

CHEMISTRY

Standard 12

(Semester III)



PLEDGE

India is my country.
All Indians are my brothers and sisters.
I love my country and I am proud of its rich and varied heritage.
I shall always strive to be worthy of it.
I shall respect my parents, teachers and all my elders and treat everyone with courtesy.
I pledge my devotion to my country and its people.
My happiness lies in their well-being and prosperity.

રાજ્ય સરકારની વિનામૂલ્યે યોજના હેઠળનું પુસ્તક



Gujarat State Board of School Textbooks

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PREFACE

The Gujarat State Secondary and Higher Secondary Education Board has prepared new syllabi in accordance with the new national syllabi prepared by N.C.E.R.T. based on N.C.F. 2005 and core-curriculum. These syllabi are sanctioned by the Government of Gujarat.

It is a pleasure for the Gujarat State Board of School Textbooks to place before the students this textbook of **Chemistry Standard 12 (Semester III)** prepared according to the new syllabus.

Before publishing the textbook, its manuscript has been fully reviewed by experts and teachers teaching at this level. Following suggestions given by teachers and experts we have made necessary changes in the manuscript before publishing the textbook.

The Board has taken special care to ensure that this textbook is interesting, useful and free from errors. However, we welcome any suggestion, from people interested in education, to improve the quality of the textbook.

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FUNDAMENTAL DUTIES

It shall be the duty of every citizen of India

- (A) to abide by the Constitution and respect its ideals and institutions, the National Flag and the National Anthem;**
- (B) to cherish and follow the noble ideals which inspired our national struggle for freedom;**
- (C) to uphold and protect the sovereignty, unity and integrity of India;**
- (D) to defend the country and render national service when called upon to do so;**
- (E) to promote harmony and the spirit of common brotherhood amongst all the people of India transcending religious, linguistic and regional or sectional diversities; to renounce practices derogatory to the dignity of women;**
- (F) to value and preserve the rich heritage of our composite culture;**
- (G) to protect and improve the natural environment including forests, lakes, rivers and wild life, and to have compassion for living creatures;**
- (H) to develop the scientific temper, humanism and the spirit of inquiry and reform;**
- (I) to safeguard public property and to abjure violence;**
- (J) to strive towards excellence in all spheres of individual and collective activity so that the nation constantly rises to higher levels of endeavour and achievement;**
- (K) to provide opportunities for education by the parent or the guardian, to his child or a ward between the age of 6-14 years as the case may be.**

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About This Textbook...

It has been decided by the Central Government of India, that only one competitive examination will be conducted at national level for the study of higher education. As a result of this planning, the formation of Core-Curriculum took place. The meaning of this was that there must be same syllabus in the subjects of Science Stream for national competitive examination. The same syllabus can be possible if the book is prepared according to NCF-2005.

Hence, by the Gujarat State Higher Secondary Education Board, a new Chemistry syllabus in Chemistry was prepared by experts and teachers on the basis of core-curriculum and NCF-2005.

Gujarat State Government being attempting for 'Education without Burden' plan will give comfort to students. Gujarat State Board of School Textbooks made positive arrangements for students to have advantage of the expertship of the teachers from Schools and Colleges having their own teaching experience, and experience in drawing questions for GUJCET examination as well as Higher Secondary Examination Board. The writers associated with the writing of this book have written units which are reviewed by other teachers, experts and reviewers and tried to prepare this book useful at national level by carrying out proper additions and alterations.

One important matter has been added. Changes have been expected in different words in this new book viz. atomic mass instead of atomic weight, molecular mass instead of molecular weight, enthalpy instead of energy, bar instead of atmosphere as well use of unit pascal. The word like reactivity will appear to be unknown but its inclusion in the modern study was found to be essential. In addition to this, in this existing book, instead of the nomenclature, units etc. the modern SI units, method of nomenclature etc. as in NCERT book are used in the text. This will appear somewhat new but being very useful in competitive examinations and to counteract the new challenges and to obtain achievement in present education system, it should be accepted.

Competitive examinations like JEE, NEET are being conducted. SI units are used in the question papers. In our GUJCET examination, SI units not being used, students were finding it difficult at the above competitive examination but we are sure that the students will make the name of Gujarat, as a state of great pride at national level.

The subject content, presentation, examples are included in this book in such a way that the students will find easy in understanding. Attempt has been made at each level even then, if teacher, friend or anybody will send suggestion for attainment of completeness, the Gujarat State Board of School Textbook will acknowledge with thanks and will include in the revised edition or new re-print.

'To send proper suggestion is your work and to implement it is our work.' By keeping this goal, the students of Gujarat State may obtain success at national level being the object, all will join in these is our expectation and request.

– Authors



Unit

1

Solid State

1.0 Introduction

You have gained information about five states, in previous standards. They are solid, liquid, gas, plasma and BEC (Bose-Einstein Condensate). We are more familiar with first three states. You have studied about liquid and gas in standard-11, in the units on liquid state and gaseous state. You have also studied the characteristic properties of liquids, etc. In this unit, we shall study in detail the solid state. The study of structure of solids and their properties etc. is called **Solid State Chemistry**.

We know that solid substance has definite shape and volume. In addition to this we shall study about many phenomena associated with chemistry including this statement. We are familiar with solid substances, because our life and everyday life are associated with solid. Different solid substances are used for different uses. In solids, their different compositions and properties are associated. If we study solid, information about its properties and by carrying out changes in it, we can have many uses of solids viz. substances used in superconductors and plastics for packing can be prepared. Solid substance differs from liquid and gas in one aspect and that is fluidity. Hence, liquid and gas are called **fluids** but in solid, the ions, molecules are in some definite form and arranged in a systematic manner. Hence, they have definite shape and so it is not a fluid. There can be two types in solid-crystalline and amorphous. In a crystalline solid, arrangement of atoms or ions is systematic.

We shall study in this unit, the arrangement of atoms or ions and their relationship with their properties and what changes we can make in these properties so that desired and useful innumerable solid substances can be obtained.

1.1 Classification of Compounds on the basis of Binding Forces (Molecular, Ionic, Covalent, Metallic)

Most of the solid substances are crystalline viz. metals like copper, iron, silver, etc., non metals like phosphorus, sulphur, and in ionic form-crystals of sodium chloride, potassium chloride and molecular solid like naphthalene.

The classification of solid substances on the basis of intermolecular attraction forces involved in them, can be made into four classes (1) Molecular solids (2) Ionic solids (3) Metallic solids and (4) Covalent network solids.

(1) Molecular solids : The molecules present in the molecular solid are its constituent particles. They can be classified into three parts as below :

(a) Nonpolar molecular solids : Elements like argon, helium or molecules formed by nonpolar covalent bonds. Elements like dihydrogen, dichlorine, diiodine etc. can be included in this type of solids. The atoms or molecules in this type of solid possess the weak **dispersion forces** or **London forces**. You have studied about these types of forces in standard-11. Solids of this type possess low melting points and they are soft and non conductor of electricity. At normal temperature and pressure, they are in liquid or gaseous state.

(b) Polar molecular solids : The solids like SO_2 etc. generally possess polar covalent bond. The molecules of such solids are bound by relatively strong polar-polar interactions. They are also soft and nonconductor of electricity. Their melting points are higher than those of nonpolar molecular solids. Even then, they are in gaseous or liquid state at normal temperature. Solid SO_2 and solid NH_3 are solids of this type.

(c) Molecular solids containing hydrogen bond : In this type of solids, atoms like H form polar covalent bond by combining with electronegative atoms like F, O or N. The strong hydrogen bonding in them, keep them in bound state. Substance like ice is the example of this. They are also non-conductors of electricity. At room temperature and pressure they are volatile liquids or soft solids. In the molecule of ice, four molecules of water are attracted by hydrogen bond. It gets separated from the hydrides of other elements of the same group because of hydrogen bond.

(2) Ionic solids : The constituent particles of ionic solids are ions. The cations and anions of such substances are attracted by strong Coulombic forces and so they possess forced molecules in three dimensional directions. They are hard and brittle. Their melting points and boiling points are higher because of strong attraction between positive and negative ions in the solid. Though ions are present in such substances, even then, they do not conduct heat or electricity because they are bound by strong attraction forces between positive and negative ions. But if they are dissolved in water or are melted in solid state, their ions get separated and so they conduct electricity.

(3) Metallic solids : Most of the metals are in solid state and so metal possesses positively charged nucleus around which free electrons are arranged. They are arranged in a systematic way. Electrons are spread in the form electron sea around the nucleus of atom of the metal. These electrons do not remain confined to any nucleus but are moving around the nuclei like the flow of water in the sea and these free electrons allow electricity and heat to conduct. When electric field is applied, they move, but in the new situation electron makes its arrangement around the nuclei. When heat is supplied to metal, the thermal energy is spread everywhere by the free electrons. In addition, metals have lustre and in some cases have colours. This is due to the presence of free electrons. They are ductile and malleable.

(4) Covalent solids : In the whole crystal, the adjoining atoms form covalent bond in larger proportion and so it results into different crystalline solids. They are called 'Giant molecules'. Many diversities are found in these compounds because they possess covalent bond-directional properties. Their molecules are bound tightly and hence they possess very high boiling points. Some decompose before being melted. They are not conductors of electricity. Diamond and graphite are the examples of this type. Graphite is soft and good conductor of electricity because its structure is specific. Three atoms of carbon in graphite form three covalent bonds by sp^2 hybridisation and the fourth electron remains free. It keeps

one layer of graphite combined with other layer. Thus layers consisting of hexagonal structure having sp^2 hybridisation are formed in graphite and the fourth electron keeps distance of 340 pm between the layers and it conducts electricity because it is free. The different layers of graphite can move creating friction with each other and so graphite is a good solid lubricant. In contrast to this, tetrahedral structure is formed by sp^3 hybridisation in diamond and all its four corners are combined with other carbon atoms of diamond and spread in three dimension. Hence, it is very hard. It cannot conduct electricity because it has no free electrons. Thus, it can be seen that in the two allotropes of the same element, if intermolecular forces and hybridisations formed are different, there is a great change in their properties.

In the following table 1.1, four types of solids and their properties are shown.

Table 1.1 Different types and properties of solids

Type of solid	Constituent particles	Attraction forces	Example	Physical nature	Melting point	Electrical conductivity
(1) Molecular solid						
(i) Non polar	Molecules	Dispersion or London forces	Ar, CCl_4 , H_2 , I_2 , CO_2	Soft	Very low	Non conductor
(ii) Polar	Molecules	Dipole-Dipole-inter attraction	HCl, SO_2 , NH_3	Soft	Low	Non conductor
(iii) Hydrogen bond possessing	Molecules	Hydrogen bond	H_2O (ice)	Hard	Low	Non-conductor
(2) Ionic solid	Ions	Coulombic or Electrostatic	NaCl, MgO, ZnS, CaF_2	Hard but brittle	High	Solid state, non-conducting but molten or aqueous solution conductor.
(3) Metallic solid	Positive ion in sea of delocalised electrons	Metallic bond	Fe, Ca, Mg, Ag	Hard but ductile and malleable	Comparatively very high	Conductors in solid and molten states
(4) Covalent or Network solids	Atoms	Covalent bond	SiO_2 (Quartz) SiC (Carborandum) C (Diamond) C (Graphite)	Hard	Very high	Non conductor Conductor (Exception)

1.2 Crystalline and Amorphous solid substances

Solid substances are available in crystalline and amorphous forms. There is difference in their structure and formation.

Crystalline solid substances are rigid and incompressible. They have definite shape. Their geometrical structures are systematic and definite. The reason for this is the regular and definite arrangement of molecules or ions in three dimensional space. They have got definite and sharp melting points. The examples of this type of crystalline solid are NaCl, KCl etc.

Amorphous substances are also rigid and incompressible but they have no definite geometrical shapes. The periodicity of the definite formation or geometry of amorphous substances is not observed

even when the atoms or ions are bound very tightly. Their melting points are not sharp, they possess some range of temperatures. The examples of such amorphous substances are glass, rubber etc. In the following table 1.2, the differences between crystalline and amorphous solids are given.

Table 1.2 Differences between crystalline and Amorphous solid substances

Property	Crystalline solid	Amorphous solid
(1) Shape	Definite shape and possessing characteristic geometry.	Irregular shape
(2) Melting point	Definite and sharp melting point which is the characteristic of the crystal of solid.	Becomes soft gradually during the small temperature range i.e. have no definite and sharp melting point.
(3) Fusion enthalpy	Definite and characteristic fusion enthalpy	Not definite and characteristic fusion enthalpy
(4) Cleavage property	Divided into two parts by cutting the crystal with sharp tool like knife. The surface of the new part obtained is plain and soft i.e. it is as original one	Divided into two parts cutting the crystal with sharp tool like knife but the surface of new part obtained is not as the original one. It is irregular.
(5) Nature	True solid	Pseudo solid or supercooled liquids
(6) Order of Arrangement of constituent particles.	The order is maintained till a long range	The order is maintained in a short range
(7) Effect of temperature	The graph (temperature \rightarrow time) obtained on cooling after heating is not a curvature. The temperature remains definite during crystallisation	The graph (temperature \rightarrow time) obtained on cooling after heating is a curvature. Temperature range is obtained during crystallisation.
(8) Properties	Their properties like electrical conductivity, thermal conductivity, mechanical strength and refractive index are different in different directions.	Their properties like electrical conductivity, thermal conductivity, mechanical strength and refractive index are same in all directions

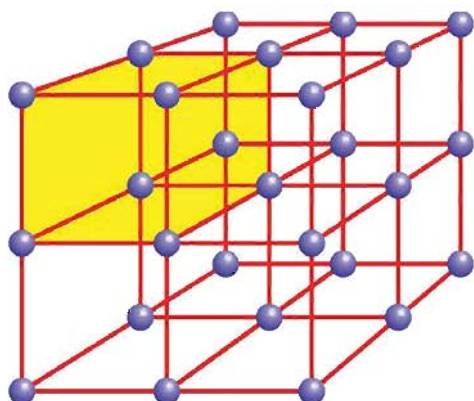


Fig. 1.1 Part of the three dimensional cube lattice and its unit cell.

1.3 Unit cell (Two Dimensional and Three Dimensional Lattice)

The smallest particle of a substance is known as atom or molecule. Similarly the smallest portion to know crystal of solid is called the unit cell; thus the smallest portion possessing the chief characteristics of a crystalline solid is called **unit cell**. Such unit cells are arranged with each other in three dimensional directions and the formation of crystal results. This type of arrangement is called crystal lattice (word 'Jalak' is used in Gujarati for lattice). As shown in fig 1.1 each particle is shown as point. Thus the systematic three dimensional arrangement of points in space is called

crystal lattice. In fig 1.1 the part of the crystal lattice is shown. There are 14 possibilities of such three dimensional lattices called Bravais lattice. Some of the characteristics of crystal lattice are as follows :

- (1) Each point in the lattice is called lattice point or lattice position (location).
- (2) Each point in the crystal lattice represents one constituent particle which can be an atom, molecule or ion.
- (3) The lattice points are connected by straight lines, so that the geometry of the lattice can be indicated.

Unit cell is the smallest part of the crystal lattice, which is repeated in different directions in three dimensions and the complete lattice is formed.

The characteristics of unit cell are as follows :

- (1) Its dimensions are on its three edges a, b and c . These edges may be perpendicular to one another or may not be perpendicular.
- (2) The angles between the edges are α (between edges b and c), β (between edges a and c) and γ (between edges a and b). Thus unit cell becomes characteristic by parameters a, b, c and α, β and γ . These parameters are shown in fig 1.2

It is necessary to note here, that we can show two dimensional figures in book but it is difficult to show three dimensions. Hence, this structure can be well understood by the use of models.

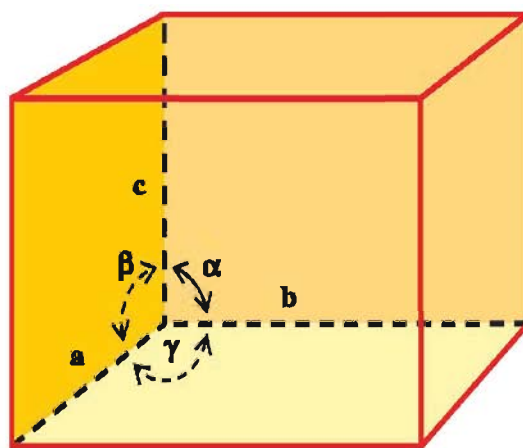


Fig. 1.2 Dimensions of Unit Cell

Primitive and Centred Unit Cells : The unit cell can be divided into two parts : (a) Primitive unit cell (b) Centred unit cell.

(a) Primitive Unit cell: When constituent particles are arranged on the eight corners of the unit cell, it is called primitive cell.

(b) Centred Unit cell : When one or more constituent particles are arranged at other places (sites) in addition to the sites of the corners, it is called **centred unit cell**. Centred unit cells are of three types (1) Face centred unit cell (2) Body centred unit cell (3) End centred unit cell.

(1) Face centred unit cell : In this type of unit cell one particle is arranged in the centre of each face (side) in addition to particles arranged on each corner of the unit cell.

(2) Body centred unit cell : In this type of unit cell one particle is arranged on the centre of the body in addition to each particle arranged on the four corners of the unit cell.

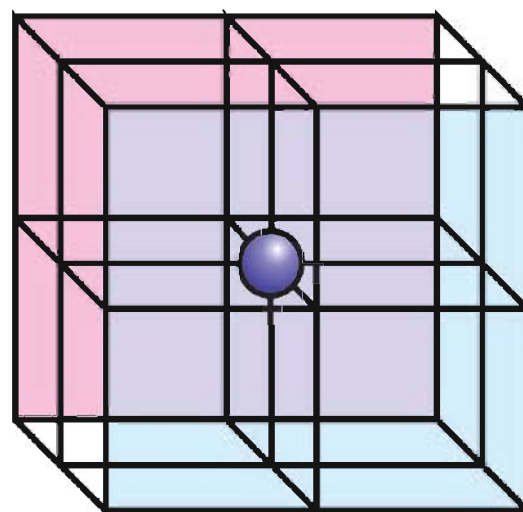
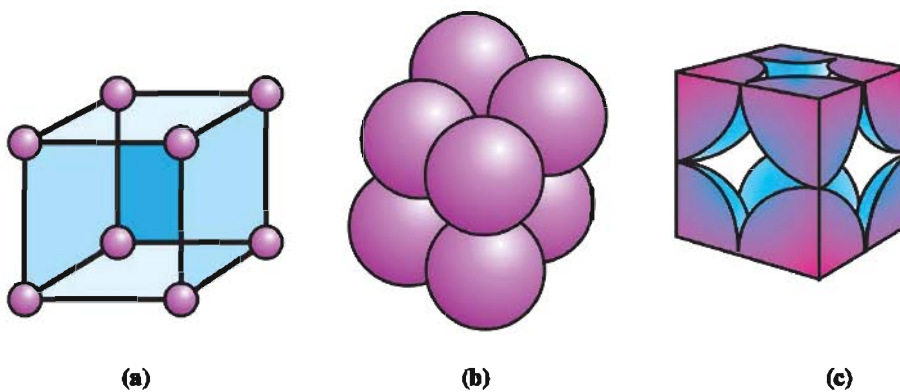
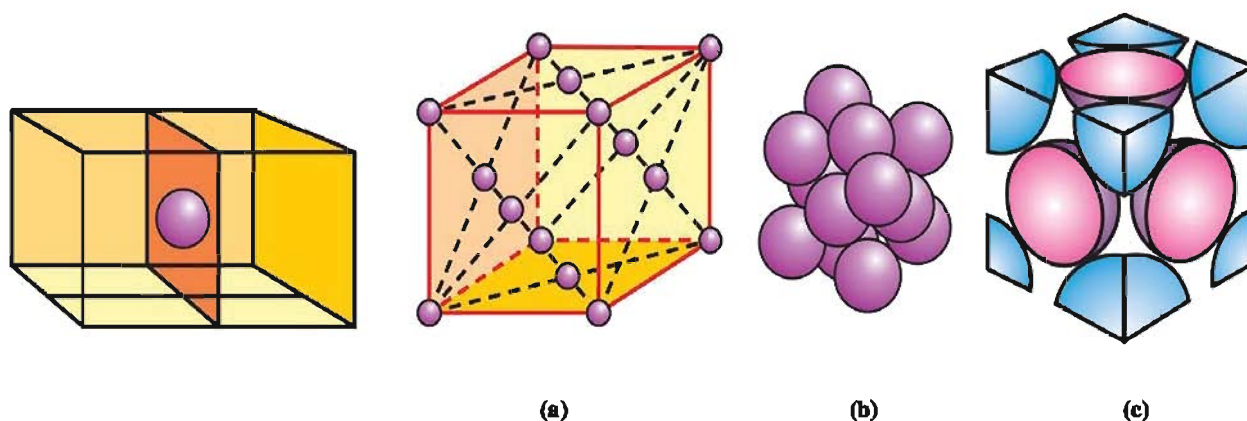


Fig. 1.3 Atom on each corner of a simple cubic cell is shared with 8 atoms



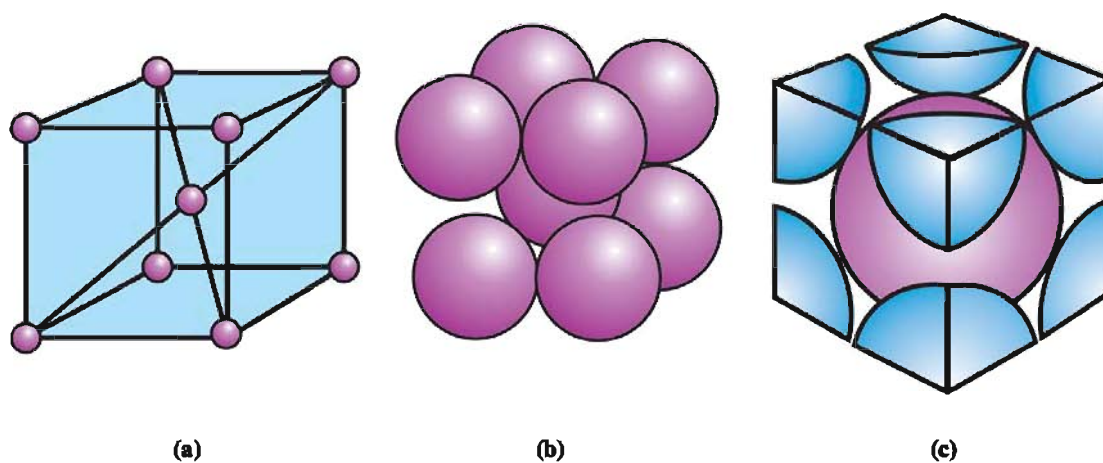
Primitive unit cell

(a) Open space filling structure (b) Space filling structure
(c) Actual portions of atoms belonging to unit cell



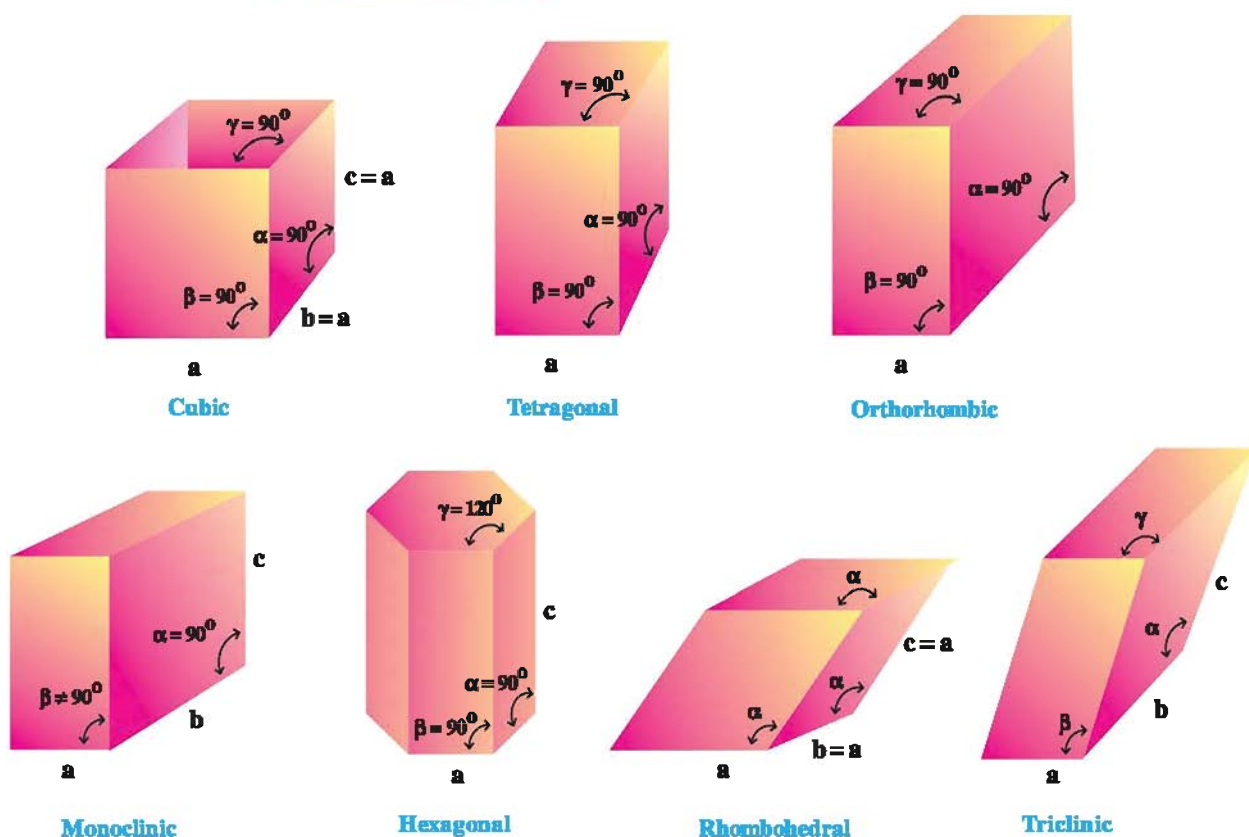
An atom at face centre of unit cell
is shared between 2 unit cells

Structure (a) open structure (b) space filling structure
(c) actual portions of atoms belonging to one unit cell



A body centred cubic unit cell (a) open structure (b) space filling
structure (c) actual portions of atoms belonging to one unit cell.

(3) End-centred unit cell : In such a unit cell one constituent particle is present at the centre of any two opposite faces besides the ones present at its corners.

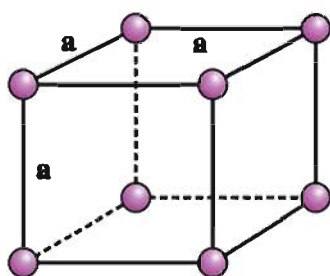


Primitive Cells

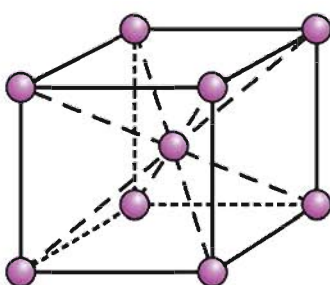
There are in all seven types of primitive cells which are shown below in table 1.3

Table 1.3 Seven primitive unit cells and deviation possible as centred unit in them

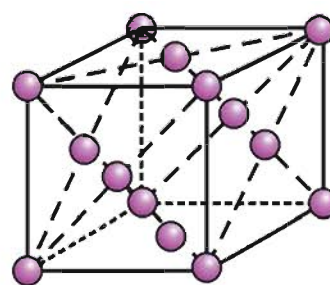
Sr.	Crystal System	Possible variations	Axial distance or distance of edge	Axial angle	Example
1.	Cube	Primitive Body centred Face centred	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	NaCl, ZnS, (zinc blende), Cu
2.	Tetragonal	Primitive, Body centred	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	White tin, SnO_2 , TiO_2 , CaSO_4
3.	Orthorhombic	Primitive Body centred Face centred End centred	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	Rhombic sulphur, KNO_3 , BaSO_4
4.	Hexagonal	Primitive	$a = b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma = 120^\circ$	Graphite, ZnO, CdS
5.	Rhombohedral or Trigonal	Primitive	$a = b = c$	$\alpha = \beta = \gamma \neq 90^\circ < 120^\circ$	Calcite (CaCO_3) Cinnabar (HgS)
6.	Monoclinic	Primitive End centred	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta = 90^\circ$	Monoclinic sulphur $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$
7.	Triclinic	Primitive	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	$\text{K}_2\text{Cr}_2\text{O}_7$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, H_3BO_3



Primitive (or simple)

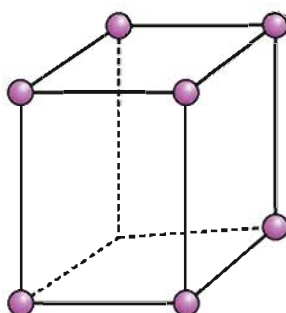


Body-centred

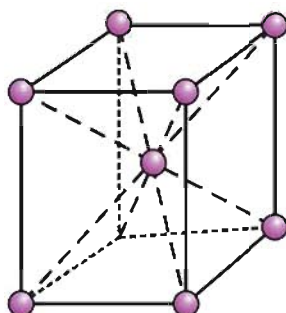


Face-centred

The three cubic lattice : all sides of same length, angles between face all 90°

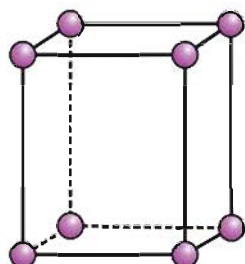


Primitive

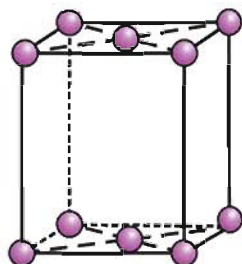


Body-centred

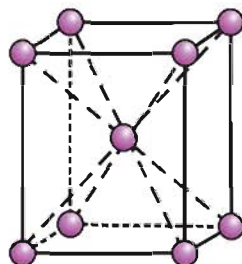
The two tetragonal : one side different in length to the other, two angles between face all 90°



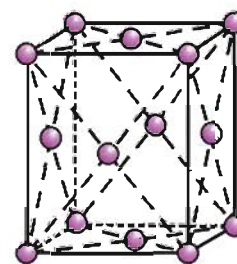
Primitive



End-centred

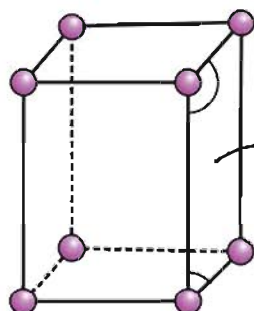


Body-centred

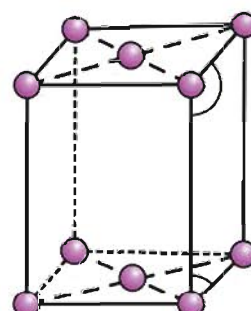
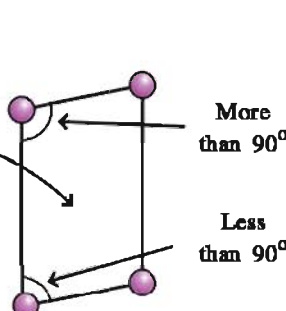


Face-centred

The four orthorhombic lattice : unequal sides, angles between face all 90°



Primitive



End-centred

The two monoclinic lattice : unequal sides, two faces have angles different to 90°

1.4 Calculation of Volume Occupied by Atoms in Unit cell

The arrangement of molecules atoms, or ions in unit cells of different crystals is different. We shall study about the close packing efficiency of atoms in different unit cells.

Packing efficiency : The packing of constituent particles (atoms, molecules or ions) may be of any type but some free space is left out which is called **hollowness** or **void**. The percentage of total space volume occupied by particles is called **packing efficiency**. We shall now carry out calculations of packing efficiency of different structures.

(1) Packing efficiency in simple cubic lattice : The atoms are only on the corners of the cube in simple cubic lattice. The particles touch each other along the edges.

The relation between the side or the edge length of a cube and the radius of each particle will be $a = 2r$.

The volume of cube in any unit cell $= a^3 = (2r)^3 = 8r^3$

Each cubic unit cell possesses only one atom.

Hence, the volume occupied by one atom $= \frac{4}{3}\pi r^3$

Now packing efficiency

$$= \frac{\text{Volume of one atom}}{\text{Volume of cubic unit Cell}} \times 100 \%$$

$$= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100 = \frac{\pi}{6} \times 100 = 52.36 \%$$

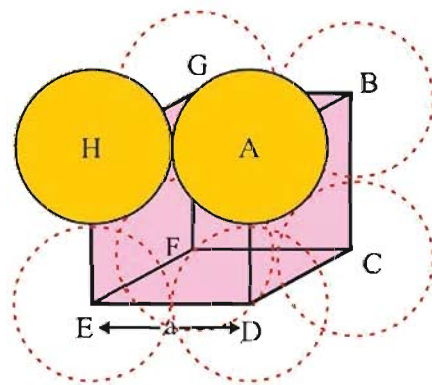


Fig. 1.4 Packing efficiency of cubic lattice unit cell

(2) Packing efficiency of body centred unit cell : As shown in figure 1.5, the atom in the centre touches two other atoms diagonally arranged. Hence, in ΔEFD ,

$$b^2 = a^2 + a^2 = 2a^2$$

$$\therefore b = \sqrt{2} a$$

Now, in ΔAFD ,

$$c^2 = a^2 + b^2 = a^2 + 2a^2 = 3a^2$$

$$\therefore c = \sqrt{3} a$$

The diagonal length of body centred cube $c = 4r$, where r is radius of the atom because, all the three spheres touch diagonally.

$$\therefore \sqrt{3} a = 4r$$

$$\therefore a = \frac{4}{\sqrt{3}} r$$

The total number of atoms in this type of arrangement is 2 and so its volume will be $2 \times \frac{4}{3}\pi r^3$

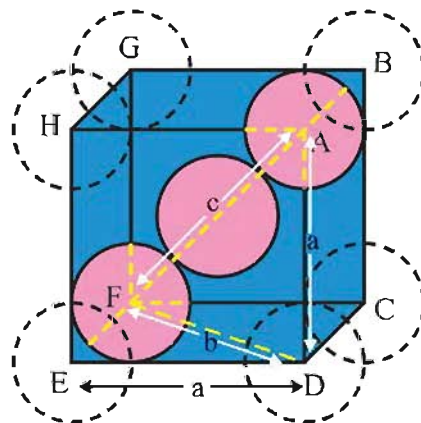


Fig. 1.5 Packing efficiency of body centred unit cell

$$\text{Volume of cube } a^3 = \left(\frac{4}{\sqrt{3}}r\right)^3$$

$$\text{Now, packing efficiency} = \frac{\text{Volume occupied by two spheres in unit cell}}{\text{Total volume of unit cell}} \times 100$$

$$= \frac{2 \times \frac{4}{3} \pi r^3}{\left[\left(\frac{4}{\sqrt{3}}\right)r\right]^3} \times 100 \% = \frac{\frac{8}{3} \pi r^3 \times 100}{\frac{64}{(3\sqrt{3})} r^3} = 68 \%$$

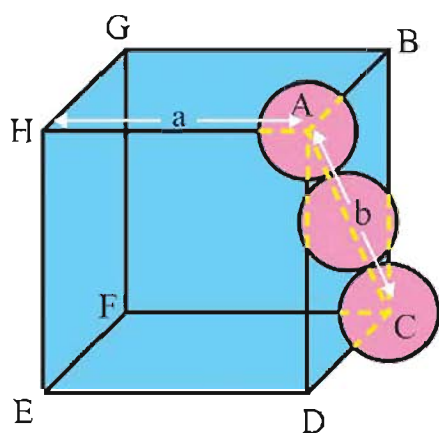


Fig. 1.6 Cubic close packing efficiency

(3) Packing efficiency in hexagonal packing (hcp) and cubic close packing (ccp) : The close packing is equally efficient in both these types. We calculate the packing efficiency of ccp structure. As shown in figure 1.6, the length of the edge of unit cell is a and the diagonal of face is $AC = b$

$$\text{In } \triangle ABC, AC^2 = b^2 = BC^2 + AB^2$$

$$= a^2 + a^2 = 2a^2 \text{ or } b = \sqrt{2} a$$

Suppose the radius of the sphere is r , then $b = 4r = \sqrt{2}a$

$$\text{or } a = \frac{4r}{\sqrt{2}} = 2\sqrt{2} r$$

As we know, four atoms or spheres are there in ccp structure and so the total volume of four spheres $= 4 \times \frac{4}{3} \pi r^3$ and the volume of cube will be a^3 or $(2\sqrt{2}r)^3$

Hence,

$$\text{packing efficiency} = \frac{\text{Volume occupied by four spheres of unit cell}}{\text{Total volume of unit cell}} \times 100$$

$$= \frac{4 \times \left(\frac{4}{3}\right) \pi r^3 \times 100}{(2\sqrt{2}r)^3} \%$$

$$= \frac{\frac{16}{3} \times \pi r^3 \times 100}{16 \sqrt{2} r^3} = 74 \%$$

It can be determined from the above three calculations that, there is maximum packing efficiency in ccp and hcp.

1.5 Close packed structures and their types (one dimensional, two dimensional and three dimensional)

We can accept atom, molecule or ion as spherical form and their arrangement in solid state by each other from all the adjoining sides and some space remains between them. Suppose we take small spheres in a closed tin and shake then and put, them all the small spheres will be arranged from all the sides but space will be left out between spheres. Particles (spheres) in the solid state possess close

packing and so there is very less space among them. Hence, if we consider component particles as hard spheres and think of their arrangement, the three situations can be possible (1) One dimensional arrangement (2) Two dimensional arrangement (3) Three dimensional arrangement. We shall study this in detail.

(1) One dimensional close packing : In this type of packing, as shown in figure 1.7 two other particles are arranged near one particle (sphere). The number of most nearby neighbour particles is called the **co-ordination number**. Thus, the co-ordination number is 2 in one dimensional close packing.



Fig. 1.7 Close packing of spheres in one dimension

(2) Two dimensional close packing : In this type of packing the rows having close packing are arranged as a stack. This arrangement can be of two types.

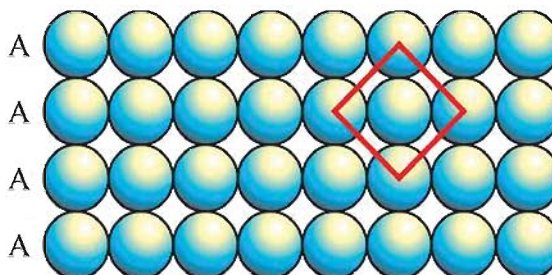


Fig 1.8(a) Square close packing

(a) In this arrangement the other particles are exactly arranged on the particles arranged in the row below them and forms a stack. Thus, the particles in the rows are aligned with each other vertically and horizontally. If we call first row as A, the second row is similar to it and so it will also be called A. Thus, one by one, each row is arranged on one another, we will have the arrangement of type AAA A...as shown in figure 1.8(a)

In this arrangement, other four spheres are arranged as neighbours around each sphere. Hence, the co-ordination number will be 4 in two dimensional arrangement. If we join the centres of the four spheres we will get a square. So this structure is called two dimensional **square close packing**.

(b) In the second method we will arrange the second row stack in slightly deviated method, so that the spheres of the second stack arrange on the depressions formed by the first stack. If we call, the first type of arrangement of stack as A then the arrangement of spheres in second stack will be a separate B type stack. Thus, if we arrange the stacks alternately then we have ABABAB....type structure. This type of structure is more rigid and more efficient packing possessing than square close packing. In this type of structure, 6 spheres are arranged around each sphere and so it is called two dimensional **hexagonal close packing** which is shown in figure 1.8 (b)

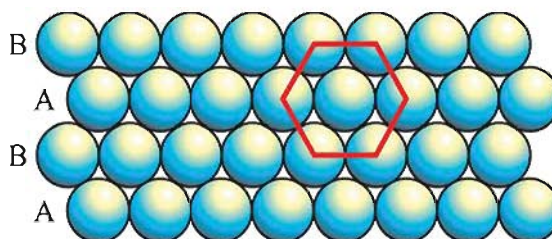


Fig 1.8(b) Hexagonal close packing of spheres in two dimensions

(3) Three dimensional close packing : All real structures or configurations we see are all three dimensional structures. Such a structure is like the arrangement of each stack in the structure. i.e. square close packing or hexagonal close packing. Now, we will study how close packing occurs in third dimension.

(i) Three dimensional close packing from two dimensional square close packing : If we arrange the stack as A and then put the second stack exactly on other sphere as on A, the spheres of first A stack and the spheres of second A stack will be exactly on the sphere of A. As shown in figure 1.9 they will remain completely and equally arranged horizontally as well as vertically.

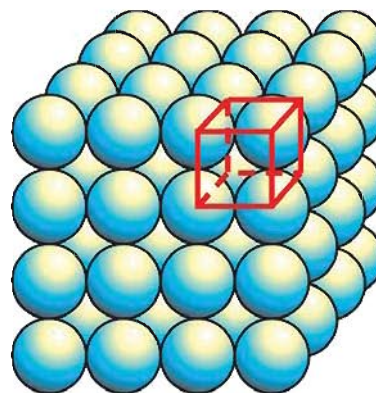


Fig. 1.9 Simple cube lattice formed by AAA...arrangement

If we call the first stack as A, then, all the stacks will be of same type i.e. AAAA....type stack. The lattice structure obtained this way is called simple cubic lattice structure and only one primary cubic unit cell is there in the unit cell.

(ii) Formation of three dimensional close packing structure from two dimensional hexagonal packing structure : Three dimensional close packing can be formed by placing one layer on the other.

(a) Arranging second layer on first layer : Suppose, we arrange the spheres of the second layer on the voids in the first layer A possessing two dimensional close packing, here the spheres are aligned differently and so we will call it layer B, which is shown in fig 1.10

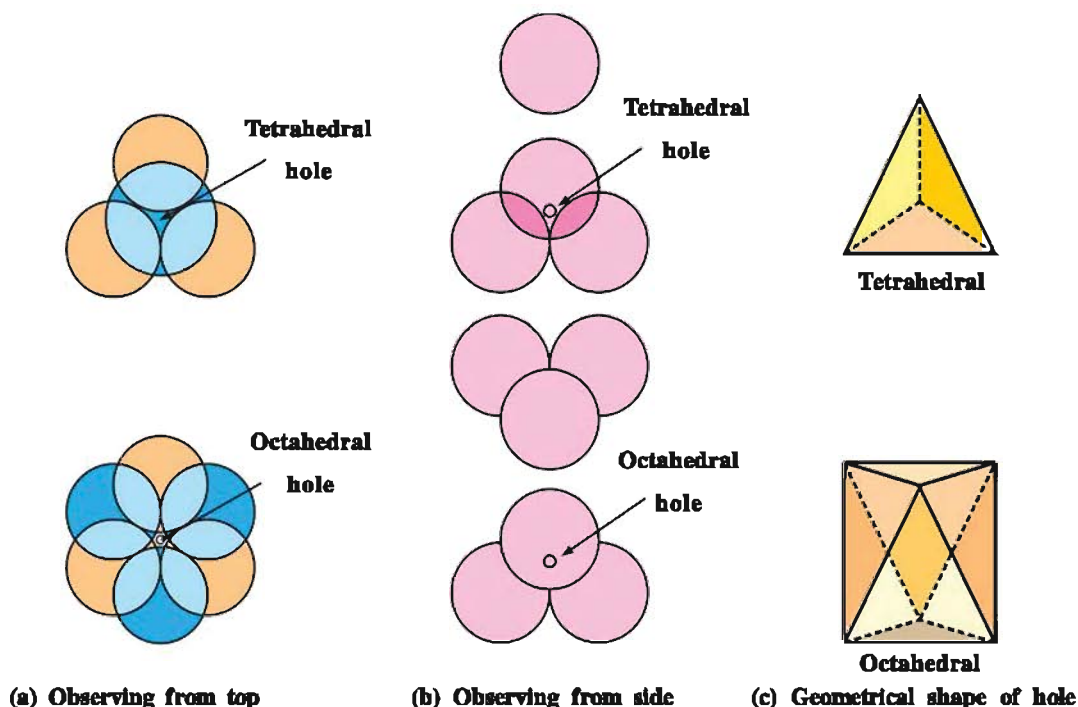


Fig 1.10 Tetrahedral and Octahedral Voids

It is clear from the figure that the triangular voids of the first layer are not completely covered by the spheres of second layer. Hence, different arrangements are possible. When the spheres of second layer are aligned on the voids of the first layer, or if it is reverse, then tetrahedral voids are formed. These voids are called **tetrahedral voids** because if the centres of the four spheres are joined, construction of tetrahedron takes place.

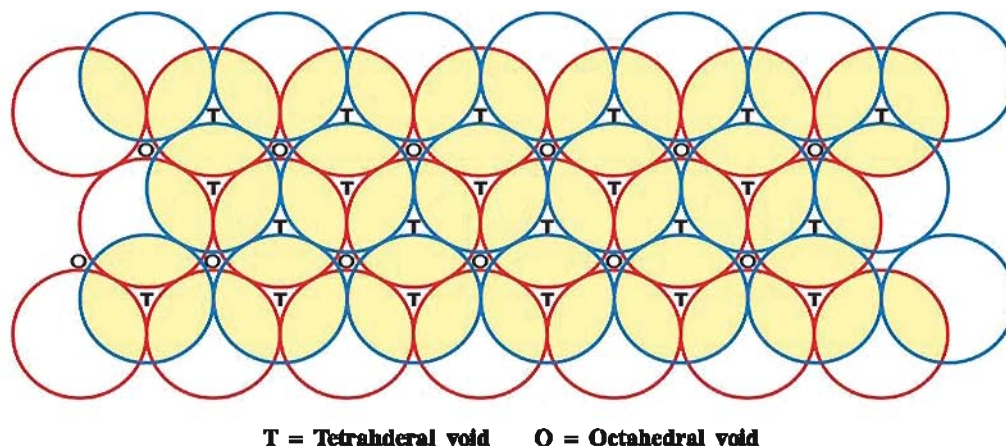


Fig 1.11 A stack of two layers of close packed spheres and voids generated in them

They are shown as T in the figure 1.11. In other places, the triangular voids of second layer are aligned as the triangular voids on the first layer their triangular shapes do not overlap. One of them indicates the triangular upper side and the second indicates towards lower side. Such voids are called **octahedral voids**. In figure 1.11 they are shown by symbol O. The number of these two types of void depends on the number of spheres of close packing.

Suppose,

The number of spheres of close packing is N.

The number of octahedral voids formed = N

The number of tetrahedral voids = 2N

Thus the number of tetrahedral voids is twice the number of octahedral voids.

(b) Alignment of third layer on the second layer : Now, suppose if we place third layer on the second layer, then there are two possibilities

(i) Covering tetrahedral voids : The tetrahedral voids of second layer will be covered by the spheres of third layer. In this situation the spheres of third layer will exactly be on the spheres of the first layer. Hence, there is repetition of the stacks formed alternately. It can be called ABAB....type stack and this structure is called **hexagonal close packing (hcp)** which is shown in fig 1.12

This type of arrangement is observed in many metals like zinc, magnesium etc.

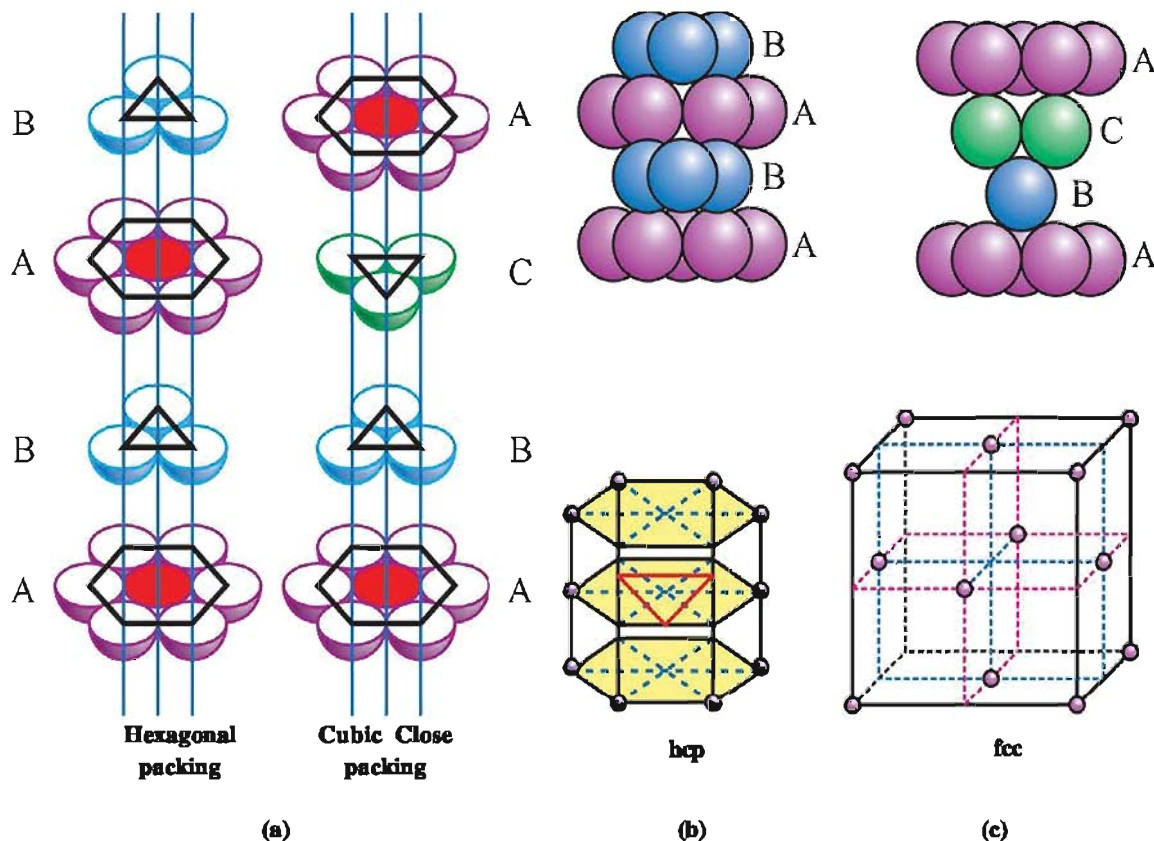


Fig 1.12 (a) Hexagonal cubic close packing exploded view showing stacking of layers of spheres (b) four layers stacked in each case and (c) geometry of packing

(ii) **Covering octahedral voids :** In this type of structure, the third layer is placed on the second layer in such a way, that the spheres of the third layer cover the octahedral voids of second layer. By doing this type of arrangement, the spheres of the third layer do not align exactly with the spheres of first layer. This arrangement can be said to be of C-type. Now, when the fourth layer is arranged, the spheres of this layer are exactly in alignment with spheres of first layer which is shown in figures 1.13. Hence, this stack is of ABCABC.....type and this type is called **cubic close packing (ccp)** or **face centred cubic (fcc)** structure. Metals like copper and silver crystallise in this type of structure.

The close packing arrangement in these two types is of maximum efficiency and about 74% of space (volume) is occupied by their crystals. It is in contact with 12 spheres and so the co-ordination number is 12 in both the constructions.

1.6 Tetrahedral and Octahedral Voids

We have learnt about tetrahedral and octahedral voids during the study of close packing structure. Tetrahedral and octahedral voids are shown in figure 1.11. It is difficult to show three dimensional figures in books but if we study with the help of models, it will be more clear.

Let us think about formula of compound and the number of voids associated in it. As seen earlier, ccp or hcp structures are formed due to close packing and two types of voids are obtained. During formation of lattice, the number of tetrahedral voids are double the number of octahedral voids. In ionic compounds the size of anion is more than that in cation. Big anions take part in close pack structure, while cations arrange in the voids. If the ions are smaller in size than the void, they are arranged in tetrahedral void and if larger then they are arranged in octahedral voids. All the tetrahedral and octahedral voids are not occupied. Only a certain fraction of the total voids is occupied. This matter depends on the formula of the compound, which will be clear from the following examples.

Example 1 : A compound is formed of two elements A and B. The atoms of element B (anion) forms cubic close packing and atoms of element A occupies all the octahedral voids. What will be the formula of the compound ?

Solution : Element B forms cubic close packing and so the number of octahedral voids will be equal to number of atoms B. All the octahedral voids are occupied by all the atoms of A and so their number will be equal to number of B. Thus elements A and B will be in 1:1 proportion; so the formula of compound will be AB.

Example : 2 The atoms of element Y form hexagonal close packing and the atoms of element X occupies $\frac{2}{3}$ portion of the number of tetrahedral voids. Write the formula of the compound formed by X and Y.

Solution : The number of tetrahedral voids formed is double the number of atoms of element Y and only $\frac{2}{3}$ part is occupied by atoms of element X. Hence, the ratio of atoms of X and Y will be $\frac{2 \times 2}{3} : 1$ or $4 : 3$. Hence the formula of the compound will be X_4Y_3 .

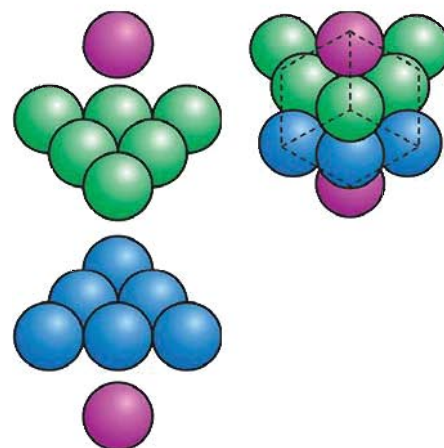


Fig 1.13

- (a) ABC ABC.... arrangement of layers when Octahedral void is covered
(b) cubic closed packing (ccp) or face centred cubic (fcc) structure.

To locate the positions of tetrahedral and octahedral voids : We have studied that there are tetrahedral and octahedral voids in the close packing structures. We will locate the positions of voids in cubic close packing (ccp) and face centred close packing (fcc).

(a) To locate positions (sites) of tetrahedral voids : Let us take ccp or fcc and divide it in eight small cubes as shown in figure 1.14. Atoms are there on the alternate corners of each of these small solids. In each small cube, total four atoms are there. If we join them with each other, they form regular tetrahedron. Hence, there will be one void in each in the structure of each unit cell (ccp) in each of the small atoms. We know that there are four atoms in each ccp structure. Hence, the number of voids is double the number of atoms.

