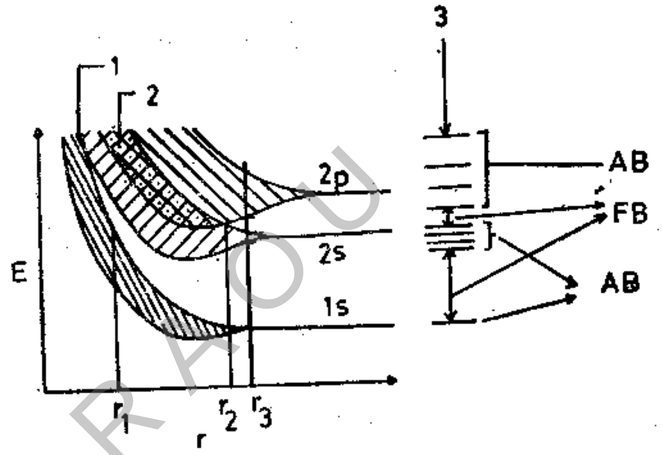


Fig. 16.4 Overlap of energy bands

It should be noted that the band width depends not on the number of atoms present but on the amount of interaction between the atomic obitals with in a band. The width of a forbidden band is greater for lower energy orbitals, compared to the higher energy orbitals. In effect, the energy band diagram for crystals will appear very much like the energy level diagram for atoms with the forbidden energies in crystals corresponding to the quantum jumps in energy from one quantum level to the next in atoms. However, in crystals the energy required of transition is small.

In the diagram the inner bands, those formed from 1s, 2s and 2p atomic orbitals are completely filled with electorns. They contain the maximum number of electrons per energy level in a band allowed by the Pauli exclusion principle. The upper bands formed from the 3s and 3p atomic orbitals contain a partially filled band and an empty band respectively. The partially filled band contains the valence electrons and is called the valence band. They empty band is called the conduction band. When an electric field is appleid, the electrons present in the filled lower energy levels cannot move because the band is completely filled, and the applied potential is not sufficient to promote the electrons to higher energy bands. In case of the electrons present in the partially filled valence band the situation is different because the electrons can move more freely into the unfilled valence bands and also into the conduction band resulting in the enhanced electron mobility which in turn gives rise to the greater conduction in the metal.

16.6 SUMMARY

Metals are differentiated from non-metals by their characteristic properties. They are a) malleability b) ductility c) electrical and thermal conductivity d) lustre e) FCC, BCC and HCP type crystal structures. They possess special interatomic attractive forces called metallic bond. Valence bond theory and Molecular orbital theory of metal bonding try to explain the properties of metals satisfactorily.

16.7 MODEL EXAMINTION QUESTIONS

I **Answer each of the following in 10 lines**

1. What is a 'band' in tems of M.O. theory or metals? How does it originate?
2. What is the difference between synchronous and pivotal resonances, according to the Pauling theory of metals?
3. Explain the concept of metallic orbital
4. Explain the concept of metallic valence.

II **Ansewer each of the following in 30 lines**

1. How do you explain the electrical conductivity of a metal?
2. How is conductivity in metals explained on the basis of valence bond theory?
3. Compare Block and Pauling theories of metallic bond.

16.8 MODEL ANSWERS TO CHECK YOUR PROGRESS

1 They are a) malleability b) ductibity c) electrical and thermal conductivity d) lustre e) F.C.C, B.C.C and H.C.P type crystal structures.

2. Due to the easy gliding over of one layer of metal atom over other layer in F.C.C type metals. eg;- Cu, Ag & Au.

BLOCK - 8

METALLURGY

Metallurgy is the study of metal extraction, their properties and alloys. Most of the metals occur in the combined state. Relatively less reactive metals like Au, Ag and Cu occur in the elemental state to a certain extent. They are said to occur in the native state or free state. The compounds of metals which occur in nature are called minerals. Metals are extracted from some minerals only. These minerals are called ores. All ores are minerals but all minerals are not ores. Iron pyrites is only a mineral of iron and not an ore. Metallurgy was known to man even around 3000 B.C. Ashoka Pillar is an example which supports that ancient indians knew the principles of metallurgy. Alchemists discovered number of metals and non-metals while they were attempting to convert cheaper metals into gold and silver.

UNIT - 17 PRINCIPLES OF METALLURGY

Contents

17.1 AIMS AND OBJECTIVES

To describe the general principles involved in the processes of extracting or isolating metals from their naturally occuring chemical compounds.

Once you complete the study and comprehension of the contents of this unit, you must be able to:

- differentiate ores from minerals
- appreciate the classification of ores into oxides, carbonates, sulphides, sulphates, chlorides and phosphates.
- give the steps involved in the extraction of a metal from its ores i.e ore dressing, concentration, roasting or calcination , smelting and refining.

17.2 INTRODUCTION

Metals occur in combined form as chemical compounds in nature. These are generally referred to as minerals. These chemical compounds may be oxides. carbonates sulphides, sulphates, chlorides or phosphates.

However, it may not be economical or beneficial to use each and every mineral for the isolation of the metal from it. For example iron occurs in nature as its oxide. (Haematite $Fe_2 O_3$ or Magnetite ($Fe_3 O_4$) and sulphide (Iron pyrites $Fe_2 S_3$). However haematite is generally employed to obtain the metal from it. The mineral which is widely employed for the extraction of the metal is commonly known as "Ore".

The extraction or isolation of metals from their ores (naturally occuring chemical compounds) is knwon to man even from Metal Ages. Metals such as copper, iron, gold, silver and alloys like bronze are familiar to men even in 3000 B.C. The process of obtianing metal from the ore is called "metallurgy". In olden days metallurgy was considered as an art rather than science.

Table 17.1 Important ores of metals.

Chemical nature	Name	Chemical formula	Important mineral
Oxides	Baddelyte	$Zr O_2$	Zirconium
	Bauxite	$Al_2 O_3 nH_2 O$	Aluminium
	Cassiterite	SnO_2	Tin
	Chromite	$Fe O, Cr_2 O_3$	Chromium
	Haematite	$Fe_2 O_3$	Iron
	Illumenite	$Fe Ti O_3$	Titanium
	Pitch Blende	$U_3 O_8$	Uranium
	Pyrolusite	$Mn O_2$	Manganese
	Thorianite	ThO_2	Thorium
	Zincite	$Zn O$	Zinc
Carbonates	Dolomite	$CaCO_3 MgCO_3$	Magnesium
	Lime Stone	$CaCO_3$	Calcium
	Magnesite	$MgCO_3$	Magnesium
Sulphides	Argentite	$Ag_2 S$	Silver
	Cinnabar	HgS	Mercury
	Galena	$Pb S$	Lead
	Pentlandite	$(Ni,Fe)S$	Nickel
	Zinc Blende	ZnS	Zinc
Sulphates	Anglesite	$Pb SO_4$	Lead
	Barytes	$BaSO_4$	Barium
	Gypsum	$CaSO_4 2H_2O$	Calcium
Chlorides	Camalite	$KCl, MgCl_2 6H_2O$	Magnesium
	Horn Silver	$AgCl$	Silver
Phosphates	MOnite	$Ca_3(PO_4)_2 H_2O$	Calcium
Silicates	Thorite	$Th SiO_4$	Thorium
	Zircon	$Zn SiO_4$	Zirconium

Check your pregress - 1

What is an ore?

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17.3 THE ORES OF METALS

Metals as described earlier, occur in nature mostly in combined form as chemical compounds of different types. These are oxides, carbonates, sulphides, sulphates, chlorides or phosphates. The important ores of different metals are listed in Table 17.1.

However some metals occur in elemental form (metallic state) too in nature. Such metals are said to occur native. These metals include silver, gold, palladium and osmium.

Ores, are always associated with sand and impurities. These impurities are called gaunge. The percentage of the impurities varies from ore to ore.

17.4 PURIFICATION OF ORES

A ore is required to be purified before it is subjected to the metallurgical processes for the isolation of the metal. This purification process mainly involves the separation of gaunge from the ore. This operation of separating gaunge from the ore is called 'concentration of the ore' or 'ore dressing'. The purification is effected by different methods. These are briefly described in the foregoing paragraphs.

a) Hand picking

The ore which occurs as big rocks is powdered and then the impurities associated with it are separated by hand picking. In this method these small bits of ore are passed over rollers and the impurities are picked out with hand while these ore bits are moving over the rollers. For example, the stone impurities associated with haematite are separated in this way by hand picking.

b) Gravity concentration method

This method employs the density difference between the ore and the impurities.

i) Washing with water

The ore is powdered in Ball Mills and washed with water flowing over it with high speeds. The lighter impurities are washed off in this water flow leaving behind the heavy ore particles. For example when Cassiterite ore is wahed with water flowing with high speeds, sand and clay are washed away leaving behind the ore.

ii) Using Wilfle table

The table is provided with wooden riffles. The ore is mixed with water and the slurry obtained is passed over these riffles, whilethe table is shaken vigorously. In this process, the heavy ore particles are collected (in a collector) at one side of the table.