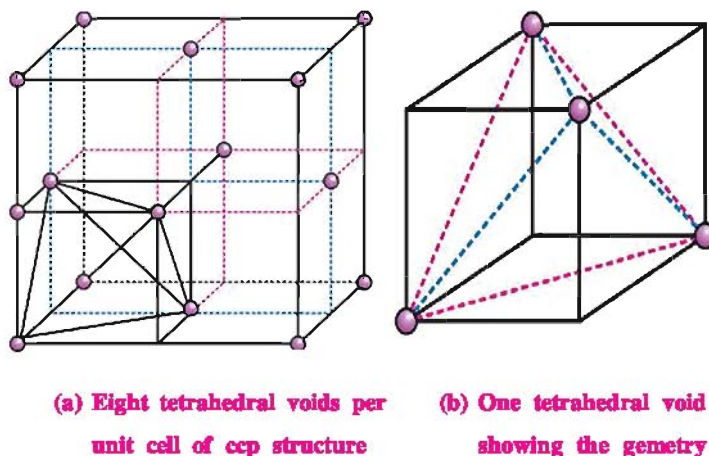


Fig. 1.14

(b) To locate positions (sites) of octahedral voids : Again we take the unit cell of cubic close packing (ccp) or face centred close packing (fcc). The body centre C of solid is not occupied but it is surrounded by atoms on six faces. If these face centres are joined octahedral structure will be formed. In this unit cell, there is one octahedral void on the centre of its each twelve edges. It is surrounded by six atoms, in which three to each unit cell are on corners and one in the centre of face and three on the one-two nearby unit cells. As the unit cell is shared by each edge of solid by four near by unit cells; accordingly octahedral void will get its location on its position.

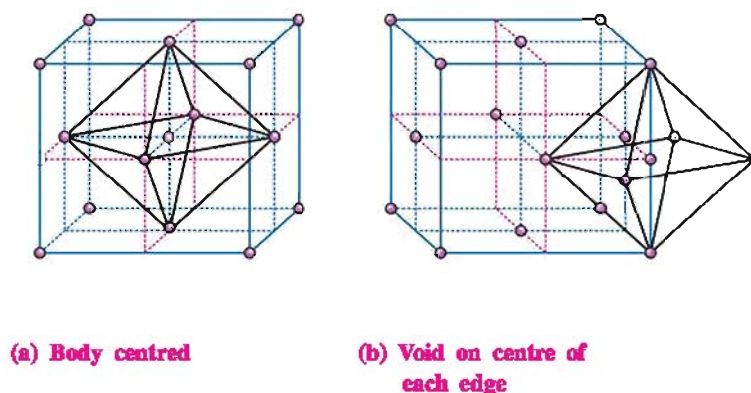


Fig. 1.15 Location of octahedral voids per unit cell of ccp or fcc structure (a) at the body centre of the cube and (b) at the centre of each edge (only one such void is shown)

Each void has only $\frac{1}{4}$ of any one cell. Thus, in cubic close packing.

Octahedral void on the body centre of solid = 1

12 Octahedral voids arranged on each edge and four unit cells = $12 \times \frac{1}{4} = 3$

Total number of octahedral voids = $1 + 3 = 4$. As we know, that in cubic close packing structure each unit cell possesses four atoms. Hence the number of octahedral voids will be equal to that number.

1.7 Calculation of number of atoms in unit cell

Each corner of a unit cell in a crystal is associated jointly with eight unit cells. Hence, its each edge of the side is associated with four sides of the unit cell and each face with two unit cells. Hence, for the structure of the crystal if atoms, molecules or ions are associated with it, then their $\frac{1}{8}$ part is occupied by corners, $\frac{1}{4}$ part by edges of sides and $\frac{1}{2}$ part by faces. The particles on corner of unit cell and the particles combined jointly with many other cells. Hence, the calculation of number of atoms can be shown as below :

8 unit cells in simple cubic unit cell, and 8 atoms of corner are shared.

Hence,

$8 \text{ corners} \times \frac{1}{8} \text{ atom per cell} = \frac{8}{8} = 1 \text{ atom}$. Thus, there is only one atom in each unit cell in simple solid crystal.

In body centred cubic unit cell, $8 \text{ corners} \times \frac{1}{8} \text{ atom per unit cell} = \frac{8}{8} = 1$ and one atom in the body centre of each unit cell; So total number of atoms will be $1 + 1 = 2$. Thus there are two atoms in each unit cell of body centred cubic cell.

In face centred cubic unit cell $8 \text{ corners} \times \frac{1}{8} \text{ per unit cell} = \frac{8}{8} = 1$ and addition 6 face centred atom $\times \frac{1}{2} \text{ atom per unit} = 3$, so total number = $1 + 3 = 4$ atoms.

Thus in face centred cubic unit cell there are 4 atoms per unit cell of crystal. The above calculations can be presented in the following table 1.4.

Table 1.4 Type of unit cell and Number of Atoms

Sr.	Type of unit cell	Number of atoms on the corner	Number of atoms in the face	Number of atoms in body center	Total atoms
1.	Simple cube	$8 \times \frac{1}{8} = 1$	0	0	1
2.	Body centred (bcc) cube	$8 \times \frac{1}{8} = 1$	0	1	2
3.	Face centred (fcc) cube	$8 \times \frac{1}{8} = 1$	$6 \times \frac{1}{2} = 3$	0	4

1.8 Point defects and their types

Before studying about the point defects let us think whether crystal is perfect or there are any imperfections. It is determined according to one estimate that in 1 mole constituent particles (6.022×10^{23} particles) there are 10^6 defects of constituent particles in the arrangement. This value

may be negligible in comparison to 6.022×10^{23} but its effect on properties, structure etc. of the crystal is definitely observed. These defects increase with increase in temperature. Thus, the crystal that appears to be ideal, has got imperfections in the arrangement of the particles and structure of the crystal. Suppose, we think the crystal to be the smallest form i.e. if we consider single crystal, even then there is probability of defects. To obtain single crystal is difficult but not impossible; but when a solid is prepared from such single crystals, there is increase in the number of defects in the solid. In the earlier standards, you have studied that the hot solution should be cooled slowly during crystallisation because there is possibility of defects to remain if it is cooled very fast. Even though you cool the solution slowly and obtain single crystal the defects remain.

It is suggested in the definition of third law of thermodynamics that the entropy of a completely pure crystalline substance is zero at absolute zero. You must have read somewhere in physics or chemistry that it is impossible to obtain absolute zero temperature. Hence, it can be said that even if we assume completely pure crystalline substance at absolute zero, there is probability of defects. With the increase in temperature, there is effect on the crystal and because of this there is displacement in position or randomness is created and the number of defects increases.

Thus, the defect can be defined as, the irregularity in the structure of crystal due to particles is the defect. There are two types of such defects. (1) Point defect and (2) Line defect. The point defect is due to the irregularity around the atoms or points in the ideal structure of crystalline substance, while line defects are due to the irregularity or deviation in the ideal arrangement of the entire rows of lattice points. Both these types of defects are called crystal defects.

The types of defects are two - (A) Stoichiometric and (B) Non-stoichiometric. In addition to these two types of point defects, there is third type of defect (C) Impurity defect. We shall now study them in detail.

(A) Stoichiometric defect : This is such a point defect that it does not disturb the stoichiometry of the solid. It is called an **intrinsic** or **thermodynamic** defect. It changes with temperature. This is also of two types (i) Vacancy defect and (ii) Interstitial defect.

(i) Vacancy defect : Some of the sites of the lattice are vacant i.e. there is vacancy instead of particle. Such a crystal is called a crystal having vacancy defect (Fig 1.16) Because of this, there is decrease in density of the substance because the number of atoms in unit cell decreases. If the substance is heated, such defects develop.

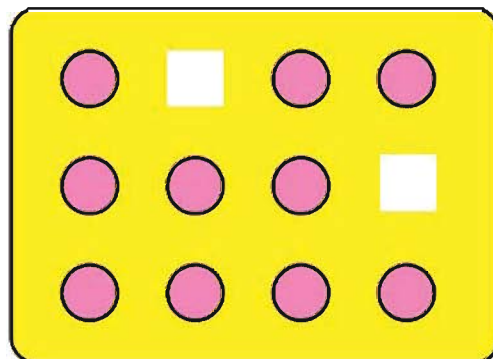


Fig. 1.16 Vacancy defect

(ii) Interstitial defect : In some crystals when the particles like atom or molecule get arranged in the interstitial sites of the crystal it is called that the crystal possesses interstitial defect. This defect increases the density of the substance because the number of atoms for unit volume increases (fig 1.17).

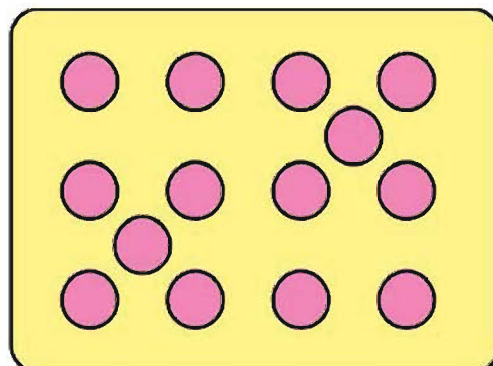


Fig. 1.17 Interstitial defect

Both the types of defects as shown above are exhibited by non ionic solids. Ionic compounds have always to maintain the electrical neutrality. This type of defect has two types (a) Schottky defect (b) Frenkel defect.

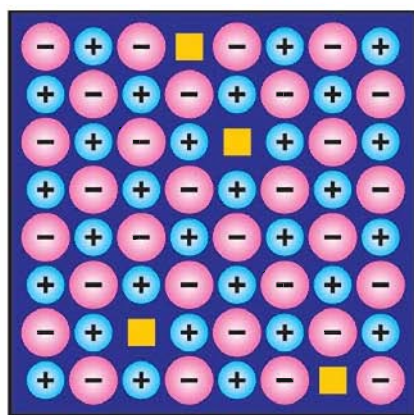


Fig. 1.18 Schottky defect

whose co-ordination numbers are high, show Schottky defect. e.g. NaCl, KCl, AgBr. It is necessary to note that AgBr shows both the types of defects- Schottky and Frenkel defects.

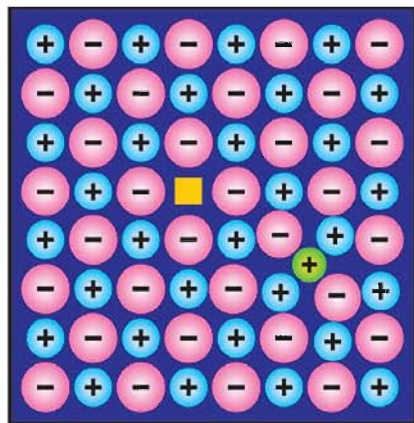


Fig. 1.19 Frenkel defect

(B) Non-stoichiometric defect : In the defects that we have studied, there was no disturbance in the stoichiometry of elements but many inorganic solids are known which possess non-stoichiometry. The constituent elements in that are in non-stoichiometric ratio. The reason for this is the defect in the crystal structure. There are two types of this defect :

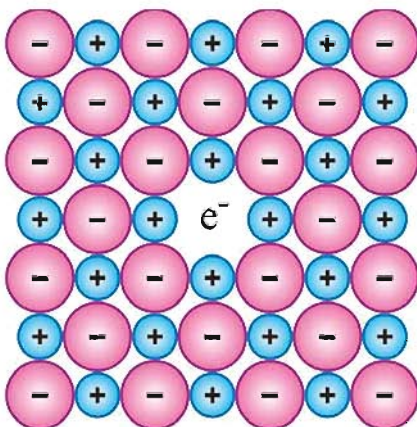


Fig. 1.20 F-centre in crystal

(a) Schottky defect : This defect is originally the vacancy defect in the ionic solid. The number of cations and anions either not available or are not arranged in the crystal will be same, because the crystal even after the defects is electrically neutral. This is shown in figure 1.18.

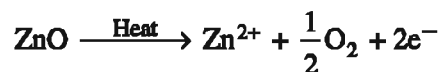
Schottky defect produces decrease in density of substance as it is in vacancy defect. The number of this defect is very significant. As mentioned earlier, there are approximately 10^6 Schottky defects per mole of NaCl crystal at room temperature. There are approximately 10^{22} ions in 1cm^3 volume. Hence, there is one Schottky defect per 10^{16} ions approximately. The cations and anions in ionic solids whose sizes are same or

(b) Frenkel defect : This defect is also shown by ionic solids. Generally the smaller ion (cation) displaces from its general (original) site and arranges in the interstitial site in the middle. Hence it creates vacancy defect and produces interstitial defect at its original sites. Frenkel defect is also called dislocation defect. There is change in the place of particle. There is no increase or decrease of them and so density of the solid does not change. Frenkel defect is observed in such ionic solid substances in which there is large difference between the ionic sizes of cations and anions. e.g. ZnS, AgCl, AgBr, AgI. The reason for this is that the ions Zn^{2+} and Ag^+ are of smaller size. This defect is seen in solid substances whose co-ordination numbers are low.

(i) Metal excess defect : Metal excess defect due to the vacancy by anion : Alkali halides like NaCl and KCl show this type of defect. Suppose sodium chloride is heated in presence of vapour of sodium, sodium deposits on the surface of the crystal. Hence, Cl^- ions diffuse in the layer of the crystal and combines with sodium atom and forms NaCl. It is due to the loss of electron in formation of Na^+ from Na atom. The electrons released diffuse in the crystal and reach the site of the anion. Because of this, there is increase of sodium in the crystal. The anionic sites occupied by unpaired electrons are called **F-centres**. (where F- is for the German word Farbenzenter indicating the coloured centres). Hence, the crystal of NaCl possesses yellow colour. When the visible light falls on the crystal of NaCl, the energy is absorbed and electron

is excited. As a result the yellow colour appears. Similarly, excess of lithium in lithium chloride crystal shows light pink colour and excess of potassium in KCl shows the violet colour due to excitation.

Excess metal defect due to presence of extra cations on the interstitial sites : Zinc oxide is a white coloured substance at room temperature. It becomes yellow when heated because it loses oxygen.



Now, Zn^{2+} increases in the crystal and so its formula will be Zn_{1+x}O . This extra Zn^{2+} ion will be arranged in interstitial site and electron will be arranged in the neighbouring interstitial site.

(ii) Metal deficiency defect : It is very difficult to prepare so many solid substances according to their stoichiometry and they possess less number of metal atoms than the calculated ones according to stoichiometry. The well known example in this is of FeO which is mostly in the form showing stoichiometry $\text{Fe}_{0.95}\text{O}$. In fact, it is in the range of $\text{Fe}_{0.93}\text{O}$ and $\text{Fe}_{0.96}\text{O}$. In the crystal FeO, some of Fe^{2+} ions are found missing and the decrease in positive charge is satisfied by Fe^{3+} ions.

(iii) Displacement defect : Some times the atoms in the lattice of the crystal are exchanged mutually from their sites to the sites of the other lattice of the crystal and produce displacement. In such cases displacement defect is observed and displacement randomness is produced. This type of defect is observed in the alloys of copper and silver.

(C) Impurity defect : Suppose we add little amount of SrCl_2 to molten NaCl, and then crystallise, then in the crystal some sites of Na^+ are occupied by Sr^{2+} (Fig.1.21) each Sr^{2+} ion displaces two Na^+ ion. It occupies one site and second site remains vacant. Thus the number of cationic vacancy is same as the number of Sr^{2+} ions. The other examples is the solid solution of CdCl_2 and AgCl .

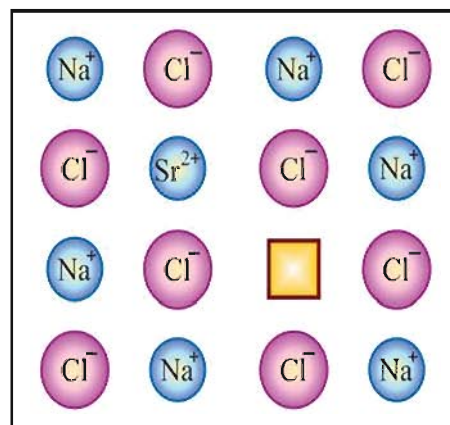


Fig. 1.21 Entry of Na^+ from NaCl by Sr^{2+} in vacancy defect

Band theory in Metals : It is accepted in the band theory that there are two bands in a metal or substance. One valence band in which the valence electrons of the substance are included. The second band over this band is called conduction band. For the electrical conductance of a substance, there must be electrons in the conduction band. The space between these two bands is called **energy gap**. The distance of this energy gap is more important for the electrons of valence band to go to conduction band. As the energy gap is less in metals, the electrons can easily go to conduction band from valence band. Hence, the conduction of electricity in metals is very easy and so they are called good conductors. In some substances, the distance of energy gap is more and so in normal conditions the electrons from valence band are not able to go to conduction band and so conduction of electricity does not occur. Hence, they are called non-conductors. Non-metals are mostly non-conductors. The situation in between these two is that of semiconductors. There are four electrons in the valence band of semimetal like silicon. They are not free. Hence, silicon under normal conditions, does not conduct electricity and is a non-conductor but if the temperature is increased or special types of radiations are impinged on it, the electrons of the valence band go to conduction band and conduction of electricity takes place. The vacant places created in the valence band are occupied by other electrons of the substance. These electrons go in less

proportion and so under definite conditions they become electrical conductor and so they are called semiconductors. Thus, conductor; non-conductor and semiconductor can be explained on the basis of band theory and distance between conductance band and valence band-energy gap.

1.9 Electrical and Magnetic effects of defects-Band theory in metals

A great range is observed in electrical conductances of solid substances. The solid substances are showing electrical conductivities from about 10^{-20} to $10^7 \text{ Ohm}^{-1} \text{ m}^{-1}$. Hence, the solid substances can be divided into three sections on the basis of their electrical conductivities. (1) Electrical conductors (2) Electrical non-conductors (c) Semi- conductors.

(1) Electrical conductors : The substances whose electrical conductivities are in the range of 10^4 to $10^7 \text{ Ohm}^{-1} \text{ m}^{-1}$ are conductors or good conductors. Generally metals are included in such solid substances.

(2) Electrical non-conductors : The solid substances, whose electrical conductances are very less i.e. 10^{-20} to $10^{-10} \text{ Ohm}^{-1} \text{ m}^{-1}$ are called electrical non-conductors(insulators).

(3) Electrical semiconductors : The solid substances whose electrical conductances are in the range 10^{-6} to $10^4 \text{ Ohm}^{-1} \text{ m}^{-1}$ are called electrical semiconductors.

Conduction of Electricity in Metals : The conduction of electricity in conductors is either by electrons or through ions. Metals conduct electricity by electrons while electrolytes conduct electricity through ions. Metals conduct electricity in solid or molten states and their conductance depend on the number of electrons in the valence shells available in their atom. The atomic orbitals which form molecular orbital are very near to each other that a band is formed. It overlaps with this half filled band or the valence band which is just above the conductance band. When electric current is passed the electrons conduct it easily and the metal shows electrical conductance.

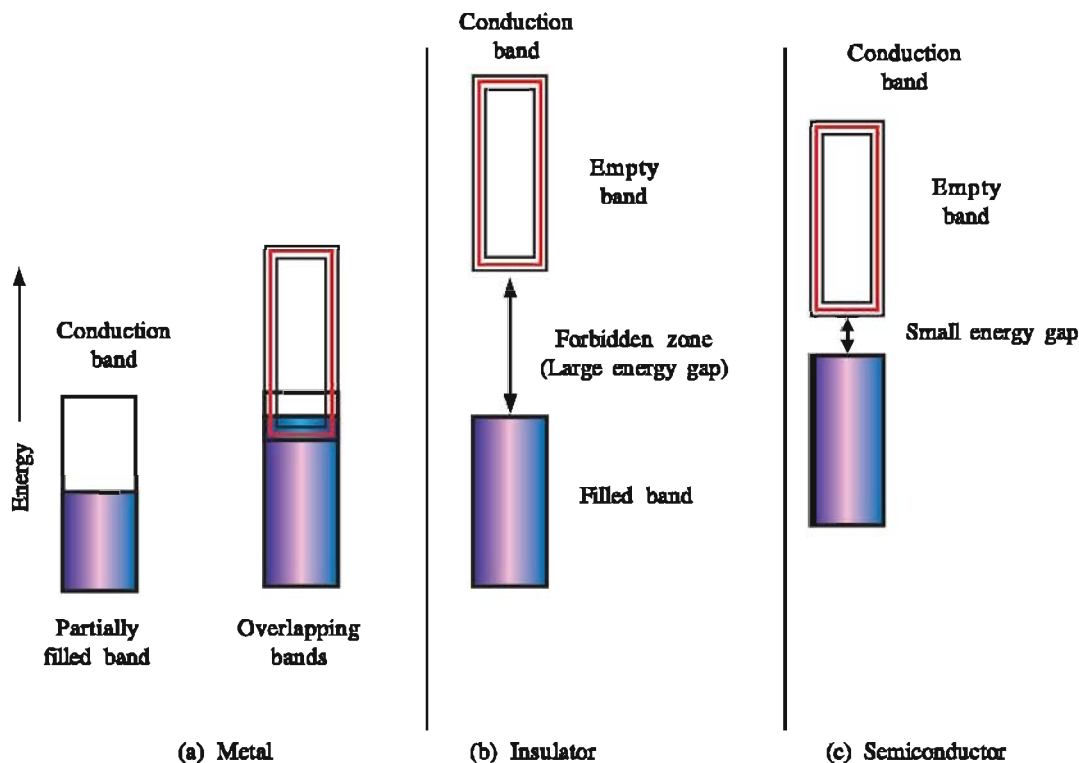


Fig 1.22 Distinction in (a) Metals (b) Insulators and (c) Semiconductors

If the vacant space (gap) is more between the filled valence band and the upper unfilled band (conduction band) the electrons cannot jump into conduction band and so the substance conducts very less amount of electricity or it does not conduct and so it acts as a non-conductor.

Electrical conductance in Semiconductors : In the case of semiconductors, the distance between valence band and conduction band is less (Fig.1.22). Hence, some of the electrons can go from valence band to conduction band, and so it will conduct less amount of electricity. The electrical conductivity of semiconductor increases with increase in temperature because, the energy obtained by increase in temperature can make the electrons jump from valence band to conduction band. Hence, the conduction of electricity becomes easy and more. Thus, semiconductor may appear as non conductor at normal temperature but with increase in temperature it appears to be a good conductor. Elements like silicon and germanium show this type of behaviour and so they are called intrinsic semiconductors. The electrical conductance of such semiconductors is so low that its practical use cannot be made, but if any suitable substance in some suitable proportion is added to it as an impurity, its conductance can be increased. This process is called '**doping**'. This doping can be carried out by adding electron rich and electron deficient elements (in comparison to the intrinsic semiconductors-silicon and germanium). These impurities can be known as electron defects in them.

We will take two general examples. Suppose a semiconductor like silicon or germanium (in which there are four electrons in valence shell) is doped with electron rich element e.g. P or As (in which five electrons are there in valence shell) then, we obtain semiconductor with one excess electron. As electron is more and it possesses negative charge, so the doped semiconductor obtained is called **semiconductor of negative type or n-type**.

Similarly, if elements like B, Al or Ga (which have three electrons in their valence shell) are doped with the silicon or germanium, there will be deficiency of electron. Such doped semiconductors are called **positive type semiconductor or p-type semiconductors**. You must have studied in detail about semiconductors in physics.

n and p-type semiconductors are used in preparation of many electronic parts or components. Diode is the combination on n-type and p-type semiconductors which is used as rectifiers. It is used in transistors. By combination of semiconductors of the type pnp or npn can be prepared having different properties. With the help of the photodiode, light energy can be converted to electricity. Semiconductors like gallium arsenide (Ga As) have created a revolution by things having such semiconductors because of their very fast response.

It is interesting to know that transition metals show notable differences in electrical conductances, Oxides like TiO , CrO_2 , ReO_3 behave like metals. ReO_3 possesses conductance and appearance like metallic copper. Other oxides like VO , VO_2 , VO_3 and TiO_2 show metallic properties or nonconductors which depend on temperature.

Magnetic properties : We know that electron possesses electric charge and it also moves. Hence, it possesses magnetic property. Electron is present in each substance and shows magnetic properties associated to some extent with them. In each atom, electron behaves like a very small magnet. Its magnetic moment can be produced from its two types of motion, one is the motion around the nucleus and the second on its own axis. Thus electron being a particle possessing electric charge and having this type of motion, it can be considered as a loop of current which possesses magnetic moment. Thus, permanent rotation and orbital magnetic moment are associated with each electron. The magnitude of magnetic moment is very small. Its measurement is done in Bohr magneton units. Its value is $9.27 \times 10^{-24} \text{ Am}^2$.

Thus, substances can be divided into five types on the basis of their magnetic properties : (1) Paramagnetic (2) Diamagnetic (3) Ferromagnetic (4) Antiferromagnetic and (5) Ferrimagnetic. We shall study all these five types.

(1) Paramagnetism : The paramagnetism is due to unpaired electrons. Paramagnetic substances are weakly attracted in presence of magnetic field. In absence of magnetic field their magnetism is removed. The paramagnetism is due to one or more unpaired electrons, because they are attracted by magnetic field. Cu^{2+} , Fe^{3+} , Cr^{3+} , O_2 etc. are the examples of such paramagnetic substances.

(2) Diamagnetism : Diamagnetism substances are weakly repelled by magnetic field. NaCl , H_2O , C_6H_6 , N_2 etc. are the examples of such substances. They are weakly attracted or repelled of magnetic field and are in opposite directions. The substances in which all the electrons are paired or there is no unpaired electrons, show the diamagnetic property. The pair formed by the spin of electrons in corresponding opposite directions cancel the magnetic moment and so they lose the property of magnetism.

(3) Ferromagnetism : Substances like iron, cobalt, nickel, gadolinium, CrO_2 etc. possess very strong attraction in presence of magnetic field. Such substances are called ferromagnetic substances. In addition to strong attraction, these substances become permanently magnetic. In solid state, metal ions of ferromagnetic substances are arranged as Domains in a small area, collectively in a group. Each of such domains acts as a small magnet. In the nonmagnetic piece of ferromagnetic substance these domains are arranged randomly and their magnetic moments are cancelled. When substance is placed in the magnetic field, all the domains are oriented in the direction of magnetic field. Fig 1.23(a) and so strong magnetic effect is produced.

If magnetic field is removed, the alignment in the domain is maintained and hence ferromagnetic substances become permanent magnets.

(4) Antiferromagnetism : Substances like MnO show antiferromagnetism. The formation of their domains is similar to the ferromagnetic substances but the domains are oriented opposite to each other and so cancel the magnetic moment of each other. Fig 1.23 (b).

(5) Ferrimagnetism : When the magnetic moments of domains in substances are arranged parallel or antiparallel to each other but are in unequal number, the substance is called ferrimagnetic substance. Fig 1.23 (c).

They are more weakly attracted in comparison to ferro-magnetic substance. Substances like magnetite (Fe_3O_4), Ferrites (MgFe_2O_4) and ZnFe_2O_4 show ferrimagnetism. Such substances when heated lose ferrimagnetism and become paramagnetic.

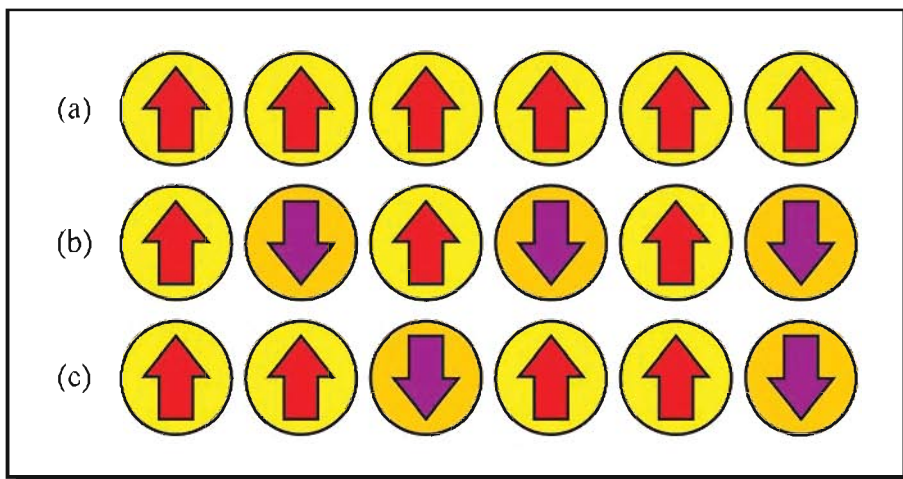


Fig. 1.23 Schematic alignment of magnetic moments in (a) ferromagnetic (b) antiferromagnetic and (c) ferrimagnetic

SUMMARY

There are three main states of matter-solid, liquid and gas. In addition to these, other two states are plasma and Bose-Einstein condensate. We have studied the solid state of matter. Solid substance has definite mass, volume and shape because the positions (sites) of their component particles are definite. They are arranged near to each other and there are strong interattraction forces. There are two main types of solids-crystalline and amorphous. In crystalline substance structure, arrangement definite melting etc. are systematic and so more information about it is given in this unit. The arrangement, of constituent particles in amorphous substances are systematic upto a small distance so they have no definite shape, and definite melting points. They can be known as supercooled liquids, while in crystalline solids, there are definite melting points, systematic arrangement, characteristic shape, etc. There is strong interaction between its component particles, they possess specific properties. The solid substances can be divided into different sections on the basis of their structure and attraction forces etc. viz. Molecular ionic, metallic, covalent etc. They all show notable differences in their properties.

The constituent particles are systematically arranged. On its basis the structure of crystal forms. The smallest particle of a crystal is called unit cell and in the crystal, these unit cells are arranged in three dimensional directions. Such an arrangement is called lattice structure. Different types of lattice structures is called Bravais lattice. Unit cell is of primitive type in which the particles are on the corners or in the centre. Face-centred, body centred and end-centred are the crystals of this type. Primitive cells are of seven types. Lattice having high efficiency because of close packing of particles, lattice is formed, in which hexagonal close packing (hcp), cubic close packing (ccp), face centred close packing (fcc) are important. Their packing efficiencies are different. It is about 54 % in ccp, about 68 % in bcp and about 74 % in fcp. Because of the arrangement of different types of crystal structure there are holes or spaces called voids. They are of two types-tetrahedral and octahedral. The number of tetrahedral voids is double the number of octahedral voids.

Crystals are not so perfect as they appear. There are imperfections in them which we call defects. These types of defects may be of different types viz. non-stoichiometric, stoichiometric, impurity, point defects etc. From these, Schottky and Frenkel defects are observed in ionic crystals. Because of the decrease in number of constituent particles in Schottky defect, there is decrease in density in Frenkel defects because the constituent particles are arranged in interstitial sites. Crystal like AgBr shows both types of the defects. By making use of such defects, some elements or constituents can be added in their places and crystals which are very useful can be obtained. It is called doping. By use of elements like aluminium or boron, pnp type semiconductor and by addition of elements like arsenic and gallium npn type semiconductors can be prepared. They can be used in transistors etc.

The crystals show different magnetic properties on the basis of the electrons present in them and their arrangement, viz. paramagnetic- in which there is effect of magnetic field and is due to unpaired electrons. In diamagnetic substances, no effect is observed of magnetic field. It indicates paired electronic configuration. In addition, metals like iron, cobalt, nickel show specific type of magnetic effect. It is called ferromagnetism. If permanent arrangement takes place due to the effect of magnetic field, ferromagnetism is observed and if no effect is observed it is antiferromagnetism.

Conductors can be divided into three types-good conductors which allow the electric current to pass through them; which do not allow electric current to pass through them called non conductors and those which conduct electricity when heated or by impingment of radiation of some special type are called semiconductors.

The conduction of electricity in substances can be explained on the basis of band theory. It can be explained on the basis of two bands- one conduction band and second valence band. Conduction band is at higher energy level than valence band. Hence the space between the two is known as energy gap. If electron can easily go from valence band to conduction band, it becomes good conductor. If electron can be sent by giving some energy (by increase in temperature), it is called semiconductor and if it is not possible to send the electrons, it is called non-conductor. In other words, it can be said that larger space difference between the two bands, more difficult it will be to send electrons from valence band to conduction band and more the nonconductor. Thus, the study of metals, ionic solids, molecular solids, covalent solids etc. and their uses from these studies, structure of crystal etc. is called 'solid state chemistry'.

EXERCISE

1. Select the proper choice from the given multiple choices :

- (1) What type of solid is sodium chloride ?
(A) Ionic (B) Molecular (C) Covalent (D) Metallic
- (2) The melting points of ionic solids are
(A) Very high (B) Normal (C) Very low (D) Abnormal
- (3) What type of solid is quartz ?
(A) Ionic (B) Molecular (C) Covalent (D) Metallic
- (4) What type of crystal structure is of silver metal ?
(A) fcc (B) Simple cube (C) bcc (D) Metallic
- (5) What is the percentage packing efficiency of simple cube ?
(A) 53.26 (B) 68.0 (C) 74.0 (D) 52.36
- (6) How many times is the number of octahedral voids as compared to tetrahedral voids ?
(A) 4 (B) 8 (C) 2 (D) 0.5
- (7) What is the number of atoms in the unit cell of body centred cube ?
(A) 2 (B) 1 (C) 4 (D) 6
- (8) What is the number of atoms in face centred cube ?
(A) 2 (B) 1 (C) 4 (D) 6
- (9) In which of the following compounds Schottky defect is present ?
(A) NaCl (B) ZnS (C) SiO₂ (D) SrCl₂
- (10) In which of the following compounds Frenkel defect is present ?
(A) NaCl (B) ZnS (C) KBr (D) SrCl₂

- (11) Which of the following compounds shows metal deficiency defect ?
(A) $\text{Fe}_{0.95}\text{O}$ (B) $\text{Fe}_2\text{O}_{3.6}$ (C) Fe_3O_4 (D) $\text{FeS}_{1.6}$
- (12) Which of the following elements is a semiconductor ?
(A) Na (B) Al (C) Fe (D) Ge
- (13) Which type of semiconductor is obtained by doping Si with B ?
(A) n-type (B) p-type (C) pnp-type (D) npn-type
- (14) With which element, the conductivity of ReO_3 is matching ?
(A) Copper (B) Zinc (C) Iron (D) Aluminium
- (15) Which of the following will be paramagnetic ?
(A) O_2^{2-} (B) Cr^{3+} (C) Na^+ (D) Cu^+
- (16) Which theory is useful in explaining electrical conductivity in conductors and semiconductors ?
(A) Pauli's principle (B) Avogadro's theory
(C) Band theory (D) Hybridisation theory

2. Write the answers of the following in short :

- (1) Write types of solids on the basis of binding forces.
- (2) Give examples of crystalline and amorphous solids.
- (3) Write the definition of unit cell.
- (4) Mention the types of packing in solids.
- (5) What is meant by tetrahedral and octahedral voids ?
- (6) Mention the number of atoms in the unit cell of different types of solids.
- (7) Write one example, of each of conductor, semiconductor and non-conductor.
- (8) What is band theory explaining conductivity ?
- (9) Write four types of magnetic properties.
- (10) What is meant by defect ? Mention the types of defects in solid.

3. Write answers of the following questions :

- (1) Explain giving examples, ionic and molecular solids.
- (2) Explain network solid compounds with example.
- (3) Write three differences of amorphous and crystalline solid substances.
- (4) Explain the types of different solids and write their characteristics.
- (5) Calculate number of atoms in body centred and face centred cubic solids.
- (6) Calculate the volume occupied by atoms in simple cube.
- (7) Explain the tetrahedral and octahedral voids by drawing diagram.

- (8) Describe the band theory explaining conductivity in semiconductor.
- (9) Explain ferromagnetism and antiferromagnetism
- (10) What is meant by doping ? Explain giving example.

4. Write the answers of the following in detail :

- (1) Explain two dimensional and three dimensional close packing.
- (2) Mention characteristics of face centred and body centred cubes.
- (3) Calculate the volume occupied by atoms in body centred cube.
- (4) Write types of defects and describe Schottky and Frenkel defects.
- (5) Write in detail about metal deficiency and non-stoichiometric defects.
- (6) Explain band theory about conductivity in solid substances.
- (7) Explain in detail, ferromagnetism, ferrimagnetism and antiferromagnetism.
- (8) Write a detailed note on energy gap, conduction band and valence band.



Unit

2

Solution

2.1 Introduction

When two or more than two substances mix and form a uniform or homogeneous mixture, such a mixture is called solution. The proportion of a component or components which is less in a solution is/are called solute and the proportion of component which is more in the solution is called a solvent. There can be one solvent and one or more than one solute components in a solution. The solution having one solute and one solvent component is called binary solution. In a homogeneous mixture the diameter of the molecular particles is 10^{-9} meter. In a homogeneous mixture the different components cannot be separated by physical methods, like filtration, sedimentation, boiling or centrifugation.

2.2 Types of Solutions

The solutions can be found in three states; Solid, Liquid and Gas. The solute and solvent can also be in three states. The physical state of the resulting solution can be decided on the basis of physical state of solute and solvent. The types of solution and their examples are given in table 2.1

Table 2.1 Types of solutions and their examples

Sr. No.	Type of solution	Physical state		Examples
		Solute	Solvent	
1.	Solid solution	Solid	Solid	Alloy formed from copper and zinc (Brass), Zinc amalgam-Zinc dissolved in mercury (Zn/Hg) adsorption of H_2 gas on Pd.
		Liquid	Solid	
		Gas	Solid	
2.	Liquid solution	Solid	Liquid	Homogeneous mixture of sugar and water. Homogeneous mixture of water and ethanol. Homogeneous mixture of CO_2 gas in water.
		Liquid	Liquid	
		Gas	Liquid	
3.	Gaseous solution	Solid	Gas	Homogeneous mixture of camphor in N_2 gas. Air containing moisture Mixture of H_2 and O_2 gas.
		Liquid	Gas	
		Gas	Gas	

When solute and solvent molecules experience attractive interaction between them, a solution is formed. For example solution is formed by strong attractive interaction between water and ethanol molecules but there is almost negligible interaction between water and benzene, their solution is not formed (it remains insoluble). Thus, solution can be formed if the solute or solvent has following characteristics.

- (i) If the number of –OH group in organic compound is more in a solute, it is more soluble in water. More the number of –OH group more is the solubility e.g., Glycerol is more soluble in water than ethanol.
- (ii) Most of the polar solutes dissolve in polar solvents. e.g., HCl in water.
- (iii) Most of the non-polar solutes dissolve in non-polar solvents. e.g., Napthalene in benzene.
- (iv) Most of the ionic solutes are soluble in water because they are ionic even in solid state. e.g., NaCl in water.

If water is the solvent in the solution, the solution is known as **an aqueous solution**. If water is not the solvent, the solution is known as **non-aqueous solution**. In a non-aqueous solution, generally benzene, ether, carbon tetrachloride etc. are used as non-aqueous solvents.

2.3 Units of Concentration

The quantitative proportion of solute and solvent are different in different solutions. The amount of solute in a unit volume of solution or unit weight of solvent is called **concentration of solution**. There are different ways to express concentration of solutions. Normality formality, molarity, molality mole-fraction, weight-fraction (% W / W) are units of concentration which you have studied in unit 1.9 of Semester-I. You will study some other units of concentration in this unit.

(1) Formality : Ionic compounds are in ionic form even in the solid state and not in molecular form. Hence formula mass is taken instead of molecular mass and so the concentration is known as formality. The sum of the atomic masses of the atom, in the proportion formula of the compound is called its formula mass. e.g. compounds like potash alum, the molecular formula of alum is $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$; hence its molecular mass will be 948 gram mole^{-1} the proportion formula of alum is $KAl(SO_4)_2 \cdot 12H_2O$ and so the value of its formula proportion mass is 474 gram formula mass. Hence, at normal temperature **if one gram formula mass of the substance (solute) is dissolved in one litre solution it is called one formal solution and this type of concentration is called formality. It is indicated by the symbol F.**

$$\text{Formality (F)} = \frac{1000 \times \text{mass of solute (gram)}}{\text{Formula mass of solute} \times \text{volume of solution (ml)}}$$

When 474 gram potash alum is dissolved in water and the solution is made to one litre, its concentration is called one formal. Formality unit is more used in pharmacy and medicinal science disciplines.

Example 1 : Calculate the formality of solution in which 948 gram potash alum is dissolved in 5 litre solution.

Solution : The formula mass of potash alum is 474 gram $(\text{formula mass})^{-1}$.

$$\begin{aligned} \text{Formality of potash alum (F)} &= \frac{1000 \times \text{mass of solute (gram)}}{\text{Formula mass of solute} \times \text{volume of solution (ml)}} \\ &= \frac{1000 \times 948}{474 \times 5000} = 0.4 \text{ F} \end{aligned}$$

The formality of this potash alum solution will be 0.4 F

(2) Volume percentage (% V / V) : The volume of solute (ml) dissolved in 100 ml solution, is expressed as volume percentage (% V / V). Such a solution is called, percent proportion with reference to the volume of solute.

Mathematically it is written as below :

$$\% \text{ V/V} = \frac{100 \times \text{volume of solute}}{\text{volume of solute} + \text{volume of solvent}} = \frac{100 \times \text{volume of solute (ml)}}{\text{volume of solution (ml)}}$$

For example 10% V/V solution of ethanol in water means 10 ml ethanol dissolved in water and made the volume of solution equal to 100 ml. Generally **solution in which solute and solvent both are in liquid form gives liquid solution. The concentration of such solution is indicated by this unit.**

Example 2 : Calculate the % V / V of a solution in which 200 ml ethanol is dissolved in 2 litre aqueous ethanol solution.

Solution : 2 litre aqueous ethanol solution means 2000 ml aqueous solution.

$$\text{Now, } \% \text{ V / V} = \frac{100 \times \text{volume of ethanol (ml)}}{\text{volume of solution (ml)}} = \frac{100 \times 200}{2000} = 10 \%$$

The concentration of aqueous ethanol solution is 10% V/V.

Example 3 : How many ml of kerosene is required to prepare 5 litre of 15% V/V kerosene in petrol solution ?

Solution : 5 litre solution = 5000 ml solution

$$\text{Now, } \% \text{ V/V} = \frac{100 \times \text{volume of kerosene (ml)}}{\text{volume of solution (ml)}}$$

$$\therefore 15 = \frac{100 \times \text{volume of kerosene}}{5000}$$

$$\text{Volume of kerosene} = \frac{15 \times 5000}{100} = 750 \text{ ml}$$

\therefore 750 ml kerosene will be required to prepare 15% V/V 5 litre solution.

(3) Mass by volume percentage (% W/V) : The mass of solute dissolved in 100 ml solution is called mass by volume percentage (% W/V). Such a solution is called percent weight proportion with reference to the mass of solute. Mathematically, it is written as below :

$$\% \text{ W/V} = \frac{100 \times \text{mass of solute (gram)}}{\text{volume of solution (ml)}}$$

For example 5% W/V aqueous solution of sugar means 5 gram sugar is dissolved in 100 ml solution. Generally the concentration of solutions is expressed by this unit in pharmacy and medicinal fields.

Example 4 : How many gram of sugar will be required to prepare 5% W/V 2 litre aqueous solution ?

Solution : 2 litre solution = 2000 ml solution

$$\text{Now, } \% \text{ W / V} = \frac{100 \times \text{weight of sugar (gram)}}{\text{volume of solution (ml)}}$$

$$\therefore 5 = \frac{100 \times \text{weight of sugar}}{2000}$$

$$\therefore \text{The weight of sugar} = \frac{5 \times 2000}{100} = 100 \text{ gram.}$$

100 gram of sugar will be required to prepare 5% W/V 2 litre solution.

Example 5 : Calculate the % W/V, containing 200 gram urea dissolved in 5 litre solution.

Solution : 5 litre solution = 5000 ml solution.

$$\% \text{ W/V} = \frac{100 \times \text{weight of urea (gram)}}{\text{volume of solution (ml)}} = \frac{100 \times 200}{5000} = 4 \%$$

The concentration of urea solution will be 4 % W/V.

(4) Parts per million : (ppm) : Some times the amount of the solute in solution is very much less, and so the concentration is expressed as parts per million. (ppm) viz. Pollutant in pollution of air, the amount of O₂ gas dissolved in sea-water pollutants in pollution of water etc. are expressed by this unit. Parts per million can be expressed by three different ways as parts per million by mass to mass, parts per million by mass to volume and parts per million by volume to volume.

Parts per million by mass to volume : The amount of solute in milligram dissolved, in one litre solution is called parts per million by mass to volume.

$$\text{parts per million by mass to volume} = \frac{\text{amount of solute (mg)}}{\text{amount of solution (litre)}} \quad (2.1)$$

So the unit of parts per million by mass to volume can be written as mg litre⁻¹

Now to express the amount of solute in gram and volume of solution in ml in equation (2.1),

$$\begin{aligned} \text{Parts per million by weight to volume} &= \frac{\text{amount of solute (gram)}}{\text{amount of solution (ml)}} \times 10^6 \\ &= \frac{\text{amount of solute (micro gram)}}{\text{volume of solution (ml)}} \end{aligned} \quad (2.2)$$

So the unit of parts per million by mass to volume can also be written as micro gram ml⁻¹

Example 6 : Calculate the parts per million by mass to volume for 2 litre solution in which 2×10^{-6} kg sulphur is dissolved.

Solution : 2 litre solution = 2×10^3 ml

mass of sulphur (solute) = 2×10^{-6} kg = 2×10^{-3} gram

\therefore parts per million by mass of volume = $\frac{\text{amount of solute (gram)}}{\text{volume of solution}} \times 10^6$

$$= \frac{2 \times 10^{-3}}{2 \times 10^3} \times 10^6 = 1$$

Parts per million by mass to volume for solution will be 1 micro gram ml^{-1}

With the change in temperature the values of molality, mole fraction, percentage by mass, parts per million by mass to mass are not changed because these units do not include the term volume which depends on temperature; while with the change in temperature the molarity, normality, percentage by volume to volume, percentage by mass to volume, formality, parts per million by volume to volume, parts per million by mass to volume values are changed; because these units include the term volume which depends on temperature.

2.4 Solubility of Gases (Solubility of Gaseous Solute in Liquid Solvent)

At a given temperature and pressure the maximum amount of gaseous solute that can be dissolved in a specified amount of solvent is called solubility of gaseous solute. Factors which effect the solubility of gaseous solute in liquid solution formed by homogeneous mixture of gaseous solute and liquid solvent are given as under.

(i) Nature of gaseous solute and the solvent : The solubility of gases like H_2 , O_2 and N_2 are less in water but their solubility is more in ethyl alcohol; also the solubility of gaseous solute like H_2S and NH_3 is more in water, while their solubility is less in ethyl alcohol. So the solubility depends on the nature of gaseous solute and then also the nature of solvent.

(ii) Effect of temperature : The solubility decreases with increase in temperature for gaseous solute in liquid solvent. Generally with increase in temperature the solute dissolved in solution bubbles out and hence, with the increase in temperature the solubility of a gaseous solute decreases. Such an effect can also be explained by Le-Chatelier principle for an equilibrium as follows.



The dissolution of gaseous solute in liquid solvent is an exothermic process. On increasing the temperature for such a reaction, according to Le-Chatelier principle the equilibrium shifts towards left hand side i.e., reverse direction. So the solubility of solute decreases.

(iii) Effect of pressure : The solubility of gaseous solute in liquid solvent increases by increasing pressure of gaseous solute present on the surface of solution. The concentration of gas dissolved in solution increases as shown in 2.1 (a) the upper part is gaseous solute while the lower part is solution obtained by dissolving gaseous solute in liquid solvent. Equilibrium is established between gaseous solute

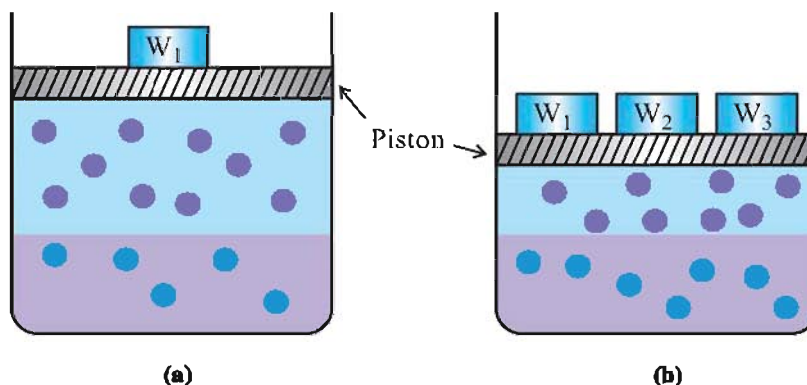


Fig. 2.1

The effect of pressure on solubility of gas. The concentration of dissolved gas is directly proportional to the pressure of gas upon the solution

and solution at temperature T_1 and pressure P_1 , and hence the rates of molecules entering into solution and the dissolved gaseous molecules leaving the solution are equal. Now as shown in figure 2.1 (b) at temperature T_1 , the pressure increases from P_1 to P_2 , the volume accommodated by gaseous solute on the surface of solution decreases and hence the number of molecules of solute in unit volume increases. So the number of gaseous molecules striking the surface of solution increases and thus increases the solubility and at the end equilibrium is established. Hence, the solubility of gaseous solute increases due to the increase in the pressure of gaseous molecules in the solution.

Henry's law : The quantitative relation between solubility of gaseous solute in liquid solvent and pressure was given by Henry in 1803. It can be expressed as "The solubility of a gaseous solute in a liquid solvent at definite temperature is directly proportional to the pressure of the gas." On the basis of this, Henry's law can be expressed as **"The solubility of a gaseous solute in a liquid solvent at constant temperature is directly proportional to the pressure of gaseous solute."**

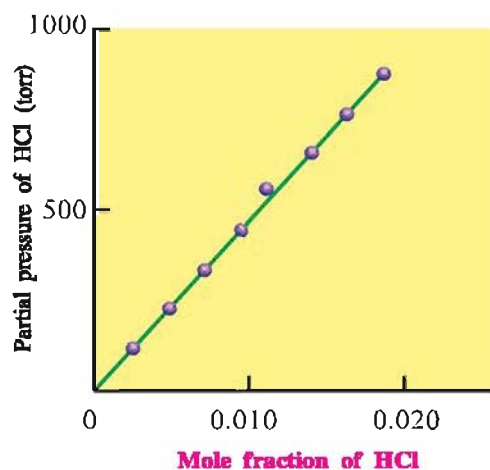


Fig. 2.2

Mole fraction of HCl in its solution in cyclohexane

Contemporarily Dalton independently concluded that the solubility of a gaseous solute in liquid solution is a function of the partial pressure of the gas. "If the mole fraction is considered for the solubility of gaseous solute then the partial pressure of a gaseous solute over the solution is directly proportional to the mole-fraction of the gaseous molecules". In the solution X is mole fraction of gaseous solute dissolved in unit volume of solvent and its partial pressure is p , then according to Henry's law it is expressed as

$$p \propto X$$

$$p = K_H \cdot X \quad \text{where, } K_H \text{ is Henry's constant.}$$

If in the solution mole-fraction of gas is X and its partial pressure is p and graph is plotted between them, the graph is a straight line as indicated in fig 2.2. The value of the slope is equal to value of K_H . The unit of K_H is bar. The values of Henry's constant are different for different gaseous solutes, at constant temperature. This indicates that K_H is a function of the nature of the gas. The values of K_H also change with change in temperature for all the gaseous solutes which are given in table 2.2

Table 2.2 Values of Henry's Constant for Some Selected Gases in Water

Gas	Temperature (K)	K_H (kbar)	Gas	Temperature (K)	K_H (kbar)
He	293	144.97	Argon	298	40.3
H ₂	293	69.16	CO ₂	298	1.67
N ₂	293	76.48	Formaldehyde	298	1.83×10^{-5}
N ₂	303	88.4	Methane	298	0.413
O ₂	293	34.86	Vinyl chloride	298	0.611
O ₂	303	46.82			

The following results can be obtained from the K_H values shown in table 2.2

- (1) The solubility of gaseous solute is lower with the higher values of K_H .
- (2) The K_H values increase as temperature increase which means the decrease in solubility of gaseous solute.

Limitations of Henry's law :

- (i) This law is applicable to the gaseous solutes which show only ideal behaviour at high temperature and low pressure.
- (ii) This law is applicable to solute which does not undergo association or dissociation when the solute is dissolved in solvent.
- (iii) This law is applicable to gaseous solute which does not form any product by the chemical reaction, when gaseous solute is dissolved in liquid solvent.

Uses of Henry's law : Henry's law is used in industrial field and to explain some biochemical reactions :

- (i) To increase the solubility of CO₂ gas in cold-drinks, soda-water, beer, champagne, the gases are filled in bottle at high pressures and then sealed.
- (ii) Due to higher partial pressure of oxygen gas entering into the lungs, it reacts with haemoglobin and forms oxyhaemoglobin. The partial pressure of oxygen gas is low in tissue. Hence, the oxygen is released from the oxyhaemoglobin itself and is useful in the utilisation of the function of cell.
- (iii) The sea-divers use the cylinders filled with mixture of 2 % dioxygen gas and 98% helium gas during the diving in sea. Nowadays a cylinder filled with 11.7 % He, 56.2 % N₂ and 32.1 % O₂ gas mixture are used.

Example 7 : Calculate the solubility of CO₂ in water in term of mole fraction if partial pressure of CO₂ is 2×10^{-8} bar at 298 K temperature, the K_H value for CO₂ is 6.02×10^{-4} bar.

Solution : According to Henry's law $p_{CO_2} = K_H \cdot X_{CO_2}$

$$\begin{aligned} \therefore X_{CO_2} &= \frac{p_{CO_2}}{K_H} = \frac{2 \times 10^{-8} \text{ bar}}{6.02 \times 10^{-4} \text{ bar}} \\ &= 3.322 \times 10^{-5} \end{aligned}$$

The solubility of CO₂ gas in water in terms of mole fraction will be 3.322×10^{-5}

Example 8 : Calculate the partial pressure of He gas over the solution, having 2.4×10^{-3} mole fraction of gas in its saturated solution at 273 K temperature. The value of Henry's constant is 6.71×10^{-6} bar.

Solution : According to Henry's law, $p_{\text{He}} = K_{\text{H}} \cdot X_{\text{He}}$

$$= 6.71 \times 10^{-6} \times 2.4 \times 10^{-3}$$

$$= 1.61 \times 10^{-8} \text{ bar}$$

The partial pressure of the gas will be 1.61×10^{-8} bar.

Example 9 : How many millimoles of CO_2 gas will dissolve when CO_2 gas is passed in 900 ml water at 298 K temperature. The value of K_{H} is 6.02×10^{-4} bar and partial pressure of CO_2 gas is 2×10^{-8} bar.

Solution : Mole fraction of $\text{CO}_2 = \frac{p_{\text{CO}_2}}{K_{\text{H}}} = \frac{2 \times 10^{-8}}{6.02 \times 10^{-4}}$

$$= 3.322 \times 10^{-5}$$

Now the density of water is 1 gm ml^{-1} . Hence, the mass of 900 ml water can be taken as 900 gram.

$$\therefore \text{Mole of } \text{H}_2\text{O} = \frac{w}{M} = \frac{900}{18} = 50 \text{ mole}$$

Suppose the moles of CO_2 is n then the total moles $= (n + 50) \approx 50$ can be taken.

$$\therefore \text{Mole fraction of } \text{CO}_2 = \frac{\text{mole of } \text{CO}_2}{\text{total mole}}$$

$$3.322 \times 10^{-5} = \frac{n}{50}$$

$$\begin{aligned} \therefore n &= 3.322 \times 10^{-5} \times 50 \\ &= 1.661 \times 10^{-3} \text{ mole} \\ &= 1.661 \times 10^{-3} \times 10^3 \text{ millimole} \\ &= 1.661 \text{ millimole} \end{aligned}$$

$\therefore \text{CO}_2$ dissolved in 900 ml water will be 1.661 millimole.

2.5 Solubility of Solid Solute in Solid Solvent

When solid solute is dissolved in solid solvent it gives solid solution. The molecules are arranged in two ways :

(1) Substituted solid solution : As shown in fig 2.3, the size of solid solute and solid solvent are almost the same, then the solute atoms are arranged in solvent atoms and the solute atoms are substituted in arrangement of atoms forming solid solution. Such type of solution is known as substituted solid solution, e.g. brass, bronze, steel, monel metal etc.

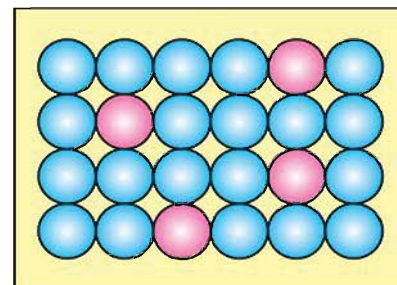


Fig. 2.3

(2) Interstitial solid solution : As shown in figure 2.4 when the sizes of solid solute and solid solvent have vast difference then the small atoms are arranged in the interstitial holes formed between big atoms. Such type of solutions are called interstitial solid solution. e.g. Tungsten carbide (WC).

Solubility of solid solute in liquid solvent : At constant temperature and pressure when the maximum amount of solid solute is dissolved in given liquid solvent then the concentration of solute is called its solubility. Now, no more solute can be dissolved in solution, so such a solution is called saturated solution. In a saturated solution the equilibrium is established between solid solute and solution.



It is not necessary that all the solid solutes will dissolve in all the liquid solvents. For example ionic solids like NaCl or KCl are soluble in polar solvent like water but not soluble in non-polar solvent like benzene or carbon tetrachloride, because generally ionic solid solutes, dissolve in polar liquid solvents. Similarly non-ionic compounds like naphthalene will dissolve in non-polar solvents like benzene, but does not dissolve in polar solvent like water. Thus the solubility of solute depends on the nature of solute and solvent. Moreover the solubility depends upon another two important factors like temperature and pressure.

Effect of temperature : When solid solute is dissolved in liquid solvent and solution is obtained then the equilibrium is established as given below :



If such reaction in equilibrium is endothermic then according to Le-Chatelier's principle, on increasing the temperature, the forward reaction will occur and hence the solubility will increase, and if such reaction is exothermic, then on increasing the temperature according to Le-Chatelier's principle, the reverse reaction will occur and hence the solubility will decrease.

Effect of pressure : Solid solute substances when dissolved in liquid solvents give liquid solutions. Here, the substances are related with reactions may be in solid or liquid state which possess the non-compressible property, so the effect of pressure is very less or negligible.

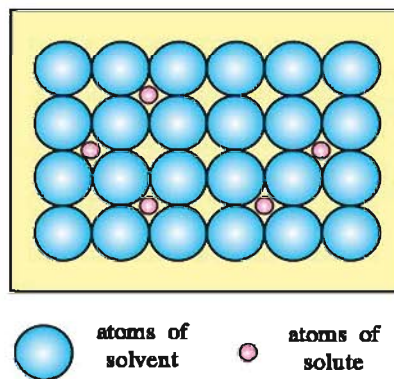


Fig. 2.4

2.6 Solution-Colligative Properties

When solute substances are dissolved in pure solvent, the solutions are obtained. Some properties of solvent change viz. the vapour pressure of a solution prepared from a solvent is less than that of pure solvent, while the boiling point increases and freezing point decreases. The osmotic pressure also changes. The change in these properties depend on number of molecules of solute but not on nature of solute. Such properties are called colligative properties of solution. For example by taking 1m aqueous solution of glucose, NaCl and BaCl₂ and if the colligative properties are studied, it is observed that all the solutions have equal molal concentration, yet the number of particles present are not equal. In glucose solution the concentration of number of particles of solute are 1 m, in NaCl solution the concentration of number of particles are 2 m and in BaCl₂ solution the concentration of number of particles is 3 m, Hence, their colligative properties are in proportion of 1:2:3 respectively. So these colligative properties do not depend upon the concentration of solution but depend on the concentration of the number of particles of solute present in the solution.

2.7 Vapour pressure of solution

A solid solute on dissolving in liquid solvent forms a solution. We have studied, such solutions. Now, let us study the vapour pressure of binary solutions which are obtained by dissolving solid solute in liquid solvent and liquid solute dissolved in liquid solvent. Solid solutes do not have remarkable vapour pressure but liquid solute and liquid solvent have vapour pressures. **At certain temperature the rate for the process of vapour to liquid phase and liquid to vapour phase becomes equal and hence equilibrium is established.** Due to this at certain temperature **pressure of vapour on surface on the solution become constant which is called vapour pressure of solution at that temperature.** The factors which affect the vapour pressure are given below.

(i) The nature of liquid : The weaker the intermolecular forces between the molecules of liquid, the greater is the vapour pressure. This is because more and more molecules of liquid are converted into vapour phase and hence the vapour pressure is more.

(ii) Temperature : Higher the temperature of liquid, more is the vapour pressure, because the kinetic energy of the molecules increases due to increase in temperature and hence more and more molecules leaving the surface of liquid and obtain the vapour phase and its vapour pressure increases.

2.8 Raoult's Law (For Non-volatile Solute)

When solid solute dissolves in liquid solvent and liquid solution is formed its vapour pressure can be understood by simple experiment given below. As shown in figure 2.5, take two equal containers A and B and fill pure solvent and solution of non-volatile solute in same solvent in the containers respectively. Initially in both containers, keep the level of both the liquids (solvent and solution) same, it will be found that the level of solvent is more reduced than the level of solution, because in container A having solvent, its surface has totally solvent molecules and hence more vapour is formed. While in container B having solution, the surface has both solute and solvent molecules. So in

containers B the fraction of surface covered by solvent molecules gets reduced as a result the number of molecules escaping from the surface is reduced and hence vapour pressure is reduced in container B. Thus, the vapour pressure of a solution prepared from a solvent is always less than that of pure solvent. The lowering of vapour pressure of solution was studied by Raoult and a law was proposed in 1887, which is called Raoult's law. According to Raoult's law **"If dilute and ideal solution is prepared by dissolving non-volatile solute in a volatile solvent, the relative lowering of vapour pressure of the solution is equal to the mole fraction of the dissolved solute."**

Proof of Raoult's law : For binary solution, Raoult's law is generally expressed as. **"For any solution the partial vapour pressure of each volatile component in the solution is directly proportional to its mole fraction."** The binary solution in which non-volatile solute is dissolved in the solution, the vapour is only due to solvent. If the vapour pressure of solvent is denoted by p_1 and its mole-fraction by X_1 then mathematical form is

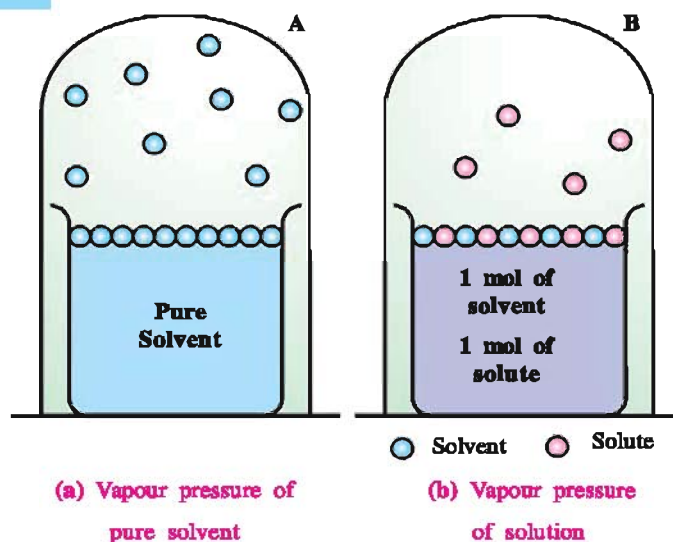


Fig. 2.5 Vapour pressure of solution

$$p_1 \propto X_1$$

$$p_1 = X_1 \cdot p_1^0 \quad (2.3)$$

(where p_1^0 is proportionality constant and its value is equal to the vapour pressure of pure solvent)

As shown in fig 2.6 the graph of vapour pressure against mole-fraction of solvent is straight line, which states the Raoult's law-when the value of mole fraction X_1 is one, then $p_1 = p_1^0$ which is clear from the graph. Now from equation (2.3).

$$\frac{p_1}{p_1^0} = X_1 \quad (2.4)$$

But $X_1 = \frac{n_1}{n_1 + n_2}$ where, n_1 and n_2 are the moles of solvent and solute respectively. Putting value of X_1 in equation (2.4) the equation is $\frac{p_1}{p_1^0} = \frac{n_1}{n_1 + n_2}$. Now subtracting each side from 1.

$$1 - \frac{p_1}{p_1^0} = 1 - \frac{n_1}{n_1 + n_2}$$

$$\therefore \frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2} \quad (2.5)$$

but $\frac{n_2}{n_1 + n_2} = X_2$ i.e., mole fraction of solute. Putting this value in equation (2.5)

$$\frac{p_1^0 - p_1}{p_1^0} = X_2 \quad (2.6)$$

Thus, the solution obtained by dissolving non-volatile solute in pure volatile solvent the relative lowering of vapour pressure of the solution is equal to the mole-fraction of the dissolved solute (X_2).

For very dilute solution $n_2 \ll n_1$, hence putting $n_1 + n_2 \approx n_1$ in equation (2.5)

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1} \quad (2.7)$$

but $n_2 = \frac{w_2}{M_2}$ and $n_1 = \frac{w_1}{M_1}$; putting this values in equation 2.7

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1} \quad (2.8)$$

where, w_1 = mass of solvent, M_1 = molecular mass of solvent

w_2 = mass of solute, M_2 = molecular mass of solute

For very dilute solutions, the molecular mass of solute can be calculated from equation (2.8).

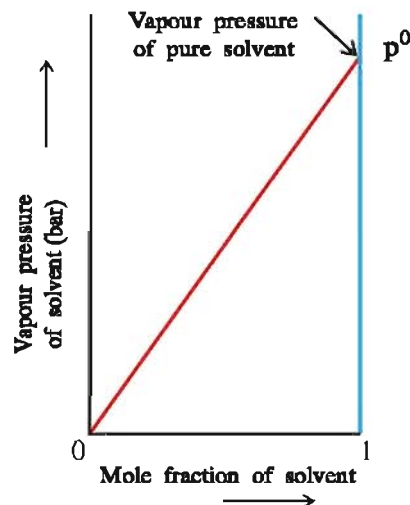


Fig. 2.6 Raoult's law.

The relation between mole fraction of solvent and vapour pressure of solution

Limitations of Raoult's law :

- (1) This law is applicable to very dilute solutions.
- (2) This law is applicable to ideal solution.
- (3) This law is applicable to solutions, whose heat of dilution does not change.
- (4) It is applicable to solutions whose total volume is equal to the sum of the volumes of solute and solvent, if they are in liquid state.
- (5) This law is applicable to the non-electrolyte aqueous solutions which do not undergo any dissociation or association when solute is dissolved in solvent.

2.9 Raoult's Law (For Volatile Solute and Volatile Solvent)

When both volatile liquids are the solute and the solvent then the vapour pressure of the solution is due to vapour pressure of both solute and solvent. According to Raoult's law for such a solution the vapour pressure of both the solute and solvent will be proportional to their mole-fractions.

Suppose in a binary solution X_A is the mole-fraction of solute A and its partial pressure is p_A and X_B is the mole fraction of the solvent B and its partial pressure is p_B then according to Raoult's law $p_A \propto X_A$ and $p_B \propto X_B$.

According to experimental observations Raoult's law can be proved that if the vapour pressure of solute is p_A^0 and vapour pressure of pure solvent is p_B^0 then,

$$p_A = p_A^0 X_A \quad (2.9) \quad \text{and} \quad p_B = p_B^0 X_B \quad (2.10)$$

Now according to Dalton's law of partial pressure the total pressure in the closed vessel will be,

$$\text{Total pressure } P = p_A + p_B$$

Now putting values of p_A and p_B from equation (2.9) and (2.10)

$$\begin{aligned} \text{Total pressure } p &= p_A^0 X_A + p_B^0 X_B \\ &= p_A^0 (1-X_B) + p_B^0 X_B \quad (\because X_A = 1-X_B) \\ &= p_A^0 - p_A^0 X_B + p_B^0 X_B \\ &= p_A^0 + (p_B^0 - p_A^0)X_B \end{aligned} \quad (2.11)$$

In the same way,

$$\begin{aligned} \text{total pressure } p &= p_A + p_B \\ p &= p_A^0 X_A + p_B^0 X_B \\ &= p_A^0 X_A + p_B^0 (1-X_A) \quad (\because X_B = 1-X_A) \\ &= p_A^0 X_A + p_B^0 - p_B^0 X_A \\ &= p_B^0 + (p_A^0 - p_B^0)X_A \end{aligned} \quad (2.12)$$

Following conclusions can be drawn from the equations (2.11) and (2.12).

- (1) Total vapour pressure of the solution can be related to mole fraction X_A or X_B of any component.
- (2) The total vapour pressure of the solution varies linearly with the mole fraction of the component A or B.
- (3) Depending on the vapour pressure of the pure components A and B, the total vapour pressure of the solution change with the change of the mole fraction of component A or B.

If graph is plotted between p_A or p_B with mole fraction X_A or X_B then as shown in fig 2.7, according to equation (2.11) if $p_B^0 > p_A^0$ i.e., component B is more volatile compared to component A then minimum total vapour pressure obtained of the solution is p_A^0 and the maximum total vapour pressure is p_B^0 . When $X_A = 1$ then the total vapour pressure over the solution is p_A^0 and when $X_B = 1$ then total vapour pressure over the solution is p_B^0 which is clear from equation (2.11) and (2.12).

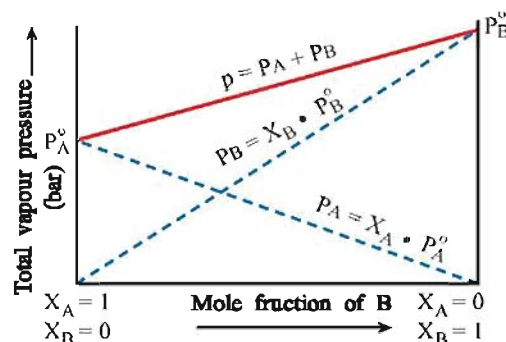


Fig. 2.7 Total vapour pressure \rightarrow mole fraction

If at equilibrium stage, Y_A and Y_B are the mole-fractions of component A and component B in vapour phase respectively then at equilibrium the partial pressure p_A and p_B of each component can be obtained by equations given below :

$$p_A = Y_A \cdot P_{\text{total}}$$

$$p_B = Y_B \cdot P_{\text{total}}$$

Raoult's law (for gaseous solute and liquid solvent) : When gaseous solute is dissolved in liquid solvent and solution is prepared, then according to Raoult's law its vapour pressure can be given as follows :

$$p_A = p_A^0 \cdot X_A \quad (2.13)$$

But if gaseous solute is dissolved in liquid solvent, then its solubility can be given by Henry's law as given below:

$$\text{Solubility } p = K_H \cdot X_A \quad (2.14)$$

By comparing Raoult's law-equation (2.13) and Henry's law-equation (2.14) if both the constant (like p_A^0 and K_H) are different but the volatile component or partial pressure of gas is directly proportional to its mole fraction. It can therefore be said that solubility of a gas and vapour pressure of solution follows Henry's law and Raoult's law respectively.

Ideal solution : The solution which obeys the Raoult's law over the entire range of concentrations is known as ideal solution. The ideal solution has two other important properties like.

- On mixing solute and solvent if solution is obtained, then for this reaction, change in enthalpy (ΔH) is zero.
- If solute and solvent are in liquid state then on preparing solution, the change in volume (ΔV) is zero. For understanding ideal behaviour of solution, the components A and B of solution, when they are in pure form, there are A-A and B-B type intermolecular interaction forces. Besides that in binary solution also A-B type attractive intermolecular interactions will also be present. If the intermolecular, attractive forces between A-A and B-B are nearly equal to the intermolecular attractive force between A-B, the solution becomes ideal. (This leads to the formation of an

ideal solution). For example mixture of Bromoethane and chloroethane, Benzene and toluene, Hexane and heptane, Chlorobenzene and bromobenzene.

Non-ideal solutions : When a solution does not obey Raoult's law over the entire range of concentration then it is called non-ideal solution. This solution is also called real solution. The vapour pressure of such solution is either higher or lower than that predicted by Raoult's law. The intermolecular attractive forces between A-A and B-B are not equal to the intermolecular attractive forces between A-B for such solution. The value of ΔH and ΔV will not be zero. For example mixture of phenol and aniline, mixture of chloroform and acetone, mixture of HCl and water, mixture of HNO_3 and water give non-ideal solutions.

Example 10 : Calculate the vapour pressure for 4% W / W aqueous solution of urea at 298 K temperature. The vapour pressure of water is 0.025 bar.

Solution : According to Raoult's law,

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1}$$

Now 4 % W/W urea solution means 4 gram urea in 96 gram water and $p_1^0 = 0.025$ bar

$$\therefore n_1 = \frac{w_1}{M_1} = \frac{96}{18} = 5.33 \text{ mole of water}$$

$$n_2 = \frac{w_2}{M_2} = \frac{4}{60} = 0.0667 \text{ mole of urea}$$

Now putting these values of p_1^0 , n_1 and n_2 in Raoult's law equation,

$$\frac{0.025 - p_1}{0.025} = \frac{0.0667}{5.33}$$

$$\therefore 0.025 - p_1 = \frac{0.0667 \times 0.025}{5.33} = 0.000313$$

$$\therefore p_1 = 0.025 - 0.000313 = 0.02469 \text{ bar}$$

The vapour pressure of 4 % W/W aqueous solution of urea will be 0.02469 bar.

Example 11 : The vapour pressure of chlorobenzene and bromobenzene are 0.350 bar and 0.500 bar respectively. Find the vapour pressure of solution obtained by mixing 11.25 gram chlorobenzene with 31.4 gram bromobenzene.

Solution : The molecular masses of chlorobenzene and bromobenzene are 112.5 and 157 gm mol^{-1} respectively.

$$\therefore \text{mole of chlorobenzene} = \frac{w}{M} = \frac{11.25}{112.5} = 0.1 \text{ mole}$$

$$\text{mole of bromobenzene} = \frac{w}{M} = \frac{31.4}{157} = 0.2 \text{ mole}$$

$$\therefore \text{Total moles} = (0.1 + 0.2) = 0.3$$

$$\therefore \text{The mole fraction of chlorobenzene} = X_1 = \frac{0.1}{0.3} = \frac{1}{3}$$

$$\text{mole fraction of bromobenzene} = X_2 = \frac{0.2}{0.3} = \frac{2}{3}$$

$$\text{Here, } p_1^0 = 0.350 \text{ bar and } p_2^0 = 0.500 \text{ bar}$$

Now according to Raoult's law,

$$\begin{aligned} \text{total vapour pressure} &= p_1^0 + (p_2^0 - p_1^0) X_2 \\ &= 0.350 + (0.500 - 0.350) \times \frac{2}{3} \\ &= 0.350 + \frac{0.150 \times 2}{3} \\ &= 0.350 + 0.100 = 0.450 \text{ bar} \end{aligned}$$

\therefore The vapour pressure of solution will be 0.450 bar.

2.10 Elevation in Boiling Point

The temperature at which the vapour pressure of any liquid (solvent or solution) becomes 1 bar (1 atmosphere), is known as boiling point of that liquid. (solvent or solution). At any temperature the vapour pressure of solution is less than that of pure solvent from which it is prepared, and vapour pressure increases on increasing temperature. At 373 K (373.15 K) temperature the vapour pressure of pure water becomes 1 bar and hence it starts boiling. Now if solution is prepared by adding non-volatile solute (like sugar), the vapour pressure of solution decreases. So as to make its vapour pressure equal to 1 bar it has to be heated. On heating solution starts boiling. Thus the boiling point of solution is higher than that of pure solvent. The increase in boiling point is called **elevation in boiling point (ΔT_b)**.

Molal elevation constant : Increase in boiling point of a solution prepared by dissolving one gram molar mass of non-volatile solute in one kilogram of solvent is called molal elevation constant (K_b). For example 342 gram sugar or 60 gram urea or 180 gram glucose is dissolved in one kilogram water means by dissolving one molecular mass of a substance the increase in boiling points (ΔT_b) of these solutions are same. Thus, increase in boiling point depends upon the number of molecules of solute and not on the nature of solute, so it is colligative property of solution.

Molal elevation and molal elevation constant : Figure 2.8 shows the relation between vapour pressure and temperature for pure solvent and its solutions.

Suppose the boiling point of pure solvent is T_b^0 and the boiling point of solution is T_b , then increase in boiling point $\Delta T_b = T_b - T_b^0$ is elevation in boiling point. Experimental observation

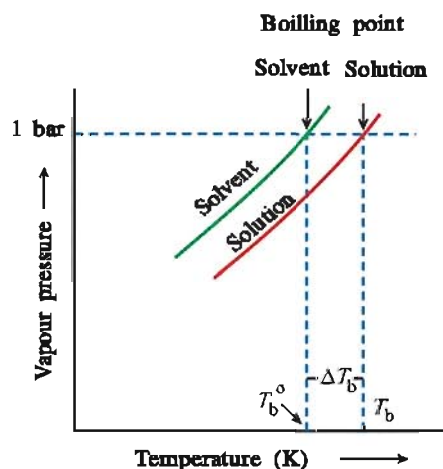


Fig. 2.8 The relation between vapour pressure and temperature

indicates that molal elevation (ΔT_b) is directly proportional to the molal concentration of solute dissolved in dilute and ideal solution. So it is written in mathematical form as

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b \times m \quad (2.15)$$

$$\text{but molality } m = \frac{1000 \times w_2}{M_2 \times w_1}$$

Putting this value in equation 2.15

$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1}$$

$$\therefore K_b = \frac{\Delta T_b \times w_1 \times M_2}{1000 \times w_2} \quad (2.16)$$

where K_b = Molal elevation constant

w_1 = mass of solvent

w_2 = mass of solute

M_2 = molecular mass of solute

ΔT_b = elevation in boiling point.

Elevation in boiling point for one molal solution is called solvent's molal elevation constant (K_b). Its unit is Kelvin kilogram mole⁻¹ (K kg mole⁻¹).

Example 12 : Calculate the boiling point of solution which is prepared by dissolving 6 gram of urea in 2 kg of water. Molal elevation constant for solution is 3.2 K kg mole⁻¹.

Solution : $\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1}$

$$K_b = 3.2 \text{ Kkgmole}^{-1}$$

$$w_2 = 6 \text{ Gram}$$

$$w_1 = 2 \text{ Kilogram} = 2000 \text{ gram} \quad M_2 = 60 \text{ gram mole}^{-1}$$

$$= \frac{3.2 \times 1000 \times 6}{60 \times 2000} = 0.16 \text{ Kelvin}$$

$$\therefore \text{The boiling point of urea solution} = \text{boiling poing of solvent} + T_b \\ = 373 \text{ K} + 0.16 \text{ K} = 373.16 \text{ K}$$

\therefore The boiling point of urea solution will be 373.16 K.

Example 13 : How many gram of glucose should be added to 5 kg of water, so that the boiling point increases from 373 K to 373.5 K. The molal elevation constant of solvent is 2.2 K kg mole⁻¹.

Solution : Elevation in boiling point

$$\Delta T_b = 373.5 \text{ K} - 373 \text{ K} = 0.5 \text{ K}$$

$$\Delta T_b = \frac{K_b \times 1000 \times w_2}{M_2 \times w_1}$$

$$\Delta T_b = 0.5 \text{ K} \quad K_b = 2.2 \text{ K kg mole}^{-1}$$

$$w_2 = ? \quad M_2 = 180 \text{ gram mole}^{-1}$$

$$w_1 = 5 \text{ kg} = 5000 \text{ gram}$$

$$w_2 = \frac{\Delta T_b \times M_2 \times w_1}{1000 \times K_b}$$

$$= \frac{0.5 \times 180 \times 5000}{2.2 \times 1000} = 204.5 \text{ gram}$$

\therefore 204.5 gram glucose should be dissolved in 5 kg water.

2-11 Depression in freezing point

Freezing point of substance (solvent or solution) is a temperature at which the solid and liquid phase of the substance (solvent or solution) are in equilibrium and at that temperature (Freezing point) the vapour pressure of the solid and liquid phase of the substance (solvent or solution) are same.

The freezing point of solution is lower than that of pure solvent from which the solution is prepared. Thus, decrease in freezing point of solution from solvent is called depression in freezing point (ΔT_f). Freezing point of solution is less than that of solvent from which it is prepared, because according to Raoult's law vapour pressure of solution is less compared to that of solvent to which the non-volatile solute is added to form that solution. So at lower temperature the vapour pressure of liquid. Solution and pure solid solvent becomes equal, that temperature is the freezing point of solution. Thus, the freezing point of solution is less than freezing point of pure solvent.

Molal depression constant : "Decrease in freezing point of a solution prepared by dissolving one gram molar mass of non-volatile solute into one kilogram of solvent is called molal depression constant (K_f). For example 60 gram urea or 180 gram glucose or 342 gram sugar i.e. one gram molar mass of solute on dissolving in 1 kg of solvent, the lowering in freezing points are equal, because depression in freezing point depends on number of molecules of solute dissolved in the solution and not on the nature of solute, so it is a colligative property.

Depression in freezing point and molal depression constant : The values of vapour pressure at different temperatures for pure solvent and solution prepared from that solvent are shown in figure 2.9.

Suppose the freezing point of pure solvent is T_f^0 and freezing point of solution is T_f then depression in freezing point $\Delta T_f = T_f^0 - T_f$ is known as depression in freezing point. Experimental results shows that it is directly proportional to the molal concentration of solute. So it is written in mathematical form as

$$\Delta T_f \propto m$$

$$\therefore \Delta T_f = K_f \times m \quad (2.17)$$

But molality $m = \frac{1000 \times w_2}{M_2 \times w_1}$. Putting values in equation (2.17)

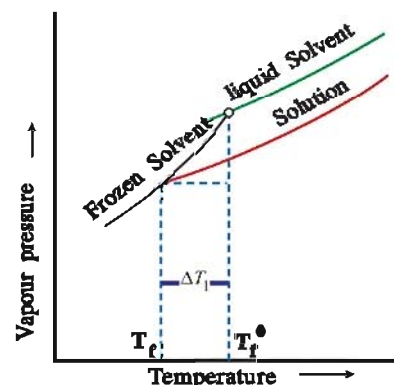


Fig. 2.9 The relation between vapour pressure and temperature (mole depression constant)

$$\therefore T_f = \frac{K_f \times 1000 \times w_2}{M_2 \times w_1}$$

$$\therefore K_f = \frac{\Delta T_f \times w_1 \times M_2}{1000 \times w_2} \quad (2.18)$$

where, K_f = molal depression constant

w_1 = mass of solvent

w_2 = mass of solute

M_2 = molar mass of solute

ΔT_f = depression in freezing point.

Depression in freezing point for one molal solution is called molal depression constant (K_f) and its unit is Kelvin kilogram mole⁻¹ (K kg mol⁻¹).

Example 14 : Find the freezing point of solution obtained by dissolving 1.8 gram glucose in 500 gram water. The value of K_f for solvent is 1.8 K kg mol⁻¹.

Solution : $\Delta T_f = \frac{K_f \times 1000 \times w_2}{M_2 \times w_1}$

$$K_f = 1.8 \text{ K kg mol}^{-1}$$

$$w_2 = 1.8 \text{ gram}$$

$$M_2 = 180 \text{ gram mol}^{-1}$$

$$w_1 = 500 \text{ gram}$$

$$= \frac{1.8 \times 1000 \times 1.8}{180 \times 500} = 0.036$$

Now freezing point of pure solvent is 273 K.

$$\begin{aligned} \therefore \text{Freezing point of solution} &= \text{freezing point of solvent} - \Delta T_f \\ &= 273 - 0.036 \text{ K} = 272.964 \text{ K} \end{aligned}$$

\therefore The freezing point of solution will be = 272.964 K.

Example 15 : How many grams of urea must be dissolved in 2000 grams of water so that depression in freezing point is 0.2 K. The K_f for solvent is 2.0 K kg mol⁻¹.

Solution : $\Delta T_f = \frac{K_f \times 1000 \times w_2}{M_2 \times w_1}$

$$\therefore w_2 = \frac{\Delta T_f \times M_2 \times w_1}{1000 \times K_f}$$

$$K_f = 2 \text{ K kg mol}^{-1}$$

$$w_2 = ?$$

$$M_2 = 60 \text{ gram mol}^{-1}$$

$$w_1 = 2000 \text{ gram}$$

$$\Delta T_f = 0.2 \text{ K}$$

$$\therefore w_2 = \frac{0.2 \times 60 \times 2000}{1000 \times 2} = 12 \text{ gram}$$

\therefore 12 gram urea will have to be dissolved in 2000 gram water.

2.12 Osmosis, Osmotic pressure and its Uses

When a semipermeable membrane is kept between two solutions having different concentrations or between a solvent and a solution, a spontaneous flow of solvent starts from a solution, having lower concentration to higher concentration, or from a solvent to a solution respectively. This phenomenon is called **Osmosis**. The meaning of Greek word osmosis is to push. Semipermeable membrane can allow only solvent molecules but will not allow solute molecules. As shown in figure 2.10, CuSO_4 solution is filled on one side and on other side pure water or dilute CuSO_4 solution.

After some time it is observed that spontaneously the water molecules flow towards the CuSO_4 solution and hence the difference is observed in level of liquids on both the sides of semipermeable membrane. Such spontaneous flow will just stop when equilibrium is established between them.

Some examples of osmosis are found in nature and in daily life. For example the dry grapes get swollen when kept in water, wilted flower revives when placed in water; blood cell collapse when placed in salty water. In all these phenomena the boundary of all the substances bounded by semipermeable membrane and hence osmosis is observed. Some examples of natural semipermeable membranes are animal cell wall, plant cell wall, urinary bladder of animal. While artificial semipermeable membrane are parchment paper, cellophane, butter paper, copper ferrocyanide $\text{Cu}_2[\text{Fe}(\text{CN})_6]$. In such artificial semipermeable membranes, the copper ferrocyanide is one of the best artificially prepared semipermeable membrane.

Osmotic pressure : As shown in fig 2.11 on one side of semipermeable membrane (SPM) a solution and on other side pure water are filled. As the time passes, the spontaneous flow of solvent starts towards solution, hence the difference in levels of the pure solvent (water) and solution is observed. Hence by applying minimum pressure on the solution that just stops the flow of solvent towards the solution across the semipermeable membrane is called osmotic pressure of solution.

Example of osmotic pressure :

- (1) Plants absorb water from soil through their roots is due to osmosis.
- (2) Water assimilated by the plants moved into the different parts of plant is due to osmosis.
- (3) Due to osmosis the water reaches into the different parts of the animal body.
- (4) Opening of flower and closing of flower is also controlled by osmosis.
- (5) Bursting of red blood cell when placed in water is also due to osmosis.
- (6) Rapid growth of the plants and germination of seeds is due to osmosis.

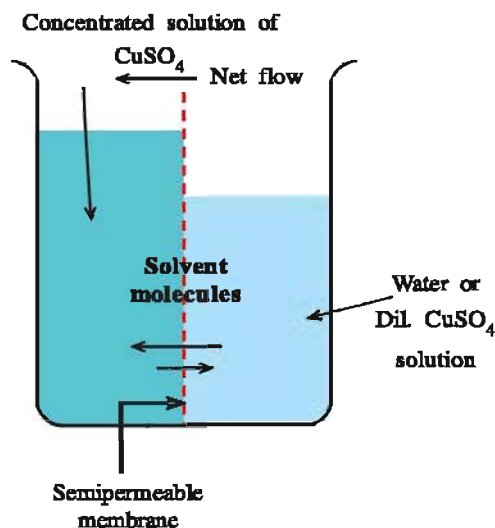


Fig. 2.10 Osmosis

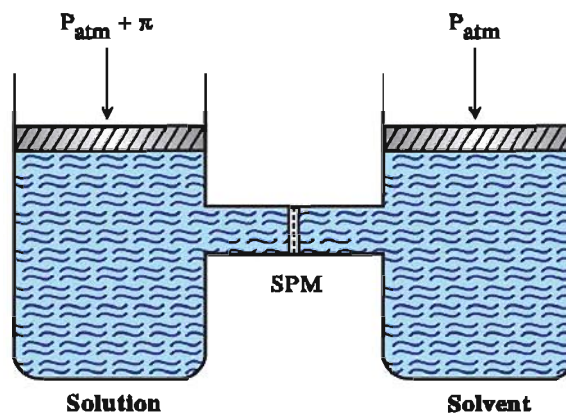


Fig. 2.11 Osmosis pressure

2.13 Laws of osmotic pressure

van't-Hoff and Pfeiffer suggested that the solute in the dilute solution behaves like a gas. The osmotic pressure of dilute solution is equal to pressure of gas if the solute is in gaseous form at that temperature and occupy the volume equal to that of solution. So van't Hoff derived laws similar to gas laws like Boyle, Gay-Lussac and Avogadro's law for dilute solution.

(i) Boyle's-van't Hoff Law : "At constant temperature the osmotic pressure (π) is directly proportional to the molar concentration of the solution." It can be written mathematically as follows:

Putting this value

$$\pi \propto C \text{ but } C = \frac{n}{V}$$

$$\pi \propto \frac{n}{V} \quad (2.19)$$

where, n = number of moles of solute V = volume of solution (litre)

$$\frac{n}{V} = \text{molar concentration}$$

Putting in equation (2.19) $n = 1$ mole,

$$\pi \propto \frac{1}{V} \quad (2.20)$$

$$\pi = K \frac{1}{V}$$

$$\therefore \pi V = K \quad (2.21)$$

Equation (2.21) is similar to Boyle's law : $PV = K$

(ii) Gay-Lussac-van't Hoff law : If the concentration of solution is constant then osmotic pressure of solution is directly proportional to absolute temperature. It can be written mathematically as

$$\pi \propto T \quad (2.22)$$

$\pi = KT$ where, K = proportionality constant.

$$\frac{\pi}{T} = K \quad (2.23)$$

Equation (2.23) is of the form $\frac{P}{T} = K$ regarding Gay-Lussac's law for gases.

(iii) Avogadro's-van't-Hoff law : The number of molecules in the same volume of different solutions having the same osmotic pressure at the same temperature. It can be written mathematically as

$$\pi \propto n \quad (2.24)$$

Now, according to equation (2.20).

$$\pi \propto \frac{1}{V} \text{ (Boyle-van't-Hoff Law).}$$

According to equation (2.22)

$$\pi \propto T \text{ (Gay-Lussac-van't-Hoff Law)}$$

$$\pi \propto n \text{ (Avogadro-van't-Hoff Law)}$$

$$\pi \propto \frac{nT}{V}$$

$$\pi = \frac{nRT}{V} \text{ where, R is proportionality constant and its value is equal to that of gas constant.}$$

$$\therefore \pi V = nRT \quad (2.25)$$

where π = Osmotic pressure in bar V = volume of solution in litres

n = number of moles of solute R = gas constant

T = absolute temperature in Kelvin.

Equation 2.25 is similar to simple gas equation $PV = nRT$

Now, putting value of $n = \frac{w}{M}$ in equation (2.25)

$$\pi V = \frac{wRT}{M}$$

$$\pi = \frac{wRT}{MV} \quad (2.26)$$

where w = mass of solute, M = molar mass of solute

2.14 Iso-Osmotic (Isotonic) Solutions

The solutions having same osmotic pressure at given temperature are called **Iso-osmotic (Isotonic) solutions**. If such solutions are separated by semipermeable membrane no osmosis occurs, between them. The vapour pressures of iso-osmotic solutions are equal so such solution are known as iso-osmotic or isotonic solutions. Concentration of isotonic solutions are equal. For example the osmotic pressure associated with fluid inside blood cell is equivalent to that of 0.91 % W/V NaCl solution, same way 0.1 M H_2SO_4 solution is isotonic with 0.3M glucose solution. If the osmotic pressures of two different solutions are different it means that concentrations are different then, solution whose osmotic pressure is less it is known as **hypotonic** with comparison to higher osmotic pressure solution. A solution whose osmotic pressure is higher, in comparison to solution having less osmotic pressure is called **hypertonic solution**. This means that for the solution having less osmotic pressure the prefix hypo and for the solution having more osmotic pressure the prefix hyper is used. For example less than 0.91% W/V pure NaCl solution is hypotonic compared to fluid inside human blood but pure NaCl solution having concentration more than 0.91 % W/V is hypertonic with respect to fluid inside human body.

Example 16 : Calculate the osmotic pressure at 300 K temperature of a solution having 18 gram glucose dissolved in 5 litre solution.

Solution : Osmotic pressure $\pi = \frac{wRT}{MV}$

$$M = 180 \text{ gram}$$

$$w = 18 \text{ gram}$$

$$V = 5 \text{ Litre}$$

$$T = 300 \text{ K}$$

$$R = 8.314 \times 10^{-2} \text{ bar lit K}^{-1} \text{ mol}^{-1}$$

$$\therefore \pi = \frac{18 \times 8.314 \times 10^{-2} \times 300}{180 \times 5}$$

$$\therefore \pi = \frac{18 \times 8.314 \times 10^{-2} \times 300}{900} = 0.4988 \text{ bar}$$

\therefore The osmotic pressure of the glucose solution will be 0.4988 bar.

Example 17 : 6 gram of urea is dissolved in 2 litre solution at 300 K temperature. How many grams of NaCl should be dissolved in 5 litre solution so that it becomes iso-osmotic with urea solution ?

Solution : As the temperature and gas constant R have same values, for both solutions; so for such iso-osmotic solutions, it can be written directly.

$$\frac{\text{mole of urea}}{\text{volume of urea solution}} = \frac{\text{mole of NaCl}}{\text{volume of NaCl solution}}$$

$$\therefore \frac{0.1}{2} = \frac{\text{moles of NaCl}}{5} \quad (\because \text{moles of urea } \frac{w}{M} = \frac{6}{60} = 0.1 \text{ mole})$$

$$\therefore \text{moles of NaCl} = \frac{0.1 \times 5}{2} = 0.25 \text{ mole}$$

Now in NaCl, ($\text{Na}^+ + \text{Cl}^-$) the number of particles is two and for isotonic solution the number of particles required is 0.25 mole number of particles, so the mole of NaCl will be half

$$\begin{aligned} \text{number of mole of NaCl} &= \frac{0.25}{2} \\ &= 0.125 \text{ mole} \end{aligned}$$

$$\begin{aligned} \text{Amount of NaCl in gram} &= \text{no. of mole} \times \text{molar mass} \\ &= 0.125 \times 58.5 \\ &= 7.31 \text{ gram} \end{aligned}$$

\therefore 7.31 gram NaCl should be dissolved so that it becomes isotonic with urea solution.

2.15 Methods of Determining the Molecular Mass

To determine the molecular mass of any substance, the different methods used are as given below :

- (1) Using Raoult's law.
- (2) Molal elevation measurement method.
- (3) Molal depression measurement method.
- (4) Osmotic pressure measurement method.

Let us study these methods in detail.

(1) Using Raoult's law : For the solution obtained by dissolving non-volatile solute in pure volatile solvent equation (2.8) was derived earlier. Using this equation the molecular mass can be determined.

According to equation (2.8)

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1} \quad \text{OR}$$

$$M_2 = \frac{p_1^0}{p_1^0 - p_1} \times \frac{w_2 \times M_1}{w_1}$$

At given temperature the solution is prepared by dissolving w_2 gram non-volatile solute into w_1 gram solvent having vapour pressure, p_1^0 and molecular mass M_1 . Now the vapour pressure of the solution (p_1) is determined and putting the values obtained at the end of the experiment in equation (2.8) the molar mass (M_2) of solute can be found.

Example 18 : Calculate the molar mass of unknown substance, when 20 gram non-volatile substances dissolved in 360 gram water at 298 K temperature. The vapour pressure of water is reduced to 0.0238 bar from 0.0242 bar.

Solution : According to Raoult's law

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1}$$

$$p_1^0 = 0.0242 \text{ bar}$$

$$p_1 = 0.0238 \text{ bar}$$

$$w_2 = 20 \text{ gram}$$

$$M_2 = ?$$

$$w_1 = 360 \text{ gram}$$

$$M_1 = 18 \text{ gram mole}^{-1}$$

$$\therefore \frac{0.0242 - 0.0238}{0.0242} = \frac{20 \times 18}{M_2 \times 360}$$

$$\therefore \frac{0.0004}{0.0242} = \frac{1}{M_2}$$

$$\therefore M_2 = \frac{0.0242}{0.0004} = 60.5 \text{ gram mole}^{-1}$$

Molar mass of unknown substance will be 60.5 gram mole⁻¹.

(2) Molal elevation measurement method : When solution is prepared by dissolving non-volatile solute in pure volatile solvent, for such a solution according to equation (2.16) molar mass of non-volatile solute can be determined. According to equation (2.16).

$$K_b = \frac{\Delta T_b \times w_1 \times M_2}{1000 \times w_2}$$

$$\therefore M_2 = \frac{K_b \times 1000 \times w_2}{\Delta T_b \times w_1} \quad (2.27)$$

At given temperature the solution is prepared by dissolving w_2 gram solute in w_1 gram solvent having molal elevation constant K_b and by experimental observation for that solution elevation in boiling point (ΔT_b) is obtained. Putting these values in equation (2.27) molar mass of solute is obtained by the calculation.

Example 19 : 0.75 gram unknown substance is dissolved in 200 gram water and solution is prepared. If the elevation in boiling point is 0.15 K and molal elevation constant is 7.5 K kg mole⁻¹ then find the molar mass of unknown substance.

Solution : The molar mass of unknown substance

$$M_2 = \frac{K_b \times 1000 \times w_2}{\Delta T_b \times w_1}$$

$$K_b = 7.5 \text{ K kg mol}^{-1}$$

$$w_2 = 0.75 \text{ gram}$$

$$\Delta T_b = 0.15 \text{ K}$$

$$w_1 = 200 \text{ gram}$$

$$\begin{aligned} \therefore M_2 &= \frac{7.5 \times 1000 \times 0.75}{0.15 \times 200} \\ &= 187.5 \text{ gram mole}^{-1} \end{aligned}$$

\therefore The molar mass of unknown substance will be 187.5 gram mole⁻¹.

(3) Molal depression measurement method : When non-volatile solute is dissolved in pure volatile solvent and solution is prepared then, for such solution equation (2.18) as derived earlier, can be used so that the molar mass of non-volatile solute (M_2) can be determined. According to equation (2.18.)

$$K_f = \frac{\Delta T_f \times w_1 \times M_2}{1000 \times w_2}$$

$$\therefore M_2 = \frac{K_f \times 1000 \times w_2}{\Delta T_f \times w_1} \quad (2.28)$$

At given temperature the solution is prepared by dissolving w_2 gram solute in w_1 gram solvent having molal depression constant K_f and by experimental observation in depression of temperature for that solution (ΔT_f) is obtained. Putting these values in equation 2.28 molar mass of solute can be obtained by the calculation.

Example 20 : 2 gram unknown substance is dissolved in 500 gram water and solution is prepared. The depression in freezing point is 0.06 K. If the molal depression constant for solvent is 5 K kg mole⁻¹, then find the molar mass of unknown substance.

Solution : Molar mass of unknown substance $M_2 = \frac{K_f \times 1000 \times w_2}{\Delta T_f \times w_1}$

$$K_f = 5 \text{ K kg mole}^{-1}$$

$$w_1 = 500 \text{ gram}$$

$$\Delta T_f = 0.06$$

$$w_2 = 2 \text{ gram}$$

$$\begin{aligned} M_2 &= \frac{5 \times 1000 \times 2}{0.06 \times 500} \\ &= 333.3 \text{ gram mole}^{-1} \end{aligned}$$

The molar mass of unknown substance will be 333.3 gram mole⁻¹

(4) Osmotic pressure measurement method : In fixed amount of solvent if fixed amount of solute is dissolved and solution is prepared at fixed temperature and the osmotic pressure is noted and then by using formula given below, the molar mass of substance can be calculated.

$$\text{Molar mass of unknown solute substance } M = \frac{\text{mass of unknown solute} \times RT}{\text{osmotic pressure} \times \text{volume of solution}}$$

This method is more useful for the determination of molar masses of protein polymer and macromolecules; because during experimental observation the values obtained for elevation in boiling point, depression in freezing point is very less (nearly 10^{-5} K); So it is difficult to measure them accurately; nearly the pressure as small as 10^{-3} bar can be measured in mm unit. Besides this the biomolecules like protein are not stable at high temperature, so their molar masses can not be obtained by molal elevation method or molal depression method, but at room temperature can be obtained by osmotic pressure measurement method, besides this the solubility of polymer substances is very less so they can be prepared as dilute solutions and for dilute solutions the observation which are obtained can be easily noted in the osmotic pressure measurement method.

While in other methods the observation values obtained are very small, so it is difficult to measure them. In osmotic pressure measurement method the concentration of solution is measured in molarity instead of molality. So the osmotic pressure measurement method is more useful than other methods.

Example 21 : At 300 K temperature 1.5 gram unknown substance is dissolved in solvent and made the volume 1.5 litre of the solution. Its osmotic pressure is found to be 0.2 bar. Calculate the molar mass of unknown substance.

Solution : Molar mass of unknown substance

$$M = \frac{\text{mass of unknown substance} \times RT}{\text{osmotic pressure} \times \text{volume of solution}}$$

$$= \frac{1.5 \times 8.314 \times 10^{-2} \times 300}{0.2 \times 1.5} = 124.71 \text{ gram mole}^{-1}$$

Molar mass of unknown substance will be 124.71 gram mole⁻¹

2.16 Abnormal molecular mass and van't Hoft factor

The various relations for the colligative properties are applicable to the non-electrolyte solution and also the solutes which do not undergo any dissociation or association in the solution; because due to dissociation or association of solute the number of particles, which indicate concentration gets decreased or increased. When polar solute is dissolved in polar solvent; the solute is polar so it is ionised in solution and number of particles in solution increases e.g. NaCl, K₂SO₄, FeCl₃ and Fe₂(SO₄)₃ when dissolved in water get ionised, and the number of particles obtained are 2, 3, 4 and 5 respectively. It is called dissociation. Due to increase in number of particles; using colligative properties; the value of molar mass obtained is less than the actual molar mass. The molar mass obtained by experimental method is called abnormal molar mass. Besides this some solute molecules when dissolved in solvent, more than two molecules combine and form associated molecules, and this process is called association. e.g. Acetic acid or benzoic acid when dissolved in solvent like benzene, then two molecules of solute associate and hence the number of molecules in solution decreases. For such type of solution the real molar mass of solute can not be obtained, by using method based on colligative properties. The experimental molar mass value is more than real molar mass value and such experimental molar mass obtained is also called

abnormal molar mass. The colligative properties of solution is applicable to only dilute solution because concentrated solution means the concentration of solution is higher, so the solute molecules are so close to each other that they exert appreciable molecular forces of attraction. As a result real molar mass can not be obtained on the basis of colligative properties; So abnormal molar mass is obtained. To obtain real molar mass scientist van't-Hoff in 1880 introduced one factor which is known as van't Hoff's factor (i).

$$\begin{aligned}\text{van't Hoff factor (i)} &= \frac{\text{Normal molar mass of solute}}{\text{Abnormal molar mass of solute}} \\ &= \frac{\text{Theoretical molar mass of solute}}{\text{Experimental molar mass of solute}} \\ &= \frac{\text{Observed colligative property}}{\text{Theoretical colligative property}}\end{aligned}$$

By introducing van't Hoff factor (i) the formula to obtain molar mass can be written as follows:

$$\text{Raoult's law : } \frac{p_1^0 - p_1}{p_1^0} = i \frac{n_2}{n_1 + n_2} \approx i \frac{n_2}{n_1}$$

$$\text{Elevation in boiling point : } \Delta T_b = i K_b \cdot m$$

$$\text{Depression in Freezing point : } \Delta T_f = i K_f \cdot m$$

$$\text{Osmotic pressure of solution : } \pi = i \frac{nRT}{V}$$

The value of van't Hoff factor (i) is less than one; when there is an association of the solute and it is more than one when there is dissociation. The value of (i) is equal to 1 when there is no association or dissociation of solute. The values of van't Hoff factor (i) for some solutions are given in table 2.3

Table 2.3 Values of van't Hoff factor (i) at various concentrations for NaCl, KCl, MgSO₄ and K₂SO₄

Salt	values of i			van't Hoff Factor i for complete dissociation of solute
	0.1 m	0.01 m	0.001 m	
NaCl	1.87	1.94	1.97	2.00
KCl	1.85	1.94	1.98	2.00
MgSO ₄	1.21	1.53	1.82	2.00
K ₂ SO ₄	2.32	2.70	2.84	3.00

Degree of dissociation : The proportion of the mass of the given solute in the solution which gets dissociated is called degree of dissociation (α)

$$\text{Degree of dissociation } (\alpha) = \frac{i-1}{n-1}$$

where i = van't Hoff factor

Degree of association (X) : The proportion of the mass of the given solute in the solution which gets associated, is called degree of association (X).

$$\text{Degree of association (X)} = (1-i) \frac{n}{n-1}$$

where i = van't Hoff factor, n = no. of molecules combined due to association.

Example 22 : The depression in freezing point is 0.24 K obtained by dissolving 1 gram KCl in 200 gram water, calculate van't-Hoff factor. The molal depression constant is $1.86 \text{ K kg mole}^{-1}$.

Solution : Molar mass of solute (KCl)

$$\begin{aligned} &= \frac{1000 \times K_f \times \text{mass of KCl}}{\Delta T_f \times \text{mass of solvent}} \\ &= \frac{1000 \times 1.86 \times 1}{0.24 \times 200} = 38.75 \text{ gram mole}^{-1} \text{ (experimental value)} \end{aligned}$$

Now the molar mass = $39 + 35.5 = 74.5 \text{ gram mole}^{-1}$

$$\begin{aligned} \text{van't Hoff factor (i)} &= \frac{\text{Theoretical molar mass of KCl}}{\text{Experimental molar mass of KCl}} \\ &= \frac{74.5}{38.75} = 1.92 \end{aligned}$$

The value of van't Hoff factor (i) for KCl will be 1.92

Example 23 : Find the degree of association when 1.0 gram benzoic acid, dissolved in 25 gram benzene is having depression in freezing point 0.81 K. The molal depression constant for solvent is $4.9 \text{ K kg mole}^{-1}$.

Solution : molar mass of benzoic acid,

$$\begin{aligned} &= \frac{1000 \times K_f \times \text{mass of benzoic acid}}{\Delta T_f \times \text{mass of solvent}} \\ &= \frac{1000 \times 4.9 \times 1}{0.81 \times 25} \\ &= 242 \text{ gram mole}^{-1} \\ &= \text{abnormal (experimental) molar mass of benzoic acid.} \end{aligned}$$

$$\begin{aligned} \text{van't Hoff factor (i)} &= \frac{\text{Theoretical molar mass of benzoic acid}}{\text{Experimental molar mass of benzoic acid}} \\ &= \frac{122}{242} \approx 0.5 \end{aligned}$$

van't Hoff factor (i) for benzoic acid is 0.5

Now, degree of association

$$\begin{aligned} X &= (1 - i) \left(\frac{n}{n-1} \right) \\ &= (1 - 0.5) \left(\frac{2}{2-1} \right) \\ &= 0.5 \times 2 = 1 \end{aligned}$$

Example 24 : Calculate degree of dissociation (α) for $K_3[Fe(CN)_6]$ when depression in freezing point is 0.062 K for 0.01 m $K_3[Fe(CN)_6]$ aqueous solution. The molal depression constant (K_f) for solvent is 1.86 K kg mole⁻¹.

Solution : The depression in freezing point (theoretical) of solution.

$$\Delta T_f = K_f \cdot m = 1.86 \times 0.01 = 0.0186 \text{ K}$$

$$\begin{aligned} \text{van't Hoff factor (i)} &= \frac{\text{Experimental depression in freezing point}}{\text{Theoretical depression in freezing point}} \\ &= \frac{0.062}{0.0186} = 3.33 \end{aligned}$$

When $K_3[Fe(CN)_6]$ is dissolved in water the total number of ions = 3 + 1 = 4 due to its ionisation .



$$\begin{aligned} \text{The degree of dissociation } (\alpha) &= \frac{i-1}{n-1} \\ &= \frac{3.33-1}{4-1} = 0.778 \end{aligned}$$

The degree of dissociation for $K_3[Fe(CN)_6]$ will be 0.778

Example 25 : The depression in freezing point is 0.69 K when 2 gram phenol is dissolved in 100 gram benzene. If it is associated as dimeric then find its degree of association. The molal depression constant for solvent is 5.12 K kg mole⁻¹.

Solution : The theoretical molar mass = 94 gram mole⁻¹.

$$\begin{aligned} \text{The experimental molar mass of phenol} &= \frac{1000 \times K_f \times \text{mass of solute}}{\Delta T_f \times \text{mass of solvent}} \\ &= \frac{1000 \times 5.12 \times 2}{0.69 \times 100} \\ &= 148.4 \text{ gram mole}^{-1} = \text{abnormal molar mass of phenol} \end{aligned}$$

$$\text{van't Hoff factor (i)} = \frac{\text{Theoretical molar mass of phenol}}{\text{Experimental molar mass of phenol}}$$

$$= \frac{94}{148.4}$$

$$= 0.633$$

The degree of association for phenol (X) = $(1 - i) \frac{n}{n - 1}$

$$= (1 - 0.633) \frac{2}{2 - 1}$$

The degree of association for phenol will be 0.734

SUMMARY

- When two or more than two substances are mixed and they form a uniform or homogeneous mixture, it is called solution.
- The proportion of component which is more in the solution is called a solvent and the proportion of a component or components which is less in a solution is/are called solute.
- There can be one solvent and one or more solute components.
- The solution having one solute and one solvent component, is called binary solution.
- There are three types of solution solid solution, liquid solution, gaseous solution.
- The physical state of a solvent in a given solution becomes the physical state of that solution.
- Polar solute dissolves in polar solvent and non polar solute dissolves in non polar solvent and forms homogeneous mixture (solution).
- If the number of -OH group is more in a solute, then it is more soluble in water.
- Most of polar solutes dissolve in polar solvents.
- If water is the solvent, the solution is called an aqueous solution, but if water is not the solvent, the solution is called as non-aqueous solution.
- **Formality** : One gram formula mass of the substance (solute) dissolved in one litre solution is called one formal solution.

$$\text{Formality (F)} = \frac{1000 \times \text{mass of solute (gram)}}{\text{formula mass of solute} \times \text{volume of solution (ml)}}$$

- **Volume percentage (% V/V)** : The volume of solute (ml) dissolved in 100 ml solution is expressed as volume percentage (% V/V).

$$\% \text{ V/V} = \frac{100 \times \text{volume of solute}}{\text{volume of solution}}$$

- **Mass by volume percentage : (% W/V) :** The mass of solute dissolved in 100 ml solution is called mass by volume percentage (% W/V).

$$\% \text{ W/V} = \frac{100 \times \text{mass of solute}}{\text{volume of solution}}$$

- **Parts per million (ppm) :** Sometimes the amount of the solute in solution is very much less and so the concentration is expressed as parts per million (ppm).

parts per million can be expressed in three different ways : (1) Parts per million by mass to mass, (2) Parts per million by mass to volume and (3) Parts per million by volume to volume.