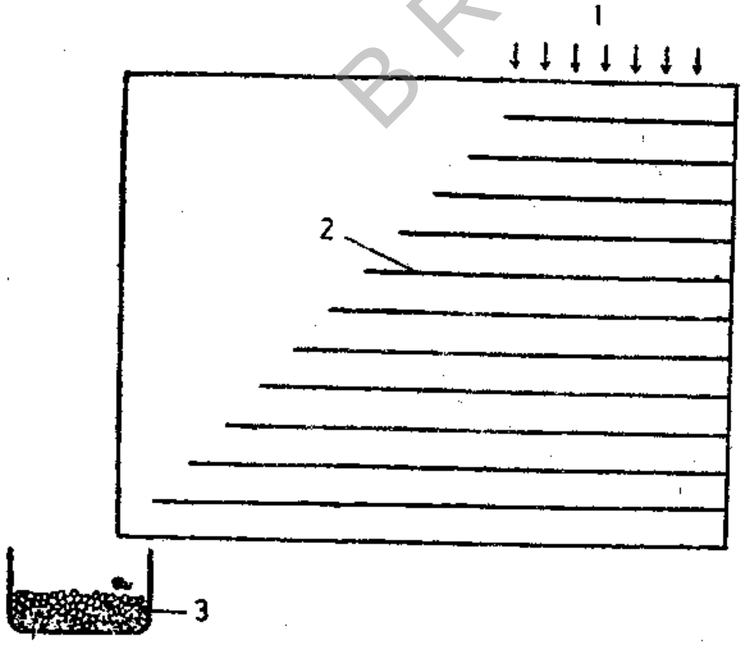

Fig. 17.1 Wilfle Table
1. Slurry (water + ore) 2. Wooden Riffles 3. Collector.

iii) Jig's method

When the ore is available as large lumps, this method is generally used. In this method 'Jig' is used and the method is therefore called Jig's method. In this Jig, Fig 17.2 a perforated screen immersed in water is present. The ore is placed on this screen and water is forced from below. The mixture of ore and gaunge then gets suspended in water. By repreating this process of forcing water a number of times, the gaunge being lighter in density floats on water and the ore accumulates at the bottom. The gaunge is then separated.

c) Flotation process

This method is specially useful when it is required to separate small particles of ore from the gaunge. This method of separation finds application in the purification of sulphide ores.

The ore is pulvarized and is made into pulp with water. The pulp is placed in water taken in a tank along with some pine oil. A chemical called sodium ethyl xanthate is then added and air is blown into the mixture with the help of tubes containing small holes. The tubes are then rotated vigorously, when froth full of bubles is formed. The particles of ore float on this froth. The gaunge particles reach the bottom of the tank and settle down. The pure ore particles are then separated from the froth.

Generally the froth formed due to air bubbles when air is bubbled through the mixture, will not be stable and the bubbles break down. Therefore to keep the froth in the stable form, some chemicals are added. These are called frothers.

In a similar way, chemicals such as sodium ethyl xanthate used to make the ore particles adhere firmly to the froth are called Collectors. The chemicals such as sodium cyanide used to improve froth flotation are called activators. Substances such as lime and sodium carbonate are added to the floatation tank to keep the pH of the mixture constant. These are called Conditioners.

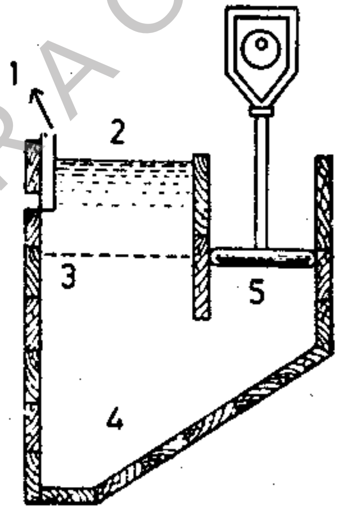

Fig. 17.2 Jig's method
1. ore outlet 2. Water level 3. screen 4. water 5. piston

iv) Magnetic separation

This method is employed if either the ore or the impurities associated with it (but not both) is magnetic in nature. For example, tin ore (tin stone), is associated with the magnetic impurity called wolfram. It is therefore easy to separate tinstone from the associated impurity. In a similar way the method can be used in the purification of pyrolusite (manganese ore) from the associated magnetic impurities of magnetite.

magnetite.

In this method the ore is pulverized and passed over a conveyer belt, passing over a magnetic roller. The magnetic and non-magnetic components of the ore are separated.

v) Electro magnetic separation

This method is applicable when the ore particles are better electrical conductors compared to the impurity particles. So they are attracted effectively and therefore move along with the roller without getting repelled by the roller. The gaunge particles are separated with the help of a brush attached to the roller.

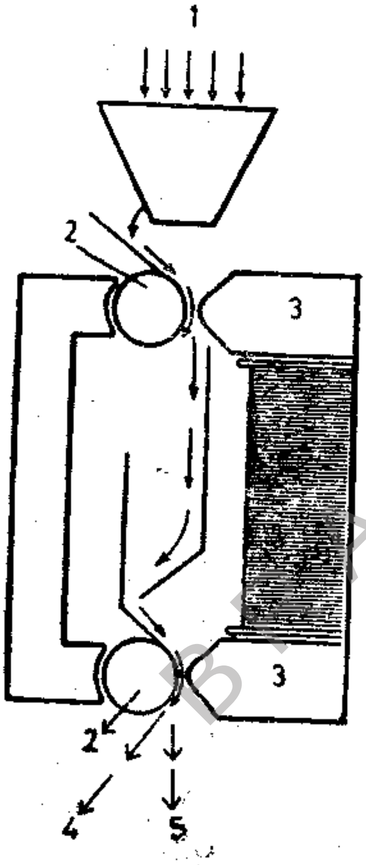

Fig. 17.3 Electro magnetic separation
1. Ore 2. Induced magnetic rollers. 3. Electro magnetic poles
4. Magnetised ore. 5. Non magnetised ore.

vi) Electro static separation

This method is generally applicable to separate metals which occur native or in the form of highly conducting sulphide ores from the impurities.

In this process a charged roller will be moving as shown in the figure 17.4

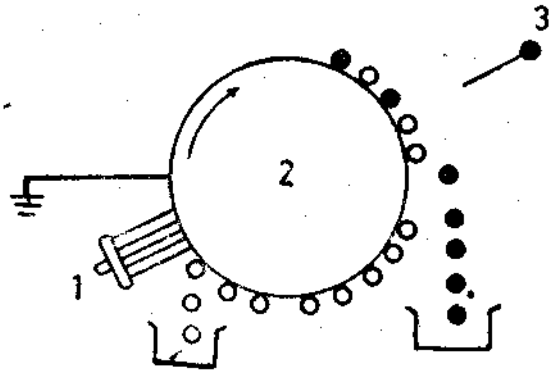

Fig. 17.4 Electro static separation
1. Brush 2. Roller 3. Electrode.

The roller is earthed through a wire and an aelectrode at high negative potential is placed near the roller. Finely powdered dry ore is then put on the roller to form a thin layer. These ore particles get negatively charged due to the electrode and will be accumulated on the roller. The accumulated particles being good conductors transfer the negative charge to the roller and gradually become positively charged. The particles are also positively charged, The low conducting gaunge particles will not be able to transfer their charge.

vii) Liquation process

This method is used in cases where the ore is relatively easily melted than the impurities.

For example, the impurities associated with the antimony ore, stitnite undergo melting at relatively higher temperatures than the ore itself. At 548°C, the ore undergoes melting and the liquid comes out through the pores, when the ore is subjected to high temperatures in a porous pot made from refractory material. The impurities remain in the vessel.

17.5 FLUXES AND SLAGS

It is not always possible to separate the solid impurities (gaunge) completelyfrom the ore by the mthods described earlier. It is also not possible to melt the gaunge at ordinary furnace temperatures and separate it in the liquid form. However, by adding some foreign substance which can chemically react with the gaunge, it is possible to melt the gaunge at lower temperatures. The foreign substance added is called flux and the substance formed by the chemical reaction between flux and gaunge is called slag. The melting point of slag is generally less than the melting point of either the flux or the gaunge.

Gaunge + Flux = Slag

The fluxes are of two types a) Acid flux and b) Basic flux

Silica (SiO_2) is used as acid flux. This occurs in nature in different forms such as sand, quartz and rock. If the gaunge possesses alkaline properties, the acid flux is used. For example the gaunge FeO (Feerrous oxide) associated with copper pyrites is separated through the addition of silica.

$$\underset{\text{gaunge}}{FeO} + \underset{\text{flux}}{SiO_2} \rightarrow \underset{\text{slag}}{Fe\ SiO_3}$$

If the gaunge possesses acid properties, the basic flux is used. For example the gaunge, SiO_2 (sand) associated with haematite is separated through the addition of lime stone ($CaCO_3$). Calcium carbonate decomposes first to give calcium oxide the later combines with SiO_2 to form the slag.

$$\begin{array}{lll} CaCO_3 & \rightarrow & CaO + CO_2 \\ CaO + SiO_2 & \rightarrow & CaSiO_3 \\ \text{flux} \quad \text{gaunge} & & \text{slag} \end{array}$$

Types of slags

It is made clear earlier in the unit 17.3 that the chemical substance is formed when a flux is added to an ore to remove the gaunge from it. For a chemical thus formed to act as a slag, it is required to possess the following charcteristics:

i) It should be easily liquifiable and the liquid thus formed should flow freely.

ii) It shall have lower specific gravity than the metal. This makes the slag float on the metal.

iii) It shall have lower heat capacity. This prevents the heating of metals to high temperature.

iv) It should be able to dissolve the impurities easily.

The slags are classified as acidic and basic depending on whether the acidic oxide is in excess or basic oxide is in excess in the slag.

For example, $(CaO)_4\ SiO_2$ is called basic slag where as $(CaO)_2(SiO_2)_3$ is called acidic slag. On the othe rhand $CaO\ SiO_2$ is called neutral slag since both acidic and basic oxides are equal in proportion.

The slags are good bye-products. They are used in the laying of (a) roads and (b) in the manufacturer of cement, fertilizers and building materials.

Check your progress - 2

What do you mean by flux?

....

....

....

....

17.6 FURNACES

In the metallurgical processes i.e. in the processes of extraction of metals form their ores, there is a need to heat a mixture of ore and another chemical substance to very high temperatures. For example in the extraction of iron form its ore haematite, the ore is heated with lime to high temperatuers. The room or the device where the mixture of ore and the chemical substance is heated to higher temperatures is referred to as Furnace. The size shape and the building material of the furnace depend on the nature of chemical reactions that takes place in the furnace.

The furnances are generally constructed with heat resistance bricks and their outer sides are lined with steel plates. The furnance is generally heated with a fuel (gas, liquid or solid) or electrically. The fuels frequently used are coal, petroleum oil, natural gas, producer gas and water-gas.

Furnances are basically classified into four types depending on.

1. the chemical nature of the metallurgical process
2. the mode of burning of the fuel

3. the mode of movement of the charge in the furnace and
4. the mode of transfer of heat to the charge.

The furnaces are also usually classified on the basis of structure as

a) Shaft Furnaces
b) Reverboratory Furnaces
c) Muffle Furnaces
d) Electrical Furnaces

a) Shaft Furnaces

This type of furnace is usually cylindrical or rectangular in shape. Coke is generally used as the fuel. The charge added ffrom the top of the furnace moves down due to gravity. Hot air is blown upwards from the bottom through tuyers. These furnaces are employed in metullurgical processes involving smelting and roasting. The Blast furnace used in the manufacture of iron and the furnace used to prepare copper matte from copper pyrites are examples of such furnaces.

b) Reverbaratory furnaces

These furnaces have specific shpae as shown in figure 17. 7. These are constructed with furnace bricks. These contain large hearths. The roof of the furnace is curved and made of silica bricks. solid and liquid charges are used in these furnaces. The charge is added though hopper fixed to the roof. Fire boxes or burners arranged at the lower part of the furnace are used to burn the fuel. The roof of the furnace helps to reflect and radiate the heat towards the charge.

Open hearth furnace used in the manufacture of steel belongs to this type.

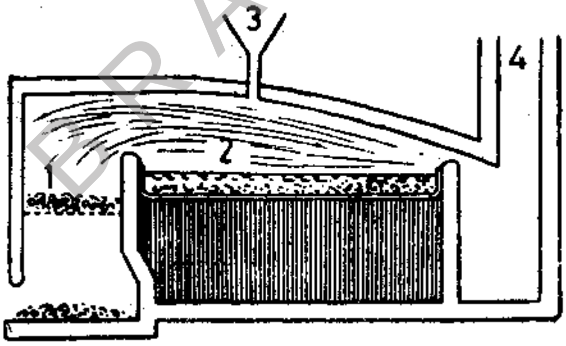

Fig. 17. 5 Reverberatory Furnaces
1. fire Box 2. Hearth 3. hopper 4. chimney

c) Muffle furnaces

In this type of furnaces, the charge and the fuel do not have direct contact. They are placed in two different rooms separated by heat conducting wall (Fig. 17.6)

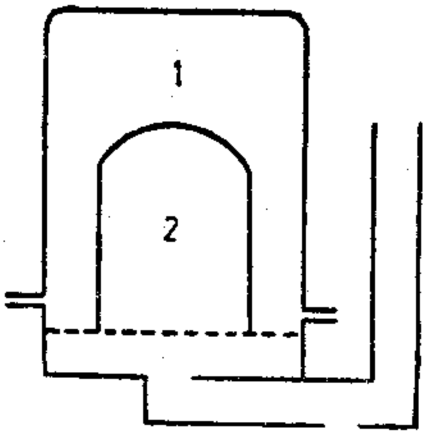

Fig. 17.6 Muffle furnace
1. fuel room 2. charge room

These furnaces are generally employed to burn furnace bricks.

d) Electrical furnaces .

These furnaces are important at places where electrical power is cheap. In these furnaces, the electrical energy is used to produce heat energy. These are basically of two types i) Arc furnaces ii) Electrical resistance furnaces. These are shown in figures 17. 7 and 17.8

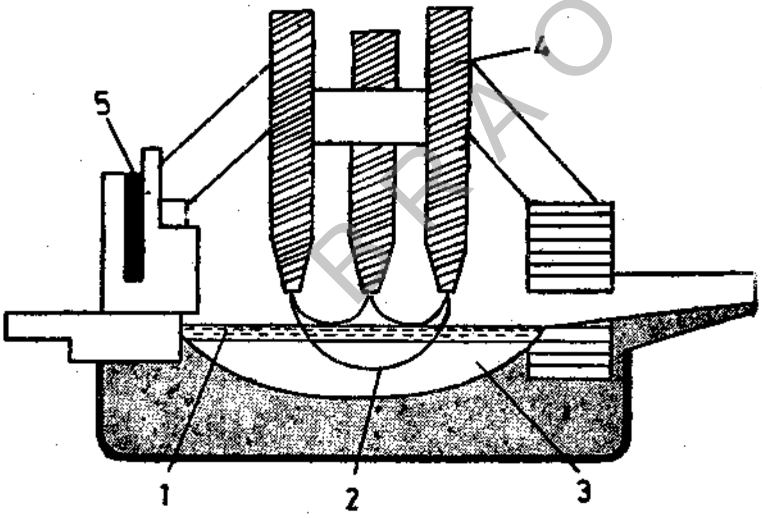

Fig. 17.7 Arc furnace
1. Melted metal 2. electric arc 3. metal 4. electrode 5. charge inlet.

In the first type of furnaces, an electric arc is used to produce the necessary heat. Carbon electrodes are used for the purpose. In the second type of furnaces, electricity is passed through the resistances and the heat produced is used in the furnaces.

1. Charge 2. Resistor

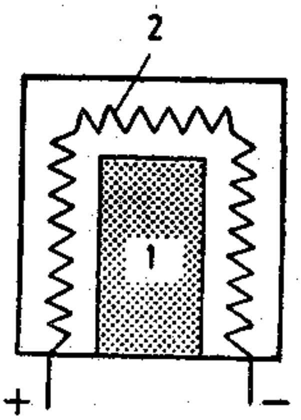

Fig. 17. 8 Electrical Resistance Furnace.

17.7 GENERAL METHODS OF EXTRACTION OF METALS FROM ORES

The method chosen depends on the chemical nature of the ore. You have already learnt that metals occur in nature as their oxides, or carbonates, or sulphides, or sulphates, or chlorides, or phosphates or silicates. Therefore specific processes or reactions are generally employed to convert the compound into the metallic state. These processes are mainly a) reduction b) roasting c) calicination d) smelting e) leaching .

a) Reduction

The reduction process is usually required in the extraction of metals from oxide and chloride ores. In the reduction of oxide ores, coke (a form of carbon) is popularly used as reducing agent. However, it offers difficulties in the case of oxides of aluminium, manganese and magnesium. But it is highly useful in the case of oxides of iron and zinc . Therefore other reducing agents such as hydrogen gas carbon monoxide, water gas, aluminium, calcium and even electricity are used in the metallurgical processes. Some exaples to illustrate the use of each of these reducing agents are given below.