- **Parts per million by mass to volume :** The amount of solute in milligram dissolved in one litre solution is called parts per million by mass to volume.

$$\text{Parts per million by mass to volume} = \frac{\text{amount of solute (mg)}}{\text{amount of solution (litre)}}$$

Unit of parts per million by mass to volume can be written mg litre^{-1}

- At given temperature and pressure the maximum amount of solute dissolved in a solvent is called its solubility
- There is effect of temperature on solubility of solid, liquid or gas.
- **Henry law :** "The solubility of gaseous solute in a liquid solvent at definite temperature is directly proportional to the pressure of the gas."
- Partial pressure of gaseous solute $p = K_H \cdot X$ where K_H is Henry's constant which depends on temperature
- Limitation and uses of Henry's law are as given in unit.
- When solid solute dissolves in solid solvent, substitutional solid solution, (brass, bronze, steel, monel metal etc.) as well as interstitial solid solution (WC) is formed.
- The solution prepared by dissolving solid solute in liquid solvent, the factor that affect the solubility are temperature and pressure these are known as colligative properties of solution.
- If a solution is prepared by dissolving solid in a solvent, vapour pressure decreases, boiling point increases and freezing point decreases.
- **Raoult's law :** Relative lowering of vapour pressure of the solution is equal to the mole fraction of the dissolved solute.

$$X_2 = \frac{p_1^0 - p_1}{p_1^0}$$

- Raoult's law has some limitations but the solution which obey Raoult's law, over the entire range of concentration is known as ideal solution and the solutions which do not obey Raoult's law are called non-ideal or real solutions.
- When volatile solute is dissolved in volatile solvent the vapour pressure of solution is the total of vapour pressure of solute and solvent both.
- When solute dissolved in solvent the increase in boiling point of solution is called elevation in boiling point.

- **Molal elevation constant** : Increase in boiling point of a solution prepared by dissolving one gram molar mass solute in one kilogram of solvent is called molal elevation constant (K_b).

$$K_b = \frac{\Delta T_b \times w_1 \times M_2}{1000 \times w_2}$$

- The depression in freezing point when one gram molar mass solute is dissolved in one kilogram of non-volatile solvent is called molal depression constant (K_f).

$$K_f = \frac{\Delta T_f \times M_2 \times w_1}{1000 \times w_2}$$

- **Osmosis** : When two solutions having different concentrations are separated by semi-permeable membrane the spontaneous flow of solvent starts from a solution with lower concentration to higher concentration it is called osmosis.
- **Osmotic pressure** : Such a spontaneous flow as above which can be stopped by applying pressure is called osmotic pressure (π).
- **Boyle's-van't Hoff law** : At constant temperature the osmotic pressure is directly proportional to the molar concentration of the solution.
- **Gay-Lussac-van't Hoff law** : If the concentration of the solution is constant then osmotic pressure of solution is directly proportional to absolute temperature. $\pi \propto T$
- **Avogadro-van't Hoff law** : In the same volumes of different solutions having similar osmotic pressure at the same temperature have same number of molecules; of the solute.
- By combining these three laws the equation $\pi = \frac{nRT}{V}$ or $\pi = \frac{wRT}{MV}$ can be derived
- The solutions having same osmotic pressure at given temperature are called iso-osmotic (Isotonic) solutions.
- The solution having lower osmotic pressure in comparison with higher concentration is called hypotonic solution. The solution having higher osmotic pressure in comparison with lower concentration is called hypertonic solution.
- **Methods to determine molar mass** :

(i) Using Raoult's law : $\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1}$

(ii) **Molal elevation constant method** :

$$\text{molar mass of solute} = \frac{1000 \times \text{mass of solute} \times K_b}{\text{elevation in boiling point} \times \text{mass of solvent}}$$

(iii) **Molal depression constant method** :

$$\text{molar mass of solute} = \frac{1000 \times \text{mass of solute} \times K_f}{\text{depression in freezing point} \times \text{mass of solvent}}$$

(iv) Osmotic pressure measurement method :

molar mass of unknown substance =

$$\frac{\text{mass of solute} \times RT}{\text{osmotic pressure of solution} \times \text{volume of solution}}$$

- The colligative properties are applicable to solutions which do not undergo dissociation or association.
- van't Hoff factor (i) is introduced for the deviation from normal behaviour.
- van't Hoff factor (i) = $\frac{\text{theoretical molar mass of solute}}{\text{experimental molar mass of solute}}$
- **Raoult's law :** $\frac{p_1^0 - p_1}{p_1^0} = i \frac{n_2}{n_1 + n_2} \simeq i \frac{n_2}{n_1}$
- **Elevation in boiling point :** $\Delta T_b = i K_b \cdot m$
- **Depression in freezing point :** $\Delta T_f = i K_f \cdot m$
- **The osmotic pressure :** $\pi = i \frac{nRT}{V}$
- **Degree of association (X) =** $(1-i) \frac{n}{n-1}$
- **Degree of dissociation (α) =** $\frac{i-1}{n-1}$

EXERCISE

1. Select the proper choice from the given multiple choices :

- (1) Which unit of concentration value is changed with change in temperature ?
(A) Normality (B) Molarity (C) % V/V (D) all of these
- (2) Which type of solution is petrol ?
(A) solid-liquid (B) liquid-liquid (C) gas-liquid (D) all of these
- (3) What is the concentration of solution in ppm when 2×10^{-6} gram CO_2 is dissolved in 10 ml solution ?
(A) 2 (B) 0.2 (C) 200 (D) 2×10^{-6}
- (4) Which of the following gas has highest solubility in ethyl alcohol ?
(A) H_2S (B) NH_3 (C) N_2 (D) CO_2
- (5) Which of the following substance has the highest solubility in water?
(A) ethanol (B) ethylene glycol (C) glycerine (D) propanol

- (6) On increasing temperature, the solubility of gaseous solute in liquid solvent
 (A) Increases (B) Decreases (C) Remains constant (D) Uncertain
- (7) On increasing temperature the value of Henry's constant
 (A) Decreases (B) Increases (C) Remains constant (D) Uncertain
- (8) Which solution has the highest effect of temperature on its vapour pressure ?
 (A) Sugar solution (B) NaCl solution (C) BaCl_2 Solution (D) Aqueous H_2S
- (9) Which of the following aqueous solution has the highest boiling point having concentration 0.02 m ?
 (A) Urea (B) NaCl (C) Na_2SO_4 (D) $\text{K}_4[\text{Fe}(\text{CN})_6]$
- (10) 0.05 M glucose solution is iso-osmotic with which of the following solutions ?
 (A) 0.10 M NaCl (B) 0.05 NaCl (C) 0.025 M NaCl (D) 1M NaCl
- (11) What is the value of van't Hoff factor for dilute FeCl_3 (aqueous) solution ?
 (A) 1 (B) < 1 (C) > 1 (D) zero
- (12) What is the value of van't Hoff factor when acetic acid is dissolved in benzene?
 (A) Zero (B) 1 (C) > 1 (D) < 1
- (13) What is the molality for 10% W/W NaOH(aq) solution ?
 (A) 2.778 (B) 2.5 (C) 10 (D) 5
- (14) For which solution the value of van't Hoff factor is one ?
 (A) NaCl (B) KNO_3 (C) glucose (D) CH_3COOH
- (15) For which solution the value of van't Hoff factor is not 1 ?
 (A) Glucose (B) Sugar (C) Fructose (D) Acetic acid
- (16) The real vapour pressure for non-ideal solution is than by Raoult's law
 (A) more (B) less (C) equal (D) (A) and (B) both
- (17) Which of the following solutions is hypotonic ?
 (A) 0.1 M NaCl (B) 0.1 M sugar (C) 0.1M Na_2SO_4 (D) 0.1 M FeCl_3
- (18) The total pressure for volatile components A and B is 0.02 bar at equilibrium. If the mole fractions of component A is 0.2, then what will be partial pressure of component B ?
 (A) 0.02 bar (B) 0.04 bar (C) 0.016 bar (D) 0.2 bar
- (19) Which of the following solutions is hypertonic ?
 (A) 0.1 M FeCl_3 (B) 0.1 M NaOH (C) 0.1 M Urea (D) 0.1 M Na_2SO_4

2. Write the answers of the following questions in short :

- (1) Define solution.
- (2) What is solvent and solute in solution ?
- (3) Write types of solutions.
- (4) Which type of solutions are air containing moisture, zinc amalgam and dry air ?
- (5) Define : Formality, Solubility, ppm
- (6) Write effect of temperature on solubility of solute.
- (7) Give example of interstitial solid solution.
- (8) Define saturated solution.
- (9) What is molal elevation ?
- (10) What is molal depression ?
- (11) Write Boyle-van't Hoff law.
- (12) What is osmosis ?
- (13) What is osmotic pressure ?
- (14) What is abnormal molecular mass ?
- (15) Write formula for degree of association (X).
- (16) What is binary solution ?
- (17) When the value of van't Hoff factor will be more than one ?
- (18) What is iso-osmotic solution ?
- (19) To determine the molar mass of polymer; which method is more useful ?
- (20) What is freezing point ?

3. Answer the following questions :

- (1) Write about types of solid solution with examples.
- (2) Write about gaseous solution with examples.
- (3) Explain % V/V in short.
- (4) Explain unit ppm with example.
- (5) Write the factors affecting the solubility of solute in aqueous H_2S solution ?
- (6) Write uses of Henry's law.
- (7) Explain substitutional solid solution in short.
- (8) Explain interstitial solid solution in short.

- (9) Write any two uses of osmotic pressure.
- (10) Explain molal elevation measurement method.
- (11) Explain association and dissociation.
- (12) What are colligative properties of solution ?
- (13) Why van't Hoff factor (i) was introduced ?

4. Explain following questions in detail :

- (1) Write Henry's law, derive the formula and write its limitation.
- (2) Explain molal elevation constant. Derive its formula.
- (3) Write Raoult's law and derive its equation.
- (4) Explain the factors affecting the solubility of solute in solution obtained by dissolving gaseous solute in liquid solvent.
- (5) Derive the formula of Raoult's law for a solution having volatile solute and solvent.
- (6) Derive the formula for molal depression constant.
- (7) Explain the different methods to determine the molar mass.
- (8) Write law of osmotic pressure and derive formula.
- (9) Explain iso-osmotic solution and write uses of osmotic pressure.
- (10) Explain abnormal molar mass and explain van't Hoff factor.
- (11) Explain and write the formula for colligative properties introducing van't Hoff factor (i).

(12) Solve the examples :

- (1) Calculate the formality of solution when 4.78 gram potash alum is dissolved in 2 litre solution.
- (2) How many ml ethanol is required to prepare 2 litre aqueous solution of ethanol solution having concentration 5% V/V.
- (3) Calculate the percentage by mass to volume for 0.2 M NaOH solution.
- (4) Calculate the ppm for solution in which 2×10^{-7} kg calcium bicarbonate is dissolved in 2 litre solution.
- (5) Calculate the solubility in mole- fraction at 300 K temperature; the partial pressure of Cl_2 gas in water is 2.5×10^{-8} bar. For Cl_2 gas the value of K_H is 7.1×10^{-4} bar.
- (6) How many millimoles of H_2S gas will dissolve in water when passed through 1 litre water, the K_H value is 5.6×10^{-4} bar and the partial pressure is 3×10^{-8} bar.
- (7) Calculate the vapour pressure of aqueous 0.1m glucose solution at 300 K temperature, the vapour pressure of water is 0.03 bar at 300 K temperature.
- (8) The vapour pressures of benzene and toluene are 0.9 and 0.85 bar respectively. Calculate the vapour pressure of solution obtained by mixing 7.8 gram benzene with 180 gram toluene.

- (9) Find the boiling point of 2.5% W/W sugar solution; the molal elevation constant for solvent is 4 K kg mole^{-1} .
- (10) How many grams of urea should be dissolved in 500 gram water so that the depression in freezing point is 0.2 K ? K_f for solvent is $3.2 \text{ K kg mole}^{-1}$.
- (11) How many grams of glucose should be dissolved in 2 litre aqueous solution at 298 K temperature so that the osmotic pressure of solution is 0.5 bar .
- (12) Calculate the osmotic pressure of 2% W/V aqueous solution of urea at 300 K temperature. This solution is iso-osmotic with what % W/V of NaOH aqueous solution.
- (13) At 298 K temperature 10 gram non-volatile unknown substance is added to 540 gram water so that the change in vapour pressure will be from 0.0335 bar to 0.033 bar ; find the molar mass of unknown substance.
- (14) Elevation in boiling point is 0.2 K when 1.5 gram unknown substance is dissolved in 500 gram water. Find the molar mass of unknown substance. Molal elevation constant for solvent is 3 K kg mole^{-1} .
- (15) 2 gram of unknown substance is dissolved in 1kg water, the depression in freezing point is 0.4 K . If the molal elevation constant is $4.5 \text{ K kg mole}^{-1}$, find the molar mass of solute.
- (16) When 5 gram unknown substance is dissolved in 10 litre solution the osmotic pressure of solution is 0.2 bar at 300 K temperature. Find the molar mass of unknown substance.
- (17) The depression in freezing point observed is 0.3 K , when 2 grams FeCl_3 is dissolved in 250 ml water. Find the van't Hoff factor. The molal elevation constant for solvent is $1.5 \text{ K kg mole}^{-1}$.
- (18) Find the degree of dissociation when 0.02M aqueous $\text{Al}_2(\text{SO}_4)_3$ solution having elevation in boiling point of 0.04 K . The molal elevation constant for solvent is $1.9 \text{ K kg mole}^{-1}$.
- (19) The depression in freezing point is 0.56 K when 1.5 gram phenol is dissolved in 100 gram toluene. If its association is dimeric then find the degree of association. Molal depression constant for solvent is 4 K kg mole^{-1} .



Unit

3

Electrochemistry

3.1 Introduction

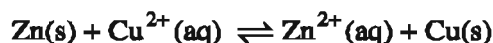
We were studying inorganic and organic chemistry. The oldest branch is inorganic chemistry. The separate branch of organic chemistry was evolved by the research on urea by Wohler, similarly the third branch of chemistry was evolved as a separate branch of chemistry called physical chemistry from the study of electrochemistry. Later on, with the progress of the time, different branches like analytical chemistry, industrial chemistry etc. came into existence which are studied in the present time.

Chemical reactions are useful for the production of electrical energy. Electrical energy is useful to express chemical reactions which are not spontaneous. The study of electrochemistry is for the production of electricity which is free energy released during spontaneous chemical reactions and this electrical energy is used for transfer for chemical reactions which are not spontaneous. Theoretical and experimental proofs are inevitable for this subject. The production of many metals, sodium hydroxide, chlorine, fluorine and many more chemicals is carried out by electrochemical methods. Batteries and fuel cells transform chemical energy to electrical energy, and so it is used in larger proportion in different instruments and appliances. The electrochemical reactions are acceptable and less polluted. So the study of electrochemistry must be done as eco-friendly for formation of new technologies.

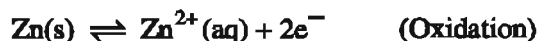
In the case of both the reactions-conduction of senses to the brain and opposite to that from brain-electrochemistry is involved. Hence, electrochemistry is a very widely developed interrelated subject. We will include the main structural points in this unit.

3.2 Electrochemical Cell

The reaction occurring in electrochemical cell is a redox reaction viz. If a thin plate of Zn metal is placed in an aqueous solution of CuSO_4 , Cu metal is deposited on zinc plate and the original blue colour of solution appears to be light blue coloured; because in this reaction Cu^{2+} is reduced and Zn metal is oxidised. This total reaction occurs as follows :



Really, this reaction is the sum of following two half reactions :



A construction can be made where by the above reactions carried out without bringing Zn and Cu reactants in contact with each other.

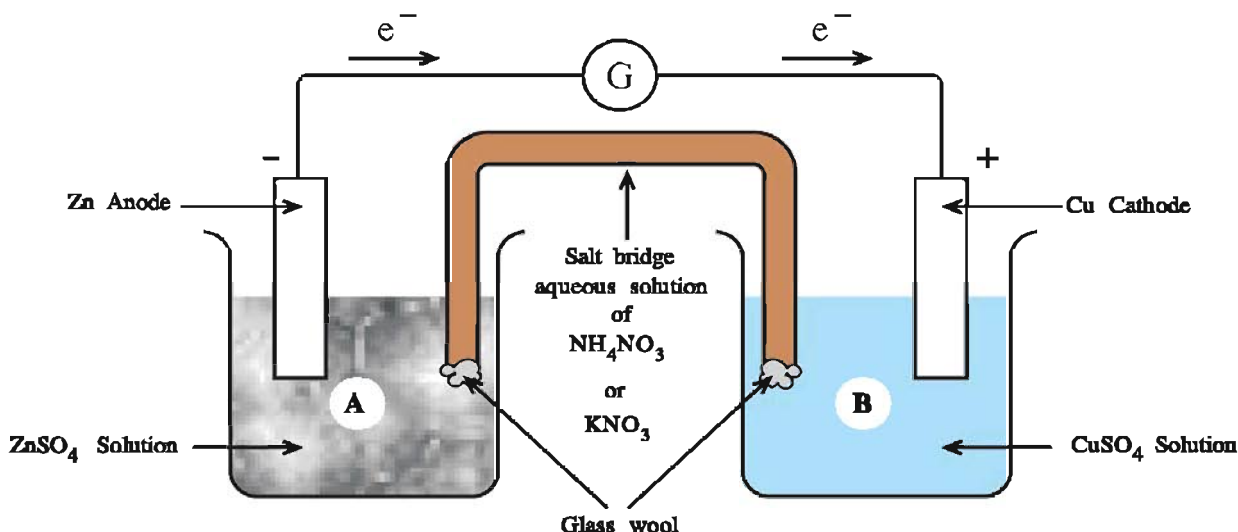


Fig. 3.1 Electrochemical cell (Zn-Cu Cell)

The contact between the reactants is to be kept only for the electron-exchange. Such a construction is called **electrochemical cell**. In the electrochemical cell, the energy produced in chemical reaction is transformed into electrical energy. The device which transforms the chemical energy into electrical energy is called **electrochemical cell**.

- (i) Aqueous solution of ZnSO_4 is in beaker A. The weighed strip of zinc metal is placed in the solution so that part of it remains outside the solution. In this half cell the strip of Zn metal is in contact with 1M aqueous solution of Zn^{2+} ions which is expressed as $\text{Zn(s)} | \text{Zn}^{2+}(\text{aq})$. Vertical line indicate contact between Zn metal strip and Zn^{2+} ions present in the solution.
- (ii) Aqueous solution of CuSO_4 is in beaker B. The weighed strip of Cu metal is placed in the solution so that part of it remains outside the solution. In this half cell, the strip of Cu metal is in contact with 1M aqueous solution of CuSO_4 , which is expressed by vertical line. $\text{Cu(s)} | \text{Cu}^{2+}(\text{aq})$. Vertical line indicate contact between Cu metal strip and Cu^{2+} ions present in the solution.
- (iii) Salt bridge is used to complete the electrical circuit and to connect the two solutions. The construction of saltbridge is like this. Aqueous solution of NH_4NO_3 is filled in U-shaped tube and its both the ends are closed by glass-wool. This tube is inverted and its one end is placed in beaker A and the other end in beaker B.
- (iv) You know that the electrical current flowing through a circuit can be measured by joining ammeter and the direction of electrical current by joining galvanometer. Hence, Ameter or galvanometer can be selected, with the help of the ammeter the flowing electrical current and the direction of flow of electron are determined.

As shown in fig 3.1, if the strips of zinc metal and copper metal are connected through galvanometer or ammeter, it shows flow of electricity from the wire.

After sometime, if both the strips are taken out, washed carefully with distilled water dried and weighed, it will be found that the weight of zinc strip has decreased and the weight of copper strip has increased. This shows that the reaction $\text{Zn(s)} \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$ must have occurred in beaker A containing solution of ZnSO_4 and the reaction $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu(s)}$ in the solution of CuSO_4 filled in beaker B.

The construction shown in fig. 3.1, is known as electrochemical cell or Galvanic cell or voltaic cell. The above special type of electrochemical cell is called Daniell cell. The strips dipped in solutions are called electrodes which is expressed as (e.g. $\text{Zn(s)} | \text{Zn}^{2+}(\text{aq})$ and $\text{Cu(s)} | \text{Cu}^{2+}(\text{aq})$). The electrode on which reduction reaction takes place is called cathode (+) and the electrode on which oxidation reaction takes place is called anode (-). If these two electrodes in electrochemical cell are connected by a copper wire in the external circuit, the current of electrons flow from anode to cathode. The U-tube filled in with solution of ammonium nitrate, used for the connection of two solutions is called **salt bridge**. The flow of current in solution occurs through the ions.

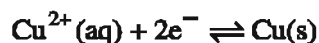
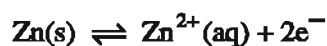
In the beaker (B) on the right hand side, copper is formed from Cu^{2+} by reduction and so, concentration of Cu^{2+} decreases due to which the solution of CuSO_4 becomes negatively charged because of SO_4^{2-} ions. The solution in the beaker (A) on left hand side Zn^{2+} ions are produced from Zn metal and so ZnSO_4 solution becomes positively charged. If it happens so, the chemical reaction of the cell will stop. Hence, both the solutions must be without any electric charge so that the reaction of cell takes place continuously. The salt bridge joining the two solutions in the beakers contains liquid medium of solution of proper salt. Hence, **the salt bridge joins the two solutions and keeps the neutrality of electrical charge.**

The cell in which the “concentrations of the ions associated with the reaction of the cell are 1 mole litre⁻¹ and if any gas is associated with the reaction, then its pressure equal to 1 bar and if temperature is 298 K, is called standard cell.

3.3 Types of Electrodes

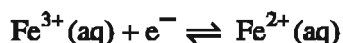
The metal strips dipped in the solution or rods of nonmetal like graphite and on whose surface reaction takes place is called an electrode. The electrodes used in electrochemical cells are mainly of three types.

(i) Active electrodes of metal : The active electrodes of metal are metals like Zn, Ni, Cu, Ag etc. Atom of this kind of electrode undergo oxidation (anode) or cation in contact gets reduced on surface (cathode). The reactions taking place on such electrodes can be shown as below :

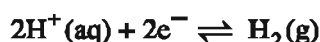


(ii) Inert electrode : Atoms of inert electrode do not experience either oxidation or reduction reaction but oxidation or reduction reaction takes place on the surface of this inert electrode. Graphite and platinum are inert electrodes. When the solutions containing Fe^{3+} and Fe^{2+} ions, are used in the

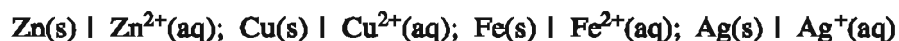
construction of the cell, platinum wire is used as the electrode. Fe^{3+} gets reduced to Fe^{2+} by receiving electron on strip of platinum or Fe^{2+} is oxidised to Fe^{3+} by giving electron to platinum wire. The reaction taking place on this type of electrode can be shown as below.



(iii) Gaseous electrode : Gaseous electrode mostly resembles the inert electrode. Here, gas is passed over the strip of platinum dipped in the solution. viz. If in hydrogen gas electrode containing $\text{H}^{+}(\text{aq})$ in solution is passed over the strip of platinum kept in the solution, then 2H^{+} are reduced and the gas H_2 is formed or 2H^{+} are formed by oxidation of H_2 gas. Here, the strip of platinum provides the surface necessary for exchange of electrons. The reaction taking place on such an electrode can be shown as below:



3.3.1 Half Cell : The metal which is kept in the aqueous solution of its salt and a system formed is called electrode. **The electrode and the solution in which it is dipped is collectively known as half cell.** The representation of half cell is done by putting a vertical line between the formulas of electrode and the active ions.



The representation of gaseous electrode is expressed by inert metal or formula of non metal, molecular formula of gas and the formula of active ions. e.g. **$\text{Pt} \mid \text{H}_2(\text{g}, 1 \text{ bar}) \mid \text{H}^{+}(\text{aq})$.**

3.3.2 Symbolic representation of cell : In symbolic representation of electrochemical cell, the representation of both the half cells used in its construction are used. If a salt bridge is used to join solutions of both the half cells, then it is expressed by \parallel (two vertical lines). But if salt bridge is not used, then \mid (single vertical line) is used. Anode is always shown on the left hand side and the cathode on the right hand side in symbolic representation of the cell. The concentration of the salt used in the construction of the cell is expressed in molarity unit in bracket after the formula or symbol of the ion. If a gaseous electrode is used in the construction of cell, then its pressure is expressed in bar units after the formula of the gas.

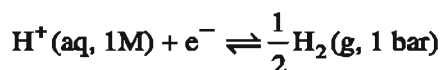


If the concentration of solution is 1M in the half cell, or pressure of gas is 1 bar and temperature is 298 K, then such a half cell is called standard half cell. By connecting of two standard half cells, standard cell is formed.

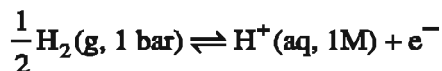
3.3.3 Standard Hydrogen Gas Electrode : The comparison of different electrodes for the tendency to release the electron or to receive the electron can be carried out by using the standard hydrogen half cell because the hydrogen electrode works as a reference to other electrode. Hence, hydrogen electrode can be taken as reference electrode. The construction of standard hydrogen gas electrode is carried out as under :

As shown in fig 3.2 a solution of 1M $H^+(aq)$ is taken in a beaker at 298 K. In this solution, the platinum strip which is electroplated with platinum black is dipped. This strip is connected with platinum wire in a tube closed at one end. Mercury is added on this wire to keep electrical contact and the other end of the wire is connected outside. Dihydrogen gas at 298 K temperature and 1 bar pressure is passed over the platinum.

When this half cell is connected with other half cell and a complete cell is formed, it acts as cathode or anode. If it acts as cathode, the following reduction reaction takes place on the platinum strip.



But if the standard hydrogen gas electrode acts as an anode the oxidation reaction takes place on the anode as shown below :



Thus, standard hydrogen gas electrode possesses the tendency to receive the electron or to release the electron. The intensity of this tendency is accepted as zero volt at all temperatures. Hence, it is easy to obtain the relative values of intensity of the tendency of receiving the electron or the tendency of releasing the electron. **The relative intensity of tendency of receiving the electron is called reduction potential E_{red} or E_{red}^0 and the relative intensity of electrodes for releasing electron is called oxidation potential E_{oxi} or E_{oxi}^0 .**

Standard hydrogen electrode works as a reference electrode for other half cells. If the tendency of the other half cell to receive electron is more than standard hydrogen gas electrode acts as an anode and if standard hydrogen gas electrode has more tendency to receive the electron, it acts as a cathode.

Hence, the dependence of another half cell as anode or cathode remains with reference to standard hydrogen electrode, so it is called reference electrode. With reference to standard hydrogen gas electrode, standard Zn-half cell act as anode while standard Cu-half cell act as cathode.

3.4 Cell potential

The electrochemical cell is a device which can transform chemical energy into electrical energy. When two electrodes are joined, then the flow of electrons due to chemical reaction will be from anode to cathode in the external circuit under produced electromotive force. This electromotive force is called cell potential E_{Cell} . If the cell is in standard state, the standard potential is expressed as E_{Cell}^0 . The voltage measured with voltmeter is really not the correct potential. **Potentiometer should be used to measure the correct potential.**

The cell potential is in fact the difference between the intensities of receiving electron of each electrode and possess the tendency to release the electron. The proof of this is obtained. From the following experimental results.



When the above cell is in operation, the following reaction takes place:

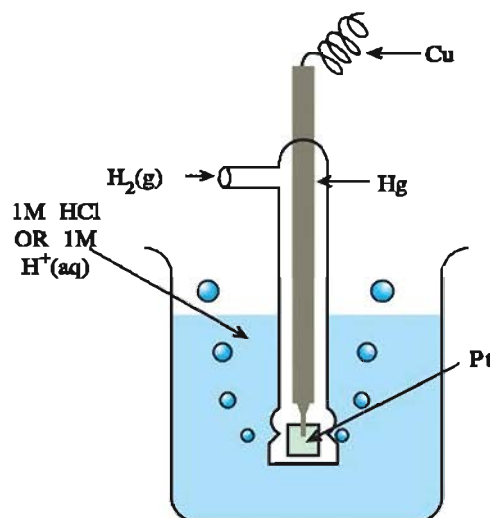
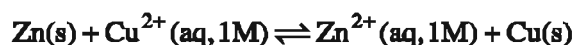


Fig. 3.2 Standard hydrogen gas electrode

Here Zn releases the electron and Cu^{2+} receives the electron. The tendency of Cu^{2+} to receive the electron is more which can be said on the basis of the above reaction.



When the above cell is in operation the following reaction takes place.



Here, Cu releases the electron and Ag^+ accepts the electron. The tendency of Ag^+ to receive electron is more than that of Cu, which can be said on the basis of the above reaction.

In the above reaction (i) the tendency of Cu, to receive electron is more than that of Zn; while in reaction (ii) the tendency of Cu to receive electron is less than that of Ag. Hence, in reaction (i) Cu electrode acts as cathode and in reaction (ii) Cu electrode acts as anode. The potential is the difference of intensities of cathode and anode to receive electrons. The absolute value of intensity of tendency to accept the electron cannot be measured because redox reaction is not completed by half cell. The value of E^0_{Cell} is the difference between the values of standard reduction potentials of two half cells. This relation is shown as below :

$$E^0_{\text{Cell}} = E^0_{\text{red (RHS)}} - E^0_{\text{red (LHS)}} \quad \text{OR} \quad E^0_{\text{Cell}} = E^0_{\text{red (Cathode)}} - E^0_{\text{red (Anode)}}$$

3.4.1 Method of determination of standard half cell potential : To obtain the potential of any standard half cell, it is connected with the standard hydrogen half cell, through salt bridge. The cell potential E^0_{Cell} of the complete cell prepared like this is measured with the help of potentiometer.

In the complete cell constructed like this, the potential of one half cell - standard hydrogen half cell is zero as it is being accepted. The potential of the other half cell will be the value equal to that of E^0_{Cell} . If the other half cell is functioning as anode the positive value of E^0_{Cell} indicating negative value of E^0_{red} of the electrode. But if it is functioning as cathode, then the value of potential E^0_{red} will be positive. If the electrochemical cell is formed by connecting zinc half cell with standard hydrogen electrode, the half cell of Zn acts as anode and hence the value of E^0_{Cell} will be equal to negative of reduction potential of Zn half cell. When the electrochemical cell is formed by connecting half cell of Cu with standard hydrogen electrode, it acts as the cathode half cell. Hence the positive value of Cu half cell will be equal to the positive value of reduction potential of half cell of Cu. The values of E^0_{red} and E^0_{oxi} of any electrode are same but the signs are opposite. The negative value of E^0_{red} shows positive value of E^0_{oxi} .

$$E^0_{\text{red}} = - E^0_{\text{oxi}}$$

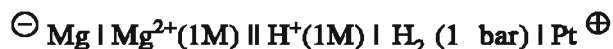
$$E^0_{\text{Mg}^{2+} | \text{Mg}(\text{red})} = -2.36 \text{ Volt}$$

$$E^0_{\text{Mg} | \text{Mg}^{2+}(\text{oxi})} = + 2.36 \text{ Volt}$$

$$E^0_{\text{Cu}^{2+} | \text{Cu}} = +0.34 \text{ Volt}$$

$$E^0_{\text{Cu} | \text{Cu}^{2+}} = -0.34 \text{ Volt}$$

Example 1 : The potential of the following given cell is 2.36 volt at 298 K. Write the equation for reaction and calculate the reduction potential of magnesium half cell.



Solution : Here, electrode of Mg is anode.

Cathode : $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{H}_2(\text{g})$ (Reduction)

Anode : $\text{Mg}(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{e}^-$ (Oxidation)

Cell Reaction : $\text{Mg}(\text{s}) + 2\text{H}^+(\text{aq}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + \text{H}_2(\text{g})$

$$E_{\text{Cell}}^0 = E_{\text{red (Cathode)}}^0 - E_{\text{red (Anode)}}^0$$

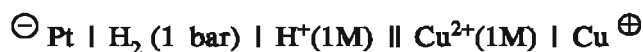
$$E_{\text{Cell}}^0 = E_{\text{H}^+ | \frac{1}{2} \text{H}_2}^0 - E_{\text{Mg}^{2+} | \text{Mg}}^0$$

$$\therefore 2.36 \text{ volt} = 0.0 - E_{\text{Mg}^{2+} | \text{Mg}}^0$$

$$\therefore E_{\text{Mg}^{2+} | \text{Mg}}^0 = -2.36 \text{ volt}$$

The standard reduction potential of this half cell $E_{\text{Mg}^{2+} | \text{Mg}}^0 = -2.36 \text{ volt}$.

Example 2 : The potential of the given following cell is 0.34 volt at 298 K temperature calculate the standard reduction potential of copper half cell.



Solution : Here, copper electrode is cathode

$$E_{\text{Cell}}^0 = E_{\text{red (Cathode)}}^0 - E_{\text{red (Anode)}}^0$$

$$\therefore E_{\text{Cell}}^0 = E_{\text{Cu}^{2+} | \text{Cu}}^0 - E_{\text{H}^+ | \text{H}_2}^0$$

$$\therefore 0.34 \text{ Volt} = E_{\text{Cu}^{2+} | \text{Cu}}^0 - 0.0$$

$$\therefore E_{\text{Cu}^{2+} | \text{Cu}}^0 = 0.34 \text{ volt}$$

The standard reduction potential of this half cell $E_{\text{Cu}^{2+} | \text{Cu}}^0 = 0.34 \text{ volt}$ and the standard oxidation potential of this half cell will be $E_{\text{Cu} | \text{Cu}^{2+}}^0 = -0.34 \text{ volt}$.

It will be understood from the above two examples that reduction potentials of standard reduction half cells are positive. Their tendency to receive electron is more than that of hydrogen. Hence, if these half cell electrodes are connected with standard hydrogen gas electrode, they will act as cathode. As contrast to this, the potentials of standard half cells of standard electrodes are negative, their tendency to receive electron is less than that of hydrogen. Hence, if the half cells of this type are constructed, they act as anode.

If, instead of standard hydrogen gas electrode any other standard half cell is used for construction of cell, then, the half cell having more negative reduction potential will act as cathode. viz. $\text{Zn}^{2+}(1\text{M}) | \text{Zn}(\text{s})$ and $\text{Cu}^{2+}(1\text{M}) | \text{Cu}(\text{s})$ half cells are joined and a complete cell is prepared then, the zinc electrode will

act as anode and copper electrode will act as cathode, because the value of $E^0_{\text{Zn}^{2+}|\text{Zn}} = -0.76$ volt which is less than the value of the $E^0_{\text{Cu}^{2+}|\text{Cu}} = 0.34$ volt. Thus the complete cell formed is $\ominus \text{Zn(s)} | \text{Zn}^{2+}(1\text{M}) || \text{Cu}^{2+}(1\text{M}) | \text{Cu(s)} \oplus$ and its standard potential can be calculated.

Cathode : $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Cu(s)}$ (Reduction)

Anode : $\text{Zn(s)} \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$ (Oxidation)

Cell reaction : $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$ (Redox)

$$\begin{aligned} E^0_{\text{Cell}} &= E^0_{\text{red (Cathode)}} - E^0_{\text{red (Anode)}} \\ &= E^0_{\text{Cu}^{2+}|\text{Cu}} - E^0_{\text{Zn}^{2+}|\text{Zn}} \\ &= 0.34 - (-0.76) = +0.34 + 0.76 = 1.1 \text{ volt} \end{aligned}$$

3.5 emf series

When potential of a cell is measured with reference to standard hydrogen electrode, the potential of second electrode is known as **Electro Motive Force** which is known in brief as emf. If the values of the reduction potentials of standard electrodes of the half cells is arranged in the decreasing order, then the series of the electrodes, formed is called emf series. Earlier importance was given to oxidation potential. Now, according to SI units importance is given to reduction potentials. The series of standard reduction electrode potentials based on the values of E^0_{red} is given in table 3.1.

Table 3.1 Standard Electrode Potentials at 298 K
Ions are present as aqueous species and H_2O as liquid;
gases and solids are shown by g and s

Reaction (Oxidised form + ne^-)	→	Reduced form)	E^0/V
$\text{F}_2(\text{g}) + 2\text{e}^-$	→	2F^-	2.87
$\text{Co}^{3+} + \text{e}^-$	→	Co^{2+}	1.81
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^-$	→	$2\text{H}_2\text{O}$	1.78
$\text{MnO}_4^- + 8\text{H}^+ + 5\text{e}^-$	→	$\text{Mn}^{2+} + 4\text{H}_2\text{O}$	1.51
$\text{Au}^{3+} + 3\text{e}^-$	→	Au(s)	1.40
$\text{Cl}_2(\text{g}) + 2\text{e}^-$	→	2Cl^-	1.36
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 2\text{e}^-$	→	$2\text{Cr}^{3+} + 7\text{H}_2\text{O}$	1.33
$\text{O}_2(\text{g}) + 4\text{H}^+ + 4\text{e}^-$	→	$2\text{H}_2\text{O}$	1.23
$\text{MnO}_2(\text{s}) + 4\text{H}^+ + 4\text{e}^-$	→	$\text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.23

Increasing strength of oxidising agent ↑	$\text{Br}_2 + 2\text{e}^-$	\rightarrow	2Br^-	1.09	↓ Increasing strength of reducing agent
	$\text{NO}_3^- + 4\text{H}^+ + 3\text{e}^-$	\rightarrow	$\text{NO(g)} + 2\text{H}_2\text{O}$	0.97	
	$2\text{Hg}^{2+} + 2\text{e}^-$	\rightarrow	Hg_2^{2+}	0.92	
	$\text{Ag}^+ + \text{e}^-$	\rightarrow	Ag(s)	0.80	
	$\text{Fe}^{3+} + \text{e}^-$	\rightarrow	Fe^{2+}	0.77	
	$\text{O}_2(\text{g}) + 2\text{H}^+ + 2\text{e}^-$	\rightarrow	H_2O_2	0.68	
	$\text{I}_2 + 2\text{e}^-$	\rightarrow	2I^-	0.54	
	$\text{Cu}^+ + \text{e}^-$	\rightarrow	Cu(s)	0.52	
	$\text{Cu}^{2+} + 2\text{e}^-$	\rightarrow	Cu(s)	0.34	
	$\text{AgCl(s)} + \text{e}^-$	\rightarrow	$\text{Ag(s)} + \text{Cl}^-$	0.22	
	$\text{AgBr(s)} + \text{e}^-$	\rightarrow	$\text{Ag(s)} + \text{Br}^-$	0.10	
	$2\text{H}^+ + 2\text{e}^-$	\rightarrow	$\text{H}_2(\text{g})$	0.00	
	$\text{Pb}^{2+} + 2\text{e}^-$	\rightarrow	Pb(s)	- 0.13	
	$\text{Sn}^{2+} + 2\text{e}^-$	\rightarrow	Sn(s)	- 0.14	
	$\text{Ni}^{2+} + 2\text{e}^-$	\rightarrow	Ni(s)	- 0.25	
	$\text{Fe}^{2+} + 2\text{e}^-$	\rightarrow	Fe(s)	- 0.44	
	$\text{Cr}^{3+} + 3\text{e}^-$	\rightarrow	Cr(s)	- 0.74	
	$\text{Zn}^{2+} + 2\text{e}^-$	\rightarrow	Zn(s)	- 0.76	
	$2\text{H}_2\text{O} + 2\text{e}^-$	\rightarrow	$\text{H}_2(\text{g}) + 2\text{OH}^-(\text{aq})$	- 0.83	
	$\text{Al}^{3+} + 3\text{e}^-$	\rightarrow	Al(s)	- 1.66	
	$\text{Mg}^{2+} + 2\text{e}^-$	\rightarrow	Mg(s)	- 2.36	
	$\text{Na}^+ + \text{e}^-$	\rightarrow	Na(s)	- 2.71	
	$\text{Ca}^{2+} + 2\text{e}^-$	\rightarrow	Ca(s)	- 2.87	
	$\text{K}^+ + \text{e}^-$	\rightarrow	K(s)	- 2.93	
	$\text{Li}^+ + \text{e}^-$	\rightarrow	Li(s)	- 3.05	

- (i) A negative E^0 means that the redox couple is a stronger reducing agent than the $\text{H}^+|\text{H}_2$ couple.
- (ii) A positive E^0 means that the redox couple is a weaker reducing agent than the $\text{H}^+|\text{H}_2$ couple.

The following information can be obtained from the series given in table 3.1.

- (1) In this series, the tendency to experience oxidation, tendency to release electron and the strength as reducing agent increases as we go from above to below.
- (2) In this series, the tendency to experience reduction reaction, tendency to accept electron and strength as oxidising agents increase as we go from below to above.
- (3) The standard potential of the complete cell formed by combination of two half cells and calculating their standard potentials. From this series, the information about which electrode will be anode and which will be cathode can also be obtained.
- (4) If the rods of the metals in this series, which have lower positions are placed in the solutions of salts of metals having higher position in the series the ion will be replaced as metals by the metal rods. e.g. The position of Fe is below than the position of Cu in emf series, if Fe rod is placed in a solution of Cu^{2+} the rod of Fe will transform Fe to Fe^{2+} and Cu^{2+} to Cu(s) .

Examples 3 : Write the symbolic representation of the cell formed by the use of following given standard half cells at 298 K. Write the cell reaction and calculate standard potential E_{Cell}^0 .



Solution : The standard reduction potential of zinc being less, it will act as anode. Hence, it will be written on left hand side in symbolic representation.

Symbolic representation of cell : $\ominus \text{Zn} | \text{Zn}^{2+} (1\text{M}) || \text{Ag}^+(1\text{M}) | \text{Ag} \oplus$

Cathode : $2\text{Ag}^+(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{Ag(s)}$ (Reduction)

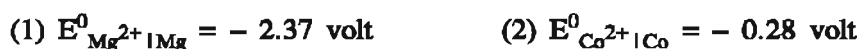
Anode : $\text{Zn(s)} \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2\text{e}^-$ (Oxidation)

Cell reaction : $\text{Zn(s)} + 2\text{Ag}^+(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + 2\text{Ag(s)}$ (Redox)

$$\begin{aligned} E_{\text{Cell}}^0 &= E_{\text{red (Cathode)}}^0 - E_{\text{red (Anode)}}^0 \\ &= E_{\text{Ag}^+|\text{Ag}}^0 - E_{\text{Zn}^{2+}|\text{Zn}}^0 \\ &= (0.80) - (-0.76) \\ &= 1.56 \text{ volt} \end{aligned}$$

In the equation the reaction at the cathode is multiplied by 2, even then the value of E_{red}^0 is not multiplied by two because, for the balancing of equation the equation of the half cell is multiplied by two but the definition of standard cell for 1M concentration does not change.

Example 4 : Write the symbolic representation of cell formed by the given two following half cells at 298 K. Write the reaction of the cell and calculate its standard potential.



Solution : As the standard reduction potential of magnesium is less, it will act as anode. Hence, it can be written on left hand side in symbolic representation.

Symbolic representation of cell : $\ominus \text{Mg(s)} | \text{Mg}^{2+} (1\text{M}) || \text{Co}^{2+}(1\text{M}) | \text{Co(s)} \oplus$

Cathode : $\text{Co}^{2+}(\text{aq}) + 2\text{e}^- \rightleftharpoons \text{Co}(\text{s})$ (Reduction)

Anode : $\text{Mg}(\text{s}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2\text{e}^-$ (Oxidation)

Cell reaction : $\text{Mg}(\text{s}) + \text{Co}^{2+}(\text{aq}) \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + \text{Co}(\text{s})$

$$\begin{aligned}E_{\text{Cell}}^0 &= E_{\text{red (Cathode)}}^0 - E_{\text{red (Anode)}}^0 \\&= E_{\text{Co}^{2+}|\text{Co}}^0 - E_{\text{Mg}^{2+}|\text{Mg}}^0 \\&= (-0.28) - (-2.37) = 2.09 \text{ volt}\end{aligned}$$

3.6 Nernst Equation

It is not necessary always that the concentration of all the species involved in electrode reaction should be unity. The potential of the electrochemical cell depends on temperature, concentration of solutions associated with cell reaction and nature of electrode. Scientist Nernst first of all gave the equation showing relation between the potential of the electrochemical cell and the concentration of solutions associated with the reaction. He mentioned that this equation can be deduced on the basis of principles of **thermodynamics**.

According to Nernst, in the electrode reaction,



The electrode potential at any concentration can be measured as the representative of the standard hydrogen electrode as follows :

$$E_{(\text{M}^{n+}|\text{M})} = E_{(\text{M}^{n+}|\text{M})}^0 - \frac{RT}{nF} \ln \frac{M}{[\text{M}^{n+}]}$$

But taking concentration of solid form M as constant,

$$E_{(\text{M}^{n+}|\text{M})} = E_{(\text{M}^{n+}|\text{M})}^0 - \frac{RT}{nF} \ln \frac{1}{[\text{M}^{n+}]}$$

$E_{(\text{M}^{n+}|\text{M})}^0$ is already known. R = gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and F is Faraday constant ($96500 \text{ coulomb mol}^{-1}$), T = Temperature in Kelvin and $[\text{M}^{n+}]$ is the concentration of that form.

We can write the concentrations of Cu^{2+} and Zn^{2+} ions in Daniell cell, in the given electrode potential.

$$\text{For cathode} : E_{(\text{Cu}^{2+}|\text{Cu})} = E_{(\text{Cu}^{2+}|\text{Cu})}^0 - \frac{RT}{2F} \ln \frac{1}{[\text{Cu}^{2+}]} \quad (1)$$

$$\text{For anode} : E_{(\text{Zn}^{2+}|\text{Zn})} = E_{(\text{Zn}^{2+}|\text{Zn})}^0 - \frac{RT}{2F} \ln \frac{1}{[\text{Zn}^{2+}]} \quad (2)$$

$$\begin{aligned}\text{Cell potential} : E_{\text{Cell}} &= E_{(\text{Cu}^{2+}|\text{Cu})} - E_{(\text{Zn}^{2+}|\text{Zn})} \\&= E_{(\text{Cu}^{2+}|\text{Cu})}^0 - \frac{RT}{2F} \ln \frac{1}{[\text{Cu}^{2+}]} - E_{(\text{Zn}^{2+}|\text{Zn})}^0 + \frac{RT}{2F} \ln \frac{1}{[\text{Zn}^{2+}]} \\&= E_{(\text{Cu}^{2+}|\text{Cu})}^0 - E_{(\text{Zn}^{2+}|\text{Zn})}^0 - \frac{RT}{2F} \ln \frac{1}{[\text{Cu}^{2+}]} + \frac{RT}{2F} \ln \frac{1}{[\text{Zn}^{2+}]}\end{aligned}$$

$$\therefore E_{\text{Cell}} = E_{\text{Cell}}^0 - \frac{RT}{2F} \ln \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \quad (3)$$

It can be said from this that E_{Cell} depends on the concentration of Cu^{2+} and Zn^{2+} ions. Its value increases with increase in concentration of Cu^{2+} and decreases with increase in concentration of Zn^{2+} .

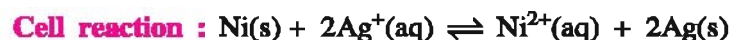
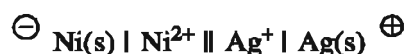
Putting the values of R, F and T and converting natural logarithm to the base-10 then, the equation (3) will be like this.

$$\frac{2.303 RT}{F} = 0.059$$

$$\text{Thus, } E_{\text{Cell}} = E^0_{\text{Cell}} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \quad (4)$$

As same number of electrons(n) are taken for both the electrodes, cell can be shown as above.

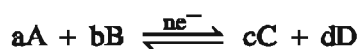
In the same way, if we have different electrons for the two electrodes, the cell can be shown as below :



It can be written according to Nernst equation as follows :

$$E_{\text{Cell}} = E^0_{\text{Cell}} - \frac{0.059}{n} \log \frac{[\text{Ni}^{2+}]}{[\text{Ag}^+]^2}$$

The general equation of electrochemical equation will be like this



According to Nernst equation,

$$E_{\text{Cell}} = E^0_{\text{Cell}} - \frac{RT}{nF} \ln K \quad \text{Where } K = \text{equilibrium constant}$$

$$= E^0_{\text{Cell}} - \frac{RT}{nF} \ln \frac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$$

The potential of non-standard half cells can be calculated by Nernst equation. If we write $\text{Co}^{2+} \mid \text{Co}$ half cell reaction as reduction reaction then it will be, $\text{Co}^{2+}(\text{aq}) + 2e^- \rightleftharpoons \text{Co(s)}$.

$$E_{(\text{Co}^{2+} \mid \text{Co})} = E^0_{(\text{Co}^{2+} \mid \text{Co})} - \frac{0.059}{2} \log \frac{1}{[\text{Co}^{2+}]}$$

But if we write $\text{Co} \mid \text{Co}^{2+}$ half cell reaction as oxidation reaction, then, it will be $\text{Co(s)} \rightleftharpoons \text{Co}^{2+}(\text{aq}) + 2e^-$

$$E_{(\text{Co} \mid \text{Co}^{2+})} = E^0_{(\text{Co} \mid \text{Co}^{2+})} - \frac{0.059}{2} \log [\text{Co}^{2+}]$$

in which the potential expressed is oxidation potential.

Example 5 : Calculate the cell potential of the following cell as 298 K.

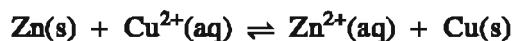
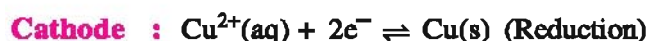


$$E^0_{(\text{Zn}^{2+} | \text{Zn})} = -0.76 \text{ volt}, \quad E^0_{(\text{Cu}^{2+} | \text{Cu})} = 0.34 \text{ volt},$$

Solution : Here zinc electrode is anode and copper electrode is cathode. Its standard electrode potential values are given. On the basis of which E^0_{Cell} can be calculated.

$$\begin{aligned} E^0_{\text{Cell}} &= E^0_{(\text{Cu}^{2+} | \text{Cu})} - E^0_{(\text{Zn}^{2+} | \text{Zn})} \\ &= 0.34 \text{ volt} - (-0.76 \text{ volt}) \\ &= 0.34 + 0.76 \\ &= 1.10 \text{ volt} \end{aligned}$$

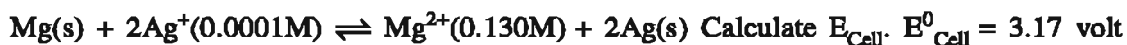
Cell reaction :



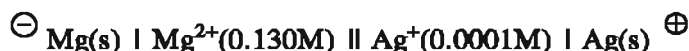
Here n equal to 2.

$$\begin{aligned} E_{\text{Cell}} &= E^0_{\text{Cell}} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \\ &= 1.10 - \frac{0.059}{2} \log \frac{[0.6]}{[0.3]} \\ &= 1.10 - 0.0295 \log 2.0 \\ &= 1.10 - (0.0295) (0.3010) \\ &= 1.10 - 0.0089 = 1.0911 \text{ volt} \end{aligned}$$

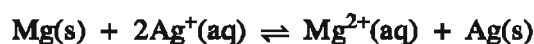
Example 6 : The following reaction occurs in the cell



Solution : The cell can be written like this



Cell reaction :



Hence n equal to 2

$$E_{\text{Cell}} = E_{\text{Cell}}^0 - \frac{RT}{2F} \ln \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2}$$

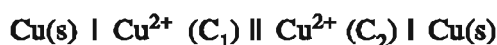
$$E_{\text{Cell}} = 3.17 - \frac{0.059}{2} \log \frac{[\text{Mg}^{2+}]}{[\text{Ag}^+]^2}$$

$$E_{\text{Cell}} = 3.17 - \frac{0.059}{2} \log \frac{[0.130]}{(0.0001)^2}$$

$$= 3.17 - 0.21 = 2.96 \text{ volt}$$

3.6.1 Concentration Cell :

If the two electrodes of the electrochemical cell are same but the concentrations of the solutions of the electrolyte are different, then it is called concentration cell, viz



The concentrations of ions change in cell reaction of concentration cell as shown below; which is the result of redox reaction. The ions of concentrated solution move towards dilute solution and so this type of cell is called concentration cell.

In this cell for the reaction $\ominus \text{Cu(s)} \mid \text{Cu}^{2+}(\text{C}_1) \parallel \text{Cu}^{2+}(\text{C}_2) \mid \text{Cu(s)} \oplus$, $E_{\text{Cell}}^0 = 0.0 \text{ volt}$

Cathode : $\text{Cu}^{2+}(\text{C}_2) + 2\text{e}^- \rightleftharpoons \text{Cu(s)}$

Anode : $\text{Cu(s)} \rightleftharpoons \text{Cu}^{2+}(\text{C}_1) + 2\text{e}^-$

Cell reaction : $\text{Cu}^{2+}(\text{C}_2) \rightleftharpoons \text{Cu}^{2+}(\text{C}_1)$

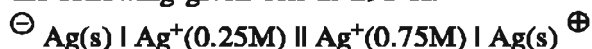
Generally reduction occurs in concentrated solution and so it will be written on right hand side and will act as cathode. The cell potential of concentration cell is calculated by the following formula.

$$E_{\text{Cell}} = E_{\text{Cell}}^0 - \frac{0.059}{n} \log \frac{[\text{C}_1]}{[\text{C}_2]}$$

Here, $E_{\text{Cell}}^0 = 0.0 \text{ volt}$ because both the electrodes are same and the values of their standard oxidation and reduction potentials are same but the sign is positive or negative and so its sum will be zero. In both the half cells, concentrations of Cu^{2+} are different, but positive ion is same in the solution. The values of electrode potentials of anode half cell and cathode half cell are same but of opposite signs. Hence, $E_{\text{Cell}}^0 = 0.0 \text{ volt}$.

$$E_{\text{Cell}} = 0.0 - \frac{0.059}{n} \log \frac{[\text{C}_1]}{[\text{C}_2]}$$

Example 7 : The standard reduction potential of $\text{Ag}^+ \mid \text{Ag}$ half cell is 0.80 volt. Calculate the potential of the following given cell at 298 K.