Carbon

$$ZnO + C \xrightarrow{950^\circ} Zn + Co$$

$$SnO_2 + 2C \xrightarrow{1300^\circ} Sn + 2CO$$

Carbon monoxide

$$Fe_2O_3 + 3CO \xrightarrow{700^\circ} 2Fe + 3CO_2$$

Water gas

$$2\,NiO + \underbrace{(CO + H_2)}_{\text{water gas}} \xrightarrow{300^\circ} 2\,Ni + CO_2 + H_2O$$

Hydrogen

$MoO_3 + 3\ H_2 \rightarrow Mo + 3\ H_2O$

$WO_3 + 3\ H_2 \rightarrow W + 3H_2O$

$WCl_6 + 3\ H_2 \rightarrow W + 6\ HCl$

Aluminium emtal

The metal combines with oxygen in a highly exothermic process. This fact is used to reduce the oxides of chromium and manganese to their metals. An initial temperature of 600°C is generally required for the purpose. The process is generally known as Alumino-thermite process.

$CrO_3 + 2\ Al \rightarrow Al_2O_3 + 2\ Cr$

$3\ Mn_3O_4 + 8\ Al \rightarrow 4\ Al_2O_3 + 9Mn$

Magnesium, Calcium metal

Rubidium oxide is reduced with magnesium to get the metal.

$Rb_2O_3 + 3\ Mg \rightarrow 3\ MgO + 2\ Rb$

The halides of titanium and uranium are reduced with magnesium and calcium respectively.

$TiCl_4 + 2\ Mg \xrightarrow{700^\circ} 2\ MgCl_2 + Ti$

$UCl_4 + 2\ Ca \rightarrow U + 2CaCl_2$

b) Roasting

In the process of roasting, the ore in the non-molten state is heated alone or along with other substances to high temperatures in presence of air. The process of roasting involves oxidation of the metal. However the metal may be converted to its oxide, sulphate or chloride depending on the nature of the ore and the composition of the charge. Based on this fact, the roasting process is classified as oxidizing roasting, sulphatising roasting and chloridsing roasting. These are illustrated by the following chemical reactions.

Oxidising roasting

$2\ ZnS + 3O_2 \rightarrow 2\ ZnO + 2\ SO_2$
$2\ Nis + 3O_2 \rightarrow 2\ Nio + 2\ SO_2$

Sulphatising roasting

$ZnS + 2O_2 \rightarrow ZnSO_4$

$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$

$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O$

Chloridising roasting

$AgS + 2\ NaCl + 2O_2 \rightarrow Na_2SO_4 + 2\ AgCl$

c) Calcination

In this process, the ore in the non-molten state is heated to high temperatures to expel the volatile substances in the ore. This process is widely used in the case of carbonate ores.

$$ZnCO_3 \rightarrow ZnO + CO_2$$
$$CaCO_3 \rightarrow CaO + CO_2$$

d) Smelting

In this process, the metal, or its sulphide is separated in the liquid form from its ore. This is a pyrochemical process, ie. a process where a chemical reaction is effected at high temperatures. The conversion of haematite into iron in the liquid state and production of a mixture of coppersulphide and iron sulphide (matte) from copper iron pyrites are good exmaples for processes involving smelting.

e) Leaching

In this process, the ore is treated with acid, alkali or even with water a number of times under suitable conditions to convert them into the metallic compounds of higher purity than the ores. Few examples are given below.

Acid leaching

$$2\,Cu_2S + 5O_2 \rightarrow 2\ CuO + 2\ CuSO_4$$
$$2\,CuO + H_2SO_4 \rightarrow 2\,CuSO_4$$
$$UO_3 + H_2SO_4 \rightarrow UO_2\,SO_4 + H_2O$$

Alkali leaching

$$Al_2O_3 + 2\,NaOH \rightarrow 2\,NaAlO_2 + H_2O$$

$$UO_3 + 3Na_2CO_3 \rightarrow H_2O \rightarrow Na_4\,UO_2\,(CO_3)_3 + 2\,NaOH$$

Cyanide leaching

$$2\,Ag_2S + 8\,NaCN + O_2 \rightarrow 4\,Na\,[Ag(CN)_2] + 2Na_2\,SO_4$$

17. 8 PURIFICATION OF EXTRACTED METALS

The metals extracted from ores by the methods mentioned earlier are not generally of very high purity. Hence, it is essential that these extracted metals are further purified. The general methods of purification are.

a) Liquation b) Distillation c) Poling d) Cupellation
e) electrolysis and f) Zone refining

a) Liquation

The method is useful in th epurification of low melting metals. In this purification process, the impure metal is heated slowly on the roof of the inclined hearth. The metal melts and flows down. The unmolten impurities remain on the hearth. Tin is purified in this way.

b) Distillation

The process is generally used to purify volatile metals. The impure metal is taken in the retort and heated. The metal volatalizes and escapes out as the vapour leaving behind the impurities. The vapours of the metal are condensed to get the pure metal. Zinc, cadmium and mercury are purified by this method.

c) Poling

This method is generally applicable metals containing oxides of the same metal as impurities. The molten metal is stirred with green logs of wood in presence of carbon powder. The gases evolved in the process would help to reduce the oxide impurities back to metals.

d) Cupellation

Cupel is a crucible made from bone-ash. The impure metal is placed in the cupel and melted. Hot air is blown over the cupel. In this process, the metallic impurity gets preferentially oxidised. A part of the metal oxide thus formed is carried away by the air and the remaining part is absorbed by the material of the cupel. Impure silver containing lead is purified by this method, lead is converted as lead monoxide and is removed.

e) Electrolysis

Impure metals such as copper, silver, gold are purified by this method. In this process the impure metal is takne generally as the anode pure form of the metal is taken generally as the cathode. A solution of the metal salt is taken together with other electrolytes as the electrolytic bath. For example, in the purification of silver, silver nitrate and potassiumcyanide are taken as the electrolytes in the bath. The metal from the anode in the pure form is deposited on the cathode, while the impurities in the anode collect at the bottom of the electrolytic cell. This collection is called anode mud.

f) Zonerefining

This method is specially applicable to obtain metals of highest purity. For exmaple germanium of high purity used in transisitors is prepared by this method. The impure metal is made into a long rod and placed in a silica boat (Fig. 17.9). The whole set up is unclosed in quartz tube. An induction coil surrounds the tube. The coil is first placed at one end of the boat and its position changed gradually. When the current flows through the coil, heat is genrated. The heat thus generated melts the part of the impure metal in the boat under the coil. The position of the coil is now changed. In the new position, the part under the coil is melted, but in the mean time, the earlier molten metal solidifies.

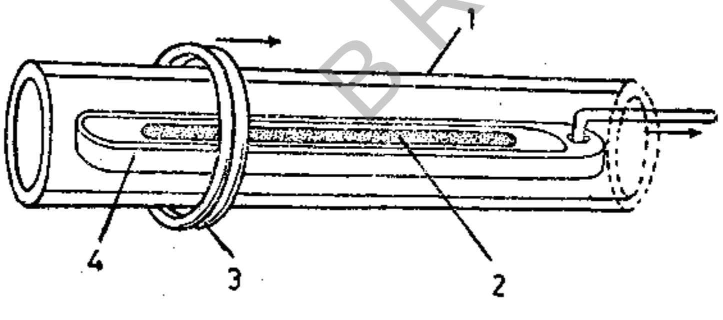

Fig. 17.11 Zone melting
1) Quartztube 2) Metal rod 3) Induction coil 4) silica boat

By this process the pure solid metal is formed at one end and the impurities are collected at the other end.

17.9 SUMMARY

Ores and minerals may not be same. Minerals from which metals can be extracted profitably are ores. Some of the metals occur in the native state. Extraction of a metal from its ore consists of the following steps- a) ore dressing b) ore concentration c) roasting or calcination d) smelting and e) metal refining. In this unit all the above are presented in detail.

17.10 MODEL EXAMINATION QUESTIONS

I Answer the following in 10 lines each.

1. Explain in detail the gravity concentration method and floatation method used in ore dressing.
2. Describe the magnetic and elctro-static methods of ore dressing.
3. Describe briefly the reverboratory and muffle furnaces.
4. Discuss briefly the reduction methods used in the extraction of metals.
5. Explain the terms roasting, calcination and smelting.
6. Describe liquation and distillation methods of purification of metals.
7. Discuss the principles underlying the metal purificatoin methods, cupellation, electrolysis and poling.

II. Answer the following in 30 lines each.

1. Discuss the gereral principles underlying the methods of isolation f metals from ores.
2. Describe the different methods purified?
3. How are impure metals purified?
4. Describe the different types of furnaces employed inthe metallurgical processess.

17.11 MODEL ANSWERSTO CHECK YOUR PROGRESS

1. Any compound of a metal present in nature from which the metal can be extracted profitably is called an ore.
2. Substance that is added in the smelting step of extrqaction of a metal from the concentrated ore to remove gaunge is called flux.

   flux + ganuge → slag

Author: Dr. V. Seshagiri

UNIT - 18 METALLURGY OF SILVER, GOLD, CHROMIUM, NICKEL AND URANIUM

Contents

18.1 AIMS AND OBJECTIVES

The main aim of this unit is to discuss about the metallrgy of silver, gold, chromium, nickel, uranium.

Once you completely study and understand the contents of this unit you must be able to:

- give the composition of the ores of Ag, Au, Cr, Ni and U
- describe the steps involved in the extraction of the above, metals from ores
- explain the methods of refining of the above metals
- differentiate flux, gaunge and slag
- give the uses of these metals
- describe in brief the important processes of isolation of metals
- mention briefly the important alloys of these metals
- discuss the important uses of the metals.

18.2 ISOLATION OF SILVER

18.2.1 Introduction

Silver is known to man even in olden days (3000 B.C). The metal was used in the preparation of coins by Indians and egyptians. India used the metal in the preparation of medicines.

18.2.2 Occurrence

Silver occurs native as well as in the combined form. It occurs in the native state together with gold, copper, mercury and platinum. In the combined state it occures mostly in the sulphide form. The important ores of silver are.

1.	Argentite or Silver glance,	$Ag_2 S$
2.	Horn Silver or Cerargyrite	AgCl'
3.	Pyrargyrite	$3Ag_2 S Sb_2 S_3$ or (Ag_3SbS_3)
4.	Proustite	$3 Ag_2 S, As_2 S_3$

Galena (PbS) is generally associated with silver ores. Therefore lead obtained from galena usually contains silver. This lead is therefore called argentiferrous lead. Most of the silver in the world is isolated in Mexico, United Staes and Canada.

18.2.3 Isolation processes

Silver is isolated from its ores by three important processes. These are:

i) Amalgamation process
ii) Cyanide Process
iii) Desilverization of lead process

These methods are briefly described here.

Amalgamation process

This is an old method and it is not in wide use these days. The sulphide ore is crushed into powder an dmixed with water to prepare pulp. Then salt, roasted sulphide ore and mercury are added. The whole mass is then crushed with the help of animals such as horses for about four weeks. The sulphide ore generally contains copper sulphate too. Thus the mixture contains copper ions, chloride ions and silver sulphide. These ions and mercury help to separate Ag from the ore. The reactions involved can be represented as

$$Ag_2 S + Cu^{++} + 2\,Cl^- \rightarrow 2\,AgCl + CuS$$

$$2\,AgCl + Hg \rightarrow 2\,Ag + Hg_2 Cl_2$$

$$Ag + Hg \rightarrow Ag\ (Hg)$$

The silver thus formed reacts with mercury and forms the amalgam. Mercury can be separated from the amalgam by distillation. But silver contains traces of gold and platinum. The metal is therefore further purified by electrolytic process.

Cyanide process

Silver is isolated from sulphide ore as well as chloride ore by this method. The method is based on two important reactions of silver. These are 1) the solubility of silver salts in alkali cyanides to form cyano complex of silver.

$$AgX + 2\ NaCN \rightarrow \frac{NaAg\,(CN)_2 + NaX}{\text{Complex}}$$

2) Silver is displaced in the metallic state from the complex on reaction with metals such as zinc and aluminium in presence of an alkali.

$$Zn + 2\ Na\ Ag\ (CN)_2 + 4\ Na\ OH \rightarrow Na_2\ ZnO_2 + 4\ NaCN + 2\ H_2\ O + 2\ Ag$$

The sulphide ore (AgS) or the chloride ore (AgCl) is pulverized and mixed with dilute solution of sodium cyanide (0.5%). The solution is agitated vigorously and air is blown into it. In this process, sodium argento cyanide, a complex salt of silver is formed.

$$Ag_2S + 4\ NaCN \rightarrow 2\ Na\ [Ag\ (CN_2\ ] + Na_2\ S$$
$$Ag\ Cl + 2\ NaCN \rightarrow Na\ [Ag\ (CN_2\ ] + Na\ Cl$$

The air bubbled into the solution helps to push forward the reactions to completion.

The argentocyanide solution is then separated from the impurities and finely divided zinc or aluminium is added to it. To facilitate, preicpitation of metallic silver, alkali is added to the solution.

$$Zn + 2\ Na\ [Ag\ (CN)_2 + 4\ NaOH \rightarrow Na_2\ ZnO + 4\ NaCN + 2H_2\ O + 2\ Ag$$
$$Al + 3\ Na\ [\ Ag\ (CN)_2 + 3\ NaOH \rightarrow 3\ Ag + 6\ NaCN + Al\ [OH]_3$$

The silver formed is separated and excess of zinc is removed by treatment with H_2SO_4. Ag is purified by fusion with Borax.

Desilverization of Lead process

Silver is generally associated as an impurity with lead ore, galena (PbS). Thus the lead isolated from such galena is also associated with silver as impurity. Such lead is called argentiferrous lead. The associated silver of such lead is isolated by cupellation. However for this process to be effective, the percentage of silver in lead should be greater than one percent. Hence the first step in the process of isolation is to raise the percentage of silver in argentiferrous lead. This is achieved by two processes namely Parkes process and Pattinson's process. These processes are described briefly.

Parkes process

The process invovles the melting of argentiferrous lead at about 420° C and addition of zinc. At the temperature of the experiment, zinc also melts and molten silver dissolves in zinc to form solid solution. This alloy of zinc-silver dissolves in zinc to form solid solution. This alloy of zinc-silver floats on the surface of the molten lead. When the molten mass is cooled, zinc-silver alloy solidifies first. This solid is separated and distilled in a retort in presence of carbon. In the process, zinc goes out as vapour leaving behind mostly silver together with some lead. Thus the percentage of silver in lead is increased. This argetiferrous lead is cuppelled to get pure silver.

The process is made possible because of the following facts.

a) Silver dissolves to a greater extent in molten zinc than in molten lead.
b) The melting point of zinc-silver alloy is higher than that of pure lead.
c) The density of zinc-silver alloy is less than that of lead.

Pattinson process

This process is based on the principle of fractional crystallisation of lead from molten argentiferrous lead. Argentiferrous lead is taken in iron vessels and melted and gradually cooled. During cooling lead separates out first, leaving the mother liquor rich in silver. Lead is separated from the mother and the later is subjected to further cooling. By this cycle of operations, mother liquor richer in silver will be obtained. This is separated, cooled and subjected to cupellation.

Purification of silver

Silver is purified electrolytically. Impure silver is made anode, silver nitrate solution is made the eletrolyte and iron is taken as cathode. During eletrolysis, silver separates as pure metal at the cathode.

18.2.4 Uses of silver

1) Sivler is mainly used as coinage metal and in the preparation of ornaments.
2) Silver salts are used in photography and medicine

18.3 ISOLATION OF GOLD

18.3.1 Introduction

One of the first metals which attracted man's attention even in Metal ages is gold. We are all familiar with alchemical efforts to convert base metals into gold. Gold is produced to large extent in South Africa, Canada, United States of America, Russia. Of course Karnataka in India is known for gold production.

18.3.2 Occurrence

Gold occurs as Vein gold in Auriferrous quatz. Gold also occurs native (i.e. in the elemental state) as small particles in alluvial gravel and sand. Many a time gold occurs together with platinum, palladium, mercury, copper, lead and even iron. In small amounts gold is present in iron pyrites. In the combined state it occurs rarely as telluride. For example sylvanite $(Ag\ Au)_2\ Te$) is an exmaple for such compound.

18.3.3 Isolation of gold

Gold is isolated from allurial sands and auriferrous quartz by separating the associated impurities. Basically two methods are employed for the purpose of this separation. These are 'washing methods' and 'dissolution methods'.

A. Washing methods

These methods can be broadly stated as (a) Panning, (b) sluicing (c) Hydraulic mining and (d) dredging. These will be described in brief in the following lines.

a) Panning

This process involves taking of the alluvial sand in trays and washing with water. This method is a very old one and is usually applicable when the sands contain considerable amounts of gold.

The alluvial sand is taken in large circular trays (about 30 cm in diameter) and mixed with water. Later the tray is rotated rapidly with hands. The lighter impurities (sand, clay etc) get mixed with water and are thrown out of the tray during this rotation along side the rim of the tray. The heavier gold particles settle at the bottom of the tray. By repeating the process of this rotation of the tray, almost all the impurities are removed and pure gold settles down.

b) Sluicing

This process involves the washing of alluvial sands with water in long wooden sluices (A sluice is similar to a small drain pipe). The sluice contains some wooden riffles. When the alluvial sand is taken at one end and water is forced with pressure, the lighter sand and clay go along with water leaving heavier gold particles at the riffles. Thus after several repetitions gold settles behind the riffles and the imurities get washed out with water.

c) Hydraulic mining

This process is similar in principle to the one described earlier. (b) However the washing is done in this process directly in the mines Water is forced under pressure into the mines containing the alluvial sands and auriferous quartz. The impurities are washed out as done in the earlier process. Gold gets collected at the bottom.