Solution :

Cathode : $\text{Ag}^+(0.75\text{M}) + \text{e}^- \rightleftharpoons \text{Ag(s)}$ (Reduction)

Anode : $\text{Ag(s)} \rightleftharpoons \text{Ag}^+(0.25\text{M}) + \text{e}^-$ (Oxidation)

Cell reaction : $\text{Ag}^+(0.75\text{M}) \rightleftharpoons \text{Ag}^+(0.25\text{M})$

It appears from the above equation that when cell is in operation the ions of concentrated solution move towards the dilute solution. For this cell, $E_{\text{Cell}}^0 = 0.0$ volt

$$\begin{aligned} E_{\text{Cell}} &= E_{\text{Cell}}^0 - \frac{0.059}{n} \log \frac{[C_1]}{[C_2]} \\ &= 0.00 - \frac{0.059}{1} \log \frac{0.25}{0.75} \quad (\text{Here taking } n = 1) \\ &= -0.059 \times \left(\log \frac{1}{3} \right) = -0.0592 \times (\log 1 - \log 3) \\ &= -0.059 \times (-0.4771) = +0.0282 \text{ volt} \end{aligned}$$

Example 8 : The reduction potential of half cell $\text{Cu}^{2+} | \text{Cu}$ is 0.34 volt. Calculate the potential of the given following cell.



Solutoin :

Cathode : $\text{Cu}^{2+}(1\text{M}) + 2\text{e}^- \rightleftharpoons \text{Cu(s)}$ (Reduction)

Anode : $\text{Cu(s)} \rightleftharpoons \text{Cu}^{2+}(0.1\text{M}) + 2\text{e}^-$ (Oxidation)

Cell reaction : $\text{Cu}^{2+}(1\text{M}) \rightleftharpoons \text{Cu}^{2+}(0.1\text{M})$
(C₂) (C₁)

In concentration cell, the ions of the solution travel towards dilute solution and in concentration cell $E_{\text{Cell}}^0 = 0.00$.

$$\begin{aligned} E_{\text{Cell}} &= E_{\text{Cell}}^0 - \frac{0.059}{n} \log \frac{[C_1]}{[C_2]} \\ &= 0.00 - \frac{0.059}{2} \log \frac{(0.1)}{(1.0)} \quad (\text{Here taking } n = 2) \\ &= -0.0295 \times \log \frac{0.1}{1} = -0.0295 \times \log \frac{1}{10} \\ &= -0.0295 \times (-1) = 0.0295 \text{ volt} \end{aligned}$$

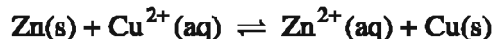
The potential of concentration cell is comparatively less. As the ions from the concentration solution travel towards dilute solution, there is an effort for equalisation of same concentration of both the half cells.

If the value of the potential of the cell obtained is negative it is believed that the electrode which was assumed to be anode is in fact cathode and the electrode which was assumed to be cathode is in fact anode.

3.7 Some Applications of Cell Potentials

- (1) On the basis of the values of cell potential the equilibrium constant of the reaction taking place in the cell can be calculated.
- (2) By construction of proper cell and on the basis of its potential value the pH of acidic solutions and ionic product of water can be calculated.
- (3) Some titrations can be carried out using cell potentials.

Calculation of Equilibrium constant : Daniell cell (fig.3.1) possesses closed circuit and we have, noted the following reaction.



In the cell indicating this reaction, the concentration of Zn^{2+} increases and the concentration of Cu^{2+} decrease with the lapse of time. At this time, the potential of the cell can be read on the voltmeter or potentiometer in which the decrease in volt will appear. After some time, we can record that there is no change in concentrations of Cu^{2+} and Zn^{2+} ions at that time. This situation is the indication of equilibrium. In this case, Nernst equation can be written as follows :

$$E_{\text{Cell}} = E_{\text{Cell}}^0 - \frac{2.303 RT}{2F} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \text{ or}$$

$$E_{\text{Cell}} = E_{\text{Cell}}^0 - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

But at equilibrium $\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = K_C$ Hence, the above equation can be written for this reaction (reaction equation) and $T = 298 \text{ K}$.

$$\therefore E_{\text{Cell}}^0 = \frac{2.303 RT}{nF} \log K_C \quad (5)$$

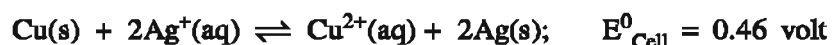
$$E_{\text{Cell}}^0 = \frac{0.059}{2} \log K_C = 1.1 \text{ volt } (\because E_{\text{Cell}}^0 = 1.1 \text{ volt})$$

$$\log K_C = \frac{(1.1 \times 2)}{(0.059)} = 37.288$$

$$\text{At } 298 \text{ temperature } K_C = 1.941 \times 10^{37}$$

Thus, equation (5) shows the relation between standard electrode potential and the equilibrium constant for the reaction taking place. Thus, it is difficult to measure equilibrium constant; but the calculation related to E^0 can be carried out.

Example 9 : Calculate the equilibrium constant of the reaction.



Solution :

$$E_{\text{Cell}}^0 = \frac{0.059}{2} \log K_C = 0.46 \text{ volt or}$$

$$\log K_C = \frac{0.46 \times 2}{0.059} = 15.593$$

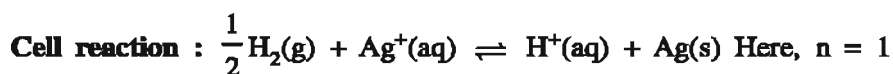
$$\therefore K_C = 3.92 \times 10^{15}$$

Example 10 : The potential of the following given cell is 1.02 volt at 298 K temperature. Calculate the pH of HCl solution. ($E^0_{\text{Ag}^+|\text{Ag}} = 0.80$ volt).



$$\begin{aligned} \text{Solution : } E^0_{\text{Cell}} &= E^0_{\text{red (Cathode)}} - E^0_{\text{red (Anode)}} \\ &= E^0_{(\text{Ag}^+|\text{Ag})} - E^0_{(\text{H}^+|\frac{1}{2}\text{H}_2)} \\ &= 0.80 - 0.0 \end{aligned}$$

$$E^0_{\text{Cell}} = 0.80 \text{ volt}$$



$$E_{\text{Cell}} = E^0_{\text{Cell}} - \frac{0.059}{n} \log \frac{[\text{H}^+]}{[\text{Ag}^+]}$$

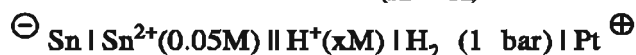
$$1.02 = 0.80 - 0.059 \log \frac{[\text{H}^+]}{[0.01]}$$

$$\frac{0.22}{0.059} = -\log [\text{H}^+] + (-2.0)$$

$$3.729 = \text{pH} - 2.0$$

$$\therefore \text{pH} = 5.729$$

Example 11 : The potential of the given following cell is 0.096 volt at 298 K temperature. Calculate pH of HCl solution ($E^0_{(\text{Sn}^{2+}|\text{Sn})} = -0.14$ volt)



$$\begin{aligned} \text{Solution : } E^0_{\text{Cell}} &= E^0_{(\text{H}^+|\frac{1}{2}\text{H}_2)} - E^0_{(\text{Sn}^{2+}|\text{Sn})} \\ E^0_{\text{Cell}} &= 0.0 - (-0.14) = 0.14 \text{ volt} \end{aligned}$$



$$E_{\text{Cell}} = E^0_{\text{Cell}} - \frac{0.059}{n} \log \frac{[\text{Sn}^{2+}]}{[\text{H}^+]^2}$$

$$\therefore 0.096 = 0.14 - 0.0295 \log \frac{(0.05)}{[\text{H}^+]^2}$$

$$\therefore \frac{-0.096 - 0.14}{0.0295} = -\log \frac{(0.05)}{[\text{H}^+]^2}$$

$$\therefore \frac{-0.044}{0.0295} = -\log (0.05) + 2\log [\text{H}^+]$$

$$\therefore \frac{0.044}{0.0295} = -1.3010 + 2 \log [H^+]$$

$$\therefore -1.491 = -1.3010 + 2 \log [H^+]$$

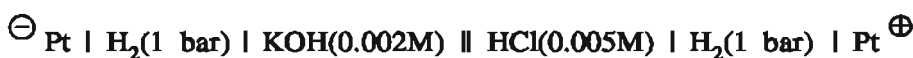
$$\therefore 1.491 + 1.3010 = -2 \log [H^+]$$

$$\therefore 1.491 + 1.3010 = 2 \times \text{pH}$$

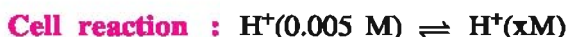
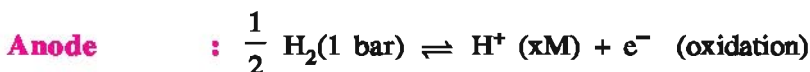
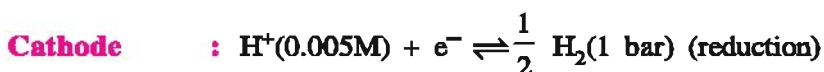
$$\therefore \frac{2.792}{2} = \text{pH}$$

$$\therefore \text{pH} = 1.396$$

Example 12 : The potential of the given following cell is 0.53 volt. Calculate the ionic product (K_w) of water.



Solution :



The change is only in concentrations of H^+

$$\therefore E^0_{\text{Cell}} = 0.00 \text{ volt in this cell.}$$

The concentration of OH^- in 0.002 M KOH is 0.002 M. In any aqueous solution, existence of H^+ and OH^- is there and the product of their concentration is K_w . Hence, for KOH solution,

$$[\text{H}^+][\text{OH}^-] = K_w, \text{ but } [\text{OH}^-] = 0.002 \text{ M}$$

$$\therefore [\text{H}^+] \text{ in KOH solution} = \frac{K_w}{(0.002)}$$

$$E_{\text{Cell}} = E^0_{\text{Cell}} - \frac{0.059}{1} \log \frac{(\text{Concentration } \text{H}^+ \text{ in KOH solution})}{(\text{Concentration } \text{H}^+ \text{ in HCl solution})}$$

$$0.53 = 0.00 - \frac{0.059}{1} \log \frac{K_w/0.002}{0.005}$$

$$\frac{0.53}{0.059} = -\log \left(\frac{K_w}{0.002 \times 0.005} \right) = -\log K_w + \log (10^{-5})$$

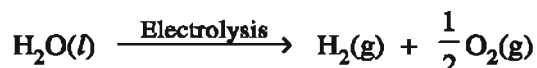
$$8.983 = -\log K_w - 5.0$$

$$\log K_w = -8.983 - 5.0 = -13.983$$

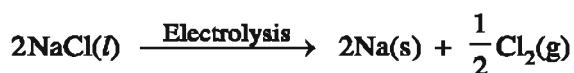
$$\therefore K_w = \text{antilog } \bar{14}.017 = 1.04 \times 10^{-14}$$

3.8 Electrolysis

Electrolysis is redox reaction. In electrolysis, electrical energy is transformed to chemical energy. The apparatus used for this is called electrolytic cell. When electric current is passed through an aqueous solution of electrolyte or molten electrolyte, by dipping proper electrodes in the solution, this type of redox reaction resulting from oxidation and reduction reactions at the electrodes, of products are obtained. The result of this type of redox reaction is known as electrolysis. viz. If few drops of sulphuric acid are added to distilled water and it is electrolysed with inert electrodes of platinum, dihydrogen gas is produced at the cathode and dioxygen gas at the anode.



Similarly, by electrolysis of molten sodium chloride, sodium metal is obtained at the cathode and dichlorine gas at the anode.



Faraday's laws of Electrolysis : Scientist Michael Faraday, in 1834, established the following relations, regarding the amounts of the products obtained by the reaction and the quantity of the electricity used for it. They are called Faraday's laws of electrolysis.

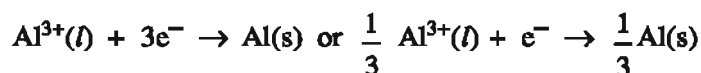
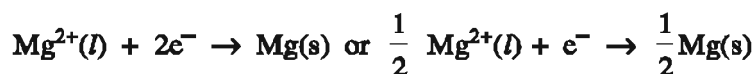
(i) First law : The amount of products produced at the electrodes by electrolysis are directly proportional to the quantity of the electricity passed through the electrolytic cell. If W is the mass of the product produced and Q is value of the quantity of electricity passed, then $W \propto Q$.

(ii) Second law : If the different electrolytic cells, containing different electrolytes are joined in series and same quantity of electricity is passed through them, then the amounts of products obtained at the electrodes are directly proportional to their equivalent weights.

$W \propto Eq$, where, W = Mass of product obtained and Eq = Equivalent weight of product.

After the establishment of above Faraday's laws, in the starting years of the twentieth century, the knowledge about the electronic configuration of the atom was developed and hence the basic information about redox reaction could be obtained. During this, the concept of mole was also accepted. Hence, the **modern presentation** of Faraday's law was made as follows:

"The products, obtained at the electrodes by oxidation and reduction half-reactions have the relation with the moles of the products and stoichiometry of the reaction and the quantity of electricity." The explanation of this law can be understood in detail by the following illustrations.



This reduction half cells indicate that if 1 mole electrons electric current is passed, 1 mole sodium, $\frac{1}{2}$ mole magnesium and $\frac{1}{3}$ mole aluminium masses will be respectively obtained.

The quantity of electricity passed by 1 mole electrons is called one Faraday. It is expressed as F.

The electric quantity on one electron is 1.602×10^{-19} coulomb

Hence, the electric quantity of one mole of electron is

$$1 \text{ Faraday (F)} = 1.602 \times 10^{-19} \times 6.022 \times 10^{23} \text{ electron mole}^{-1} \\ = 96487 \text{ } (\cong 96500) \text{ Coulomb mole}^{-1} \text{ (electron)}$$

In Coulomb unit, 1 Faraday = 96487 coulombs

But generally **96500** coulombs is accepted for calculations.

If I ampere current is passed through electrolytic cell for t seconds, the quantity of electricity Q in coulomb units can be calculated by the following equation.

$$Q = I \times t \text{ (I = electric current in amperes, t = time in seconds)}$$

The amounts of substances liberated at the electrodes depend upon the quantity of electricity passed. If quantity of electricity equal to 1 Faraday is passed then $\frac{1}{n}$ mole substance will be liberated at the electrode; where n is the number of moles of electrons associated with the reaction at the cathode.

Table 3.2 Electricity Quantity and Electrolysis

Sr	Reaction occurring at the electrode	Number of moles of electron	Quantity of electricity (F)	$\frac{\text{Moles}}{\text{F}}$
1.	$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	1	1	1
2.	$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	2	2	$\frac{1}{2}$
3.	$\text{Al}^{3+}(\text{l}) + 3\text{e}^- \rightarrow \text{Al}(\text{s})$	3	3	$\frac{1}{3}$
4.	$2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2\text{e}^-$	2	2	$\frac{1}{2}$
5.	$2\text{H}_2\text{O}(\text{l}) \rightarrow \text{O}_2(\text{g}) + 4\text{H}^+(\text{aq}) + 4\text{e}^-$	4	4	$\frac{1}{4}$

The efficiency of the electrolytic cell is not always 100 percent. Hence, the efficiency of the cell can be calculated by the following formula.

$$\text{Efficiency of cell (\%)} = \frac{\text{Experimental value of product}}{\text{Theoretical value of product}} \times 100$$

Example 13 : In the electrolysis of aqueous solution of CuCl_2 copper is deposited on the negative electrode and chlorine gas liberated on the positive electrode at 800 K temperature and 1 bar pressure. How much copper and chlorine gas will be liberated if 2.0 ampere current is passed for 1 hour ? ($F = 96500$ Coulomb) ($\text{Cu} = 63.5\text{u}$, $\text{Cl} = 35.5 \text{ u}$) ($R = 0.08314 \text{ bar Litre mol}^{-1} \text{ K}^{-1}$).

Solution : We will calculate the total quantity of electricity passed according to the definition $Q = I \times t$

$$\text{Quantity of electricity} = 2 \times 60 \times 60 = 7200 \text{ coulomb}$$

$$= \frac{7200}{96500} = 0.075 \text{ F}$$

Reaction occurring at cathode : $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$
(2 mole) (63.5 gram mole⁻¹)

In the above reaction, 2F are associated with 1 mole Cu. Hence, the Cu associated with 0.075 F.

$$\begin{aligned} \text{mole of Cu} &= \frac{0.075}{2} = 0.0375 \text{ mole} \\ &= 0.0375 \times 63.5 \\ &= 2.38 \text{ gram Cu will be obtained.} \end{aligned}$$

Similarly,

At the anode $2\text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2 (\text{g}) + 2\text{e}^-$

i.e. 1 mole Cl_2 gas is associated with 2F quantity of electricity.

$$\text{Cl}_2 \text{ gas associated with } 0.075 \text{ F quantity of electricity} = \frac{1 \times 0.075}{2} = 0.0375 \text{ mole}$$

According to simple gas equation. $PV = nRT$

The volume of Cl_2 gas at 300 K temperature and 1 bar pressure

$$\begin{aligned} &= \frac{0.0375 \times 0.08314 \times 300}{1} \\ &= 0.9353 \text{ litre} \end{aligned}$$

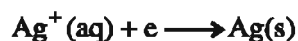
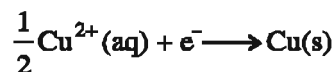
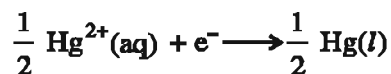
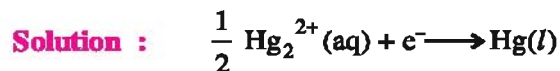
Example 14 : How much O_2 gas will be collected at the anode at 300 K temperature and 1 bar pressure if 2.5 ampere electric current is passed for one hour in electrolysis of aqueous solution of Na_2SO_4 . ($F = 96500$ coulomb) [1 mole gas volume is 22.4 litre at STP].

Solution : $2\text{H}_2\text{O}(\text{l}) \rightarrow 4\text{H}^+(\text{aq}) + \text{O}_2(\text{g}) + 4\text{e}^-$
1 mole 4F (22.4 litre at STP)

The volume of liberated O_2 at 300 K temperature and 1 bar pressure

$$\begin{aligned} &= \frac{2.5 \times 60 \times 60}{96500} \times \frac{1}{4} \times \frac{22400}{1} \times \frac{300}{273} \times \frac{1}{1} \\ &= 573.93 \text{ ml} \end{aligned}$$

Example 15 : 2.68 ampere electric current is passed for 1 hour from the solutions of $\text{Hg}_2(\text{ClO}_4)_2$, $\text{Hg}(\text{ClO}_4)_2$, CuSO_4 and AgNO_3 . How many moles of each metal will be deposited on cathode ?



As the electrolytes are arranged in the series and same quantity of electricity will pass through them.

$$\text{Quantity of electricity} = 2.68 \times 3600 = 9648$$

$$= \frac{9648}{96500} = 0.09998 \text{ F} = 0.1 \text{ F}$$

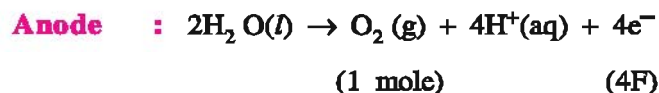
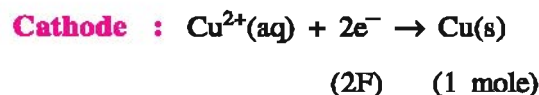
Thus, 0.1F quantity of electricity will pass through each electrolyte. Hence, as shown earlier 0.1 mole Hg_2^{2+} , 0.05 mole Hg^{2+} , 0.05 mole Cu^{2+} and 0.01 mole Ag^+ will be reduced to metal getting deposited on the cathode.

Example 16 : How many grams of Cu and what volume of O_2 gas will be obtained at 300 K temperature and 1 bar pressure by passing 10 ampere current for 193 minutes from an aqueous solution of CuSO_4 ? The efficiency of the electrolytic cell is 80% ($\text{Cu} = 63.5 \text{ u}$).

Solution : The quantity of electricity passed = $I \times t$
 $= 10 \times 193 \times 60 \text{ coulomb}$

$$= \frac{10 \times 193 \times 60}{96500} = 1.2 \text{ F}$$

Chemical reactions :



According to the reaction; by passing 2 Faraday electric current 1 mole Cu and by passing 4 Faraday electric current 1 mole O_2 gas are produced.

For Cu : when 2 Faraday electric current is passed 1 mole Cu will be obtained

When 1.2 Faraday electric current is passed $\frac{1.2}{2} = 0.6$ mole Cu will be obtained.

Weight of copper = $0.6 \times 63.5 = 38.1$ gram

As the efficiency of the cell is 80 % so, $\frac{38.1 \times 80}{100} = 30.48$ gram Cu will be obtained.

For O_2 gas, when 4 Faraday, electric current is passed 1 mole O_2 gas is produced.

When 1.2 Faraday electric current is passed $= \frac{1.2}{4} = 0.3$ mole O_2 gas will be obtained.

According to simple gas equation, $PV = nRT$

$$V = \frac{nRT}{P} = \frac{0.3 \times 0.08314 \times 300}{1} = 7.4826 \text{ litre.}$$

As the efficiency of the cell is 80 % so, $\frac{7.4826 \times 80}{100} = 5.986$ litre

Example 17 : 0.972 gram Ag is obtained by passing 5 ampere electric current for 193 seconds through an aqueous solution of silver nitrate ($AgNO_3$) between graphite electrodes, calculate the efficiency of the electrolytic cell.

Solution : The quantity of electricity passed = $I \times t$

$$= 5 \times 193 = 965 \text{ coulomb}$$

$$= \frac{5 \times 193}{96500} = 0.01 \text{ Faraday}$$

Cathode : $Ag^+ (aq) + e^- \rightarrow Ag(s)$

According to the reaction when 1 Faraday of electric current is passed 1 mole Ag is obtained. So, 0.01 Faraday electric current is passed, 0.01 mole Ag will be obtained.

\therefore Weight of Ag = mole of Ag \times atomic weight of Ag

$$= 0.01 \text{ mole} \times 108 \text{ g mol}^{-1} = 1.08 \text{ gram Ag will be obtained}$$

This is the value obtained by calculation and so it is considered as theoretical value. 0.972 gram Ag is released in the electrolytic cell during electrolysis. it becomes experimental value.

$$\text{Efficiency of the cell} = \frac{\text{Experimental value}}{\text{Theoretical value}} \times 100$$

$$= \frac{0.972 \times 100}{1.08} = 90\%$$

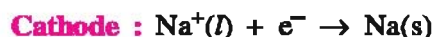
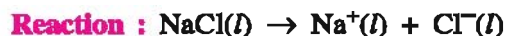
The efficiency of the cell is 90%.

3.9 Products Obtained by Electrolysis

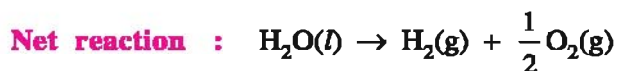
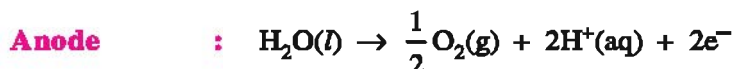
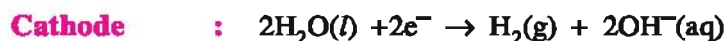
Which products will be obtained by electrolysis of aqueous solutions of salts depend upon the nature of the electrodes used for it, concentration of solutions and the electromotive force. Some of the illustrations strengthening this statement are given below :

3.9.1 Electrolysis of NaCl :

(a) Electrolysis of molten NaCl : Na metal and Cl_2 gas are obtained on the cathode and anode respectively when molten NaCl is electrolysed using cathode of steel and anode of graphite.

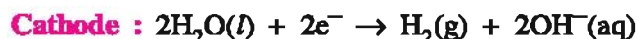


(b) Electrolysis of dilute aqueous solution of NaCl : When dilute aqueous solution of NaCl is electrolysed using graphite electrodes, dihydrogen gas at cathode and dioxygen gas at anode are obtained by net reaction of only electrolysis of water. In dilute solution as concentration of Cl^- ion is less, Hence, dioxygen O_2 is obtained instead of Cl_2 . Similarly reduction $\text{Na}^+(\text{aq})$ on cathode being difficult it is difficult to have its reduction on cathode. Instead of Na, H_2 gas is obtained by reduction of H_2O and $\text{OH}^-(\text{aq})$ are formed.



Thus, the electrolysis of dilute aqueous solution of NaCl, in fact is the electrolysis of water.

(c) Electrolysis of Concentrated Aqueous Solution of NaCl : During the electrolysis of concentrated aqueous solution of NaCl between graphite electrodes, takes place by following reaction. As concentration of Cl^- is more in concentrated solution of NaCl, Cl^- ions are oxidised at the anode instead of H_2O and so Cl_2 gas is obtained.

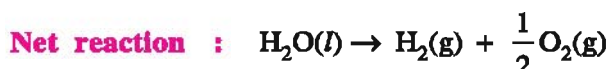
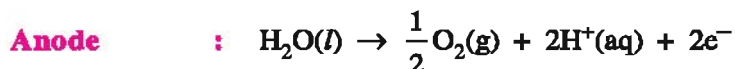
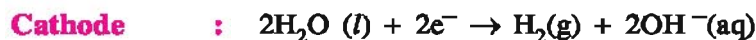


$\text{Na}^+(\text{aq})$ ions of the solution does not undergo reduction reaction because reduction of H_2O is easier, H_2 gas is obtained at the cathode. Thus, by electrolysis of concentrated aqueous solution of NaCl, Cl_2 gas is obtained at the cathode and Na^+ ions of the solution combine with OH^- near the cathode and gives NaOH.

It is observed from all the above three illustrations, that different products are obtained by electrolysis of a substance in its different concentrations and also in its molten state.

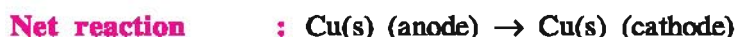
3.10 Electrolysis of aqueous solution of Na_2SO_4

In the electrolysis of dilute aqueous solution of Na_2SO_4 between graphite electrodes, O_2 gas is obtained at the anode and H_2 gas is obtained at the cathode in the net reaction of electrolysis of water. Reduction at Na^+ ion and oxidation of SO_4^{2-} ions being difficult, these ions do not experience the reaction.



3.11 Electrolysis of aqueous solution of CuSO_4

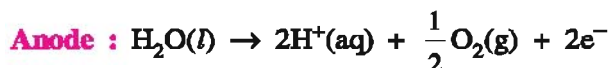
(a) If the electrolysis of aqueous solution of CuSO_4 between copper electrodes, is carried out, the copper of anode deposits on the cathode as the net reaction. The copper electrode (anode) being active, it experiences oxidation reaction during electrolysis.



As the reaction proceeds (cathode) further, the weight of copper anode decreases because the anode of copper being active produces Cu^{2+} by experiencing oxidation reaction.

Copper metal $\text{Cu}(s)$ is deposited at the cathode by experiencing reduction reaction and so weight of cathode increases. If electrolysis is carried out using impure copper as anode at proper electrical potential the impurities which do not experience oxidation, remain in the solution. In the metallurgy of copper, the inert metals like Au, Pt which do not experience oxidation, are released from the anode and deposited at the bottom of the cell. It is called **anode mud**.

(b) If electrolysis of aqueous solution of CuSO_4 between inert electrodes like graphite or platinum is carried out, the reactions take place as follows:



The oxidation of SO_4^{2-} in the solution is difficult in comparison to oxidation of H_2O . H_2O gets oxidised and $\text{H}^+(aq)$ and O_2 gas are produced. The reduction take place of $\text{Cu}^{2+}(aq)$ ion and they are removed from the solution. In this electrolysis, copper is deposited on cathode and O_2 gas is produced anode and H_2SO_4 is produced in solution.

Electrolysis being very important reaction, production of metals like Na, Ag, Al and production of NaOH, KOH and refining (purification) of metals like Cu, Ag, Au are carried out by electrolysis. Electrolysis-reaction is also used in electroplating of metals.

3.12 Gibbs' Free Energy and Cell Potential

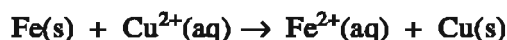
You have necessary information about Gibbs' free energy in thermodynamics. You have studied in detail that for spontaneous reactions the free energy of the system decreases that means the change in free energy becomes negative. For the electrochemical cells, when electrodes are connected the chemical reactions occur spontaneously and so the value of ΔG is negative. If the potential of the cell is E_{Cell} and if n Faraday electricity is obtained from the cell then, $\Delta G = -nFE_{\text{Cell}}$

where F is Faraday constant. The above equation for a standard cell can be written like this $\Delta G^0 = -nFE_{\text{Cell}}^0$

If the evolved electrical energy is completely transformed into electrical work then, $\Delta G = W_{\text{electrical}} = -nFE_{\text{Cell}}$

Thus, change in free energy is equivalent to electrical work.

Example 18 : The electric current is produced in an electrochemical cell by the given following reaction.



If 0.85 Faraday electricity is obtained from standard cell, then what maximum work can be done ? The value of potential of this standard cell is 0.78 volt.

Solution : Maximum electrical work $\Delta G^0 = W_{\text{electrical}} = -nFE_{\text{Cell}}^0$

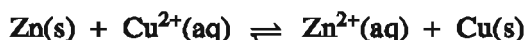
$$= -0.85 \times 96500 \times 0.78$$

$$= -63979.50 \text{ volt coulombs}$$

$$= -6.398 \times 10^4 \text{ joules (1 volt coulombs = 1 joule)}$$

The equilibrium constant of a cell reaction can be calculated on the basis of value of cell potential. For this we will see the following example.

Example 19 : Calculate the equilibrium constant and free energy change of given following reaction for Daniell cell at 298 K temperature.



Cell potential = 1.1 volt ($F = 96500$ coulomb)

Solution : For this reaction $n = 2$,

$$\Delta G^0 = -nFE_{\text{Cell}}^0 = -RT \ln K = -2.303RT \log K$$

$$\log K = \frac{nFE_{\text{Cell}}^0}{2.303RT}$$

$$= \frac{2 \times 96500 \times 1.1}{2.303 \times 8.314 \times 298}$$

$$\log K = 37.2074$$

$$K = 1.61 \times 10^{37}$$

$$\Delta G^0 = -nFE_{\text{Cell}}^0 = -2 \times 96500 \times 1.1 \text{ volt coulomb}$$

$$= -212300.0 \text{ joule} = -2.123 \times 10^5 \text{ joule}$$

3.13 Difference between Electrochemical Cell and Electrolytic Cell

The difference between electrochemical cell and electrolytic cell can be understood by the following points :

Electrochemical cell	Electrolytic cell
(1) Chemical energy is transformed to electrical energy in this cell.	(1) Electrical energy is transformed to chemical energy in this cell.
(2) Electrical energy is produced by spontaneous redox reaction	(2) Redox reaction takes place by supplying electrical energy does not take place on its own.
(3) Two electrodes are generally in two different vessels containing solutions.	(3) Both the electrodes are dipped in the same vessel containing solution of electrolytes or molten salts.
(4) The electrode on which reduction occurs is called cathode and the electrode on which oxidation occurs is called anode.	(4) The electrode which is connected to the positive electrode of battery is called anode and oxidation takes place there and similarly the electrode connected to the negative electrode of the battery is called cathode and reduction takes place there.
(5) Salt bridge is required in construction of this cell.	(5) Salt bridge is not required in the construction of this cell.
(6) e.g. Daniell cell, Galvanic cell, storage cell	(6) e. g. Electroplating, Electrowinning

3.14 Electrolysis for Industrial Products

As shown in the table 3.3, important chemicals are obtained at the cathode and anode

Table 3.3

Sr.	Electrolyte	Cathode	Anode
1.	NaCl (Molten)	Na	Cl ₂
2.	NaCl (concentrated solution)	H ₂ , NaOH in solution	Cl ₂
3.	NaCl (dilute solution)	H ₂	O ₂
4.	Al ₂ O ₃	Al	O ₂ , CO ₂
5.	KHF ₂ in anhydrous HF	H ₂	F ₂

3.15 Electrical Conduction

Substances are of two types-solid or liquid from electrical conduction point of view.

Solid or liquid substances which conduct electric current are called conducting substances and from which the electric current does not conduct are called insulators.

Generally, two types of conducting substances are available (1) Metallic conductors and (2) Conduction of electricity through solutions of electrolytes.

(1) Metallic conductors : Metals and alloys are electric conductors. The conduction of electricity through them is due to the delocalised electrons in the outer orbit of the atoms of metals. There is no chemical change in the substance during electrical conduction but in physical change, the temperature increases.

(2) Conduction of electricity through solution of electrolytes : The substances which release ions in water by ionisation are called electrolyte substances and such solutions are called electrolytic solutions. If electric current is passed through aqueous solutions of acid, base as well as salts, the electrical conduction takes place through ions. It is necessary to know the concept of electrical resistance to understand the electrical conduction in electrolytic substances.

Less proportion of conduction of electricity occurs due the resistance of the ions present in the solutions of electrolytes. If more is the resistance by ions, less will be the conduction of electricity and lesser the resistance by ions, more will be the conduction of electricity. The electrical resistance is expressed by R and is measured by Wheatstone bridge.

The resistance of a uniform conductor is directly proportional to its length (l) and inversely proportions to its area of cross section (A)

$$R \propto \frac{l}{A}$$

$R = \rho \frac{l}{A}$ where, R = Resistance, A = Area of cross section, l = length, ρ = proportionality constant.

The proportionality constant (ρ) is called resistivity or specific resistance. The SI unit of resistivity is ohm meter (Ω m) but mostly ohm cm (Ω cm) unit is used.

3.16 Resistivity (Specific Resistance)

The resistance of a conductor having one meter length and one square meter of unit cross sectional area is called its **resistance (specific resistance)**.

$$1 \Omega \text{ meter} = 100 \Omega \text{ cm or } 1 \Omega \text{ cm} = 0.01 \Omega \text{ m}$$

Conductivity : The inverse of resistance R is **called conductivity G** .

$$G = \frac{1}{R} = \frac{A}{\rho \cdot l} = K \frac{A}{l} \quad \text{where } K = \frac{1}{\rho} \quad K = G \cdot \frac{l}{A}$$

The SI unit of conductivity is **Siemens** which is expressed as **S**. It is expressed as ohm^{-1} or Ω^{-1} or mho or \mathcal{U} .

Specific conductivity : The inverse of resistivity is called specific conductivity. It is accepted by IUPAC that specific conductivity be accepted as conductivity. Hence, the word conductivity is used instead of specific conductivity. The value of $\frac{l}{A}$ in the formula of conductivity is the cell constant of the apparatus used to measure conductivity. Its value can be determined from $\frac{l}{A}$ or in chemistry, by using a solution of KCl of known concentration. Its value is determined at the experimental temperature by measuring its conductivity and obtaining its value from literature. The obtained conductivity G is multiplied by **cell constant** and so specific conductivity is obtained which is expressed as K from the Greek word kappa.

$$\text{Specific conductivity } K = \text{observed conductivity } G \times \text{cell constant}$$

The SI unit of specific conductivity is S m^{-1} or S cm^{-1} . The conductivity of the conductor having unit length of 1 meter and unit area of cross section 1 square meter is S m^{-1} . $1 \text{ S cm}^{-1} = 0.01 \text{ S m}^{-1}$.

Table 3.4 The values of conductivity by of some selected materials at 298.15 K

Material	Conductivity S m ⁻¹	Material	Conductivity S m ⁻¹
Conductors		Aqueous-solutions	
Sodium	2.1×10^3	Pure water	3.5×10^{-5}
Copper	5.9×10^3	0.1 M HCl	3.91
Silver	6.2×10^3	0.1 M KCl	0.14
Gold	4.5×10^3	0.1 M NaCl	0.12
Iron	1.0×10^3	0.1 M CH ₃ COOH	0.047
Graphite	1.2×10	0.01 M CH ₃ COOH	0.016
Insulator		Semiconductors	
Glass	1.0×10^{-16}	CuO	1×10^{-7}
Teflon	1.0×10^{-18}	Si	1.5×10^{-2}
		Ge	2.0

It is clear from the above table, that the values of conductivities of different substances have very large difference. This depends on the characteristics of substance; temperature, pressure are also the factors affecting the measurement of conductivity.

The classification of conducting substances is carried out on the basis of the magnitude of their conductivity values, as follows :

(1) Good conductors : As the conductivities of metals and alloys are more, they are called good conductors. Some non metallic substances like graphite, organic polymers are also good conductors.

(2) Insulators : The conductivity of glass and ceramic substances is in very less proportion and so they are called insulators.

(3) Semiconductors : The values of conductivities of the substances, which are in between the values of good conductors and insulators are known as semiconductors. Silicon, germanium, gallium arsenide etc. are semiconductors.

The resistivities of some substances are zero and their conductivities are extremely high. They are called superconductors. Earlier metals and alloys were considered superconductors at low temperature (0 to 15 K) but many ceramic substances and mixed oxides are known as superconductors at higher temperature (150 K).

The conduction of electricity through metals is called metallic or electronic conduction. It occurs due to migration of electrons. The electronic conductivity depends on the following factors :

- (1) Structure of metal and its characteristics.
- (2) The number of electrons in the valence shell of atoms of metal.
- (3) The electrical conductivity of metal decreases with increase in temperature.

There is no change in the structure of the metal during electrical conduction.

3.17 Ionic Mobility

The proportion of hydrogen and hydroxyl ions in water is very less, 10^{-7} M. Because of this, water is known as bad conductor of electricity (conductivity = $3.5 \times 10^{-5} \text{ S m}^{-1}$).

When electrolyte is dissolved in water, the conductivity of solution increases due to ionisation of the electrolyte in water. The conductivity of the solution is mostly due to the ions present in the solution. This type of conductivity is called ionic conductivity. The dependence of ions conductivity is on the following factors :

- Nature of the added electrolyte
- The size of the ions produced and their hydration.
- The nature of the solvent and its viscosity
- Concentration of electrolyte
- Temperature

In the ionic solutions, when electric current is passed, electrochemical reactions take place and the structure of solution changes.

Molar conductivity : The solutions of different electrolytes in the same solvent have different conductivities at the same temperature. The reason for this is the size of ions produced and the electrical charge on the ions. The migration of ions under the effect of concentration of electrolyte and electrical pressure are responsible for different conductivities. So it is more meaningful to express the conductivities of these solutions as molar conductivities.

Molar conductivity is expressed as Λ_m (Greek alphabet lambda).

$$\text{Molar conductivity } \Lambda_m = \frac{K \times 1000}{C}$$

where, K = (Kappa) specific conductivity, C = Concentration of solution in unit of molarity.

The unit of molar conductivity is $\text{mho cm}^2 \text{ mol}^{-1}$. If the concentration of solution is taken in normality or gram equivalent weight, then the unit will be $\text{mho cm}^2 \text{ gm eq}^{-1}$.

The changes in conductivity of the solution with changes in its concentration : If there is change in concentration of electrolyte dissolved in solution then its conductivity as well as molar conductivity changes. In both weak and strong electrolytes the conductivity increases with decreases in concentration of solution. With the decrease in concentration of solution, the number of ions in unit volume carrying electric charge increases. It is clear from this fact that the conductivity of solution increases.

The electrical conduction by the solution of electrolyte a given concentration having unit volume, between two platinum electrodes possessing unit cross section and at a distance of unit length is called conductivity of solution.

The above fact will be clear from the following formula.

$$G = \frac{KA}{l} = K, \text{ Taking the units } A \text{ and } l \text{ in the unit meter or cm.}$$

Thus, the conductivity of V volume having 1 mole electrolyte solution between two electrodes possessing unit cross section and at a distance of unit length is called **molar conductivity**.

$$\Lambda_m = \frac{KA}{l} = K \quad l = 1 \text{ and } A = V \text{ (volume of solution of electrolyte)}$$

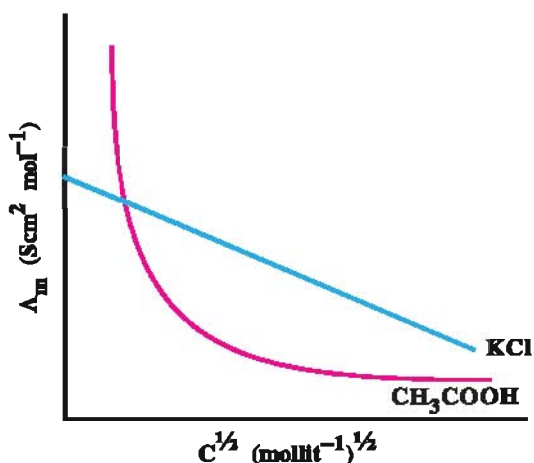
$$\therefore \Lambda_m = K \cdot V$$

If the total volume V of a solution of 1 mole electrolyte is increased, the concentration of the solution decreases and so the molar conductivity increases. When the value of concentration becomes about zero i.e. at infinite dilution the molar conductivity is called limiting molar conductivity or molar conductivity at infinite dilution. Limiting molar conductivity is expressed as Λ_m^0 and gives different proportions of ions which may be more or less. Hence, one which gives more ions will show more conductivity. It is called strong electrolyte viz. Aqueous solutions of NaCl, KCl, MgCl_2 , KNO_3 . If an electrolyte ionises less in aqueous solution and gives less number of ions and therefore shows less conductivity is called weak electrolyte e.g. Aqueous solutions of CH_3COOH , NH_4OH , HCN.

Conductivity of strong electrolytes : There is increase in the value of Λ_m of a strong electrolyte on dilution of its solution.

$$\Lambda_m = \Lambda_m^0 - AC^{\frac{1}{2}}$$

If a graph of values of Λ_m against $C^{\frac{1}{2}}$ is plotted, a straight line is obtained. The intercept of this graph will be the value of Λ_m^0 and the value of the slope will be A . The value of A depends on the type electrolyte (its dissociation into positive ion and negative ion), given solvent and temperature. NaCl, KCl, CaCl_2 and MgCl_2 are strong electrolytes having 1:1, 1:1, 2:1, and 2:1 type valencies. The values A are same for all the same type of electrolytes.



Conductivity of weak electrolytes : The study of changes in conductivity with dilution was carried out by scientist Ostwald. It was found that the conductivity of weak electrolyte increases more with dilution. This type of study is known as **Ostwald's law** of dilution.

The degree of dissociation is very less for such weak electrolyte like acetic acid having more concentration. When a solution of such electrolytes having 1 mole electrolyte is diluted, and with that volume increases and with that the degree of dissociation increases. As a result the number of ions increases and **molar conductivity (Λ_m)** also increases. It is clear from the graph that the molar conductivity at infinite dilution increases in the form of a curve when the graph of Λ_m^0 for such solutions is extrapolated towards X-axis, The value of **limiting molar conductivity** at infinite dilution (almost zero concentration) is not obtained.

The values of limiting molar conductivity at such electrolytes can be obtained by Kohlrausch's law of independent migration.

The value of degree of dissociation for such an electrolyte at the given concentration will be as below :

$$\text{Degree of dissociation } (\alpha) = \frac{\text{Molar conductivity of the solution of a given concentration } \Lambda_m}{\text{Molar conductivity of the solution at infinite dilution } \Lambda_m^0}$$

$$\text{We know that, } K = \frac{C\alpha^2}{(1-\alpha)} \text{ where, } K = \text{Dissociation constant of weak electrolyte,}$$

C = concentration of solution, α = degree of dissociation of weak electrolyte

$$= \frac{C \Lambda_m^2}{\Lambda_m^0 \left(1 - \frac{\Lambda_m}{\Lambda_m^0} \right)} = \frac{C \Lambda_m^2}{\Lambda_m^0 \left(\frac{\Lambda_m^0 - \Lambda_m}{\Lambda_m^0} \right)}$$

Example 20 : The conductivity of 0.001028 mole litre⁻¹ acetic acid is $4.95 \times 10^{-5} \text{ S cm}^{-1}$. If the limiting molar conductivity of acetic acid is $390.5 \text{ S cm}^2 \text{ mol}^{-1}$ calculate dissociation constant.

$$\text{Solution : } \Lambda_m = \frac{K}{C} = \frac{4.95 \times 10^{-5} \text{ S cm}^{-1}}{0.001028 \text{ mol L}^{-1}} \times \frac{1000 \text{ cm}^3}{\text{L}} = 48.15 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^0} = \frac{48.15 \text{ S cm}^2 \text{ mol}^{-1}}{390.5 \text{ S cm}^2 \text{ mol}^{-1}} = 0.1233$$

$$K_a = \frac{C\alpha^2}{1-\alpha} = \frac{0.001028 \text{ mol L}^{-1} \times (0.1233)^2}{1-0.1233}$$

$$K_a = 1.78 \times 10^{-5} \text{ mol L}^{-1}$$

3.18 Kohlrausch's law of Independent migration of Ions

The value of molar conductivity (Λ_m) for different electrolytes can be obtained. In addition, the values of molar conductance (Λ_m) will also change with change in concentration. It is found from the study that a straight line graph is obtained for the molar conductivity (Λ_m) at different concentrations of the strong electrolyte like KCl. In this graph, the value of limiting, molar conductivity extended to zero concentration (infinite dilution), the intercept is obtained or molar conductivity (Λ_m^0) at infinite dilution will be obtained. But for weak electrolyte like CH_3COOH the graph of molar conductivity at different dilutions of weak electrolyte does not give straight line but a curve. So their intercepts obtained are not correct and the true values of molar conductivity at infinite dilution cannot be obtained.

Scientist Kohlrausch studied the Λ_m^0 values of some strong electrolytes. He observed some characteristics viz. The difference between the value of Λ_m^0 of two strong electrolyte like NaX and KX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) was found to be same. e.g.,

$${}^0\Lambda_m \text{KCl} - {}^0\Lambda_m \text{NaCl} = {}^0\Lambda_m \text{KBr} - {}^0\Lambda_m \text{NaBr} = {}^0\Lambda_m \text{KI} - {}^0\Lambda_m \text{NaI} = 23.4 \text{ mho cm}^2 \text{ mol}^{-1}$$

$$\text{Similarly, } {}^0\Lambda_m \text{NaBr} - {}^0\Lambda_m \text{NaCl} = {}^0\Lambda_m \text{KBr} - {}^0\Lambda_m \text{KCl} = 1.8 \text{ mho cm}^2 \text{ mol}^{-1}.$$

It can be concluded from this study, that the molar conductivity of a strong ionic electrolyte is equal to the sum of the molar ionic conductivity of the positive ion and the molar ionic conductivity of negative ion. ${}^0\Lambda_m \text{NaCl} = {}^0\lambda_m \text{Na}^+ + {}^0\lambda_m \text{Cl}^-$

If the electrolyte gives ν_+ and ν_- ions due to dissociation, then their molar conductances, can be written as ${}^0\Lambda_m = \nu_+ {}^0\lambda_{m+} + \nu_- {}^0\lambda_{m-}$ (where, ${}^0\lambda_{m+}$ and ${}^0\lambda_{m-}$ respectively are ionic molar conductivity of positive and negative ion.)

From this, Kohlrausch's law can be written as follows. **"The molar conductivity of an electrolyte at infinite dilution ${}^0\Lambda_m$ is the sum of the values of the molar conductivities of positive ion and negative ion present in them ${}^0\lambda_{m+}$ and ${}^0\lambda_{m-}$ ".**

In the use of Kohlrausch's law, the molar conductivity at infinite dilution for a weak electrolyte can be obtained by adding or subtracting the values of molar conductivities at infinite dilution of the solutions of proper strong electrolytes. This will be clear from the following example.

Suppose the molar conductivity of weak electrolyte CH_3COOH is to be determined, then it can be obtained by determining molar conductivities of strong electrolytes like CH_3COONa , HCl and NaCl ; then computing.

$${}^0\Lambda_m \text{CH}_3\text{COOH} = {}^0\Lambda_m \text{CH}_3\text{COONa} + {}^0\Lambda_m \text{HCl} - {}^0\Lambda_m \text{NaCl}$$

According to Kohlrausch law,

$$\begin{aligned} {}^0\Lambda_m \text{CH}_3\text{COOH} &= {}^0\lambda_m \text{CH}_3\text{COO}^- + {}^0\lambda_m \text{Na}^+ + {}^0\lambda_m \text{H}^+ + {}^0\lambda_m \text{Cl}^- - ({}^0\lambda_m \text{Na}^+ + {}^0\lambda_m \text{Cl}^-) \\ &= {}^0\lambda_m \text{CH}_3\text{COO}^- + {}^0\lambda_m \text{Na}^+ + {}^0\lambda_m \text{H}^+ + {}^0\lambda_m \text{Cl}^- - {}^0\lambda_m \text{Na}^+ - {}^0\lambda_m \text{Cl}^- \end{aligned}$$

$${}^0\Lambda_m \text{CH}_3\text{COOH} = {}^0\lambda_m \text{CH}_3\text{COO}^- + {}^0\lambda_m \text{H}^+$$

Table 3.5 Limiting molar conductivity for some ions in water at 298 K

ion	${}^0\lambda$ ($\text{S cm}^2\text{mol}^{-1}$)	ion	${}^0\lambda$ ($\text{S cm}^2\text{mol}^{-1}$)
H^+	349.6	OH^-	199.1
Na^+	50.1	Cl^-	76.3
Ca^{2+}	119.0	CH_3COO^-	40.9
Mg^{2+}	106.0	Br^-	78.1
		SO_4^{2-}	160.0

Example 21 : Calculate the limiting molar conductivities of CaCl_2 and MgSO_4

Ion	Limiting molar conductivity $\text{S cm}^2 \text{mol}^{-1}$
Ca^{2+}	119.0
Mg^{2+}	106.0
SO_4^{2-}	160.0
Cl^-	76.3

Solution : According to Kohlrausch's law,

$$\begin{aligned}
 \text{(i)} \quad \Lambda_m^0 \text{CaCl}_2 &= \Lambda_m^0 \text{Ca}^{2+} + 2\Lambda_m^0 \text{Cl}^- \\
 &= 119 + 2(76.3) \\
 &= 271.6 \text{ S cm}^2 \text{mol}^{-1}
 \end{aligned}$$

$$\begin{aligned}
 \text{(ii)} \quad \Lambda_m^0 \text{MgSO}_4 &= \Lambda_m^0 \text{Mg}^{2+} + \Lambda_m^0 \text{SO}_4^{2-} \\
 &= 106.0 + 160.0 \\
 &= 266.0 \text{ S cm}^2 \text{mol}^{-1}
 \end{aligned}$$

Example 22 : If the values of limiting molar conductivities of NaCl , HCl , and CH_3COONa are 126.4, 425.9 and $91.0 \text{ S cm}^2 \text{mol}^{-1}$ respectively, then calculate the limiting molar conductivity of acetic acid.

$$\begin{aligned}
 \text{Solution :} \quad \Lambda_m^0 \text{CH}_3\text{COOH} &= \Lambda_m^0 \text{H}^+ + \Lambda_m^0 \text{CH}_3\text{COO}^- \\
 &= \Lambda_m^0 \text{H}^+ + \Lambda_m^0 \text{Cl}^- + \Lambda_m^0 \text{CH}_3\text{COO}^- + \Lambda_m^0 \text{Na}^+ - \Lambda_m^0 \text{Cl}^- - \Lambda_m^0 \text{Na}^+ \\
 &= \Lambda_m^0 \text{HCl} + \Lambda_m^0 \text{CH}_3\text{COONa} - \Lambda_m^0 \text{NaCl} \\
 &= (425.9 + 91.0 - 126.4) = 390.5 \text{ S cm}^2 \text{mol}^{-1}
 \end{aligned}$$

3.19 Batteries

Commercial cells and Fuel cells :

Any battery is a source for obtaining electric current. In a cell (battery) the chemical energy obtained by chemical reaction in it, is transformed to electrical energy.

Dry cell, Ni-Cd storage cell, lead storage cell, fuel cell etc. are included in the cells for industrial use. It can be divided into two types. (1) Primary cell and (ii) Secondary cell.

(1) Primary cell : The cell which is dead after a long use and which cannot be regenerated i.e. which cannot be reproduced, is called **primary cell**. e.g. Dry cell.

(2) Secondary cell : The cell which can be regenerated or reproduced is called **secondary cell**. e.g. lead storage cell and Ni-Cd storage cell.

3.19.1 Dry cell : This type of dry cell or primary cell was first of all prepared by French Scientist Leclanche in 1867. Hence, **it is also called Leclanche cell**.

In this cell, there is a thin porous layer of paper on inner side of a cylinder of zinc metal, closed at the bottom. In this cylinder, graphite rod is placed in the centre so that it does not touch the bottom and small amount of mixture of MnO_2 and carbon is filled, the remaining part is filled with a paste of the mixture of NH_4Cl and ZnCl_2 and the mouth of the cylinder is sealed with a special type of wax in a such a way that graphite rod is slightly outside. The insulating layer of thick paper is applied on the outer part of the cylinder (Fig. 3.3)

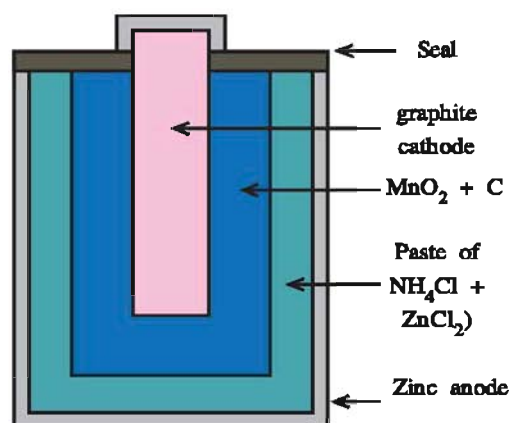


Fig. 3.3 Dry cell

When the cylinder of zinc and the rod of graphite are connected by a conducting wire, zinc acts as anode and the rod of graphite in the contact of MnO_2 acts as a cathode. The reactions occurring at these electrodes are as follows :

Reaction at cathode : $2\text{MnO}_2 + 2\text{NH}_4^+ + 2e^- \rightarrow \text{Mn}_2\text{O}_3 + 2\text{NH}_3 + \text{H}_2\text{O}$

Reaction at anode : $\text{Zn(s)} \rightarrow \text{Zn}^{2+}(\text{aq}) + 2e^-$

In fact, the product-containing manganese-obtained depends on the time of continuous use and the interval between times of the two uses. The potential of this cell is about 1.5 volt. Here oxidation of Mn (III) to Mn (IV) can not be possible by reversing the direction of the current and so, once this cell is dead means has become useless, it cannot be regenerated or reproduced. Hence this cell is known as primary cell. Dry cell is not really dry because wet paste of NH_4Cl and ZnCl_2 is filled in it. If this cell is completely dry, then the electric current cannot pass through it. To obtain more voltage, two or more cells are joined in series and more voltage can be obtained; so dry cell is used in torch, transistor, radio and other big or small electronic devices.

Mercury cell : Mercury cell is a systematic device to produce low electric current. It is used mostly in hearing aids, watches etc. In this cell layer of zinc-mercury (Zn-Hg) is in the form of anode and paste of mercuric oxide and carbon is as cathode. In it, electrical paste filled is prepared from KOH and ZnO. The reactions occurring at the electrode in this cell are as under :

Carbon rod (Cathode)

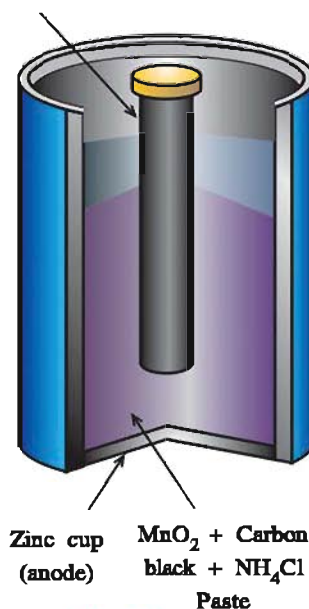


Fig. 3.4

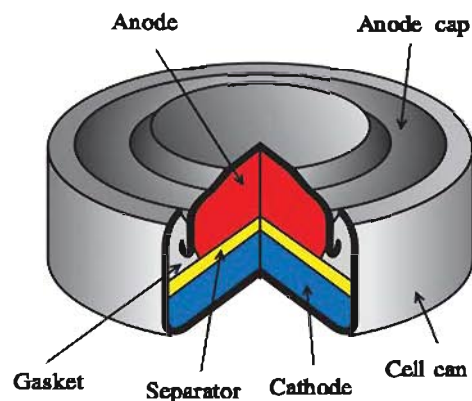
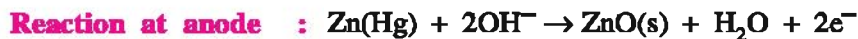
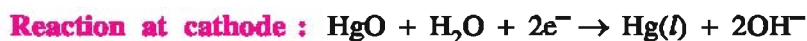


Fig. 3.5 Mercury cell



The complete equation of these reactions is as follows :



The cell potential of this cell is about 1.35 volt and during the whole life of this cell, no ions are produced in the complete reaction.

3.19.2 Secondary cells : The cells which can be regenerated or reproduced are called secondary cells. Lead storage cell and Ni-Cd storage cells are secondary cells.

Lead storage cell : When two or more cells are joined in series to obtain more voltage which can be recharged are called storage cells.

In the construction of this cell, sponge like lead plate and thin plate of lead on which layer of PbO_2 is applied are dipped in 38 % (W/W) concentration sulphuric acid containing vessel. When these two plates are connected by conducting wire the following discharging reactions take place and electric current is produced.

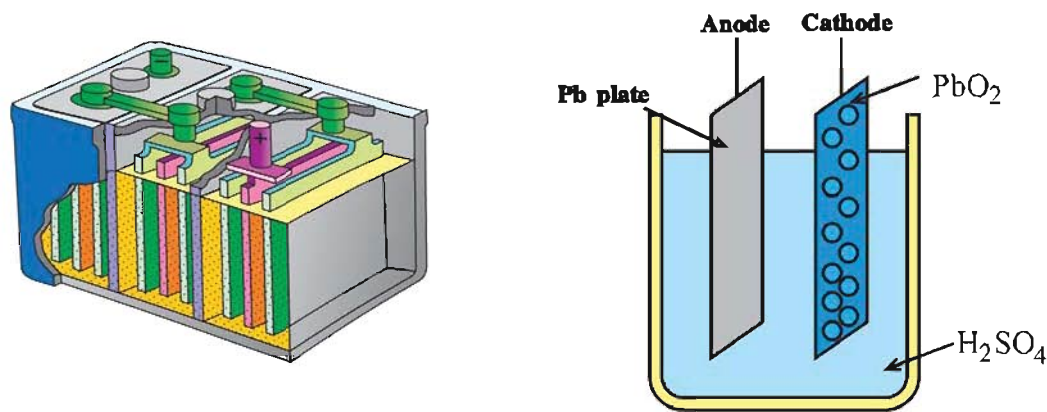
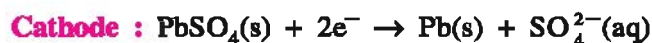


Fig. 3.6 Lead storage battery

PbSO_4 produced here remains stuck to the surface of the electrodes. The cell potential of this cell is about 2 volt. When the cell is in operation the density of sulphuric acid solution in reaction decreases. In the beginning the density of the solution is $1.25\text{--}1.30 \text{ gm ml}^{-1}$ but when cell stops producing electric current, the density of the solution decreases and becomes $1.10\text{--}1.15 \text{ gm ml}^{-1}$. If the cell is joined to a high electrical voltage containing any cell and passing the electric current in opposite direction, the reverse reactions take place on the electrodes and the cell becomes capable to produce electric current again. Even then, the efficiency of the method to regenerate is not 100 %. Hence, at intervals, solution of H_2SO_4 containing 38% (W/W) concentration is to be added. After a long time use, this cell becomes useless. The charging reactions taking place in lead storage cell are as follows :



If in one vessel of lead storage cell more than one anodes and cathodes are dipped in the vessel containing solution and joining them in series, more than 2.0 volt potential can be obtained. In the car battery, six cells are joined and 12 volts can be obtained. 22 to 24 volt electric current can be obtained by combining 11 to 12 cells in series.

Ni-Cd storage cell : Nickel-cadmium cell is important as a secondary cell like the lead storage cell. Its life is more than that of lead storage cell but its production is very costly. There are charging and discharging reactions in the method of working of this cell. The complete reaction of discharging is as follows.



3.19.3 Fuel cell : The cell which can transform the energy obtained by combustion of fuels like H_2 , CO or methane, into electrical energy in only one step is called fuel cell. When hydrogen is oxidised large amount of energy is produced in the form of heat.



We know that when fuel is combusted, heat is produced. In the thermal power stations like Sabarmati, Gandhinagar, Dhuvaran, Vanakbori, etc. mainly mineral coal is used as the fuel and water is transformed into steam by this produced heat. Electricity is produced by using this steam using turbine. Maximum 35% of this combustion energy is converted to electrical energy that is, its working efficiency is much less. But, if the energy produced by combustion reaction is directly obtained in the form of electrical energy, then the wastage of energy can be decreased. This purpose is achieved in fuel cell. Different types of fuels can be used in fuel cell. **First of all, the fuel cell was presented by scientist Bacon.**

Hydrogen Fuel cell : The simple understanding of a fuel cell using hydrogen as fuel is given in fig 3.8. In a vessel, two porous carbon membranes are arranged and concentrated aqueous solution of NaOH is filled between them. This membranes work as inert electrodes. Platinum is used for electrode acting as anode and mixed powder of platinum and silver oxide is used as a catalyst in the electrode which acts as cathode. On passing hydrogen gas from anode and oxygen gas from cathode, the reactions take place at the electrodes and electric current is produced.

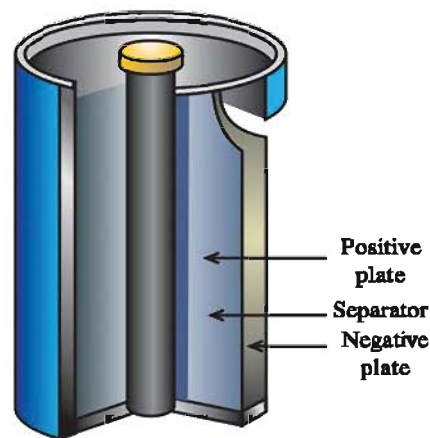


Fig. 3.7 Ni-Cd Storage battery

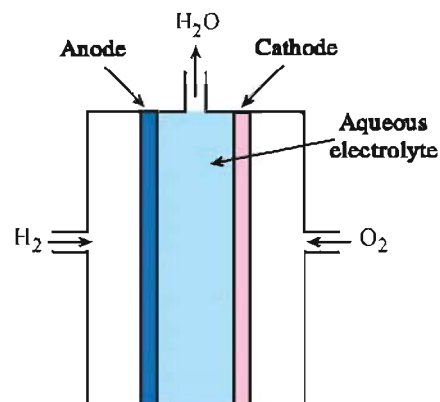
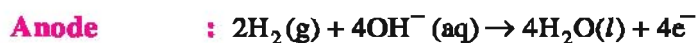


Fig. 3.8 Fuel cell



Theoretically the efficiency for the production of electricity by this type of cell can be expected to be 100% but, really, the efficiency obtained is about 70 - 75%. The potential of this cell is about 1.23 volt.

Advantages : There are number of advantages of fuel cell in comparison to other cells. Air is not polluted by fuel cell. Also, it does not create sound and possesses very high efficiency in comparison to electricity produced by thermal power stations. This type of cell was used in space shuttle programme Appolo carried out by American scientist. In addition, the vapour of water obtained during cell reaction was cooled and was used for drinking purpose. In foreign countries, the use of such fuel cells is increasing.

3.20 Corrosion

Some metals are slowly corroded in contact with air or the rust forms on iron. Green coloured salt produced on the vessels of copper and brass. The lustre of silver also fades. The reason for this is the chemical reaction between the surface of the metals and oxygen. The real reactions are mostly complicated. Even then, here we shall study the reaction with iron by the following illustration :

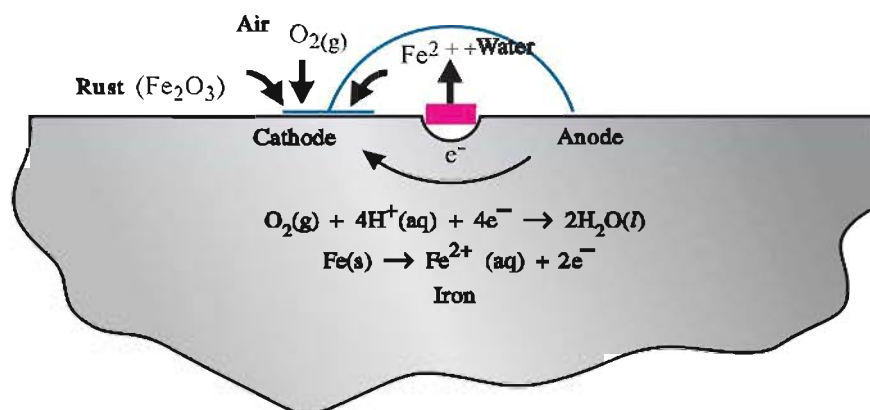
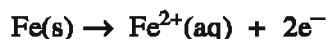


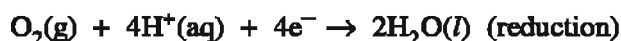
Fig. 3.9 Reaction of corrosion of iron

The arrangement of atoms can never be systematic in the rod or vessel of iron viz. In the rod, where there is a bent, its structures in a trace proportions will not be systematic. In addition, its crystal lattice is also defective. Also, there are impurities of other metals like copper is present in iron in trace proportions.

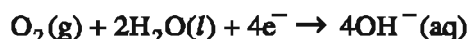
This microscopic surface being active, the atoms on the surface lose electrons easily and get transformed into positive ions. Hence, the atoms of iron near the bent on the surface of iron oxidation reaction occurs.



The molecules of water required for this reaction to occur, are available from moisture of air. Hence, the surface near the bent acts as anode. The flow of the electrons produced takes place through the rod of iron and will reach to that point on the surface where oxygen of the air will carry out reduction reaction in presence of H⁺. This point acts as cathode because following reaction takes place.



H^+ required for this reaction can also be available from dissociation of H_2CO_3 produced by dissolution of carbon dioxide in water on the surface of the iron rod. Thus, one type of electrochemical cell is formed on the surface of the iron rod and it acts as anode. The formation of rust starts from this point. Fe^{2+} ions produced by oxidation are oxidised to Fe^{3+} ions by the oxygen of the air which diffuses towards the cathode and finally $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ is formed. If H^+ are not available then oxygen dissolved in moisture get reduced by electrons.



Methods of prevention of Corrosion : Iron is an important metal industrially and in different transportation devices. A huge loss occurs in the world due to corrosion. Hence, one of the methods to prevent is that the moisture should not be allowed to have contact with the surface. This purpose is achieved by applying layer of zinc on iron. This iron is called galvanised iron. In case, if the layer of zinc from the surface of the galvanised iron is removed, even then iron does not get rusted; because the value of $E^\circ_{\text{Fe}|\text{Fe}^{2+}}$ is more than that of $E^\circ_{\text{Zn}|\text{Zn}^{2+}}$. Hence, the atoms of zinc diffuse on the open surface of iron.

In the other method of prevention of corrosion, it is the combination of metals like Mg or Zn having higher values of E°_{oxi} with the sheets of iron and buried under the soil. To prevent the iron plates of steamers, being corroded; they are connected with iron plates and then allowed to come in contact with sea water. By doing so, the plate of iron acts as cathode, and blocks of Mg or Zn as anode. These blocks are continuously corroded and so are to be replaced at intervals. Such blocks of Mg or Zn act as anode. These blocks are continuously corroded and so are **sacrificial anodes**.

In addition, to apply wax, to paint and use some chemical substances called **inhibitors** are used. By using them there is no direct contact of gases present in air with the surface of the metal. As a result chemical reaction does not occur and so corrosion is prevented.

SUMMARY

- The reaction taking place in electrochemical cell is a redox reaction.
- In electrochemical cell, chemical energy is transformed to electrical energy and produce electrical energy.
- Electrochemical cell is known as voltaic or galvanic cell.
- The salt bridge functions to connect the two solutions and to maintain electrical neutrality of solutions.
- The symbolic representation of chemical reaction $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$ is expressed as follows $\ominus \text{Zn}(\text{s}) | \text{Zn}^{2+}(1\text{M}) || \text{Cu}^{2+}(1\text{M}) | \text{Cu}(\text{s}) \oplus$ where one vertical line | indicates the electrode and two vertical lines || indicate the salt bridge.

- The types of electrodes are (i) Active electrodes of metal (ii) Inert electrodes (iii) Gaseous electrodes. The combined system consisting of electrode and the solution in which it is dipped is jointly known as half cell. The representation of half cell is made by putting a vertical line between the electrode and the formula of the active ions. e.g. $\text{Zn(s)} \mid \text{Zn}^{2+}(\text{aq})$; $\text{Fe(s)} \mid \text{Fe}^{2+}(\text{aq})$.
- The representation of gaseous electrode is made by inert metal, formula of gas and the formula of active ions e.g. $\text{Pt} \mid \text{H}_2(\text{g}) (1 \text{ bar}) \mid \text{H}^+(\text{aq})$.
- Standard hydrogen electrode acts as a reference half cell. Its standard potential is accepted as 0.0 volt. The values of standard potential of unknown electrodes are determined with the help of H-electrode.
- Electrochemical cell is a device to convert chemical energy to electrical energy.
- The flow of electrons, when two electrodes are combined, obtained on the basis of chemical reaction under the evolved electromotive force is from anode to cathode in the external circuit. This electromotive force is called cell potential E_{Cell} .
- If the cell is standard one, then the cell potential is expressed as E_{Cell}^0 . Potentiometer is used to determine the correct potential of the cell.
- Cell potential $E_{\text{Cell}} = \text{Reduction potential of } E_{\text{Cathode}} - \text{Reduction potential of } E_{\text{Anode}}$
 $E_{\text{Cell}}^0 = \text{Standard potential of } E_{\text{Cathode}} - \text{Standard potential of } E_{\text{Anode}}$
- When the potential of the electrical cell is determined with reference to hydrogen electrode, then it is known as electromotive force (emf).
- Nernst equation $E_{\text{Cell}} = E_{\text{Cell}}^0 - \frac{0.059}{n} \log \frac{[\text{C}_1]}{[\text{C}_2]}$ where the value 0.059 is the value of $\frac{2.303RT}{F}$ at 298 K temperature. ($R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and $F = 96500 \text{ coulomb}$.
- With the help of the Nernst equation, K_c equilibrium constant, pH, K_w (ionic product of water) can be determined.
- Even if the anode and cathode may be of same electrode, but if the concentrations of the solutions of their salts are different, electrochemical cell is formed which is called concentration cell. e.g. $\ominus \text{Fe(s)} \mid \text{Fe}^{2+} (0.6\text{M}) \parallel \text{Fe}^{2+} (0.8\text{M}) \mid \text{Fe(s)} \oplus$ is a concentration cell.
- Electrolytic cell is the cell of opposite type of electrochemical cell. In the electrolytic cell the electrical energy is transformed to chemical energy. During electrolysis of acidic water, hydrogen gas is obtained at the cathode and oxygen gas is obtained at the anode.
- The modern law as proposed after the first and second law of electrolysis by Michael Faraday. "The number of moles of products obtained at the electrodes by oxidation and reduction half reactions, is related with the electrical quantity passing through cell according to their stoichiometry."

- The quantity of electricity flowing by one mole electrons is called one Faraday which is expressed by the symbol F. 1 Faraday (F) = 96487 \approx 96500 coulomb.

For electric charge (Q) = electric current (I) \times time (t)

$$F = \frac{I \times t}{96500}$$

The products obtained by electrolysis,

- Viz. Na metal and Cl₂ gas are obtained by electrolysis of molten NaCl.
- In electrolysis of concentrated NaCl between graphite electrodes, Cl₂ gas is obtained and NaOH can be obtained in solution which is industrial production of NaOH.
- Impure metal is taken as anode and the electrolysis is carried out in the solution of salt of that metal, the metal can be refined and pure metal can be obtained on the cathode. The noble metals remain as anode mud.
- The electrolysis of aqueous solution of Na₂SO₄, is in fact electrolysis of water.
- The relation between Gibbs' free energy (G) and the potential of the electrochemical cell in which spontaneous reaction, can be shown by the formula. $\Delta G^0 = -nFE^0_{\text{Cell}}$

To obtain equilibrium constant from $\Delta G^0 = -nFE^0_{\text{Cell}} = -RT \ln K_C$

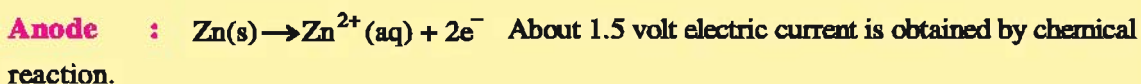
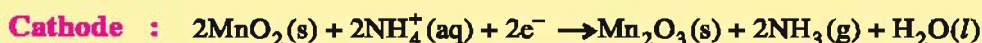
$$\log K_C = \frac{nFE^0_{\text{Cell}}}{2.303RT}$$

- The solid or liquid substances are of two types according to their electrical conduction : The substances which conduct electric current are called conductors and which do not conduct electric current are called non-conductors (insulators).
- The two types of conducting substances are (i) metallic conductors (ii) conduction of electrical current by electrolytic solutions. It is necessary to have the idea about electrical resistance in electrical conduction by electrolytic solutions, so that electrical conductivity can be understood.
- The resistance of any uniform conductor is directly proportional to its length (l) and inversely proportional to its area of cross section (A). $R \propto \frac{l}{A}$ $R = \rho \frac{l}{A}$, ρ is the proportionality constant which is called resistivity. It is also called specific resistance.
- The SI unit of resistivity is Ohmmeter (Ω m). The reciprocal or resistance R is called conductance G

$$G = \frac{1}{R} = \frac{A}{\rho l} = K \frac{A}{l} \text{ where, } K = \frac{1}{\rho}$$

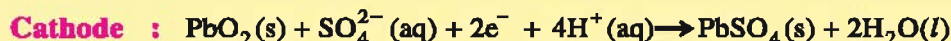
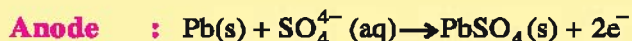
- The SI unit of conductance is Siemens expressed as S. It is expressed as ohm⁻¹, (ohm⁻¹ or Ω^{-1}) Mho (mho or U). Specific conductance which is expressed by Greek letter K (Kappa) is obtained by multiplying specific resistivity by cell constant.

- Specific conductance (K) = observed conductance \times cell constant. The SI unit of specific conductance is $S\ m^{-1}$ or $S\ cm^{-1}$.
- The classification of conducting substance is carried out on the basis of the magnitudes of the values of their conductance. (i) Good conductor (ii) Semiconductor (iii) Bad conductor (insulator). The substances whose resistivity is zero and whose conductivity is very high are called superconductors. The metals and non-metals are superconductors at 0 to 15 K temperature. The ceramic substances and mixed oxides are superconductors at 150 K temperature.
- Ionic mobility and molar conductivity $\Lambda_m = \frac{K \times 1000}{C}$ where, K (Kappa) = Conductivity
 C = molar concentration of solution. The unit of molar conductivity is $mho\ cm^2\ mol^{-1}$. If the concentration of solution is in normality or gram equivalent weight then, the unit of equivalent conductivity is $mho\ cm^2\ gmequ.^{-1}$.
- "The conduction of electricity by a solution at a given concentration of solution between two platinum electrodes at a distance of unit length having unit area of cross section is called the conductivity of solution."
- Hence, $G = \frac{KA}{l} = K$ (A and l are in unit measure)
- Molar conductivity $\Lambda_m = \frac{KA}{l} = K$ where, $l = 1$ and $A = V$ (volume of solution of 1 mole electrolyte)
 $\therefore \Lambda_m = K \cdot V$
- The molar conductivity at infinite dilution is expressed as limiting molar conductivity Λ_m^0 . The law of Kohlrausch regarding independent mobility of ions," The value of molar conductivity at infinite dilution (Λ_m^0) of an electrolyte is equal to the sum of molar conductivities at infinite dilution of positive ion and negative ion ($\lambda_{m^+}^0 + \lambda_{m^-}^0$).
- In the utility of Kohlrausch's law, the molar conductivity of weak electrolyte can be obtained by addition or subtraction of molar conductivities of suitable strong electrolytes.
- Any battery is a source of obtaining electric current. The cells for industrial use are of two types (i) primary which can not be regenerated or reproduced after a long use. (ii) Secondary cell which can be regenerated or reproduced when it has become dead after a long use. Dry cell is a primary cell and storage cell is a secondary cell. Dry cell is also called Leclanche cell. The reaction taking place in dry cell are.

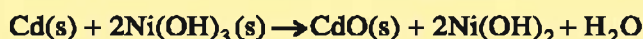


- Mercury cell is also a primary cell whose cell potential is about 1.35 volt,

Storage cell : Lead storage cell is a secondary cell. The chemical reactions are :



In this cell, about 2.0 volt electric current is produced during chemical reaction. Nickel-cadmium storage cell can be used for a long time because it possesses long life.



- Electrical energy is produced only in one step from the heat of combustion produced by the combustion of gaseous fuels. Such a cell is called fuel cell. Nowadays fuel cells are used because of less efficiency in production of electricity by thermal power station and to prevent pollution due to it.
- A loss of billions of rupees occur due to metallic corrosion. Metallic corrosion is a redox reaction in which the chemical reactions of electrochemical cell are taking place at anode and cathode. Its prevention can be carried out by inhibitors or electroplating.

EXERCISE

1. Select the proper choice from the given multiple choices :

- Which reaction takes place in electrochemical cell ?
(A) Oxidation (B) Reduction (C) Redox (D) All the given
- Which of the following reactions is for Daniell cell ?
(A) $\text{Cu}^{2+}(\text{aq}) + \text{Fe(s)} \rightleftharpoons \text{Fe}^{2+}(\text{aq}) + \text{Cu(s)}$
(B) $\text{Zn}^{2+}(\text{aq}) + \text{Mg(s)} \rightleftharpoons \text{Zn(s)} + \text{Mg}^{2+}(\text{aq})$
(C) $\text{Cu}^{2+}(\text{aq}) + \text{Zn(s)} \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$
(D) All the given reactions.
- Which cell differs from principle point of view?
(A) Storage cell (B) Electrolytic cell (C) Fuel Cell (D) Leclanche cell.
- Which phenomenon does not occur in Daniell cell ?
(A) Increase in weight of plate of Cu.
(B) The conduction of electricity takes place by salt bridge.
(C) Increase in weight of plate of Zn.
(D) There is no change in colour of ZnSO_4 solution.

- (5) The electrochemical cell stops working after sometime. Why ?
- (A) Increase of temperature
(B) The difference of cell potentials of both electrodes become zero.
(C) By reversing the direction of reaction taking place in the cell.
(D) Due to change in concentration
- (6) What is used for the measurement of accurate potential of electrochemical cell ?
- (A) Galvanometer (B) Ammeter (C) Voltmeter (D) Potentiometer
- (7) If M, N, O, P and Q are in the increasing order of their standard potentials in standard conditions of their standard half cells, then by combination of which two half cells maximum cell potential will be obtained ?
- (A) M and N (B) M and Q (C) M and P (D) M and O
- (8) $E^0_{\text{red}} =$
- (A) E^0_{oxi} (B) $-E^0_{\text{red}}$ (C) $-E^0_{\text{oxi}}$ (D) E^0_{redox}
- (9) What will be the symbolic representation of the cell for the given following reaction :
- $$\text{Fe(s)} + \text{Cd}^{2+}(\text{aq}) \rightleftharpoons \text{Fe}^{2+}(\text{aq}) + \text{Cd(s)}$$
- (A) $\ominus \text{Fe(s)} \mid \text{Fe}^{2+}(1\text{M}) \parallel \text{Cd(s)} \mid \text{Cd}^{2+}(1\text{M}) \oplus$
(B) $\ominus \text{Cd(s)} \mid \text{Cd}^{2+}(1\text{M}) \parallel \text{Fe}^{2+}(1\text{M}) \mid \text{Fe(s)} \oplus$
(C) $\ominus \text{Cd(s)} \mid \text{Cd}^{2+}(1\text{M}) \parallel \text{Fe(s)} \mid \text{Fe}^{2+}(1\text{M}) \oplus$
(D) $\ominus \text{Fe(s)} \mid \text{Fe}^{2+}(1\text{M}) \parallel \text{Cd}^{2+}(1\text{M}) \mid \text{Cd(s)} \oplus$
- (10) The solution of silver nitrate becomes coloured when pieces of nickel are added to solution of silver nitrate because
- (A) Nickel is oxidised (B) Silver is oxidised
(C) Nickel is reduced (D) Silver is precipitated
- (11) The values of standard reduction potential of X, Y and Z metals are 0.34 V, 0.80 V and -0.45 V. Mention their order of strength as reducing agent
- (A) $Z > Y > X$ (B) $Z > X > Y$ (C) $X > Y > Z$ (D) $Y > Z > X$
- (12) If one mole electrons are passed through solutions of MgSO_4 , AgNO_3 and AlCl_3 , in what mole ration the metals Mg, Ag and Al will be deposited at the electrodes ?
- (A) 1 : 1 : 1 (B) 1 : 2 : 3 (C) 2 : 1 : 3 (D) 3 : 6 : 2
- (13) What will be obtained at cathode and anode obtained respectively when electrolysis of aqueous solution of concentrated NaCl, out between graphite electrodes ?
- (A) Cl_2 and Na metal (B) H_2 and O_2
(C) Cl_2 and H_2 (D) H_2 and Cl_2

- (14) The resistance of any uniform conductor is
- in inverse proportion to its length
 - in direct proportion to its length
 - in the inverse proportion of the square of its area of cross section
 - in direct proportion of the area of its cross section.
- (15) Which is more corroded when the iron plates of steamers are connected with block of Zn metal and kept in contact of sea water ?
- Iron
 - Zinc
 - Both
 - Neither of the metals
- (16) Which is the device used for measurement of electrical resistance ?
- Voltmeter
 - Wheatstone bridge
 - Galvanometer
 - Ammeter
- (17) At which temperatures ceramic materials are known as superconductor ?
- 0 K
 - 200 K
 - 150 K
 - 15 K
- (18) l = length, R = resistance, A = area of cross section, then.
- $R \propto \frac{l}{A}$
 - $R \propto \frac{A}{l}$
 - $R \propto \frac{1}{Al}$
 - $R \propto lA$

2. Answers the following question in brief :

- What is an electrochemical cell ?
- Write the function of salt bridge ?
- Write the names of the solution used for filling in salt bridge.
- What is a gas electrode ? Describe any one of them.
- Write definition of cell potential.
- By which two instruments cell potential is determined ?
- Write Nernst equation and on the basis of which rules it can be derived.
- From which the value 0.059 is obtained in Nernst equation.
- What is concentration cell ?
- In which parameters the values of E_{Cell} and E^0_{Cell} become 0.0 volt.
- Write usefulness of cell potential.
- Write Faraday's modern law of electrolysis.
- What will be the value of cell potential under the circumstances of concentration of anode in concentration cell is more than concentration in cathode ? What it will indicate ?
- On which factors do the products obtained during electrolysis of aqueous solution of salt depend ?

- (15) What is meant by primary and secondary cells ?
- (16) Write usefulness of electrolysis.
- (17) Write the names of the chemicals used in dry cell.
- (18) Write names of catalysts used in hydrogen fuel cell.
- (19) Dry cell cannot be regenerated ? Why ?
- (20) What fault is produced in the lead storage cell so that the production of electric current is stopped ? Why ?
- (21) Write the principle of fuel cell.
- (22) Mention advantages of fuel cell.
- (23) The ring of silver has fallen into the solution of an acid ? Will there be reason to worry ? Why ?
- (24) Can the solution of copper sulphate be filled in the bucket of aluminium ? Why ?
- (25) What is emf series ?
- (26) What will you observe with naked eye when the Daniell cell is operative ?
- (27) If 1.93 ampere current is passed from an electrical conductor. How many electrons will pass through that point in one second ?
- (28) How electrical resistance is expressed and write a law pertaining to it ?
- (29) What is meant by specific conductivity ?
- (30) Write Kohlrausch's law.
- (31) Classify the conducting substances on the basis of their values of conductivity
- (32) What is indicated by $\Lambda_m^0 = \nu_+ \lambda_{m+}^0 + \nu_- \lambda_{m-}^0$?
- (33) What are called superconducting substances ? Write the effect of temperature on it.
- (34) Write reduction reaction of moisture containing oxygen gas for corrosion of metal.
- (35) Explain the terms : 'Sacrificial anode' and 'Inhibitors'.

3. Write answers of following questions :

- (1) What is electrochemical cell ? Write equation of Daniell cell and mention anode and cathode ?
- (2) Write the construction of salt bridge and explain its function.

- (3) What is electrode ? Write its types and give one example of each.
- (4) What is emf series ? Write the information available from it.
- (5) Write the reaction of the electrochemical cell formed with the help of $E^0_{Ni^{2+}|Ni} = - 0.23 \text{ V}$, $E^0_{Ag^+|Ag} = 0.80$ and give symbolic representation.
- (6) H_2 gas is liberated by reaction of Fe with HCl, but H_2 gas is not liberated when Cu reacts with HCl. Explain.
- (7) Write usefulness of cell potential.
- (8) Write Nernst equation and explain the terms involved in it.
- (9) Write laws of Faraday for electrolysis.
- (10) Explain the electrolysis of dilute aqueous solution of NaCl between graphite electrodes.
- (11) If 1.08 gram Ag is deposited on the cathode when 7.5 ampere current passed through aqueous solution of $AgNO_3$ for 200 seconds, then calculate efficiency. ($Ag = 108 \text{ u}$, $N = 14 \text{ u}$, $O = 16 \text{ u}$)
- (12) The electrolysis of aqueous solution of sodium sulphate is in fact the electrolysis of water. Explain.
- (13) Explain Gibbs' free energy and cell potential.
- (14) Find the change in free energy and equilibrium constant of an electrochemical cell having standard potentials, cell having
 $E^0_{Cu^{2+}|Cu} = 0.34 \text{ V}$ and $E^0_{Fe^{2+}|Fe} = - 0.45 \text{ V}$.
- (15) Explain resistivity and specific conductance.
- (16) Write the classification of cells which are industrially useful and give example.
- (17) Explain Lec Lanche cell.
- (18) Write methods of preventing corrosion.
- (19) Write reactions of corrosion of iron.
- (20) Find the value of E_{cell} of electrochemical cell.



$$(E^0_{Zn^{2+}|Zn} = - 0.76 \text{ V}, E^0_{Cd^{2+}|Cd} = - 0.40 \text{ V})$$

4. Write the answers of the following questions in detail :

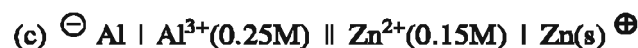
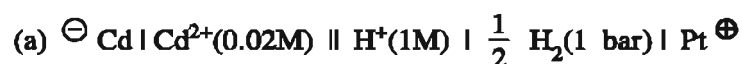
- (1) Draw the labelled diagram of electrochemical cell based on the reaction $\text{Zn(s)} + \text{Ag}^+(\text{aq}) \rightleftharpoons \text{Zn}^{2+}(\text{aq}) + \text{Ag(s)}$ and answer the following questions.
 - (i) Show the anode and the cathode and write the reactions on them
 - (ii) Show the direction of flow of electrons
 - (iii) Carry out symbolic representation
- (2) What is electrolysis : Explain the electrolysis of aqueous solution of CuSO_4 between graphite electrodes.
- (3) Explain the electrolysis of aqueous solution of CuSO_4 by active electrode of Cu and write its usefulness.
- (4) Write the Kohlrausch's law of independent migration of ions and explain.
- (5) What is storage cell ? Explain lead storage cell.
- (6) What is fuel cell ? Explain hydrogen fuel cell.
- (7) Explain metallic corrosion.
- (8) Explain ionic mobility: Explain the factors on which it depends.
- (9) Explain in detail "Standard hydrogen gas electrode."
- (10) Explain electrical conduction.
- (11) Explain molar conductivity and also explain the effect of changes in concentration on conductivity.
- (12) Explain mercury and Ni-Cd cells

(13) Calculate the following examples :

- (1) By using the standard electrode potentials given below, construct the cell having maximum and minimum potentials, write cell reactions and calculate equilibrium constant.

$$E^0_{\text{Fe}^{2+}|\text{Fe}} = -0.45 \text{ V}, E^0_{\text{Ag}^+|\text{Ag}} = 0.80 \text{ V}, E^0_{\text{Mg}^{2+}|\text{Mg}} = -2.37 \text{ V}.$$

- (2) Find the value of cell potential of the following cells at 298 K temperature



- (3) The values of standard potentials of the half cells, $\text{Sn}^{2+} | \text{Sn}$ and $\text{Ni}^{2+} | \text{Ni}$ are -0.14 V and -0.23 V respectively. Calculate the equilibrium constant at 298 K temperature.
- (4) The cell potential of the given following cell is 0.52 V at 298 K temperature, calculate the pH of HCl solution ($E^0_{\text{Cu}^{2+} | \text{Cu}} = 0.34$ V)
- $$\ominus \text{Pt} | \text{H}_2(1\text{bar}) | \text{HCl} (x\text{M}) || \text{Cu}^{2+}(0.02\text{M}) | \text{Cu(s)} \oplus.$$
- (5) The potential of the given following cell is 0.586 V at 298K temperature, calculate the ionic product (K_w) of water.
- $$\ominus \text{Pt} | \text{H}_2(1 \text{ bar}) | \text{NaOH} (0.01\text{M}) || \text{HCl} (0.01\text{M}) | \text{H}_2 (1 \text{ bar}) | \text{Pt} \oplus$$
- (6) How many grams of Cu and what volume of O_2 gas will be obtained if 18.4 ampere electric current is passed through the electrolytic cell of CuSO_4 for 1 hour and 42 minutes between graphite electrodes at 298 K temperature and 1 bar pressure ? ($\text{Cu} = 63.5\text{u}$ $\text{O} = 16\text{u}$)
- (7) How many amperes of current should be passed when aqueous solution of Na_2SO_4 is electrolysed between graphite electrodes at 300 K temperature so, that 250 ml min^{-1} O_2 gas is obtained under 1.0 bar pressure.
- (8) How many spoons can be electroplated by silver when 5 ampere current is passed through electrolytic cell of AgNO_3 for 2.7 hours ? 0.01 gram Ag layer is deposited on each spoon ($\text{Ag} = 108 \text{ u}$).
- (9) For how much time 48 ampere current should be passed through 400 ml 0.04M AgNO_3 solution during electrolysis so that Ag is completely deposited?
- (10) How many grams of Cu will be obtained by passing 4.5 ampere current through 1 litre 0.6M CuCl_2 aqueous solution by dipping inert electrodes ? What will be the change in concentration ?



Unit

4

General Principles and Processes of Isolation of Elements

4.1 Introduction

A few elements are available in free state in nature. Metal like copper, non-metals like carbon, sulphur and inert gases like helium and other are available in free form in nature. Many more metals and non-metals other than these are available naturally in combined form in the crust of the earth. As you know, that metals being important in our everyday life, they can be obtained in the form of metal from their compounds. For this, processes like extraction, isolation involving physico-chemical principles can be used to obtain metal. This total process is known as '**metallurgy**'. The methods developed and used to obtain metals are based on the economical and industrial aspects. Some principles to obtain elements are same, even then, some special methods are developed depending on the nature of the ore.

Mineral is the substance available in nature, which is present in the crust of the earth and is being dug out. All the minerals available are not useful for obtaining metal because very less amount of metal is available from them. The mineral from which metals can be obtained in good proportion is called **ore**. e.g. It is not practical to obtain aluminium from aluminosilicate but it can be obtained in good proportion from its mineral bauxite. There may not be only the element to be obtained being present but undesirable and certain earthly substances are present which can be called impurities. This is called **gangue**. The main steps to obtain metal from the ore are as follows :

(1) Concentration of ore (2) Isolation of metal from concentrated ore (3) Purification (Refining) of metal.

Thus, the total procedure to isolate metals from their ores using scientific and industrial processes is called '**metallurgy**'.

In this unit, we shall study steps for effective concentration of ores, certain general principles of metallurgy in which the thermodynamical and electrochemical aspects have been included as well as to obtain metal by reduction.

4.2 Occurrence of Metals

The abundance of different elements in the crust of the earth is different. In metals, the abundance of aluminium is the highest. Its place is third in the elements available from the earth's crust. It is about 8.3% by weight. Its chief minerals are mica and china clay. Some of the gem stones are impure forms of Al_2O_3 . e.g. Ruby contains Cr as impurity, sapphire contains Cd as impurity. The element available at second place is iron. It is available in many combined forms and it is also very important element. It is also present in combined form in the haemoglobin present in blood in our body. We shall study in this unit, the extraction of metals like aluminium, copper, iron and zinc. Principal ores of aluminium, copper iron and zinc metals are shown in table 4.1

Table 4.1 Principal Ores of some important metals

Metal	Ore	Composition proportion
Aluminium	Bauxite	$\text{AlO}_x(\text{OH})_{3-2x}$ where $0 < x < 1$
	Kaolinite (one type of china clay)	$[\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5]$
Copper	Copper pyrites	CuFeS_2
	Malachite	$\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
	Cuprite	Cu_2O
	Copper glance	Cu_2S
Iron	Haematite	Fe_2O_3
	Magnetite	Fe_3O_4
	Siderite	FeCO_3
	Iron pyrites	FeS_2
Zinc	Zinc blende or	ZnS
	Sphalerite	
	Calamine	ZnCO_3
	Zincite	ZnO

The oxide mineral is preferably selected to obtain metal from ores because SO_2 gas evolved from sulphide minerals causes pollution and their reduction is also difficult. So, bauxite for aluminium and haematite for iron etc, oxides are used. For copper and zinc, the ores mentioned in table 4.1 and their availability and the related factors are taken into consideration for the selection of ores. Before carrying out concentration of ores, they are crushed or grinded so that they become of the required size of particles.

4.3 Concentration of Ores

As we have seen earlier, there are impurities in the ores. viz. sand, clay etc. To obtain ore by removal of impurities as much as possible, is called concentration. There are many steps. The selection of these steps depends on the physical properties of the ore and the properties of the gangue. Two things are important during the concentration of ores : (1) To obtain maximum concentrated form by proper method. (2) The environment may not have any risk by the factors affecting the environment.

We shall understand one by one, all the four methods. (1) Hydraulic washing (2) Magnetic separation (3) Froth Floatation method (4) Leaching.

(1) Hydraulic washing : In this method, the principle of relative density of ore and gangue is involved so this method is also called relative density isolation. In such method, the ore is taken in a vessel and water flow is passed from the upper parts, so that the powdered ore is washed and all the light particles of the gangue are washed out. Ore is finally collected.

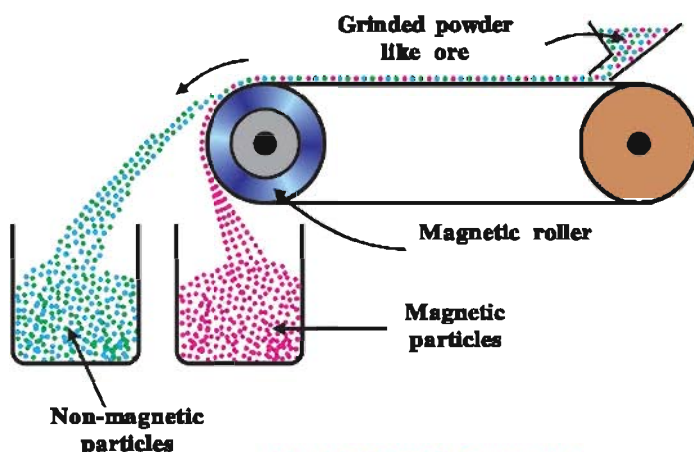


Fig. 4.1 Magnetic Separation

belt which is placed on magnetic roller. As shown in figure 4.1 the components which are being attracted are dragged towards the roller while the components which are not being attracted fall away from the roller. Thus, concentration of ore can be carried out by magnetic separation.

(2) Magnetic separation : In this method, the principle of magnetic properties of the components of the ore is involved. If any one of the ores and the gangue possesses magnetic attraction, then magnetic field can be applied. Thus, the components attracted by the magnet and not attracted by the magnet are separated. This method can be applied to the ores of iron. As shown in figure 4.1, the grinded powder like ore is placed on a magnetic roller and magnetic field is applied. The magnetic roller is also called conveyor

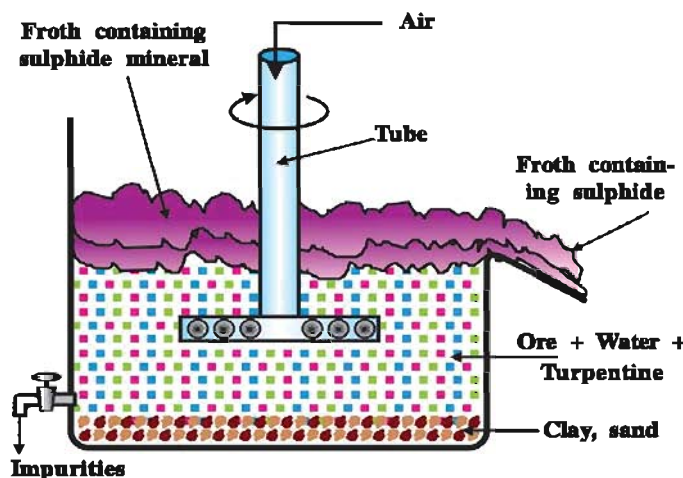


Fig. 4.2 Froth floatation method

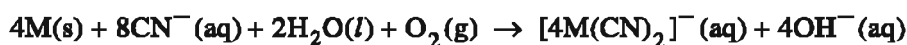
(3) Froth Floatation method : This method is mostly used for the ores containing sulphide. The ore is grinded and brought into powder form and then suspended in water. Substances which can produce froth and concentrate the ore are added to it. viz substances like pine oil, fatty acids, xanthates, turpentine etc. are added as the substances to collect the ore. As they do not mix with water, they keep the ore concentrated and moistureless. In addition froth stabilisers like cresol, aniline are also added. The particles of the mineral are wetted by substances like pine oil and the particles of the gangue are

wetted by water. As shown in figure 4.2 air is introduced in the mixture. As a result the solution gets agitated and the particles of the ore are carried on the upper part by the light froth produced. As this froth is light it is taken out by sieves skimmed off from the upper part and it is heated to obtain particles of ore. The remaining impurities remain suspended in the solution containing water. Some times two ores containing sulphide can also be separated. For this, the proportion of oil and water is properly selected and some depressants are used. viz. If NaCN is added as depressant to the ore containing ZnS and PbS, then PbS, skims off on the upper part with the froth and ZnS does not come with the froth. The reason for this may be the formation of complex - $\text{Na}_2[\text{Zn}(\text{CN})_4]$ soluble in water from the insoluble ZnS in water.

(4) Leaching : This method is used when the ore is soluble in some suitable solvent. This method can be understood by the following illustrations.

(A) Leaching of Alumina from Bauxite : As you know bauxite is the ore of aluminium which is leaching of alumina from bauxite. We shall study further in this unit.

(B) The second example of leaching is metallurgy of silver and gold. In this, leaching of silver by NaCN and leaching of gold by KCN in presence of oxygen is carried out. The metals are obtained in displaced form by the reactions as shown below :



(where M = Silver or Gold)



4.4 Extraction of Crude Metal from the Concentrated Ore

The metal to be obtained is in the ionic form of the compound of concentrated ore, so that they can be obtained by reduction. But for this, the concentrated ore has to be converted into the suitable form so that it can be reduced. viz. Sulphide ore can be reduced only after it being converted to oxide form of ore; because the reduction of oxide is easier. Steps to obtain metal from the ore can be divided into two parts :

(1) Conversion to oxide (2) Reduction of oxide to metal

(1) Conversion to oxide : For this, two reactions have to be carried out. (i) Calcination (ii) Roasting.

(i) Calcination : The ore is heated very strongly during calcination, so that all volatile substances are removed and metal oxide is left out. e.g.



(ii) Roasting : As shown in figure 4.3, the ore is heated below the melting point of the metal in a reverberatory furnace by introducing air continuously. The roasting of sulphide containing ore takes places according to the following reactions :

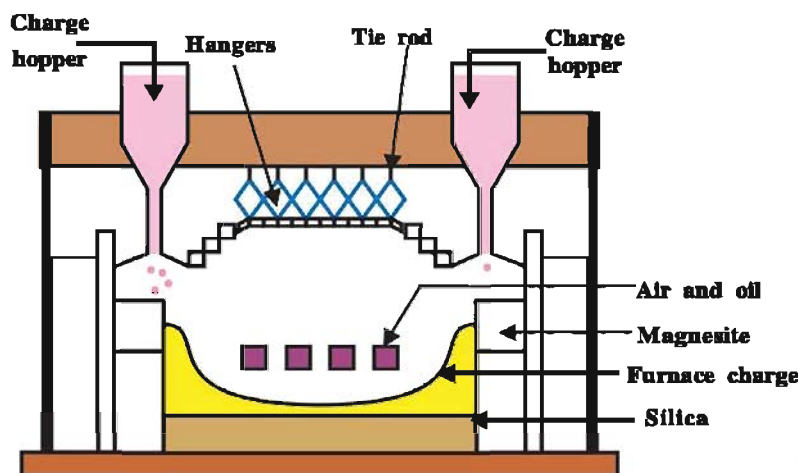
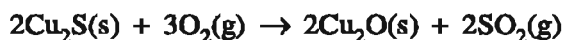
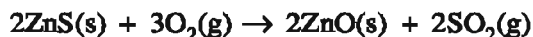
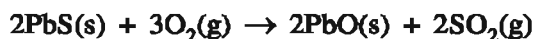
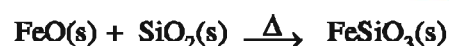


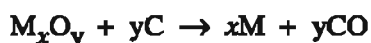
Fig. 4.3 Reverberatory furnace

If the ore of copper is containing sulphide then it is heated in reverberatory furnace. If the ore is iron containing, then silica is added to it before heating so that iron oxide combines with silica and forms iron silicate (FeSiO_3). It is known as **slag**.



Similarly, copper metal forms one mixed substance which is a mixture of Cu_2S and FeS . It is called **"Matte"**. SO_2 gas produced can be used in the manufacture of sulphuric acid.

(2) Reduction of Oxide of Ore to metal : During reduction reaction suitable reducing agent (viz. C or CO or any other metal) is used with the ore. Reducing agent like carbon combines with oxide of metal and reduces the metal oxide giving metal. viz.



Metal oxides can be reduced easily or with difficulty depending upon their stabilities. In the case of oxides which are easily reducible, common reducing agents are used and metal can be obtained by reduction. e.g. Fe metal from Fe_2O_3 . But the reduction of stable oxides like Al_2O_3 is possible by accepting the electrons. You know that acceptance or receiving of electron is the reduction reaction. Thus, the reduction reaction by accepting electron is called **electronation**. Heat is required during both the types of reduction reactions. To understand these phenomena explanation about principles, functions etc. of thermodynamics is essential. We shall study this in detail in point no 4.5.

For understanding the thermal reduction, the necessary changes in temperature, and which substance will be suitable for reduction reaction of metal oxide, the calculation of Gibbs' free energy and its interpretation is necessary. The study of metallurgy with changes in temperature is called **"Pyrometallurgy"**.

4.5 Thermodynamic Principles of Metallurgy

It is essential to have information about certain basic principles of thermodynamics. You are familiar with the terms like chemical equilibrium, equilibrium constant, Gibbs' free energy, entropy, enthalpy etc. From these, the understanding about equilibrium constant, Gibbs' free energy etc. will be useful here.

You have learnt Gibbs-Helmholtz equation $\Delta G = \Delta H - T\Delta S$, where ΔG is the change in free energy. ΔH is change in enthalpy and ΔS is the change in entropy and T is the temperature in Kelvin unit. You have also learnt the other important relation $\Delta G^0 = -RT \ln K$, where K = equilibrium constant, R = Gas constant and ΔG^0 is standard free energy change. Three values of ΔG^0 can be possible- positive, zero and negative. If the value of ΔG^0 is positive, then the reaction will not be spontaneous. If it is zero, reaction will be equilibrium state and if it is negative reaction will be spontaneous. Also the values of K can be <1 , 0 and >1 . If the value of K is < 1 , then the proportion of products will be less in comparison to reactants i.e. product obtained will be less. If it is one, then equilibrium will be there i.e. both reactants and products will be in same proportion. If it is greater than 1 the proportion of product obtained will be more. In addition to this, Le Chatelier's principle also plays an important role.

As we have seen, the negative value of ΔG will lead the reaction to products. In the equation $\Delta G = \Delta H - T\Delta S$, if the value of temperature T is increased, the value of ΔS will increase. Consequently, the product $T\Delta S$ will also increase, so that $\Delta H - T\Delta S$ or ΔG will become negative and so the reaction will go towards product.

The value of ΔG^0 is constant at definite temperature and so in the process, after mixing reactants and products the factors like concentration, temperature, pressure, affecting the reaction should be so arranged that the value of ΔG becomes negative. If it happens so, the reaction will become spontaneous in the direction towards products. Scientist H. J. T. Ellingham had studied the relations by plotting graphs of ΔG^0 versus T , and so these graphs are known as Ellingham diagrams. They are useful but have certain limitations also. We will not study it in detail here.

When reducing agent takes part in the reaction, then its oxide is formed and metal oxide gets reduced. The function of reducing agent is to make the value of ΔG^0 negative. Thus, free energy change of oxidation-reduction reaction should be zero.

On the basis of the thermodynamic principles associated with obtaining metal, it can be said that increase in temperature will lead to negative value of ΔG^0 . Hence the redox reaction should be such that the value of ΔG^0 obtained will be negative. But increase in temperature is harmful for exothermic reaction but can be advantageous for endothermic reaction. In the end, it should be kept in mind that the reducing agent should be such that its reduction reaction with metal oxide should be as spontaneous as possible. i.e. it gives maximum negative value of ΔG^0 and the efficiency of metal oxide reduction can be more. Thus, we can decide about the use of carbon, carbon monoxide, or any metal for the reduction and so the product obtained will be more or metal obtained will be more. In short, the selection of the reducing agent will depend on the magnitude of the negative value of ΔG^0 . We have studied in the unit of equilibrium that to obtain maximum product the value of equilibrium constant K should be as high as possible and the corresponding values of free energy change should be as less as possible so that the process will be advantageous. Hence, we can have combination of temperature, pressure, reducing agent in such a manner that the 'optimum' state can be formulated and maximum product, i.e. maximum amount of metal, can be obtained by reduction. Such thermodynamical principles are also called physico-chemical principles.

4.6 Electrochemical Principles of Metallurgy

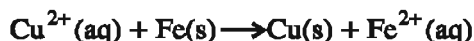
We have earlier learnt, the principles of thermodynamics, in obtaining metals from their oxides during pyrometallurgy. In addition to this, the principles of electrochemistry can be useful for reduction of metal ions present in the aqueous solutions or in molten states. For this electrolysis, or addition of some other metal (considering their reduction potentials) and ions of the metals can be reduced and

metals can be obtained. Metal can be obtained by reduction reaction during electrolysis of molten salts, in which electrochemical principles are involved. We have studied some equations viz.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0, \Delta G^0 = -RT \ln K$$

$$\Delta G^0 = -nFE^0 \text{ and } E^0 = \frac{RT}{nF} \ln K$$

From these, if we think of the equation combining thermodynamics and electrochemistry, then the equation $\Delta G^0 = -nFE^0$ is useful; where n is the number of electrons associated with the reaction, F = value of Faraday = 96500 coulomb, E^0 is the standard reduction potential of the complete cell of the redox reaction and it is the difference between standard reduction potentials of the two metals and ΔG^0 = standard free energy change. The oxidation potentials of the electrodes doing reactions will be very high and positive, so their reduction potentials will be very low and negative and so their reduction will be very difficult. But if the value of E^0 is positive, the value of ΔG^0 will be negative and so the reaction will be spontaneous. Hence, if active metal is added, into the solutions of ions of the metal which is less active, the metal ions from the solution will be reduced and converted to metal- form and the added metal will be obtained as ions in the solution. viz.



Activity : Prepare solution of copper sulphate in the laboratory. Place the iron nails in this solution. After two hours, observe what has happened? The blue colour of the solution will become light blue coloured and red particles will be deposited on the iron nails. This observation is of the reaction shown above; then explain which metal is oxidised, which metal is reduced, which ions from the solution are reduced and which ions have gone into solution by oxidation. If you have studied the unit on electrochemistry, calculate E^0_{Cell} of the reaction and calculate the value of ΔG^0 from its value and prove the use of electrochemistry in metallurgy.

Also, you do the experiment in reverse form. Place a strip of copper metal in the solution of FeSO_4 . What happens? Explain. Give reason. This type of experiment is included in your practical book.

In electrolysis, you have studied that metal ions from the solution are deposited on cathode. Always reduction will occur at cathode. For this reduction, the electrons of the cathode have entered, metal ions receive them and metal is obtained from metal ions. Generally, cathode of any metal can be used because the metal is to be deposited on the cathode. Cathode does not dissolve, but will not allow the impurities to enter, inert cathode or the cathode prepared of the metal to be obtained is advisable for use. We shall discuss this in detail in the point of metal refining.

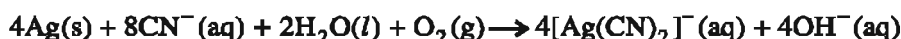
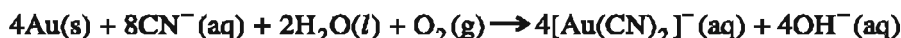
The electrolysis of molten solid can be carried out as above but if the melting point of molten solid is very high, some substances are added to bring it down which is known as flux and so electrolysis can be carried out at lower temperature. Cryolite (Na_3AlF_6) or calcium fluoride (CaF_2) is added in the process of obtaining Al from Al_2O_3 . We shall study this in detail in the extraction of aluminium metal.

4.7 Oxidation-Reduction

You have studied the different definitions of oxidation and reduction. We shall study here one of these definitions. Oxidation means loss of electron and reduction means gain of electrons. Formation of metal ions from metal by loss of electron is oxidation reaction and formation of metal from metal ions by gain of electron is reduction reaction. This method is mostly for non-metals. We shall study the following reactions which is the reaction to obtain chlorine from sea water (brine).