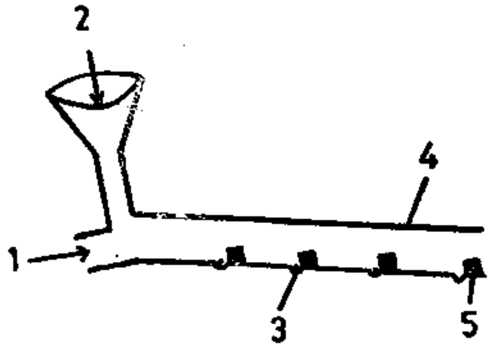

Fig. 18.1 slucing
1. Water inlet 2. Alluvial sand inlet 3.Gold particles 4. Sluice 5. Riffle

d) Dredging

This process is useful to isolate gold present in sands under river beds. A boat with a provision to bail out sands present at the river bottoms is called a dredge. This contains a wheel to which buckets are attached. As the wheel moves, these buckets one by one bail out the sands from the river beds. These sands together with water is allowed to flow over screens. The bigger particles stay back on the screen and the smaller particles pass through the screen. The material passed through the screen is collected and placed on Wiffle table and washed with water. The gold particles collect near the riffles and the impurities pass over the table.

Check your progress - 1

What is the common concentration method of heavy metal oxide ores?

....

....

....

B) Dissolution methods

There are basically three important processess. These are a) amalgamation b) cyanidation and c) chlorination.

All the three methods are based on the solubility of gold to form different chemical compounds. For example in process a) gold dissovles in mercury to form the amalgam, in process b) goldform sodium argentocyanide and in process c) gold forms gold chloride.

These compounds ar elater subjected to different chemical reaction to obtain gold in fairly pure form.

a) Amalgamation Process

Argentifierrous quartz is to be mined and broken down into pieces. These are then pulverized in a special mill in presence of water. This process results in the formation of pulp. This pulp is then passed through screens to separate the impurities from the pulp. The pulp then passes over amalgamated copper rods fixed in wooden trays. The gold particles present in the pulp react with amalgamated copper and form amalgamated gold. The impurites are collected at the bottom of the trays, where as amalgamated gold adheres to the rods. This amalgam is later scrapped and subjected to distillation in retorts. Mercury is voltalized and gets collected in erathen pots, while gold remains back in the retort. Gold obtained by this method is 60-70% pure.

b) Cyanidation

The pulverized ore is taken in tanks provided at the bottom with sieves. 0.05 to 0.1% sodium cyandie solution in 0.01 to o.5% sodiumhydroxide is added to the powdered ore taken in the tanks. The ore is completely covered with the alkaline cyanide solution and air is blown into the solution. In this process, gold present in the ore dissolves in cyanide solution and forms sodium auro cyanide complex solution.

$4\,Au + 8\,NaCN + 2\,H_2O + O_2 \rightarrow 4\,NaOH + 4\,Na[Au(CN)_2]$. This complex gold solution is drained through the sieves available at the bottom of the tanks and passed through boxes containing zinc metal powder. The complex reacts chemically with zinc and gold is precipitated.

$$4\,Na[Au(CN)_2] + 2\,Zn \rightarrow 4\,Na_2[Zn(CN)_2] + 4\,Au$$

The excess zinc metal is destroyed by adding sulphuric aicd. Precipitated gold is separated and made into rods.

In Kolar gold fields, gold is isolated by the process involving amalgamation as well as cyanidation.

c) Chlorination

This process is used to isolate gold from sulphide and arsenide ores. The ore is pulverized and roasted to give the oxide.

The roasted ore is placed in rotating cylindrical vessels and chlorine is passed into it. The ore is kept in contact with chlorine for about 36 hours. Gold reacts with chlorine to form $AuCl_3$.

$$2\,Au + 3\,Cl_2 \rightarrow 2\,AuCl_3$$

Gold chloride solution thus formed is taken in tanks and ferrous sulphate solution is added to precipitate gold.

$$AuCl_3 + 3\,FeSO_4 \rightarrow Fe_2(SO_4)_3 + Au \downarrow + FeCl_3$$

The precipitated gold is separated and made into rods.

18.3.4 Purification of gold

Gold obtained in any one of the methods mentianed above is generally 70% - 80-% pure only. Hence there is a need to further purify the metal. Electrolytic as well as chemical methods are used for the purpose.

1. Electrolytic method

Impure gold is made anode and pure gold is taken as cathode. Gold cyanide solution is taken as the electrolyte. After electrolysis, pure gold separates from impure anode and gets deposited on the cathode.

2. Chemical methods

a) **Fusion process:** Impure gold is fused with a mixture of borax and potassium nitrate in a crucible. The base metal such as copper, bismuth, lead present in gold are converted into their oxides leaving behind pure gold.

b) **Parting process:** In this process impure gold is treated with sulphuric acid, nitric acid and chlorine gas. During this treatment, metals such as silver are converted into their compounds leaving behind metallic gold

18.3.5 Uses of gold

1. Gold is used as a capital metal in banks.
2. Gold is used as covering metal on base metals in ornaments.
3. Colloidal suspensions of gold (purple of cassiums) is used as coloring material for glass and ceramics.
4. Gold is used in medicines.

18.4 ISOLATION OF CHROMIUM

18.4.1 Introduction

Chromium occurs in nature in the form of its compounds. The metal forms coloured salts and hence the name "Chromium" was given to the metal. "Chroma" in Greek means "colour". A french scientist Vayquelin discovered the metal in 1797. In 1857 Devilli prepared the metal in a state of approximate purity. Moissan in 1894 obtained chemically pure chromium.

18.4.2 Occurence

chromium widely occurs as its oxide. Important ores are

a) Chromite or chrom iron storne -- ($FeCr_2O_4$, FeO, Cr_2O_3)
b) Chrom ochre -- Cr_2O_3
c) Chromite -- Fe_2O_3, $2\,Cr_2O_3$
d) Crocoiste -- $PbCrO_4$

Turkey, Rhodisia, South Africa, Cuba, India and Russia are rich in chromium ores. In India Andhra Pradesh, Bihar, Karnataka, Maharashtra, Tamilnadu and Orissa are rich in chromium ores.

18.4.3 Isolation

Chromium is mainly extracted from chromite ore (FeO, Cr_2O_3).

The ore is concentrated by gravitational methods using Wilfley table. The concentrated ore is mixed with sodium carbonate, quick lime and roasted in a reverboratory furnace. Sodium chromate will be formed in the process.

$$4\,FeO, Cr_2O_3 + 8\,Na_2CO_3 + 7O_2 \rightarrow Fe_2O_3 + Cr_2O_3 + 8\,Na_2CrO_4 + 8CO_2$$

Sodium chromate thus formed is dissolved in water and treated with sulphuric acid when sodium dichromate is formed.

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

Sodium sulphate is separated by fractional crystallisation. Sodium dichromate solution is later evaporated to give solid dichromate. The solid dichromate is mixed with saw dust or coke and heated to high temperatures. Sodium dichromate is converted into chromium trioxide in the process.

$$Na_2Cr_2O_7 + 2C \rightarrow Cr_2O_3 + Na_2CO_3 + CO$$

Chromium trioxide thus formed is reduced to the metallic state by finely divided carbon or by aluminium metal (Gold Schmidt's Alumino Thermite process).

a. Reduction wiht carbon: Chromiumtrioxide is heated in presence of finely divided carbon at1400°C in refractory furnace.

$$Cr_2O_3 + 3C \rightarrow 2Cr + 3CO.$$

b) Reduction with aluminium: A crucible made from fire clay is used in the process. It is filled with fluorspar which acts thermal insulator. A cavity is made at the centre in this fluorspar and chromium trioxide, and aluminium powder are added. A mixture of barium peroxide (or potassium chlorate) and magensium wire placed on the mixture serves as the ignitor. The crucible is heated and magnesium wire is lighted. The heat generated in the process makes aluminium react with chromium oxide. The chemical reaction being exothermic lot of heat is generated. The temperature rise to 2500°C to 3000°C.

1. Magnesium wire
2. Barium Peroxide
3. Chromium trixide
4. Fluorspar
5. Fireclay crucible

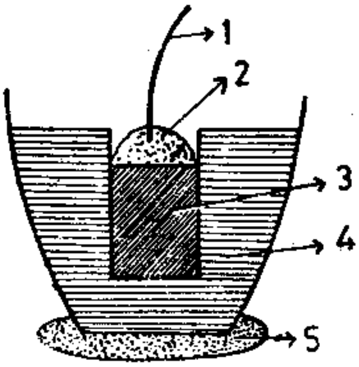

Fig. 18.2 Gold Schmidts process

$$Cr_2O_3 + 2\,Al \rightarrow Al_2O_3 + 2Cr + 130 \text{ K. Cals.}$$

At this high temperatures, chromium melts and alumina (Al_2O_3) floats on it. On cooling the metal solidifies.