The value of ΔG^0 is + 422 kJ for this reaction if we calculate the value of E^0 from this by the equation $\Delta G^0 = -nFE^0$ then, its value obtained is -2.186 V. As we have studied earlier, the value of E^0 being negative, the reaction will not occur in forward direction. Hence, if we apply external e.m.f. higher than -2.186 V, then the reaction will occur and Cl_2 gas will be obtained on anode and NaOH will remain in solution because H_2 will be obtained as gas at cathode. Formation of Cl_2 from Cl^- ions is oxidation reaction and will occur at anode. Suppose we electrolyse molten NaCl, then Cl_2 will be obtained on anode and Na metal will be obtained on cathode and NaOH will not be obtained in solution. As seen earlier in leaching sodium cyanide (NaCN) is used to obtain gold and silver. Formation of Ag^+ from Ag and Au^+ from Au are oxidation reactions. Hence, cyanide complex ions of gold and silver- $[\text{Au}(\text{CN})_2]^-$ and $[\text{Ag}(\text{CN})_2]^-$ complex ions will be obtained respectively. It can be reduced by zinc metal and so gold and silver metals can be obtained viz.



and then,



Zinc acts as reducing agent in above reactions.

4.8 Refining of Impure Metals

There is a possibility to have impurity in the metals obtained by any of the methods or processes discussed earlier. Hence, to obtain very pure metals, their refining can be carried out and refining as high as possible can be obtained. For this, the methods used for refining are applied after taking into consideration the properties of the metal, impurities present in it etc. some of these are listed below :

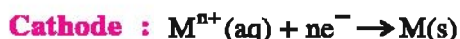
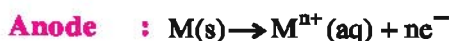
- | | | |
|-------------------|---------------------------|-----------------------------|
| (1) Distillation | (2) Liquation | (3) Electrolysis |
| (4) Zone refining | (5) Vapour phase refining | (6) Chromatographic methods |

(1) Distillation : This refining method is used for metals like zinc and mercury which have comparatively low melting points. The vapours obtained by distillation of impure metals, is cooled and the metal is obtained. The pressure is to be reduced for distillation of metal like mercury. Low pressure can be achieved by vacuum distillation method.

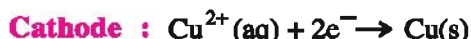
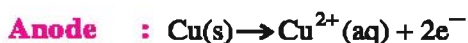
(2) Liquation : This method is used for the refining of metals like tin which have low melting points. For this, the impure metal is passed over a hot slopping surface, so that the pure metal having low melting point is obtained from the impurities which are melting at higher temperatures. The temperature of slopping surface can be adjusted.

(3) Electrolysis : In this, the impure metal is made anode and the strip of pure metal is made cathode. Now, these two electrodes are dipped in the aqueous solution of proper salt. If suitable electric current is passed in the solution, electrolysis takes place and pure metal is deposited on the cathode and the impure metal on the anode undergoes oxidation and enters into the solution as ions. Some noble metals are collected near the anode in the form of mud which is called anodic mud. In this method, the principle of electrochemistry is involved. You have earlier studied about standard potential of cell (E^0) and free energy change (ΔG). Hence, if the reduction potential is high, the ions in the solution are reduced and deposited as pure metal on the cathode. The impure metal at the

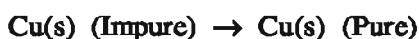
anode, enters into the solution as ions by oxidation reaction. If suitable potential is adjusted then amount of the metal obtained is directly proportional to the quantity of the electricity passed. You have studied this in the first law of Faraday's laws of electrolysis.



The refining of impure copper is carried out by this method in which the reactions take place as follows :



combining both the reactions.



Thus, pure copper metal is obtained from impure metal. Metal like zinc can also be obtained in pure form by this method.

(4) Zone Refining : Semimetals like silicon and germanium can be refined by this method. The principle of this method is that, the impurities of some metals are more soluble in molten state but is less soluble in solid state. This principle is used in the zone refining method.

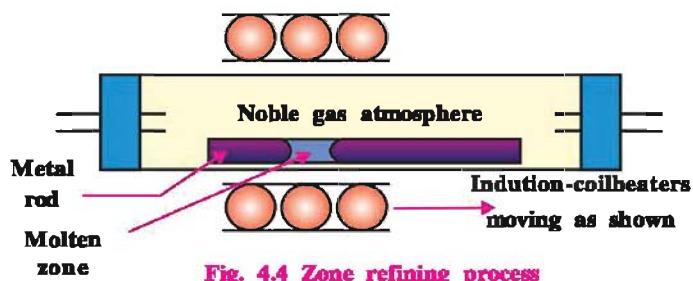


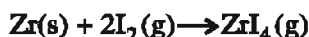
Fig. 4.4 Zone refining process

In this method spherical mobile heater is fixed at one end of the cylinder of impure semimetal. As shown in figure 4.4, the molten zone is advanced further with the heater. As the heater advances further, the impure semimetal (element) is separated from molten fluid and the impurities advance further with impure molten fluid. This method

is repeated and the heater is moved in one direction only. It is cut in cylindrical form and removed. The vapourised semimetal gets cooled and obtained in pure form. The inert gas atmosphere is created with inert gas kept in the cylinder so that there is no effect of air and heat. Very pure silicon required for semiconductors is obtained by this method. In addition to this, metals/semimetals like germanium, boron, gallium, and indium are refined by this method.

(5) Vapour phase Refining : In this method, the impure metal is reacted with suitable substance and its volatile compound is prepared which is in gaseous form and so can be collected in other vessel. Then, this volatile compound is decomposed so that pure metal is obtained and the by-product obtained can be used again and can be reacted with impure metal. Thus, there are two aspects in the principle of this method : (1) To prepare volatile compound of the said metal with any other suitable substance (2) The obtained volatile compound can be easily decomposed. If it happens so, it will be easy to obtain metal. We shall see the refining of nickel. Impure nickel is reacted with hot flow of carbon monoxide gas at 330-350 K temperature so that complex compound named nickel tetracarbonyl $[Ni(CO)_4]$ is formed. In this, nickel metal combines directly with neutral ligand like carbonyl. If nickel carbonyl compound obtained this way is heated at 450-470 K temperature, it decomposes and pure nickel metal is obtained. Obtained carbon monoxide can be used again for the formation of nickel carbonyl from impure nickel metal, so that the expenses will be less. This method was developed by scientist Mond and so it is called **Mond Carbonyl process**.

Similarly, metals like zirconium or titanium can be refined by using Van Arkel method. By this method, oxygen and nitrogen present in the form of impurities in the metals like zirconium and titanium can be removed. Impure metal is heated with iodine in an evacuated vessel. The iodides of metal being volatile, are changed into vapour.



The metal iodides obtained in this way are heated electrically on tungsten filament at 1800 K temperature so that they are decomposed and the pure metal is deposited on the wire.



(6) Chromatographic method : In this method, the principle of adsorption is involved. The adsorption order or efficiency of different metal ions on any one adsorbent is different. Hence, if the mixture of any metal ions is passed over any suitable solid adsorbent, the components (ions) in the mixture are adsorbed in different parts of the adsorbent. These adsorbed parts in the adsorbent are separated and obtained by suitable eluent because that ion or substance becomes soluble in that eluent. You will study in detail about adsorption in the unit of surface phenomena. Solid like Al_2O_3 , paper like filter paper or any suitable inert gas can be used as adsorbent. If solid substance like Al_2O_3 is used then it is filled in a glass tube and it can be used; so that the glass tube will become one column and so this chromatography is called **column chromatography**. If we cut filter paper strip and carry out separation of metal ions by suitable solvent on it, it is called **paper chromatography**. If on any suitable support, gaseous substance is used and separation is carried out, it is called **gas chromatography**. Demonstration experiments on adsorption and paper chromatography are included in your practicals book. Do it as an activity, with the help of the teacher. You will experience how interesting, nice, pleasant and innovative science is ! Some dyes, cations, anions etc. can be separated by suitable chromatographic method.

4.9 Extraction of Aluminium (Al), Copper (Cu), Iron (Fe) and Zinc (Zn) Metals

(1) Extraction of Aluminium : The extraction of Aluminium can be divided into two parts :

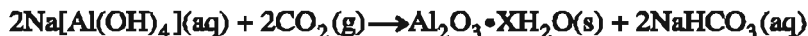
(A) To obtain pure alumina (Al_2O_3) from ore (bauxite)

(B) To obtain aluminium metal by reduction of alumina.

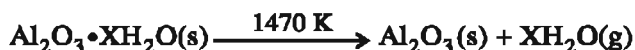
(A) To obtain pure alumina from ore (bauxite) : Bauxite is one of the principal minerals of aluminium from which aluminium is obtained. Silica (SiO_2), oxides of iron and titanium dioxide (TiO_2) are as impurities in impure bauxite. As seen earlier, the mineral bauxite is grinded and converted to small particles. Afterwards it is digested with 6 to 8% concentrated NaOH solution at 473 - 523 K temperature and 35 - 36 bar pressure. Because of this reaction amphoteric oxide Al_2O_3 reacts with base like NaOH and soluble hydrated sodium aluminate complex $\text{Na}[\text{Al}(\text{OH})_4]$ is formed which we express as sodium tetrahydro aluminate (III) according to IUPAC. The remaining components also dissolve in sodium hydroxide and form soluble sodium silicate but hydroxides of iron and titanium being insoluble get precipitated.



By filtering the solution, sodium aluminate is obtained in solution. By neutralising the solution by passing CO_2 gas, hydrated Al_2O_3 gets precipitated. At this stage, freshly prepared precipitates of Al_2O_3 or $\text{Al}(\text{OH})_3$ are added which create induced effect in precipitation of Al_2O_3 from solution.



Sodium silicate remains in solution. Insoluble hydrated alumina is filtered. On heating it at 1470 K temperature, pure alumina is obtained.



(B) To obtain pure aluminium from alumina : Al_2O_3 does not conduct electricity and its melting point is very high; so that electric current can flow before getting pure aluminium metal and

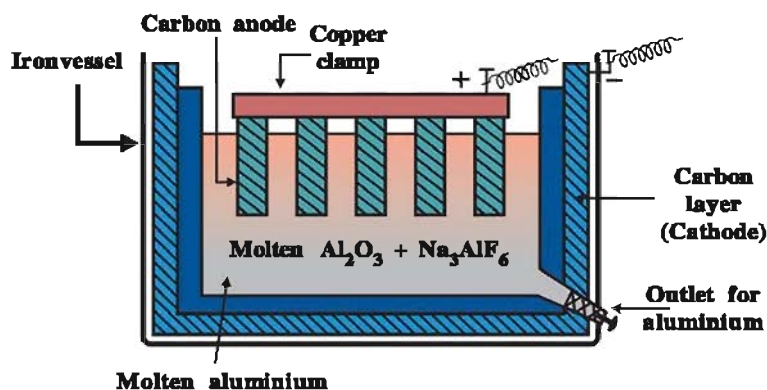
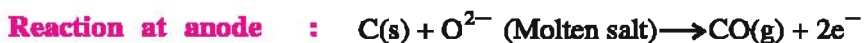


Fig. 4.5 Electrolytic cell for extraction of aluminium metal

aluminium metal can be obtained on cathode by electrolysis. Hence, substances like cryolite (Na_3AlF_6) or CaF_2 are added to Al_2O_3 . Hence, as studied earlier the physico chemical principles of thermo-dynamics are used so that the system formed is such that the value of ΔG^0 becomes more negative. This mixture is taken into an iron vessel in which there is layer of graphite on the inner side and it works as cathode. As shown in figure 4.5, carbon anodes are used and the molten $\text{Al}_2\text{O}_3 + \text{Na}_3\text{AlF}_6$ mixture is taken as electrolyte. For this, high temperature is to be maintained. Aluminium metal is obtained on graphite cathode by reduction. It is being in molten state at high temperature of the cell, aluminium comes out in the liquid form from the hole in the lower part of the cell. On cooling, aluminium metal is obtained in solid form. Thus, carbon of graphite functions as reducing agent.



This method was discovered independently by scientists Hall and Heroult and so it is known as **Hall-Heroult process**. Oxygen liberated from Al_2O_3 at anode reacts with anode because anode is made up of carbon and temperature is high, so carbon monoxide (CO) and carbon dioxide (CO_2) are formed.



Thus, carbon of the anode is used up or gets corroded. According to one estimate 0.5 kilogram

carbon is corroded or used up for 1 kilogram aluminium produced. Hence, the anodes of carbon are to be changed frequently. The production of alumina at the international level is about 100 million tons, India is producing about 1 million ton.

Uses of Aluminium : As aluminium is a light metal, it is used in the preparation of parts of aeroplane, household vessels, parts of cars for race. As it is good conductor of electricity, it was used in the electric wires. At present, its use has diminished. It can be used as reducing agent and metals like chromium manganese, are obtained from oxides of these metals. Alum is its important and useful compound. It also forms alloys like duralumin, magnalium, alnico and aluminium bronze are used in preparation of parts of the aeroplanes, parts of scientific balances, coinage, etc. Its thin sheets are used in cigarette cases, to keep hot substance hot and in packaging for the things instead of packaging by papers.

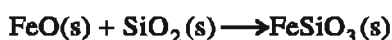
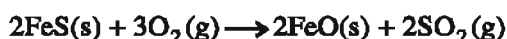
(2) Extraction of copper : For the extraction of copper, copper pyrites (CuFeS_2) is used even when many ores of copper are available. Copper available in free state, is obtained as copper metal by removal of the impurities existing with it. By this method, about 5% copper metal is obtained. If the ore is in carbonate or oxide form, it is heated with suitable reducing agent in fire furnace. Then it is heated with coke and sand so that copper metal is obtained by reduction of oxide; But if the ore is sulphide, it is not reduced directly as seen earlier and so it is to be converted to oxide. Sulphur dioxide gas produced during this reaction, causes pollution in atmosphere. Wet metallurgical process is used for pyrites ores of lower grade; while dry metallurgical process is used for the higher grade of pyrite ores. As copper has more attraction for sulphur, its reduction is difficult. With the increase in temperature, this attraction also increases. Iron has got more attraction for oxygen. Dry metallurgical method can be divided into five steps : (i) Concentration (ii) Roasting (iii) Smelting (iv) Bessemerisation (v) Refining.

(i) Concentration : About 2% copper is present in copper sulphide minerals available in nature. Froth floatation process is used for concentration of ore (**Recollect :** As studied earlier froth floatation process is used for concentration of sulphide ores). The grinded mineral is suspended in water and turpentine oil or cryolite oil is added to it. Then air is blown into it, so that oil sticks to the mineral and with the bubbles of the air it is collected as froth on the upper part and the impurities as well as waste is collected at the bottom. The froth is skimmed off with sieves. By concentrating in this way, about 25% copper containing ore is obtained.

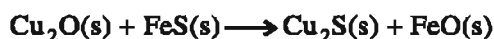
(ii) Roasting : The ore obtained by froth floatation method is roasted in air so that moisture as steam, sulphur and arsenic as their oxides i.e., sulphur dioxide and arsenious oxide are removed because of high temperature. During roasting, until iron sulphide is not converted into iron oxide, cuprous sulphide is not converted to its oxide.



(iii) Smelting : The mixture obtained by roasting is smelted with sand (SiO_2) in blast furnace so that sand and iron oxide combine to form iron silicate (FeSiO_3) which is called **slag**. As it is light it floats on the mixture and so it is repeatedly removed. This iron oxide is removed as slag during the smelting.



If cuprous oxide is formed with cuprous sulphide during roasting is converted to cuprous sulphide.



FeO obtained this way can be removed as slag. Then, mixture of iron sulphide (FeS) and cuprous sulphide (Cu_2S) is seen there which is called matte. As it is heavy, it settles at the bottom of the vessel and the light slag of iron silicate - remains floating, so it is easy to remove it.

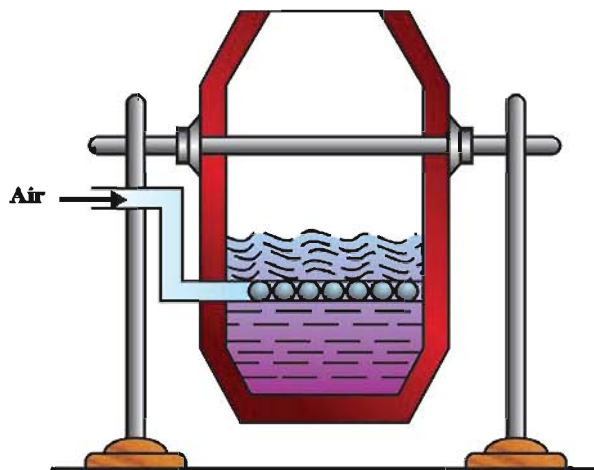
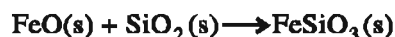
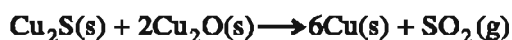


Fig. 4.6 Bessemerisation

(iv) Bessemerisation : The iron left out in the mixture is removed in Bessemerisation process. For this the fluid (mixture) obtained by smelting is poured in Bessemer's converter and required amount of sand is added. Then the converter is kept in vertical position as shown figure 4.6. Air at high pressure is introduced into it, so that iron sulphide is converted to iron oxide which combine with sand and form iron silicate (slag).



During Bessemerisation, cuprous oxide is formed by oxidation of cuprous sulphide only after all the iron sulphide is converted to iron oxide. When cuprous oxide is formed in the sufficient proportion, introduction of air is stopped. Because of self oxidation between cuprous sulphide and cuprous oxide, copper is obtained in fluid state.



Copper is taken out in fluid state, from the Bessemer converter. As this copper gets cold, bubbles of sulphur dioxide gas from the fluid are evolved. Hence, it appears that blisters are there on the surface of copper and is called **blister copper**. This copper is about 95% pure. Mainly impurities of sulphur and iron are present in it. Impurities like Zn, Si, As, Sb, Bi, Au, Pt are present in trace amounts.

(v) Refining :

(A) Thermal Refining : Blister copper is heated in presence of air in furnace, so that volatile oxides of As, Sb, etc. are removed. Silicates of Fe, Bi, Zn etc. float as slag on copper, which are removed. The remaining impurities like Ag, Au, Pt, can not be removed. During this some cuprous oxide is produced which dissolves in copper and so it becomes brittle. Hence, to stop this, powder of coal is spread on the fluid copper and the fluid is shaken with the freshly cut branches of tree. Because of the heat of copper, destructive distillation of branches of wood produces gas like methane. It reduces cuprous oxide to copper. Copper obtained this way is about 99.5% pure. It being very strong, it is used for common uses.

(B) Electrolysis : Copper obtained by thermal refining contains some impurities and so it is not a good conductor of electricity. Noble metals like Ag, Au and Pt are present in it and so it is advisable to obtain them. Hence electrolysis method is used for obtaining very pure copper. As shown in figure 4.7, solution of copper sulphate in dilute sulphuric acid is taken as an electrolyte, in a vessel. In this, small strips or rod of impure copper is dipped as the anode and strip of pure copper is dipped as cathode. As the electric current is passed through the solution, following reactions take place at anode and cathode during electrolysis.

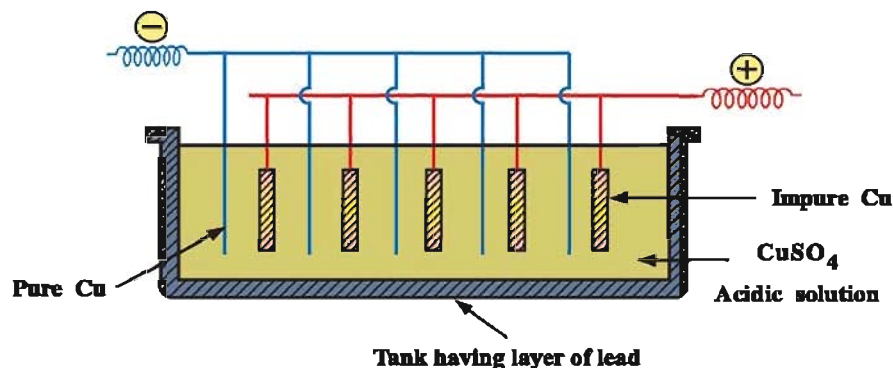


Fig. 4.7 Electrolysis of copper

Anode : $\text{Cu(s) (Impure)} \longrightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$ (Oxidation)

Cathode : $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu(s)}$ (Reduction)

Net reaction : $\text{Cu(s) (Impure)} \longrightarrow \text{Cu(s) (Pure)}$

Thus, as long as electric current is passed, copper of impure copper gets oxidised and enters into the solution as copper ions and the copper ions of the solution are changed to copper metal by reduction reaction which is deposited on the cathode. As noble metals like Ag, Au and Pt are not oxidised, they are collected below the anode which is known as **anode mud**. Ag, Au and Pt metals can be obtained from it. The purity of copper obtained at the cathode is about 99.96 to 99.99%.

Uses of copper : Copper is used in preparation of electrical appliances, tubes of boiler, sheet, household vessels, currency coins and also it is added to gold ornaments so that they become strong. It is also used for obtaining metals like Ag and Au from their ions in the solutions of their salts, by reduction. In addition to this, it is also used in preparation of many more alloys. Some of the known alloys of copper are brass, bronze, german silver, Monel metal, Bell metal, Delta metal, constantan, Muntz metal, phosphor bronze, aluminium bronze etc.

(3) Extraction of Iron metal : From the ores of the iron, haematite (Fe_2O_3) is used to obtain iron. There are three steps for this.

(i) Roasting and Calcination (ii) Reduction and smelting (iii) Refining.

(i) Roasting and Calcination : The oxide form ore containing iron is first roasted by heating with some coal in a furnace, so that the volatile impurities like the moisture and carbon dioxide obtained due to decomposition of carbonate are removed. Ferrous oxide is oxidised to ferric oxide which does not combine with silica and does not form slag, in the smelt. The mixture in the furnace becomes porous.

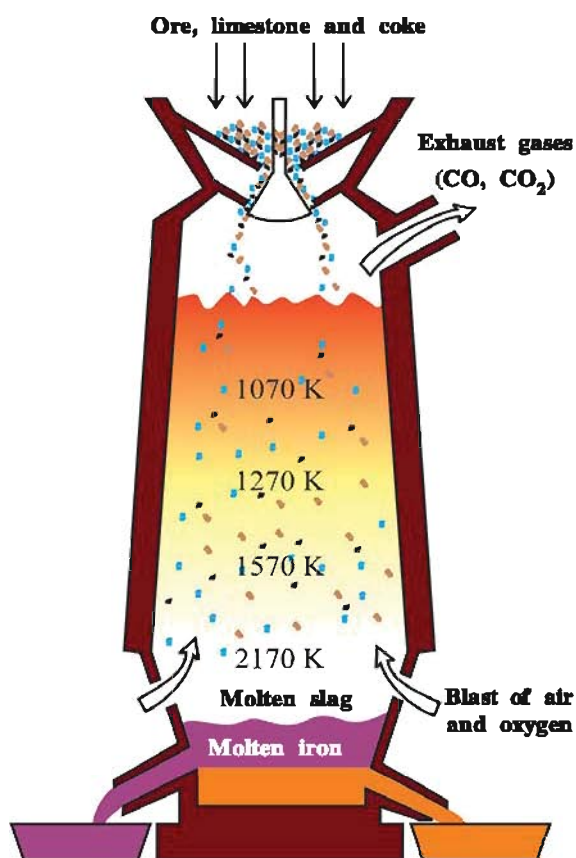
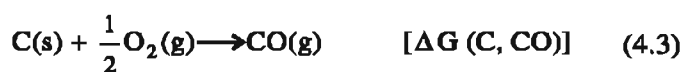
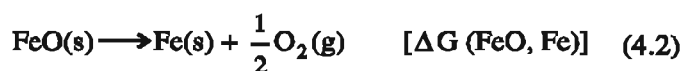


Fig. 4.8 Blast furnace

(ii) Reduction and smelting : The porous mixture obtained by roasting is mixed with lime stone. Coke, etc. are added into the blast furnace from the upper part as shown in figure 4.8. Here, oxide is reduced to iron metal. Thermodynamics is useful in understanding the reactions occurring in blast furnace e.g. How carbon monoxide formed from coke, carries out reduction ? Why such a furnace is selected ? The main function of this furnace is to carry out the following reactions :



The coke can carry out reduction directly. CO gas is formed by combination of carbon with oxygen available from FeO.



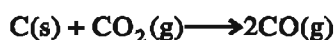
Reaction 4.1 is obtained by computation of simple reaction (4.2) and (4.3). Hence, the free energy change of the reaction ($\Delta_r G$) will be as follows.

$$\Delta_r G = \Delta G (\text{C, CO}) + \Delta G (\text{FeO, Fe}) \quad (4.4)$$

If the value of $\Delta_r G$ obtained is negative, then only the reaction will occur. Hence, from the study of $\Delta_r G$ and temperature, the changes in $\Delta_r G$ can be studied and the temperatures of the reactions occurring in blast furnace can be controlled and the conditions can be so created that the reaction occurs. You have studied in standard 10 that blast furnace is a very tall furnace and there are different temperatures at different heights in the furnace. At the temperature 500-800 K (Range of low temperatures in blast furnace) the reaction takes place.

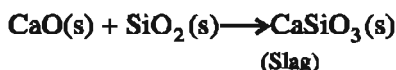
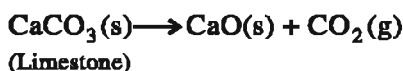
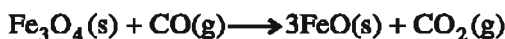
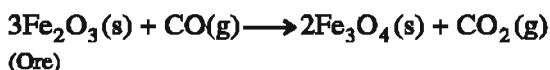


At temperatures 900 - 1500 K, (Range of high temperatures in blast furnace), following reactions occur,

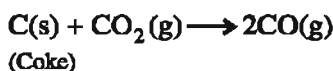


Calcium oxide obtained by the decomposition of lime stone combines with silica which is the impurity from the ore and forms slag which is removed as slag. Slag being in molten condition, separates from the iron. Hence, the reaction occurring at different temperatures in blast furnace can be shown as below :

(i) In the temperature range of 500-900 K.



(ii) At 1270 K temperature



(iii) Molten slag is formed at 2170 K temperature.

(iv) At temperature higher than 2170 K, pig iron is formed.

Iron obtained from blast furnace contains 4% carbon and many impurities. Also, it contains S, P, Si, Mn etc. in trace. It is called **pig iron**. It can be casted into different shapes. Cast iron is different from pig iron. Cast iron can be prepared by blowing hot air in the mixture of pig iron, iron scrap and coke. The proportion of carbon in it is comparatively less (about 3%). It is hard and brittle.

(iii) Refining : Wrought iron or malleable iron is the purest form of general iron. Wrought iron is prepared from cast iron in reverberatory furnace in which there is a layer of haematite. Haematite changes carbon to carbon monoxide.



Limestone is added as a flux and is removed with oxidation of sulphur, silicon and phosphorus. Metal is taken out of the furnace and passed through the rollers so that slag is removed and iron metal is obtained.

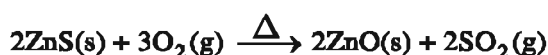
Uses of Iron : The most important form of iron is cast iron which is used in stoves, rails of railway, pipes of gutter, toys etc. because it can be casted. It is used in preparation of wrought iron and steel. Wrought iron is used in preparation of anchors, wires, bolts, chains, agricultural tools, etc. Steel has many uses. Different types of steel, having desirable properties can be prepared by mixing other metals with iron. Steel containing nickel is used in ropes, automobile, parts of aeroplanes, pendulums, measurement tap etc. Steel containing chromium is used in machines for cutting and grinding and stainless steel is used in cycles, automobiles, vessels, pans etc.

(4) Extraction of Zinc : The ores of zinc are available in forms of oxide, carbonate and sulphide. From these, the zinc sulphide ore is known as zinc blende. It is mostly used in obtaining zinc metal. Zinc

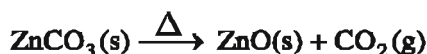
metal can be obtained by reduction with carbon. This, extraction takes place in four different steps :
(i) Concentration (ii) Roasting (iii) Reduction (iv) Refining

(i) Concentration : As studied earlier, ZnS which is the sulphide containing ore of zinc, froth floatation process is used for its concentration. It contains galena (lead sulphide-PbS) sand etc. as the impurities. It is grinded and converted to powder form. It is taken in a vessel and water is added to it. Air is passed through after adding turpentine oil. As zinc sulphide mineral is light it comes up with the light froth obtained by bubbles of air, while other impurities remain in the solution or settle down. The froth obtained by froth floatation process is frequently removed with sieves. Concentrated ore is collected. If mineral is calamine, this method is not necessary because the ore does not contain galena.

(ii) Roasting : Concentrated ore-ZnS or calamine is roasted in presence of air, so that it is converted to oxide form ZnO. If the ore is ZnS, it becomes necessary to keep in mind that it is converted to ZnO as much as possible otherwise it combines with liberated SO₂ gas and changes to zinc sulphate.

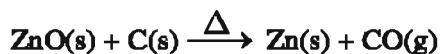


If mineral is carbonate, ZnO is obtained as follows :



Thus zinc oxide is obtained.

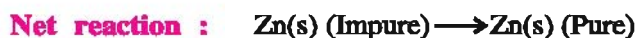
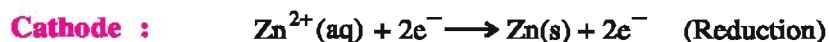
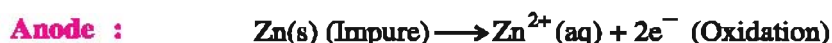
(iii) Reduction : Zinc oxide obtained by roasting is mixed with powder form coal or anthracite coal and heated in the cylindrical retort which is made up of fire clay bricks; so strongly that it becomes red hot. One end of the retort is closed and other retort is joined with the other open part so that it works as a condensor and cools the vapour of zinc that is coming out. Many such retorts can be connected in series. It is kept bent towards its mouth. When it is heated, carbon combines with oxygen of zinc oxide and forms carbon monoxide. Carbon monoxide burns with a blue flame at the end of the china clay tube. After some time the flame becomes brighter which indicates that now the vapour of metal has started forming. A small condensor which is prepared from iron and called as prolong or nozzle. It is connected with the end of each of the china clay tube; so that zinc metal gets cooled and collected in it. This metal is taken out and is casted into blocks. The zinc metal that we get on commercial basis is called **spelter**.



In the distillate coming out in the beginning, impurity of cadmium is removed, because it can be easily reduced and is more volatile than zinc.

(iv) Refining : Zinc obtained by reduction, which is called spelter contains impurities like Fe, Al, As, Sb etc. which can be removed by repeated distillation. But zinc is reacted with dilute H₂SO₄, so as to obtain pure zinc. By this reaction solution of zinc sulphate is obtained. Intensive refining of this zinc sulphate is carried out. Cadmium is precipitated by zinc dust. Iron is converted to ferric state. Al, Sb, and As are separated from solutions of suitable acidity. Afterwards, the solution is filtered out so that

pure zinc sulphate solution is obtained. As seen earlier in copper, here also impure zinc is made anode and pure zinc strip or rod is made cathode. The electrolyte is zinc sulphate solution containing dilute H_2SO_4 . Reactions occurring at anode and cathode are as follows :



Uses of zinc : Zinc is used in preparation of electrical cells, in electroplating of zinc and also in galvanising. It is used in certain alloys like brass, german silver, in combination with copper. It is used as zinc powder in reduction reactions. Metals like silver (Ag) and gold (Au) can be obtained from Ag^+ or Au^{3+} ions containing solutions by reduction with zinc. It is also used for protection of metal from corrosion by electroplating them on iron strips (galvanised iron).

SUMMARY

Metals and non-metals are associated with human life from very long time. viz. metals like iron, copper, gold, mercury, and non-metals like dioxygen and dinitrogen. We use these metals in pure form or their alloys formed by metals combined with other substances. Many reactions and processes are to be used before obtaining such metals.

Metals are mostly combined in their oxide, sulphide or carbonate compounds and very rare cases the metals are in free form. Their proportions are different in the earth's crust. The substances which are obtained from earth's crust or mines are called mineral. There can be more than one mineral for a particular metal. Same amount of metal or element is not obtained from each mineral. Hence, the part in which the maximum quantity and good quality metal can be obtained is called ore. viz. Haemetite for iron, bauxite for aluminium, copper pyrites for copper and zinc blende for zinc.

The complete process to extract metal from ore is called metallurgy. In this unit, we have studied about the extraction of certain metals from their minerals or ores. The combined form of metal alongwith impurities and earthly substances is called gangue. Three important steps are there to obtain metal from ore. (i) concentration of ore, (ii) isolation of metal from concentrated ore and (iii) refining of metal. The abundance of aluminium ore available from earth's crust has position three in the order of elements available from earth's crust. The methods used for concentration of ores are developed after taking into consideration, impurities, etc., physico-chemical principles, physical and chemical properties of the metal as well as the matters which should not be harmful to environment. Amongst the methods of concentration of ore are (1) hydraulic washing (2) magnetite separation (3) froth floatation method and (4) leaching. The principle of hydraulic washing is the relative density of gangue. Principle of magnetic attraction-repulsion is involved in magnetic separation. In froth floatation process, concentration of sulphide ore by producing artificially foam is carried out. In leaching, the principle of solubility of different solutes in different solvents is involved.

Several steps are associated with extraction of crude metal from ore. viz. conversion to oxide and reduction of oxide to metal. The steps which are followed for conversion into oxides are (1) calcination (2) roasting - by which metal is obtained in oxide form. Some substances are

added to remove certain substances viz. to remove iron oxide, sand (Silica) is added so that iron silicate (FeSiO_3) is obtained in slag form. As it is light, it can be removed. The furnaces for such functions, furnaces like reverberatory furnace, fire furnace and blast furnace are used.

After obtaining oxide of metals, they are reacted with suitable reducing agents and metals are obtained. Carbon, coal, carbon monoxide, active metal etc. can be used as reducing agents. Metallurgy studied with changes in temperatures is called pyrometallurgy. Reduction can also be carried by electrons through electric current.

The study and information about the principles of thermodynamics, chemical equilibrium, Le Chatelier's principle, as well as the study of terms like free energy change, equilibrium constant, enthalpy, entropy etc. become very essential in the process of metallurgy. For any reaction to result in products, the value of equilibrium constant should be more than 1 and the corresponding value of free energy change should be as negative as possible. Scientist Ellingham studied the relations between free energy decrease ($-\Delta G^0$) and it is known as Ellingham diagrams. The use of physico-chemical principles associated with metallurgy are explained in this unit. Oxidation means to lose electron which takes place at anode in the electrochemical cell and reduction means to gain electron which takes place at cathode in the electrochemical cell. Hence, impure metal can be oxidised with the help of anode and pure metal is reduced from the solution by reduction and gets deposited on the cathode viz. From anode of impure copper, pure copper can be obtained on the cathode. The purity of the metal obtained by this method is almost 100%. Certain metals can be converted to their complex compound forms by addition of certain substances and can be separated. Viz. reaction of metals like silver and gold with substance like sodium cyanide.

The following methods are used for refining of impure metals. (1) Distillation (2) Liquation (3) Electrolysis (4) Zone refining (5) Vapour phase refining.

Metal like mercury can be refined by distillation. Metal like tin can be refined by liquation metal like copper can be refined by electrolysis, semimetal like silicon can be refined by zone refining method and metal like nickel can be converted to gaseous compound like nickel carbonyl and then refined by vapour state method. Metals like zirconium and titanium can be refined by Van Arkel method. The ions of some metals can be obtained in pure form by chromatographic method and then metals of ions can be obtained by reduction.

In addition, the extractions of aluminium, copper, iron and zinc have been studied in this unit. This study can be shown as summary in the following table.

Sr. No.	Ore	Pure metal	Method and its name
1.	Bauxite ($\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$)	Aluminium	Hall-Heroult method - by electrolysis
2.	Copper pyrites (CuFeS_2)	Copper	Thermal refining and electrolysis method
3.	Haematite (Fe_2O_3)	Iron	Use of blast furnace method
4.	Zinc blende (ZnS)	Zinc	Electrolysis method

In addition, in this unit, the uses of each metal, their alloys with other metals etc. are also included. The products etc. obtained by extraction of metals and non- metals plays an important role in the economic condition of the country.

EXERCISE

1. Select the proper choice from the given multiple choices :

- (1) Which is the ore of aluminium ?
(A) Bauxite (B) Haematite (C) Copper pyrites (D) Zinc blende
- (2) Which is the ore of copper ?
(A) Bauxite (B) Haematite (C) Copper pyrites (D) Zinc blende
- (3) Which is the ore of zinc ?
(A) Bauxite (B) Haematite (C) Copper pyrites (D) Zinc blende
- (4) Which is the ore of iron ?
(A) Bauxite (B) Haematite (C) Copper pyrites (D) Zinc blende
- (5) Which metal is refined by zone refining method ?
(A) Copper (B) Zinc (C) Silicon (D) Aluminium
- (6) Which metal is refined by electrolysis method ?
(A) Mercury (B) Zinc (C) Tin (D) Silicon
- (7) What is name of the method used in refining of aluminium?
(A) Van Arkel (B) Bessemerisation (C) Hall-Herault (D) Heitler-London
- (8) What is called the strongly heating of ore and converted to oxide ?
(A) Roasting (B) Distillation (C) Liquefaction (D) Electrolysis
- (9) In which method do the ranges of temperature play an important role ?
(A) Electrolysis (B) Zone refining (C) Blast furnace (D) Liquation
- (10) Which principle is involved in chromatographic separation ?
(A) Precipitation (B) Hydration (C) Decomposition (D) Adsorption

2. Answer the following questions in brief :

- (1) Explain the principle of zone refining method and show which metal can be refined by it.
- (2) Explain in detail roasting and calcination.
- (3) Describe the use of carbon and carbon monoxide as reducing agent.
- (4) Electrolysis is a reduction method. Explain.
- (5) Write chemical reactions occurring in the different ranges of temperature in blast furnace.

3. Write the answers in detail, of the following questions :

- (1) Describe in brief the methods for obtaining ore from mineral.
- (2) Explain the use of physico-chemical principles in metallurgy.
- (3) Describe Hall-Herault method.
- (4) Explain the electrolysis of impure copper.
- (5) Explain in detail, the zone refining method.

4. Write in detail, the answers of following questions :

- (1) What is slag ? Why is it required and in extraction of which metal it is used ?
- (2) Discuss the physico-chemical principles regarding cryollite and calcium fluoride used in Hall-Heroult method.
- (3) Explain the terms giving suitable example-Roasting, Calcination, Refining, Electrolysis, Zone refining.
- (4) Describe in detail the method to obtain pure alumina from bauxite.
- (5) Give reasons for the following phenomena :
 - (1) The anodes of carbon have to be changed in refining of aluminium.
 - (2) Froth floatation method becomes inevitable for the ore containing sulphide.
 - (3) Iron oxide does not get reduced till there is presence of iron sulphide.
 - (4) Cryollite is added in refining of aluminium.
 - (5) In refining of metals like gold and silver, the solutions of their complex compounds are used.



Unit

5

p-Block Elements II

5.1 Introduction

We have studied in standard 11, that the last electron is filled in p-orbital in the elements of groups 13 to 18. Hence, these elements are called p-block elements. The outermost electronic configuration of these elements is ns^2np^{1-6} (Except He; Electronic configuration of He is $1s^2$). The properties of the elements of p-block, depend on their atomic size, ionisation enthalpy, electron gain enthalpy and electronegativity. A large diversity is observed in properties of elements of p-block because of absence of d-orbital in the second period and presence of d- or/and f-orbitals in the electronic configuration of third to seventh period. In addition, diversity is also observed because of the presence of metals, non-metals and semimetal elements.

5.2 Elements of Group-15

Nitrogen, phosphorus, arsenic, antimony and bismuth are included in group 15. As the first element of the group is nitrogen, it is also known as **nitrogen group**. In any group if we move from top to bottom, non-metal to semimetal and then, increase in metallic properties is observed. Nitrogen and phosphorus are non-metals, arsenic and antimony are semimetals and bismuth is a metal element. Dinitrogen gas is present in air as 78 % by volume. Nitrogen element from the earth's crust is obtained in the form of sodium nitrate- NaNO_3 (Chile salt petre) and potassium nitrate- KNO_3 (Indian salt petre). Phosphorus element is obtained from apatite minerals $\text{Ca}_5(\text{PO}_4)_3 \cdot \text{CaX}_2$ ($\text{X} = \text{F}, \text{Cl}, \text{OH}$) e.g. fluorapatite $\text{Ca}_5(\text{PO}_4)_3 \cdot \text{CaF}_2$. Phosphorus is the important component in the constitution of animals and plants. It is present in living cell as well as in bones. Phospho-protein is present in eggs and milk. The important atomic and physical properties of the elements of this group are shown in table 5.1

Table 5.1 Atomic and Physical Properties of Group 15 Elements

Property	N	P	As	Sb	Bi
Atomic number	7	15	33	51	83
Atomic mass (g mol ⁻¹)	14.01	30.97	74.92	121.75	208.98
Electronic configuration	[He]2s ² 2p ³	[Ne]3s ² 3p ³	[Ar]3d ¹⁰ 4s ² 4p ³	[Kr]4d ¹⁰ 5s ² 5p ³	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ³
Ionisation enthalpy (I)	1402	1012	947	834	703
(Δ _i H) (kJ mol ⁻¹) (II)	2856	1903	1798	1595	1610
(III)	4577	2910	2736	2443	2466
Electronegativity	3.0	2.1	2.0	1.9	1.9
Covalent radius (pm)	70	110	121	141	148
Ionic radius (pm)	171	212	222	76	103
Melting Point (K)	63	317	1089	904	544
Boiling Point (K)	77.2	554	888	1860	1837
Density (g cm ⁻³) (295 K)	0.879	1.823	5.77	6.697	9.808

5.2.1 Electronic configuration, occurrence, oxidation states :

Electronic configuration : The electronic configuration of valence shell of elements of group 15 is ns²np³. As the s-orbitals of these elements are completely filled and p-orbitals are partially filled, these elements are exceptionally stable.

Occurrence : The chief minerals of the elements of group-15 are shown in table 5.2

Table 5.2 Chief Minerals of Elements of Group 15

Elements	Structures of chief minerals and their names
Nitrogen	Approximately 78% in the form of free gas in the earth's atmosphere. Approximately 17% in animal and plant proteins, NaNO ₃ (Chile salt petre); KNO ₃ (Indian salt petre).
Phosphorus	Approximately 60% Ca ₃ (PO ₄) ₂ in bones and teeth, Ca ₉ (PO ₄) ₆ • CaF ₂ Fluorapatite; Ca ₉ (PO ₄) ₆ • CaCl ₂ Chlor aptatite; Ca ₉ (PO ₄) ₆ • Ca(OH) ₂ Hydroxyapatite.
Arsenic	As ₄ S ₄ -Rielger (Volcano regions); As ₂ S ₃ -Orpiment; FeAsS ₂ Arsenopyrites.
Antimony	Sb ₂ S ₃ -Stibine; Sb ₂ O ₄ -Antimony ore.
Bismuth	Bi ₂ S ₃ -Bismuthine; Bi ₂ O ₃ -Bismite; (BiO) ₂ CO ₃ -Bismuthspar.

Oxidation State : The common oxidation states of elements of group-15 are -3 , $+3$ and $+5$. The tendency to show -3 oxidation state decreases as we go down the group because of increase in the atomic size and metallic properties. Similarly the stability of $+5$ oxidation state also decreases as we go down in the group. When nitrogen element reacts with oxygen element, it shows $+1$ to $+5$ oxidation states. In certain oxoacids, phosphorus shows $+1$, $+3$, $+4$ and $+5$ oxidation states. The oxidation states of elements of group 15 are shown in table 5.3.

Table 5.3 Oxidation States of Elements of Group 15

Elements	N	P, As	Sb	Bi
Oxidation states	-3 to $+5$	-3 , $+3$, $+5$	$+3$, $+5$	$+3$

5.2.2 Periodicity in physical and chemical properties :

(1) Periodicity in physical properties : It can be said on the basis of table 5.1, that in the elements of group 15 with the increase in atomic number, there is general tendency of increase in atomic size, decrease in ionisation enthalpy and decrease in electronegativity. Hence, the metallic property increases with atomic number.

(i) Atomic and Ionic Radii : Going down the group 15, atomic and ionic radii increase. There is remarkable increase in the atomic radii while moving from nitrogen to phosphorus; but there is slight increase in atomic radii while going from As to Bi; the reason for this, is that in heavy elements, d-or/and f-orbitals are present. (Table 5.1).

(ii) Ionisation Enthalpy : The value of ionisation enthalpy decreases while going down the group because of increase in atomic size. The order of the first ionisation enthalpy (Δ_1H_1), second ionisation enthalpy (Δ_1H_2) and the third ionisation enthalpy (Δ_1H_3) is $\Delta_1H_1 < \Delta_1H_2 < \Delta_1H_3$ (Table 5.1). As the p-orbitals in elements of group 15 are half filled and so they possess characteristic stability. Hence, electron is not removed easily from these elements. Thus, in the same period, the values of ionisation enthalpy of elements of group 15 are more than the values of ionisation enthalpy of elements of group 16.

(iii) Electronegativity : Generally the atomic size increases with atomic number while going down the group, hence electronegativity decreases. The difference in electronegativities of heavier element is found to be less (Table 5.1).

The elements of this group are polyatomic. There are allotropes of all the elements of this group except nitrogen and bismuth.

(2) Periodicity in chemical properties :

(i) Reaction with hydrogen element : All the elements of group-15 form hydrides of the type MH_3 (where $M = N, P, As, Sb$ or Bi) by combining with hydrogen. The stability of the hydride compounds decreases as we go from NH_3 to BiH_3 in the group, but its property as reducing agent increases. The order of basicity of these hydride compounds is $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.

(ii) Reaction with oxygen element : All the elements of group-15 combine with oxygen and form two types of oxides M_2O_3 and M_2O_5 . The oxides of the elements having higher oxidation state are more acidic than the oxides of the elements having lower oxidation states. The acidic character decreases as we move down the group. The M_2O_3 type oxides of nitrogen and phosphorus are acidic, oxides of arsenic and antimony are amphoteric and oxide of bismuth is basic. This shows the development in metallic property as we go down the group.

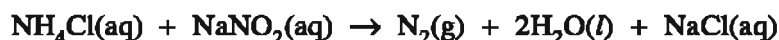
(iii) Reaction with halogen elements : The elements of group-15 react with halogens and form halide compounds of the type MX_3 and MX_5 . As there are no d-orbitals in valence shell of nitrogen atom, it is not able to form pentahalide. Pentahalides are more covalent than trihalides. All the trihalides except the nitrogen element are stable; while only one trihalide of nitrogen element- NF_3 is stable. Trihalide compounds except BiF_3 are covalent compounds.

(iv) Reaction with metal elements : All the elements of group-15 combine with metal elements and form binary compounds like Ca_3N_2 (Calcium nitride), Ca_3P_2 (Calcium phosphide), Na_3As (Sodium arsenide), Zn_3Sb_2 (Zinc antimonide) and Mg_3Bi_2 (Magnesium bismuthide). In these, the oxidation state of N, P, As, Sb and Bi is (-3).

5.3 Nitrogen

5.3.1 Preparation, Properties and Uses of Dinitrogen Gas :

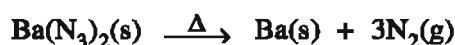
(1) Preparation of Dinitrogen : Commercially, dinitrogen is prepared by liquefaction and fractional distillation of air. As the boiling point of dinitrogen is 77.2 K, it is first obtained during distillation. While, the boiling point of dioxygen is 90 K and so remains in the vessel. In the laboratory, dinitrogen gas can be prepared by the reaction of aqueous ammonium chloride with aqueous sodium nitrite.



During this reaction, NO and HNO_3 are formed in smaller proportions. To remove them, the gas produced during the reaction is passed through the mixture of potassium dichromate and aqueous sulphuric acid. Dinitrogen gas can also be prepared by thermal decomposition of ammonium dichromate.



Very pure dinitrogen gas can be obtained by thermal decomposition of sodium or barium azide.

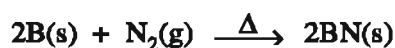
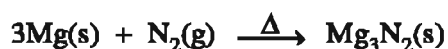
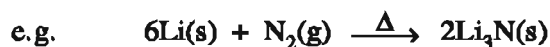


(2) Properties :

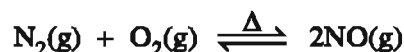
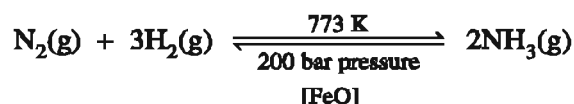
(i) Physical properties :

- Dinitrogen gas is colourless, odourless, tasteless and nonpoisonous.
- It possesses two stable isotopes ^{14}N and ^{15}N .
- It is sparingly soluble in water.
- It is inert at room temperature but its reactivity increases with the increase in temperature.

(ii) Chemical properties : At high temperature, it combines with certain metals and forms ionic nitrides while with non-metals it forms covalent nitrides.



It reacts with dihydrogen and dioxygen and forms ammonia gas and nitric oxide gas respectively.



(3) Uses :

- Dinitrogen gas is useful in industry in the manufacture of ammonia gas and other nitrogen containing compounds.
- In the metallurgical processes to maintain inert atmosphere, in electric bulbs and preparation of nitric acid.
- The reactivity of oxygen in the air is decreased because of the presence of dinitrogen gas and so it becomes useful in respiration. Liquid dinitrogen is used as coolant in preservation of biological substances and food materials.

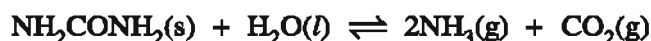
5.3.2 Distinction from other elements of group (Anomalous behaviour) :

- The diatomic molecule of nitrogen is in gaseous form as dinitrogen (N_2) while, other elements are in solid state in the form of M_4 molecule (except Bi).
- Nitrogen element does not possess allotropes but other elements possess allotropes.
- Nitrogen trioxide N_2O_3 and nitrogen pentoxide N_2O_5 are monomolecular (monomers); while the trioxides and pentoxides of other elements are bimolecular (dimers) e.g. P_4O_6 , As_4O_6 , P_4O_{10} and As_4O_{10}
- The trihydride of nitrogen element (NH_3) is non poisonous while trihydrides of other elements are poisonous, (e.g. Phosphine (PH_3), Arsine (AsH_3) etc).
- As nitrogen is non-metal, its oxide compounds possess acidic property.
- The halides of nitrogen except NF_3 are explosive, while the halides of other elements are stable.
- Because of the smaller size and higher electronegativity of nitrogen element, there is characteristic property of forming $p\pi-p\pi$ bond in it; while this property is not possessed by the other elements of the group. As a result, nitrogen element exists as dinitrogen gas having triple $\text{N}\equiv\text{N}$ bond; while other elements of the group possess P-P , As-As and Sb-Sb single bond. Bi forms metallic bond.
- There are no d-orbitals available in the orbits of nitrogen element, its maximum bonding capacity is 4. As a result it cannot form $d\pi-p\pi$ bond. The other elements of this group are able to form this type of bond. e.g. $\text{R}_3\text{P}=\text{O}$ or $\text{R}_3\text{P}=\text{CH}_2$ where R is the alkyl group. Phosphorus and arsenic elements form $d\pi-d\pi$ bonds with transition metal elements in which the compounds of phosphorus and arsenic like $\text{P}(\text{C}_2\text{H}_5)_3$ and $\text{As}(\text{C}_6\text{H}_5)_3$ act as ligands.

5.3.3 Compounds of Nitrogen Element :

(1) Ammonia (NH₃) :

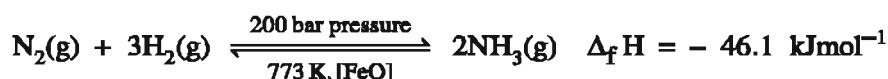
(i) **Preparation** : Ammonia gas is present in very less proportion in air. In addition ammonia gas is formed by the decay of nitrogen containing organic compounds like urea.



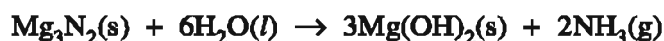
By reaction of ammonium salt with sodium hydroxide or calcium hydroxide, ammonia gas can be obtained.



Industrially ammonia gas is manufactured by Haber's process.



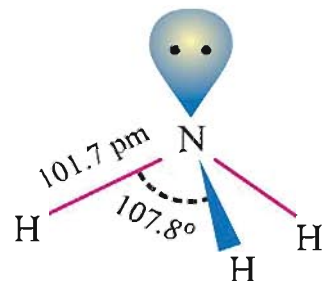
According to Le Chatelier's principle 773 K temperature, 200 bar pressure and FeO as catalyst are used alongwith K₂O and Al₂O₃ in less proportions as **promoters**. By hydrolysis of magnesium nitride, ammonia gas is obtained.



(ii) Properties :

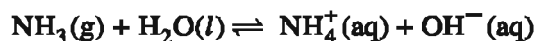
(A) Physical properties :

- Ammonia is a colourless gas with pungent smell.
- Its freezing point and boiling point are 198.4 K and 239.7 K respectively.
- Ammonia molecule possesses trigonal pyramidal structure in which three bonding and one nonbonding electron pairs are present.

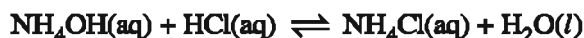


(B) Chemical properties :

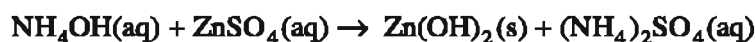
- Ammonia gas dissolves in water and forms ammonium hydroxide which acts as weak base.



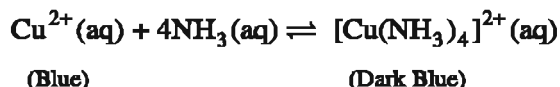
- Aqueous solution of ammonia gas reacts with acid and forms ammonium salt.



- Aqueous solution of ammonia gas forms hydroxides of metals by reaction with aqueous solutions of metal salts.



- As nitrogen atom in ammonia molecule has got non-bonding pair of electron, it acts as a Lewis base. It forms co-ordinate covalent bond with metal ion and forms complex ion.

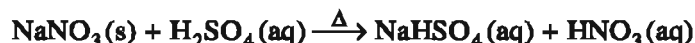


(iii) Uses :

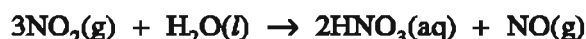
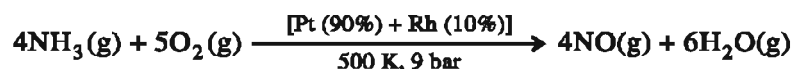
- Ammonia gas is used in the formation of nitrogenous fertilisers like ammonium nitrate, urea, ammonium phosphate and ammonium sulphate.
- It is also useful in preparation of certain important inorganic compounds like nitric acid.
- Liquid ammonia is used as refrigerant.