18.4.4 Purification of Chromium

The chromium solution (Chromic acid) together with sulphate solution is taken as the electrolyte, and pure lead is used as anode and copper is used as cathode. On electrolysis at 85°C, pure chromium is deposited on the cathode.

18.4.5 Uses of Chromium

1. Chromium is used as an alloying element in steels.
2. Its capacity to resist high temperatures is used in the construction of hearths in furnaces.
3. Chromium salts are used as coloring materials in paints.
4. Chromium salts are used extensivelky in tanning industry.
5. In glass and porcelain industry chromium salts are used as coloring materials.

18.5 ISOLATION OF NICKEL

18.5.1 Introduction

Kronsted in Germany isolated nickel for lthe first time in 1751 and named it as nickel. However, Bergmann in 1774 studied the properties of the metal in detail. Australia and Canada are importnt amongst countries which produce nickel. Finland, Russia and Greece have large deposits of nickel ores. In India, Rajasthan has large deposits of copper containing nickel.

18.5.2 Occurrence

Nickel occurs in combined form together with sulphur, arsenic, antimony, cobalt, copper and iron. The important ores are:

a)	Nickel glance	_	$NiAsS$
b)	Millerite (Nickel Blende)	-	NiS
c)	Kup fer Nickel or Nickelite	-	$Ni\ As$
d)	Pentlandite	-	$(Ni,Fe)_{11}S_{10}$

Nickel also occurs in native state in small quantities in meteorites.

18.5.3 Isolation

The metal is generally extracted from sulphide ore, pentlandite or any other sulphide ore. The ore is powdered and concentrated by floatation process. The concentrated ore is put into heaps and burnt continuously for some weeks. In this roasting process iron in the ore is converted into iron oxide, while nickel and copper remain as sulphides.

$$2FeS_2+5O_2 \rightarrow 2\,FeO + 4\,SO_2$$

The roasted ore is then mixed with coke and fluxes (Lime stone quartz) and subjected to smelting process in the blast furnace. FeO formed in the roasting process combines with silica (SiO_2) and forms ferrous silicate. Limestone decomposed into calcium oxide (CaO) and the later combines with excess silica (SiO_2) to form calcium silicate. These ferrous and calcium silicates form the slag.

$$FeO + SiO_2 \rightarrow Fe\,SiO_3$$

$$CaO + SiO_2 \rightarrow Ca\,SiO_3$$

The product remaining behind on removal of these impurities ($Fe\,SiO_3$, $Ca\,SiO_3$) is called "Matte". This matte contains copper sulphide and nickel sulphide to large extent and iron sulphide to less extent.

The matte is fused and taken in alkali lined *Besemer Convertor* together with silica (flux). Air is blown into the mixture. In this process sulphur is converted into SO_2. All the ferrous sulphide is converted into ferrous oxide (FeO). This FeO combines with silica to form iron silicate. This is finally removed as the impurity. The residue of the matte contains mostly copper sulphide and nickel sulphide with nickel ranging from 55-60% and copper 25 - 30%.

Recovery of nickel from matte

Nickel is obtained from matte by two processes:

a) Orford's Process
b) Mond's Process

a) ***Orford's Process:*** This is based on the following facts.

1) Copper sulphide dissolves in molten sodium sulphide while nickel sulphide does not dissolve.
2) The density of nickel sulphide is greater than the density of copper sulphide dissolved in sodium sulphide.
3) The nickel sulphide is oxidised in presence of oxygen to give nickel oxide
4) Nickel oxide when mixed with carbon and heated to high temperatures in graphite crucible, gives nickel.

$$2\,NiS + 3O_2 \rightarrow 2\,NiO + 2\,SO_2$$

$$2\,NiO + 2C \rightarrow 2\,Ni + 2\,CO$$

[illegible] Process — Nickel is mostly isolated from the matte by this process.

[illegible]

1) Nickel combines with carbon monoxide at 80°C to give $Ni(CO)_4$. Copper and iron do not form carbonyls under similar conditions.

2) Nickel carbonyl decomposes at 180°C to form nickel. The matte is roasted in special furnaces. Copper sul;phide and nickel sulphide are converted into their oxides in this process.

$$Cu_2S + 2O_2 \rightarrow 2CuO + SO_2$$

$$2\,NiS + 3O_2 \rightarrow 2\,NiO + 2\,SO_2$$

The oxide mixture is dissolved in hot dilute sulphuric acid. Copper oxide dissolves in the acid to give copper sulphate, while nickel oxide remains intact.

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$$

Nickel oxide is filtered and intoroduced into high tower (reducing tower) from the top. The top portion of the tower is maintained at 300°C and the bottom portion is cooled. Water gas ($CO+H_2$) is sent into the tower from the bottom. This gas reduces nickel oxide to nickel at the top portion of the tower.

$$2\,NiO + (CO + H_2) \rightarrow 2\,Ni + H_2O + CO_2$$

The nickel thus formed will be in the finely divided state. This finely divided nickel is sent into a second tower (Volatalizer tower) maintained at about 80°C. Carbon monoxide is sent into the tower from the bottom. Nickel combines with carbon monoxide to give nickel carbonyl.

$$Ni + 4\,CO \rightarrow Ni(CO)_4.$$

Nickel carbonyl is then sent into the third tower (decomposing tower) Maintained at 180°C. The tower is packed with grannulated nickel,. Nickel carbonyl undergoes decomposition on contact with these grannules and metallic nickel is deposited on the grannules. The nickel obtained in this process is nearly 99.9% pure.

$$Ni(CO)_4 \xrightarrow{Ni} Ni + 4CO$$

18.5.4 Purification of Nickel

Nickel is purified electrolytically. Impure nickel is taken as anode and pure nickel as cathode. Nikclel ammonium sulphate is used as the electrolyte. Electrolysis is carried out at 30°C when pure nickel is deposited on the cathode.

Check your Progress - 2

What happens if carbon monoxide is passed over nickel powder kept at 80°C?

18.5.5 Alloys of Nickel

Nickel forms many alloys such as german silver, nichrome, platinite, monel metal and cupro nickel.

German Silver Contains 50.50% Copper, 10-30% Nickel and 20-30% Zinc. This is used to make utensils.

Nichrome Contains 60% Nickel, 25% Iron, 15% chromium. This is used in the manufacture of resistance wires.

Platinite contains 60% Iron, 40% Nickel. This has the same coefficient of expansion as glass. It is therefore used in the manufacture of filaments in electric bulbs.

Monel metal contains 70% Nickel, 30% Copper. This resists the action by alkalis. It is therefore used in the manufacture of vessels for chemical reactions.

Cupro Nickel contains 75% copper and 25% nickel. This is used in the preparation of coins.

18.5.6 Uses of Nickel

1. Nickel is used to coat metals such as Iron to prevent rusting as well as to give it the base metal bright apperance.
2. Finely divided nickel is used as a catalyst in the reduction process. This is specially used in the hydrogenation of oils.
3. Nickel is used in the manufactuer of alloys.

18.6 ISOLATION OF URANIUM

18.6.1 Introduction

Uranium was discovered by *Klaproth* in 1789 in the mineral pitch blende. The metal is named after the planet Uranus discovered in 1781. Uranium is now a very important metal since atomic energy is being widely used these days. Monozite sands occuring in Travancore contains Uranium. Bihar and Rajasthan also have minerals containing Uranium to less extent.

18.6.2 Occurrence

The Important ores of Uranium are

1) *Pitche Blende:* U_3O_8. This contains thoria (ThO_2), lead, iron and rare earths as other constituents. This is obtained in Canada, Belgium and South Africa.

2) *Carnotite,* $K_2O, 2UO_3, V_2O_5\, nH_2O$
This is obtained in Canada.

3) *Autanite,* $CaO, 2\, UO_3, P_2O_5\, nH_2O$

18.6.3 Isolation

The isolation process involves mainly

a) The concentration of the ore and separation of U_3O_8 in the pure form and (b) reduction of U_3O_8 to the metallic state. The concentrated ore is subject to (i) chemical precipitation or (ii) ion-exchange process or (iii) solvent extraction to obtain pure U_3O_8.

The method adopted to concentrate the ore depends on the composition of the ore. The composition of the ore varies from place to place.

The ore is first crushed into powder and magnetic separation methods. Sulphide impurities are removed by floatation process.

The ore is roasted to decompose the carbonates and sulphides and expel CO_2 and SO_2 formed in the process. The volatile substances such as arsenic and antimony are also removed in the process. The roasted ore is then subjected to acid leacning or alkali leaching.

Acid Leaching

The roasted ore is taken in store vessels and is leached with sulphuric acid or nitric acid or hydrochloric cid. Generally an oxidising agent such as manganese dioxide is added to convert lower oxides into UO_3. The oxide dissolves in acid to give uranyl sulphate.

$$UO_3 + H_2SO_4 \rightarrow UO_2\,SO_4 + H_2O$$

The PH of the solution is generally kept at 2.8 and $BaCl_2$ is added to remove Radium as $RaSO_4$ along wih $BaSO_4$. The contents are filtered to separate soluble uranyl sulphate together with copper and iron sulphates. To this filtrate sodium carbonate is added, when copper, iron and manganese are precipitated as hydroxides. But uranium forms a carbonato complex. On filtration soluble carbonate complex of Uranium is separated. This is then treated with sodium hydroxide solution to precipitate sodium diuranate.

$$2Na_4\,\{UO_2\,(CO_3)_3\} + 6\,Na\,OH \rightarrow Na_2\,U_2O_7 + 6Na_2\,CO_3 + 3H_2O$$

Alkali Leaching

In this process sodium carbonate is added when UO_3 reacts with it to form complex Uranyl Carbonate.

$$UO_3 + 3\,Na_2CO_3 + H_2O \rightarrow Na_4\,\{UO_2(CO_3)_3\} + 2\,NaOH$$

The Complex carbonate reacts with NaOH to form sodium diuranate.

Preparation of U_3O_8 from Sodium Diuranate

Sodium diurante precipitate is dissolved in HCl to form Uranyl Chloride. H_2S is bubbled into the solution to precipitate copper and arsenic. These precipitates are removed and excess H_2S is expelled. Later ammonium hydroxide is added and ammonium diuranate is precipitated. This diuranate is separated and heated to 700°C to give U_3O_8.

Ion exchange process

Uranyl sulphate solution obtained in cid leaching process, is passed through anion exchange resin. The complex Uranium ions are retained on the resin. The impurities do not form complexes and as such are not retained. Compelx Uranyl sulphate ions are later eluted from the resin. Ammonium nitrate is generally used as elutant. U_3O_8 is finally precipitated from the complex uranyl sulphate.

Solvent extraction process

When the aqueous solution containing uranium salts is extracted with ether or methyl ketone, the uranium salts are extracted into the organic layer. The organic liquid is again treated with aqueous solution to extract uranium salts back into water. Uranyl nitrate is thus obtained into the aqueous solution which is later evaporated to get the crystals. The are heated to get U_3O_8.

Isolation of Uranium metal from U_3O_8.

U_3O_8 is heated in presence of cabon in an arc furnace to get the metal.

$$U_3O_8 + 4\,C \rightarrow 3\,U + 4\,CO_2$$

Uranium required for nuclear reactors, is obtained by reducing UO_3 by hydrogen.

$$UO_3 + H_2 \rightarrow UO_2 + H_2O$$

UO_2 reacts with HF at 400°C to give UF_4

$$UO_2 + 4\,HF \rightarrow UF_4 + 2H_2O$$

UF_4 is then reduced with calcium and uranium metal is obtained.

$$UF_4 + 2\,Ca \rightarrow U + 2\,CaF_2 + 134 \text{ K. Cals.}$$

18.6.4 Uses of Uranium

1. Uranium is used in the production of nuclear energy.
2. Sodium uranate is used as a coloring substance in glass land ceramic industry.
3. It is also used as catalyst in the manufacture of ammonia by Haber's process.

18.7 SUMMARY

The composition of differenet ores of Ag, Au, Cr, Ni and U is given in this Unit diffrent methods of extraction of the above metals are described. The methods of refining of the above metals and their uses are mentioned.

18.8 MODEL EXAMINATIHON QUESTIONS

I. Answer each of the following in 10 lines.

1. Discuss the principle underlying the process of desilverization of lead.
2. How is gold isolated in the amalgamation process?
3. Describe Gold Schmidt's Alumino Thermic Process.
4. Describe the steps involved in the preparation of matte in the isolation of lnickel from the sulphide ores.
5. Discuss the principle of Orford's process.
6. How is uranium ore converted into UO_3?

II. Answer each of the following in 30 lines

1. Describe the metallurgy of silver or gold in detail.
2. Mention the important ores of chromium and describe how chromium is obtained from any of these ores.
3. How is nickel isolated from its ore by Mond's process?
4. Describe how uranium is isolated from its ore pitch blend.
5. Compare and contrast the metalluyrgical process of silver and gold.

18.9 MODEL ANSWERS TO CHECK YOUR PROGRESS

1. Heavy metal oxide ores are usually concentrated by gravity process.
2. Nickel combines with carbon monoxide and forms a complex $Ni(CO)_4$.

BOOKS SUGGESTED FOR FURTHER READING

1. Physical Chemistry -- W.J. Moore
2. Principles of Physical Chemistry -- S.H. Maron & C.F. Prutton
3. physical Chemistry -- G.M. Barrow
4. Text Book of physical Chemistry -- S. Glasstone
5. Concise Inorganic Chemistry -- J.D. Lee
6. Inorganic Chemistry -- T. Moeller
7. Fundamental concepts of Inorganic Chemistry -- Gilreath
8. physical Chemistry Vol. I and Vol. II -- Telugu Academy
9. Inorganic Chemistry Vol. II -- Telugu Academy

Dr. B.R. AMBEDKAR OPEN UNIVERSITY

Faculty of Science

(Under Graduation Programme)

III YEAR - B.Sc

CHEMISTRY COURSE - III

Assignment - 1

N.B:-

1. Do not copy the answer directly from any of the books
2. As far as possible try to answer the questions independently in your own words.
3. If it is necessary to quote from any source give the correct reference.
4. Use your own fullscape pages for writing the assignment.
5. Leave sufficient margins for the comments of the evaluator.
6. Completion of this assignment normally should not take more than two hours time.

SECTION - A

Answer the following in 30 lines

1. Define Hess's law. Prove that this law is in agreement with the first law of thermodynamics.
2. How is the specific conductivity of an electrolyte varies with dilution?
3. Describe about the different methods of determination of order of a reaction?

SECTION - B

Answer the following in 10 lines

1. What is Kohlrasch law? Give its main application.
2. Describe about the protective action of Colloids.
3. Give an account of Arrhenius theory of electrolytic dissociation.

Dr. B.R. AMBEDKAR OPEN UNIVERSITY
Faculty of Science
(Under Graduation Programme)

III YEAR
CHEMISTRY COURSE - III

Assignment - 2

N.B:-

1. Do not copy the answer directly from any of the books
2. As far as possible try to answer the questions independently in your own words.
3. If it is necessary to quote from any source give the correct reference.
4. Use your own fullscape pages for writing the assignment.
5. Leave sufficient margins for the comments of dthe evaluator.
6. Completion of this assignment normally should not take more than two hours time.

SECTION - A

Answer the following in 30 lines

1. Describe in detail about Werner's coordination theory.

2. Explain the variable oxidation states and magnetic properties of transition metals on the basis of electronic configuration.

3. Discuss the composition of two important ores of Nickel. Describe the method of extraction of Nickel from one of the ores.

SECTION - B

Answer the following in 10 lines

1. What are Chelates? Give an example.

2. What are fluxes and slags? Give examples.

3. What are ligands? Give their classification.

Dr. B.R. AMBEDKAR OPEN UNIVERSITY
FACULTY OF SCIENCE

CHEMISTRY COURSE - III (PAPER-III)
MODEL QUESTION PAPER

Time: 3 hours

Max. Marks : 75
Min. Marks: 27

SECTION - A

Answer any three of the following in 30 lines 3 x 15 = 45

1. Explain the terms 'Rate Constant', order and molecularity of a reaction. Derive an expression for the rate constant of a first order reaction.
2. Describe the structural isomerism in co-ordination compounds.
3. Give the composition of two important ores of Silver. Describe the method of extraction of Silver from one of the ores.
4. Discuss Debye-Huckel theory of strong electrolytes.
5. Discuss the merits and demerits of Bayer's strain theory.
6. Discuss the cyclic structure of D-glucose.

SECTION - B

Answer any five of the following in 10 lines 5 x 6 = 30

7. Give the different forms in which the first law of thermodynamics can be expressed.
8. Discuss the magnetic properties of transition metals.
9. Explain the effective atomic number concept proposed by Sidgwick.
10. Explain the valence bond theory of metallic bond.
11. Explain the terms Roasting, Calcination and Smelting.
12. Write the phenomenon of Keto-Enol tautomerism with a suitable exmaple.
13. What are amino acids? Describe any three methods of their synthesis.
14. Write a note on gold number.
15. Write the resonance structures of Furan.
16. What are ligands? Give their classification.

Cut here