(2) Nitric acid (HNO_3) :

(i) Preparation : To prepare nitric acid in laboratory, sodium nitrate or potassium nitrate is heated with concentrated sulphuric acid in a glass retort.



Anhydrous nitric acid is obtained by distilling concentrated aqueous solution of nitric acid in presence of P_4O_{10} . Industrial production of nitric acid is carried out by catalytic oxidation of ammonia. This process is known as **Ostwald's method**, in which the following reactions are involved



The aqueous nitric acid obtained in this way is distilled and acid with 68.5 % by weight concentration can be obtained. To obtain nitric acid with 98 % concentration it is dehydrated with concentrated H_2SO_4 .

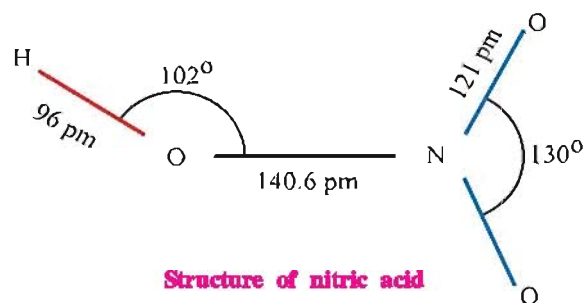
(ii) Properties :

(A) Physical properties :

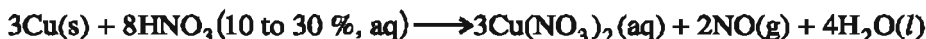
- Nitric acid is a colourless liquid.
- Its freezing point and boiling point are 231.4 K and 355.6 K respectively.
- Its density at 298 K temperature is 1.504 gram ml^{-1} .
- Nitric acid possesses planar structure in gaseous state.

(B) Chemical properties :

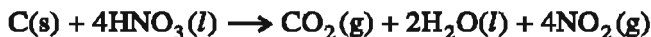
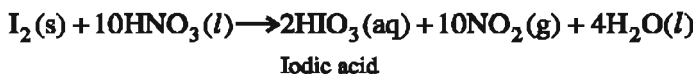
- Aqueous solution of nitric acid acts as a strong acid in which H_3O^+ and NO_3^- ions are present.



- Concentrated nitric acid is a strong oxidising agent. It reacts readily with metals except the noble metals like gold and platinum. Certain metals like Cr, Al do not dissolve in concentrated nitric acid because inert oxide layer is formed on these metals. Generally, nitrate salts are formed by reaction of metals with nitric acid. If dilute nitric acid is used in the reaction NO or N₂O are produced and if concentrated nitric acid is used NO₂ gas is produced.

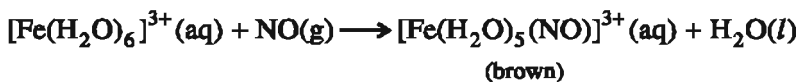
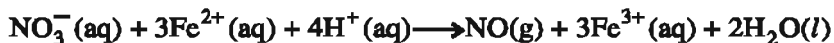


- The non-metals and their compounds are oxidised by concentrated HNO₃.



- Aqueous solution of nitric acid gives ring test. This ring test is given by NO₃⁻ ion in aqueous solution, So nitric acid also gives this test

Ring test : Freshly prepared solution of ferrous sulphate is added to aqueous solution containing NO₃⁻ ion. Then after, concentrated sulphuric acid is added slowly from the inner wall of the test tube. (if required solution is cooled). **Brown coloured ring is observed near the surface where concentrated sulphuric acid and mixed solution meet. This ring is due to formation of nitroso complex.** The ring test is carried out during inorganic qualitative analysis for detection of NO₃⁻ ion.



(iii) Uses :

- The main use of nitric acid is made in preparation of fertilisers like ammonium nitrate and explosive substances like trinitrotoluene and nitroglycerine.
- It is used as oxidising agent in rocket fuels.

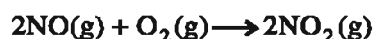
(3) Oxides of nitrogen :

Preparation, structure and properties of oxides of nitrogen : Nitrogen forms many oxide compounds in different oxidation states of nitrogen. Names of compounds of nitrogen oxides, molecular formula, oxidation states of nitrogen element, preparation and general properties are shown in Table 5.4.

Table 5.4 Oxides of Nitrogen

Name of oxide of Nitrogen	Molecular formula	Oxidation State of nitrogen element	Common methods of preparation	Physical appearance and chemical nature
Dinitrogen oxide [Nitrogen(I) oxide]	N ₂ O	+ 1	$\text{NH}_4\text{NO}_3 \xrightarrow{\Delta} \text{N}_2\text{O} + 2\text{H}_2\text{O}$	colourless gas neutral
Nitrogen monoxide [Nitrogen(II) oxide]	NO	+ 2	$2\text{NaNO}_2 + 2\text{FeSO}_4 + 3\text{H}_2\text{SO}_4 \rightarrow \text{Fe}_2(\text{SO}_4)_3 + \text{NaHSO}_4 + 2\text{H}_2\text{O} + 2\text{NO}$	colourless gas neutral
Dinitrogen trioxide [Nitrogen(III) oxide]	N ₂ O ₃	+ 3	$2\text{NO} + \text{N}_2\text{O}_4 \xrightarrow{250\text{ K}} 2\text{N}_2\text{O}_3$	blue solid, acidic
Nitrogen dioxide [Nitrogen(IV) oxide]	NO ₂	+ 4	$2\text{Pb}(\text{NO}_3)_2 \xrightarrow{673\text{ K}} 4\text{NO}_2 + 2\text{PbO}$	brown gas acidic
Dinitrogen tetroxide [Nitrogen(IV) oxide]	N ₂ O ₄	+ 4	$2\text{NO}_2 \xrightleftharpoons[\text{heat}]{\text{cool}} \text{N}_2\text{O}_4$	colourless solid/ liquid, acidic
Dinitrogen pentoxide [Nitrogen(V) oxide]	N ₂ O ₅	+ 5	$4\text{HNO}_3 + \text{P}_4\text{O}_{10} \rightarrow 4\text{HPO}_3 + 2\text{N}_2\text{O}_5$	colourless solid acidic

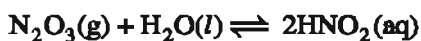
Nitric oxide (NO) partially polymerises in liquid state because of presence of one unpaired electron. It acts as dimeric molecule in solid state. Nitric oxide combines with oxygen and forms nitrogen dioxide.



Nitrogen dioxide in gaseous state forms compound having dimeric structure N₂O₄ by attaining equilibrium state as follows :



Oxides of nitrogen, react with water and forms oxoacid compounds of nitrogen.



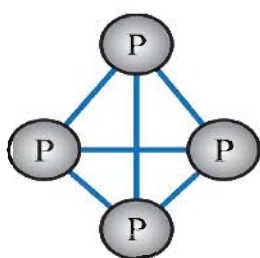
Because of this, N_2O_3 and N_2O_5 are called anhydrides of HNO_2 and HNO_3 respectively. The resonance structures of oxides of nitrogen and the information about their bonds are given in table 5.5

Table 5.5 Resonance Structures of Oxides of Nitrogen

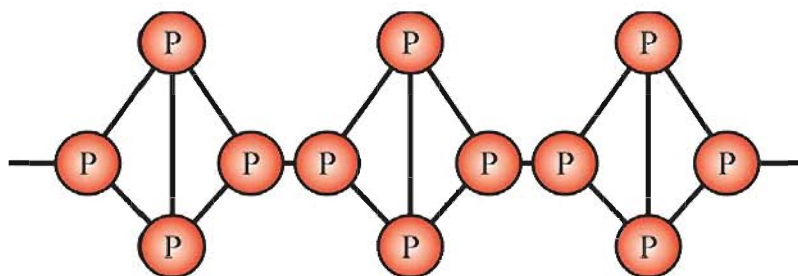
Molecular formula	Resonance structure	Details about bond
N_2O	$\text{N}=\text{N}=\ddot{\text{O}} \leftrightarrow \text{N}\equiv\text{N}-\ddot{\text{O}}:$	$\text{N}-\text{N}-\text{O}$ 113 pm 119 pm Linear
NO	$\text{:N}=\ddot{\text{O}}: \leftrightarrow \text{:N}=\ddot{\text{O}}:$	$\text{N}-\text{O}$ 115 pm
N_2O_3		 Planar
NO_2		 Angular
N_2O_4		 Planar
N_2O_5		 Planar

5.4 Phosphorus

5.4.1 Allotropes of Phosphorus : The known allotropes of phosphorus are white (yellow), red and black. The white phosphorus prepared by industrial synthesis, is poisonous and wax like white substance in which discrete tetrahedral P_4 molecules are present. Red phosphorus is nonpoisonous and it is in polymeric form. The allotropes of phosphorus are shown in figure 5.1



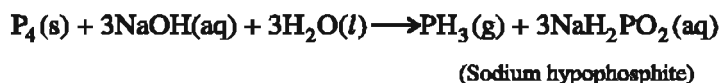
(a) White (yellow) phosphorus



(b) Red phosphorus

Fig. 5.1 Allotropes of Phosphorus

White phosphorous is insoluble in water but soluble in solvent like carbon disulphide (CS_2). It glows in the dark. In the inert atmosphere, phosphorous undergoes redox reaction with boiling NaOH solution and forms phosphine (PH_3).



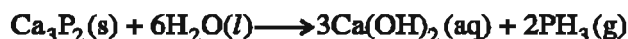
The melting point of white phosphorus is 317 K. It is highly reactive and burns when kept open in air. Hence, it is stored in water. If white phosphorus is heated at 573 K in absence of air, it is changed to stable red form. The melting point of red phosphorus is 873 K. It is less soluble in solvent like CS_2 in comparison to white phosphorus and is less reactive. Hence, it does not burn when it comes in contact with air. The more reactivity of white phosphorus is due to its abnormal structure. Because of this, strain is generated in P_4 molecule. Hence, the bond angle is 60° in geometrical structure of P_4 . Because of this, p-orbitals do not overlap head to head. As a result of this p-p bond is bent. Hence this bond is weak and reactive. As a result, white phosphorous burns as soon as it comes in contact with air.

Two forms of phosphorous found are α -black phosphorus and β -black phosphorus. α -black phosphorus is obtained by heating red phosphorus in closed tube at 803 K temperature. White phosphorus is heated under high pressure at 473 K to obtain β -black phosphorus.

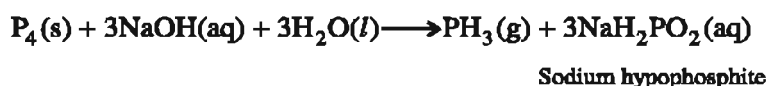
5.4.2 Compounds of Phosphorus :

(1) Phosphine (PH_3) :

(i) **Preparation** : Phosphine is obtained by reacting calcium phosphide with water or dilute hydrochloric acid.



In laboratory, phosphine is prepared by reacting white phosphorus with concentrated NaOH in inert atmosphere



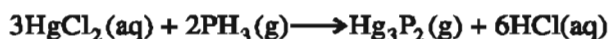
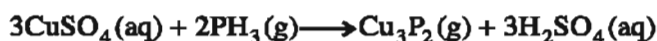
(ii) Properties :

(A) Physical properties :

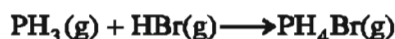
- Phosphine is a colourless gas having smell like rotten fish and is very poisonous gas.
- It is sparingly soluble in water.

(B) Chemical properties :

- Phosphine explodes when it comes in contact with oxidising agents like HNO_3 , Cl_2 and Br_2 .
- If phosphine is absorbed in aqueous solution of copper sulphate or mercuric chloride, corresponding phosphide is formed



- Phosphine is a weak base. It gives phosphonium bromide (PH_4Br) by reaction with HBr .

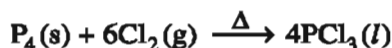


(iii) Uses :

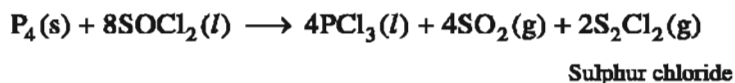
- Because of spontaneous combustion property of phosphine, it is used in Holme's signals. By making a hole in the vessel containing calcium carbide and calcium phosphide is thrown into the sea and so the gas produced burns which works as signal.
- It is used in preparation of smoke screen.

(2) Phosphorus trichloride (PCl_3) :

(i) Preparation : Phosphorus trichloride is obtained by passing dry chlorine gas on white phosphorus at high temperature.



Phosphorus trichloride is obtained by reaction of white phosphorus with thionyl chloride (SOCl_2).

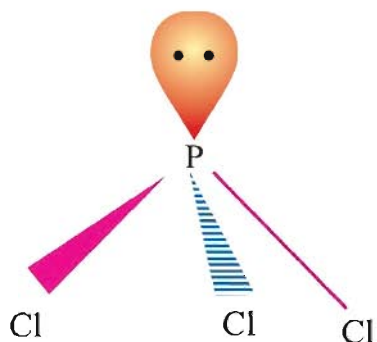


(ii) Properties :

(A) Physical properties :

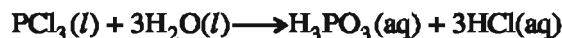
- Phosphorus trichloride is a colourless fuming liquid.
- Its boiling point is 349 K.
- It is soluble in solvents like benzene, chloroform, ether, carbon disulphide
- Its shape is pyramidal.

(B) Chemical Properties :



Phosphorus trichloride

- Phosphorus trichloride forms fumes when it comes in contact with air or water-because the P-Cl bond present in PCl_3 is decomposed and is converted into the resulting product phosphorus acid (H_3PO_3).

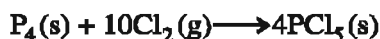


- It reacts with organic compounds having -OH group. viz. CH_3COOH , $\text{C}_2\text{H}_5\text{OH}$ as follows :

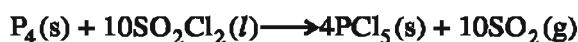


(3) Phosphorus pentachloride (PCl_5)

(i) **Preparation :** Phosphorus pentachloride is obtained by reaction of white phosphorus with excess amount of dry chlorine gas.



Phosphorus pentachloride is obtained by reaction of white phosphorus with sulphuryl chloride (SO_2Cl_2).

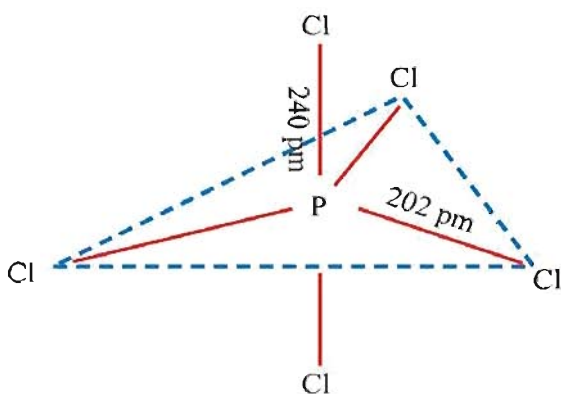


(ii) Properties :

(A) Physical properties :

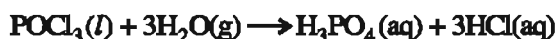
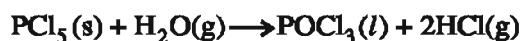
- Phosphorus pentachloride is yellowish white coloured solid substance.
- Its melting point is 440 K.
- PCl_5 possesses trigonal bipyramid shape in liquid and gaseous states.

(B) Chemical properties :



Structure of liquid or gaseous phosphorus pentachloride

- Phosphorus pentachloride is converted to phosphorus oxychloride by hydrolysis by moisture of air and finally phosphoric acid is formed.



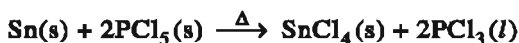
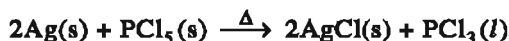
- Phosphorus pentachloride sublimes on heating but decomposes when heated more.



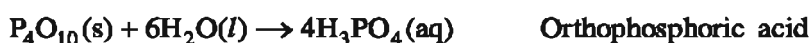
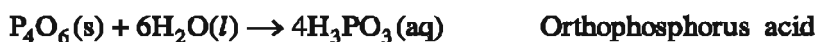
- It forms chloro compounds by reaction with organic compounds having -OH group.



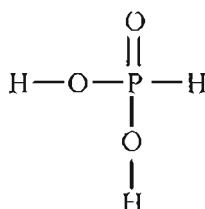
- On heating PCl_5 with metal piece, it forms corresponding metal chlorides.



(4) Oxoacids of phosphorus : Different oxoacids of phosphorus are obtained by reactions of phosphorus oxides with water.



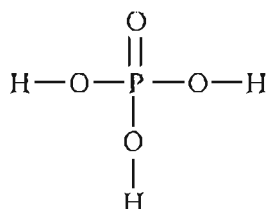
Orthophosphorus acid (H_3PO_3) is a weak diprotic acid because its only two hydrogen atoms are combined with oxygen atom. Hydrogen atom directly combined with phosphorus is not acidic because, the electronegativities of both P and H are same and so P–H bond is non polar. As all the three hydrogen atoms in orthophosphoric acid are combined with oxygen atom, it is a weak triprotic acid. In both these molecules, the other atoms around the phosphorus atom are arranged in tetrahedral shape. Also, the successive dissociation constants in both the molecules are decreasing by the approximate multiple of 10^5 .



Orthophosphoric acid (H_3PO_3)

$$\text{K}_{a1} = 1.0 \times 10^{-2}$$

$$\text{K}_{a2} = 2.6 \times 10^{-7}$$



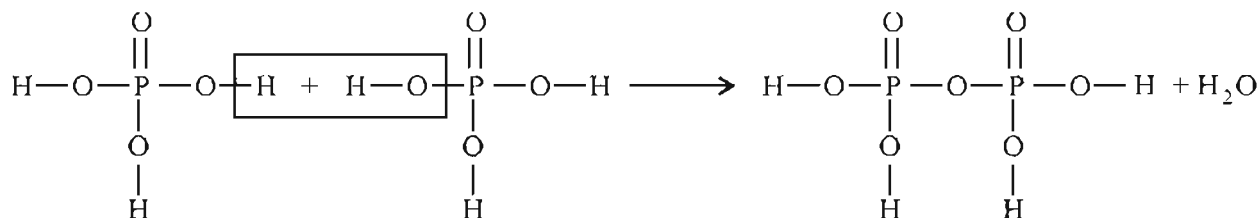
Orthophosphoric acid (H_3PO_4)

$$\text{K}_{a1} = 7.5 \times 10^{-3}$$

$$\text{K}_{a2} = 6.2 \times 10^{-8}$$

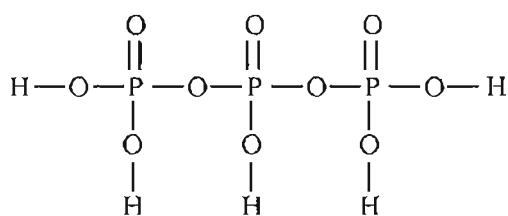
$$\text{K}_{a3} = 4.8 \times 10^{-13}$$

Diphosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$) is also called pyrophosphoric acid which is obtained by removal of one molecule of water when two molecules of H_3PO_4 combine.

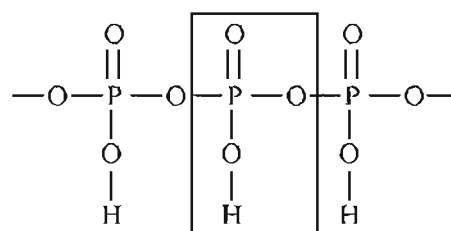


Pyrophosphoric acid

In trimetaphosphoric acid $\text{H}_3\text{P}_3\text{O}_{10}$ the HPO_3 unit is repeated three times. $(\text{HPO}_3)_n$ is known as polymetaphosphoric acid.

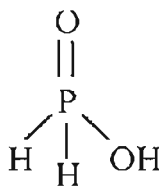


Trimetaphosphoric acid $\text{H}_5\text{P}_3\text{O}_{10}$



Polymetaphosphoric acid
(HPO_3 unit is repeated)

In all the acids, the oxidation number of phosphorus is +5. Hypophosphorus acid is also called phosphonic acid. Its formula is H_3PO_2 and the oxidation number of phosphorous is +1.



Structure of H_3PO_2

5.5 Elements of Group-16

Oxygen, sulphur, selenium, tellurium and polonium elements are included in group 16. These elements are known as **oxygen group** elements or as **chalcogens**. The important atomic and physical properties are shown in table 5.6

Table 5.6 Atomic and Physical Properties of Elements of Group-16

Properties	O	S	Se	Te	Po
Atomic number	8	16	34	52	84
Atomic mass (gm mol^{-1})	16.00	32.06	78.96	127.60	210.00
Electronic structure	$[\text{He}]2s^2 2p^4$	$[\text{Ne}]3s^2 3p^4$	$[\text{Ar}]3d^{10} 4s^2 4p^4$	$[\text{Kr}]4d^{10} 5s^2 5p^4$	$[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^4$
Ionisation Enthalpy ($\Delta_i H_1$) (kJ mol^{-1})	1314	1000	941	869	813
Electronegativity	3.50	2.44	2.48	2.01	1.76
Covalent radius (pm)	66	104	117	137	146
Ionic radius (pm)	140	184	198	221	230
Melting point (K)	55	393	490	725	520
Boiling point (K)	90	718	958	1260	1235
Density (gm cm^{-3}) (298 K)	1.32	2.06	4.19	6.25	—

5.5.1 Electronic configuration, occurrence, oxidation states :

Electronic configuration : The electronic configuration of valence shell of elements of group 16 is ns^2np^4 .

Occurrence : Oxygen element is the most abundant element available in highest proportion on the earth. Oxygen element possesses about 46.6% mass of earth's crust. In dry air oxygen is 20.9461% by volume. Sulphur present on the earth is about 0.03-0.1% by mass of earth's crust. It is available in combined forms i.e. sulphate compounds like gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), Epsom salt ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$), Baryte (BaSO_4) and sulphide compounds like galena (PbS), zinc blende (ZnS), copper pyrites (CuFeS_2). Sulphur is also present in organic compounds present in eggs, proteins, garlic, onion, hair and wool. Selenium and tellurium are available as selenide and telluride compounds. Polonium is obtained by decay of minerals of thorium and uranium.

Oxidation states : There are six electrons in valence shell of elements of group-16 i.e. two electrons are less for completion of octet. Hence, the oxidation state of such elements is -2 . The stability of -2 oxidation states of these elements decreases as we go down the group. Polonium does not show -2 oxidation state. The electronegativity of oxygen element is more and so it possesses -2 oxidation state but in OF_2 its oxidation state is $(+2)$. The other elements of this group show $+2$, $+4$, $+6$, oxidation states. Sulphur, selenium and tellurium generally show $+4$ oxidation states in compounds with oxygen and $+6$ oxidation state in compounds with fluorine. As we go down from above in the group, the stability of $+6$ oxidation state decreases and stability of $+4$ oxidation state increases. Oxidation states of elements of group 16 are shown in Table 5.7.

Table 5.7 Oxidation states of Elements

Elements	O	S	Se	Te	Po
Oxidation state	$-2, -1, +1, +2$	$-2, +2, +4, +6$	$-2, +2, +4, +6$	$-2, +2, +4, +6$	$+2, +4$

5.5.2 Periodicity in physical and chemical properties :

(1) Periodicity in physical properties : On the basis of table 5.6, it can be said that there is general tendency of increase in atomic size, decrease in ionisation enthalpy, decrease in electronegativity with the increase in atomic number of elements of group-16. Hence, the metallic property increases with increase in atomic number.

(i) Atomic and Ionic radii : The atomic and ionic radii increase with increase in number of orbits in the elements when we go down the group. As an exception, the atomic radius and ionic radius of oxygen element is comparatively less than other elements (Table 5.6).

(ii) Ionisation Enthalpy : The value of ionisation enthalpy decreases with increase in atomic number as we go down the group. The values of ionisation enthalpy of the elements of this group are comparatively less than those of the elements of corresponding period of group 15; because the elements of group 15 have half filled p-orbitals and so possess characteristic stability (Table 5.6).

(iii) Electronegativity : Amongst all the elements, after fluorine element, oxygen element has highest electronegativity. Generally, as we go down from above in the group as atomic number increases, atomic size increases and so electronegativity decreases (Table 5.6).

(2) Chemical properties :

(i) Reaction with hydrogen element : All the elements of group 16 form hydrides of the type H_2M (where $M = S, Se, Te, Po$). The acidic property of the hydride compounds increases on going from H_2O to H_2Te because as we go down from above in the group the value of dissociation enthalpy of $M-H$ bond decreases.

(ii) Reaction with oxygen element : All the elements of group 16 form oxides of two types $-MO_2$ and $-MO_3$ when react with oxygen element (where $M = S, Se, Te, Po$). Ozone (O_3) and sulphur dioxide (SO_2) are in gaseous form and selenium oxide (SeO_2) is in solid form. The property as reducing agents of these dioxide compounds, decreases as we go from SO_2 to TeO_2 . SO_2 is a reducing agent, while TeO_2 is an oxidising agent. All these oxides possess acidic nature.

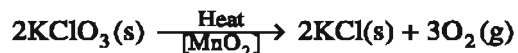
(iii) Reaction with halogen elements : Elements of group 16 react with halogens and form MX_6 , MX_4 and MX_2 type halide compounds, (where $M =$ elements of group 16 and $X =$ halogen element). The order of stability of halide compounds is $F^- > Cl^- > Br^- > I^-$. Amongst the hexahalide compounds, only hexafluoride compounds are found to be stable.

5.6 Oxygen

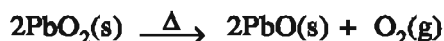
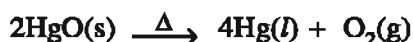
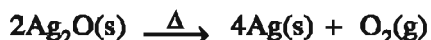
5.6.1 Preparation, Properties and uses of dioxygen gas :

(1) Preparation of Dioxygen gas : In laboratory, dioxygen (O_2) gas is prepared by following methods.

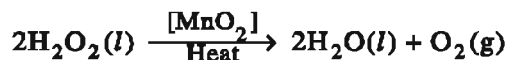
(i) By thermal decomposition of oxygen containing elements like $KClO_3$ and $KMnO_4$ or by electrolysis of acidic water.



(ii) Dioxygen gas is obtained by thermal decomposition of oxides of certain metals.



(iii) Dioxygen gas is obtained by decomposition of H_2O_2 in presence of manganese dioxide.



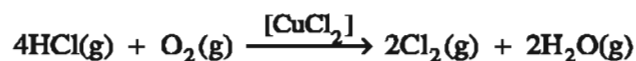
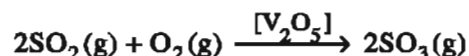
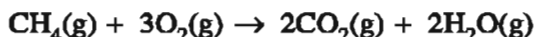
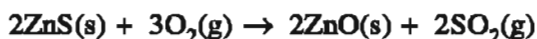
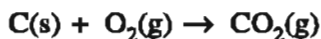
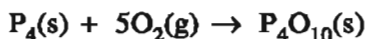
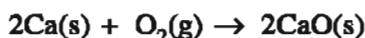
For industrial production of dioxygen gas, first carbon dioxide and water vapour are removed from air. By liquefaction and fractional distillation of remaining air mixture dinitrogen and dioxygen gases are obtained.

(2) Properties :

(i) Physical Properties :

- Dioxygen is a colourless and odourless gas.
- It possesses three stable isotopes ^{16}O , ^{17}O and ^{18}O .
- It is paramagnetic.
- About 3.08 cm^3 of dioxygen gas dissolves in 100 cm^3 of water at 293 K temperature, which is sufficient to sustain life of marine and aquatic living beings.
- It is converted in liquid form at 90 K temperature and in solid form by cooling at 55 K temperature.

(ii) Chemical properties : Dioxygen gas reacts with most of metal elements except inert (e.g. Au, Pt) and noble gas elements. The reactions of dioxygen gas with certain metal elements, non-metal elements and other compounds are shown as below :



(3) Uses :

- Dioxygen gas is useful in respiration reaction and combustion reaction.
- Dioxygen gas is useful in preparation of steel.
- Dioxygen gas is used in oxyacetylene flame. As very high temperature is obtained by this flame, it is used in welding work of metals.
- The cylinders of dioxygen gas are useful for treatment of patients in the hospital, mountaineers and divers going deep in the water as well as respiration process.

5.6.2 Distinction from other elements of group (anomalous behaviour) :

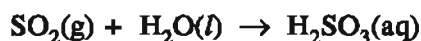
- Oxygen is in gaseous form at room temperature while other elements of the group are in solid form.
- Oxygen exists as diatomic molecule (O_2) while other elements exist as polyatomic molecule.
- Oxygen is a non-metal. With the increase in atomic number the metallic property of elements increases.

- (iv) d-orbitals are not available in valence shells of oxygen atom. Hence, it possesses lower oxidation states (-2, -1, 1, 2). While in other elements, as d-orbitals are available, the expansion of valence orbit in elements is possible. Here, these elements possess higher oxidation states (-2, 2, 4, 6). (See table 5.7)
- (v) Oxygen because of its smaller size and higher electronegativity, forms hydrogen bond with hydrogen atom in water. Hence, strong hydrogen bond is observed in water and not observed in H₂S.

5.6.3 Compounds of Oxygen :

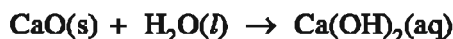
(1) Simple Oxides : Oxygen combines with other elements and forms binary compounds called oxides. As noted earlier, oxygen element combines with most of the elements of periodic table. Certain elements combine with oxygen and form more than one compounds. Oxygen element is able to form both the types ionic and covalent type compounds. Simple oxide compounds are classified as acidic, basic and amphoteric on the basis of their properties.

The oxides which give acid by reaction with water are called acidic oxides e.g. SO₂, Cl₂O₇, CO₂, N₂O₅ etc.

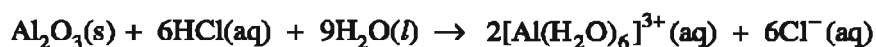


Generally oxides of non metals are acidic.

The oxide compounds which give base by reaction with water are called basic oxides. e.g. Na₂O, CaO, BaO :



Generally oxides of metal are basic. Some oxides possess both the acidic and basic nature. These oxides are called amphoteric oxides. They react with both acid and base. Some oxides are such which possess neither of the acidic nor basic nature. These oxides are called neutral oxides. e.g. CO, NO and N₂O. Al₂O₃ reacts both with acid and base as shown below and so it is amphoteric oxide.



(2) Ozone : Ozone is the allotrope of oxygen. Ozone is formed from oxygen in atmosphere in presence of sunlight at the height of 20 kilometer above sea level. This layer of ozone gas protects the earth from harmful effect of ultraviolet rays.

(i) Preparation : Ozone gas can be prepared in laboratory by the use of ozonizer of Siemens or Brodie. Ozone is obtained by passing cold and dry oxygen in presence of silent electric charge in Siemen's ozonizer.

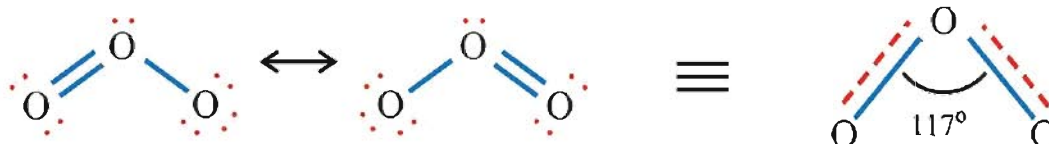


In industrial production the ozonizer of Siemens and Halteske is used in which 8000 to 10000 volt electromotive force is used between rods of aluminium. In electrolysis method, 5% ozone can be obtained at the anode by electrolysing acidic water using platinum electrodes.

(ii) Properties :

(A) Physical properties :

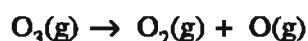
- Ozone possesses light blue colour in gaseous form, dark blue colour in liquid form and dark violet colour in solid form.
- Ozone possesses characteristic odour.
- Less proportion of ozone is not harmful but if its proportion, exceeds 100 ppm, then difficulty in respiration develops. As a result of this there is experience of headache and suffocation.
- The resonance structure of ozone are as shown below :



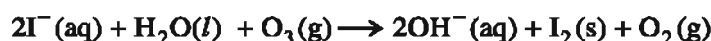
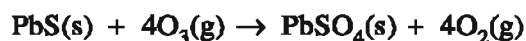
Resonance structures of ozone molecule

(B) Chemical Properties :

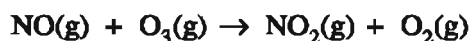
- Nascent oxygen [O] is released from decomposition of ozone. Hence, it is a strong oxidising agent.



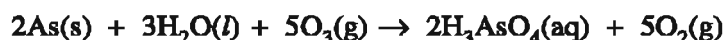
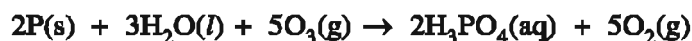
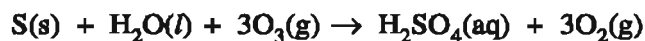
Hence, ozone gas oxidises lead sulphide to lead sulphate and iodide ion to iodine.



- Nitric oxide coming out from the exhaust of supersonic jet planes, react with ozone and form nitrogen dioxide gas.



- In the same way, it forms oxo- acids by reaction with moisture containing sulphur, phosphorus and arsenic.



(iii) Uses :

- Ozone is used to sterilise drinking water.
- It is useful as bleaching agent for bleaching of different oils, flour and starch.
- It is useful as oxidising agent in production of potassium permanganate.

5.7 Sulphur

5.7.1 Allotropes of Sulphur :

Amongst the different allotropes of sulphur, yellow rhombic sulphur (α -sulphur) and monoclinic sulphur (β -sulphur) are very important. The stable form of sulphur at room temperature is rhombic sulphur. When it is heated at 369 K temperature it is converted into monoclinic sulphur.

Rhombic sulphur (α -sulphur) : Rhombic sulphur is of yellow colour. Its melting point is 385.8 K. On evaporation of solution of sulphur prepared in CS_2 , rhombic sulphur is obtained. It is insoluble in water but soluble in organic solvents like benzene, alcohol.

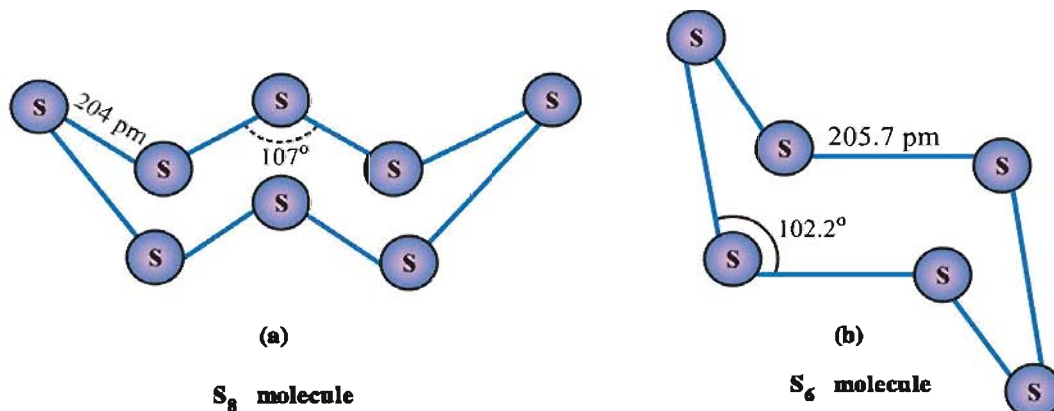


Fig. 5.2 Molecular structure of sulphur

Monoclinic sulphur (β -sulphur) : Monoclinic sulphur is soluble in CS_2 . Its melting point is 393 K. When rhombic sulphur is melted in a dish and then cooled, monoclinic sulphur is obtained. Monoclinic sulphur is stable at temperature higher than 369 K and it is changed to rhombic sulphur at lower temperatures. As contrast to this, rhombic sulphur is stable at temperature lower than 369 K but is changed to monoclinic sulphur at higher temperature. At 369 K temperature, both the allotropes are stable. This temperature is called the **transition temperature**. Both these possess S_8 molecule. In both these forms S_8 molecule is in the form of a crown which is shown in fig 5.2 (a). In the last two decades, it has been possible to prepare sulphur molecules containing 6 to 20 atoms, as a result of research. The cyclic structure of S_6 molecule is of chair form which is shown in fig 5.2 (b).

5.7.2 Compounds of Sulphur :

(1) Sulphur dioxide (SO_2) :

(i) Preparation : When sulphur is combusted in air or oxygen gas, sulphur dioxide (with about 6 to 8% sulphur trioxide) is obtained.



In laboratory, sulphur dioxide gas is obtained by reaction of hydrochloric acid with sodium sulphite.



In industries, sulphur dioxide is obtained as a bye product during roasting of sulphide mineral.

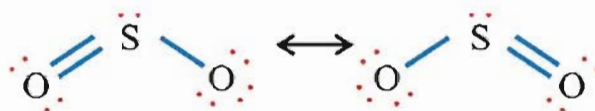


Sulphur dioxide gas obtained this way is dried and stored in liquid state under pressure in steel cylinder.

(ii) Properties :

(A) Physical Properties :

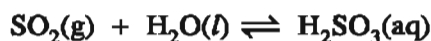
- Sulphur dioxide is a colourless gas having intense smell and possessing burning effect.
- It is soluble in water in very high proportions.
- Its boiling point is 263 K. It gets liquefied at room temperature at 2 bar pressure.
- Sulphur dioxide molecule is angular. Its resonance structures are as follows :



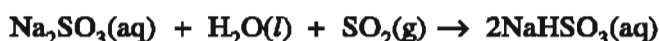
Resonance structures of SO_2 molecule

(B) Chemical properties :

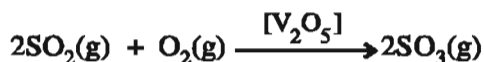
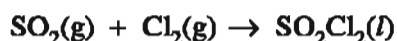
- Solution of sulphurous acid is obtained when sulphur dioxide is passed through water.



- It forms sodium sulphite in first step by reaction with NaOH which reacts with more proportion of sulphur dioxide and form sodium hydrogen sulphite.



- Sulphur dioxide reacts with chlorine gas in presence of catalyst and forms sulphuryl chloride (SO_2Cl_2). Sulphur trioxide is formed by oxidation in presence of vanadium pentoxide catalyst.



It makes coloured acidic solution of KMnO_4 colourless. Thus it acts as a reducing agent.



(iii) Uses :

- It is useful in purification of petroleum and sugar.
- It is also used to bleach wool and silk.
- To dissolve certain organic and inorganic substances liquid sulphur dioxide is used as solvent.
- Sulphur dioxide is useful in industrial production of sulphuric acid, sodium hydrogen sulphite, and calcium hydrogen sulphite.

(2) Sulphuric acid (H_2SO_4) :

(i) **Industrial manufacture** : Mainly the following steps are included in the manufacture of sulphuric acid by contact process.

- (1) To obtain sulphur dioxide gas by combusting sulphur or sulphide mineral in air.
- (2) To convert sulphur dioxide to sulphur trioxide with the help of oxygen in presence of vanadium pentoxide catalyst.
- (3) Sulphur trioxide obtained this way is absorbed in concentrated sulphuric acid and so fuming sulphuric acid or oleum ($\text{H}_2\text{S}_2\text{O}_7$) is obtained.

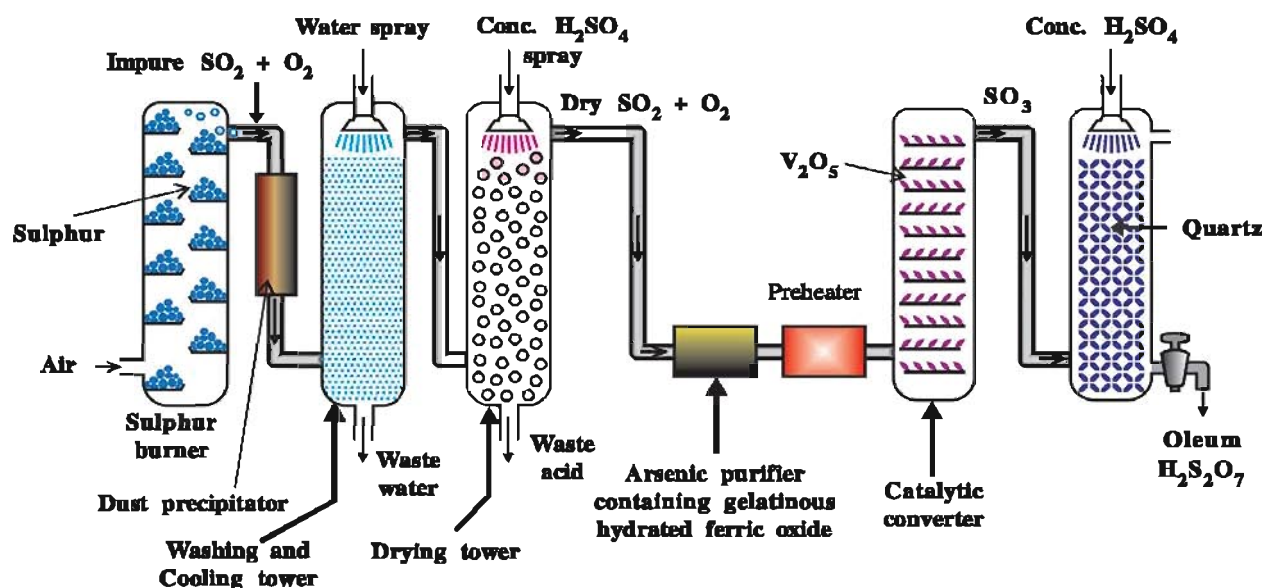
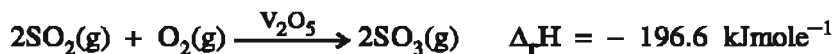
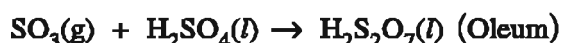


Fig 5.3 Industrial manufacture of sulphuric acid by contact process

First of all, arsenic compounds and other impurities are removed from sulphur dioxide gas and purification is carried out. The important step in production of H_2SO_4 by contact process is to prepare sulphur trioxide gas by catalytic oxidation in presence of vanadium pentoxide catalyst.



This reaction is exothermic. The volume of the system decreases during forward reaction. Hence, to obtain more product, according to Le Chatelier's principle, lower temperature and higher pressure are required. But by decreasing the temperature very low, the rate of oxidation reaction decreases. In practice, this reaction is carried out at 2 bar pressure and 720 K temperature. Sulphur trioxide gas obtained in this way is absorbed in concentrated sulphuric acid. As a result fuming sulphuric acid or oleum ($\text{H}_2\text{S}_2\text{O}_7$) is obtained. Sulphuric acid of required concentration can be obtained by its dilution with water.



96 to 98% pure H_2SO_4 can be obtained by contact process.

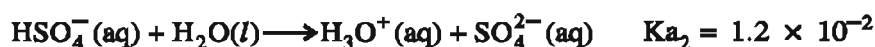
(ii) Properties :

(A) Physical properties :

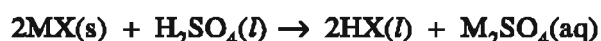
- Sulphuric acid is colourless, dense oily liquid.
- Its specific gravity at 298 K temperature is 1.84.
- Its freezing point is 283 K and boiling point is 611 K.
- It evolves heat when dissolved in water. Hence it is necessary to take utmost care when solution of sulphuric acid is prepared. For this, concentrated sulphuric acid is slowly added into water with constant stirring or ice is kept around the vessel.

(B) Chemical properties :

- The ionisation of sulphuric acid in aqueous solution takes place in two steps.

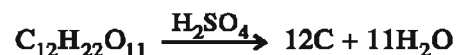


- The higher value of K_{a1} , indicates that H^+ and HSO_4^- ions are obtained by its ionisation in more proportion. The higher value of K_{a1} indicates the more strength of acid.
- Sulphuric acid forms two types of salts-common sulphate (e.g. Na_2SO_4 , CuSO_4) and acid sulphate or bisulphate or sodium hydrogen sulphate (NaHSO_4) by reaction with NaOH .
- It is used in preparation of other acids due to low volatility.



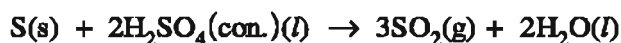
(where M = metal ion, X = F^- , Cl^- , NO_3^-)

- Concentrated sulphuric acid is a strong dehydrating substance. Gases containing moisture when passed through concentrated H_2SO_4 they become dry. (These gases must not be reacting with H_2SO_4). It removes water from organic compounds.



By this charring reaction sugar becomes black.

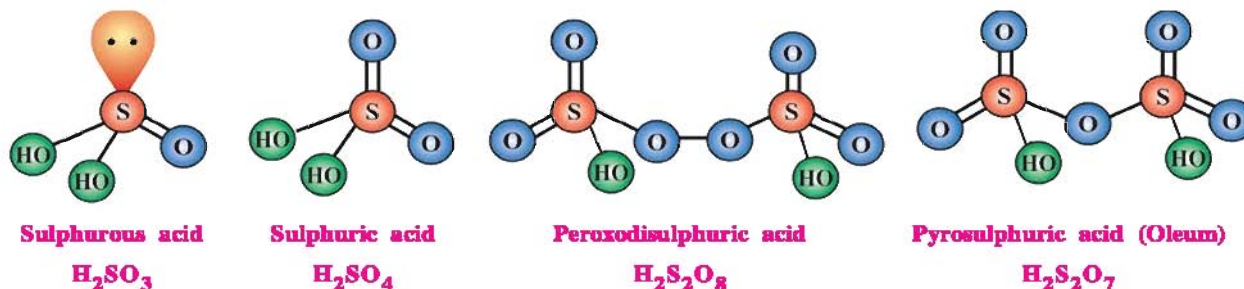
Hot concentrated sulphuric acid acts as oxidising agent. Metals and non-metals are oxidised by concentrated H_2SO_4 and sulphuric acid is reduced and converted to SO_2 .



(ii) Uses :

- Sulphuric acid is an important industrial chemical.
- As sulphuric acid is very useful in preparation of most of the chemical substances like fertilizers, dyes, synthetic fibres, soap and detergent, it is called '**King of Chemicals.**'
- It is used as reagent in laboratory.

(3) Oxoacids of sulphuric acid : Sulphur forms different types of oxoacid compounds - like H_2SO_3 , $\text{H}_2\text{S}_2\text{O}_3$, $\text{H}_2\text{S}_2\text{O}_4$, $\text{H}_2\text{S}_2\text{O}_5$, $\text{H}_2\text{S}_x\text{O}_6$ ($x = 2$ to 5), H_2SO_4 , $\text{H}_2\text{S}_2\text{O}_7$, H_2SO_5 , $\text{H}_2\text{S}_2\text{O}_8$. Here, we shall study only structures of some oxoacids. They are shown below.



5.8 Elements of group 17

Flourine, chlorine, bromine, iodine and astatine are the elements of group-17. These elements are collectively known as halogen elements. They are reactive non-metallic elements. As a whole more similarity is observed in the properties of the elements of this group. Astatine is a radioactive element. Important atomic and physical properties of the elements of this group are shown in table 5.8.

Table 5.8 Atomic and Physical Properties of Elements of group-17

Property	F	Cl	Br	I	At
Atomic number	9	17	35	53	85
Atomic mass (g mol^{-1})	19.00	35.45	79.90	126.90	210
Electronic configuration	$[\text{He}]2s^2 2p^5$	$[\text{Ne}]3s^2 3p^5$	$[\text{Ar}]3d^{10} 4s^2 4p^5$	$[\text{Kr}]4d^{10} 5s^2 5p^5$	$[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^5$
Ionisation enthalpy ($\Delta_i H_1$) (kJ mol^{-1})	1680	1256	1142	1008	—
Electron gain enthalpy (kJ mol^{-1})	−328	−349	−325	−295	—
Electronegativity	4.0	3.2	3.0	2.7	2.2
Covalent radius (pm)	64	99	114	133	—
Ionic radius (pm)	133	184	196	220	—
	F_2	Cl_2	Br_2	I_2	—
Melting point (K)	54.4	172.0	265.8	386.6	—
Boiling point (K)	84.9	239.0	332.5	458.2	—
Density (g cm^{-3}) (298 K)	1.5	1.66	3.19	4.94	—

5.8.1 Electronic configuration, occurrence, oxidation states :

Electronic configuration : The electronic configuration of valence shell of elements of group-17 is ns^2np^5 . They have one electron less for obtaining electronic configuration like their neighbouring inert elements.

Occurrence : The chief minerals of elements of group-17 are shown in table 5.9.

Table 5.9 Chief Minerals of Elements of Group-17

Elements	Structures and names of Chief Minerals
Fluorine	CaF_2 —fluorspar, Na_3AlF_6 —Cryollite, $\text{Ca}_5(\text{PO}_4)_3\text{F}$ —Fluor apatite
Chlorine	NaCl —Sodium chloride, KCl —Potassium chloride, (in form of soluble salt)
Bromine	NaBr —Sodium bromide, KBr —Potassium bromide, MgBr_2 —Magnesium bromide (in form of soluble salt)
Iodine	NaIO_3 —Sodium iodate.

Oxidation state : Amongst the elements of this group fluorine is the most electronegative element. As a result, its oxidation state is (-1) in all its compounds even then, going down from above in the group the tendency to attain positive oxidation state increases. e.g. Oxoacids of chlorine. Sometimes, the oxidation states of chlorine, bromine and iodine in their compounds are found to be $-1, +1, +3, +5, +7$.

5.8.2 Periodicity in Physical and Chemical Properties :

(1) Periodicity in physical properties : It can be said on the basis of table 5.8, that there is general tendency of increase in atomic size, decrease in ionisation enthalpy and decrease in electronegativity with increase in atomic number of elements of this group.

(i) Atomic and Ionic Radii : The atomic radii of elements of halogen group are the least in comparison to other elements in the corresponding period; because halogen elements possess maximum effective nuclear charge. e.g. fluorine element of group 17 in second period possesses least atomic radius in comparison to all the elements. As we go down from above i.e. going from fluorine element to iodine element, atomic and ionic radii increase because of increase in principal quantum number in going from fluorine to iodine.

(ii) Ionisation Enthalpy : The values of ionisation enthalpy decrease with increase in atomic size while going down from above in the group.

(iii) Electron Gain Enthalpy : The value of electron gain enthalpy of halogen elements of the period is highest negative. The reason for this is that there is one electron less than the stable electronic configuration of elements of neighbouring noble elements. The value of electron gain enthalpy goes on being less negative as we go down from above in the elements of group 17; But table 5.8 shows that the value of electron gain enthalpy of Cl atom is more negative than the value of gain enthalpy of F-element. The reason for this is that new added electron takes place in 2p-orbital of F-element and in 3p-orbital of Cl element. You have studied in unit 3, std-11 (semester-I) that there is more electron repulsion in 2p-orbital than that in 3p-orbital and so electron enters into 3p-orbital very easily.

(iv) Electronegativity : The electronegativity of halogen elements is more. The electronegativity decreases as we move down from above in group 17. The electronegativity of fluorine element is maximum amongst all the elements in the periodic table.

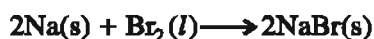
(2) Periodicity in chemical properties :

(i) Reaction with hydrogen element : All the halogen elements react with hydrogen element, and form hydrogen halide compounds; but the tendency of reaction with hydrogen decreases as we move from fluorine to iodine element. These compounds dissolve in water and form hydrohalic acids. The order of acidic strength of these acid compounds is $\text{HF} < \text{HCl} < \text{HBr} < \text{HI}$. The stability of these halide compounds decreases with decrease in value of dissociation enthalpy of H-X bond. The order of stability of compounds is $\text{HF} > \text{HCl} > \text{HBr} > \text{HI}$.

(ii) Reaction with oxygen element : Halogen elements react with oxygen element and form many oxides, and most of them are unstable. e.g. fluorine element forms two oxides OF_2 and O_2F_2 . Amongst the two, OF_2 compound is thermally stable at 298 K temperature. In oxides that are formed by elements chlorine, bromine and iodine, the oxidation state of halogen elements is +1 to +7. The order of stability of oxides is $\text{I} > \text{Cl} > \text{Br}$.

(iii) Reaction with halogen elements : Halogen elements react with other elements of their group and form compounds called interhalogen compounds e.g. XX' , XX'_3 , XX'_5 and XX'_7 compounds, where X = higher volume halogen element and X' = halogen element of small size.

(iv) Reaction with metal elements : Halogen elements react with metal elements and form corresponding metal-halide compounds. e.g. Bromine element reacts with sodium metal and forms sodium bromide.



The order of ionic character in metal halides is $\text{MF} > \text{MCl} > \text{MBr} > \text{MI}$.

5.8.3 Distinction of fluorine element from other elements of group (Anomalous behaviour) :

(i) Fluorine element has small size, more electronegativity, less value of dissociation enthalpy of F-F bond, so it shows anomalous behaviour from other elements. Ionisation enthalpy and electronegativity of element is more than the expectation, while value of atomic and ionic radii, melting point, boiling point and electron gain enthalpy are less in comparison to expected values of other elements of this group.

(ii) Fluorine forms only one stable oxoacid: while other halogen elements form many oxoacids.

(iii) Because of the presence of strong hydrogen bond, hydrogen fluoride is in liquid state while other hydrogen halides are in gaseous state.

5.9 Chlorine

5.9.1 Preparation, Properties and Uses of Dichlorine Gas :

(1) Preparation : Dichlorine gas can be prepared by any of the following reactions :

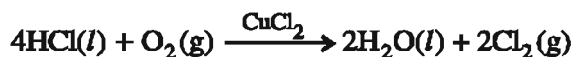
(i) By reaction of manganese dioxide with concentrated HCl, dichlorine gas is formed.



(ii) Chlorine gas is obtained by reaction of potassium permanganate with hydrochloric acid.



(iii) Deacon's process : Chlorine gas can be obtained by oxidation of hydrogen chloride with oxygen of the air in presence of catalyst $[\text{CuCl}_2]$.



(iv) Electrolysis method : Chlorine gas can be obtained by electrolysis of brine (saturated solution of NaCl), chlorine gas is deposited at the anode. Chlorine gas is obtained as a by-product in certain industries.

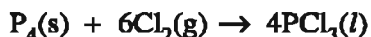
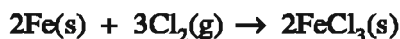
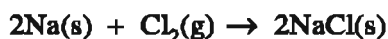
Chlorine gas can be prepared in laboratory by reactions (i) and (ii) and chlorine gas can be produced in industry by reactions (iii) and (iv).

(2) Properties :

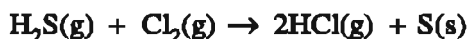
(i) Physical properties :

- Chlorine is a suffocating and intense smelling gas.
- It is 2 to 5 times heavier than air.
- It can be converted to greenish yellowish coloured liquid.

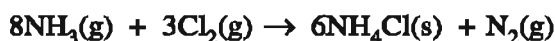
(ii) Chemical properties : Chlorine gas is a strong oxidising agent and so reacts with metals and non-metals and forms corresponding chloride compounds.



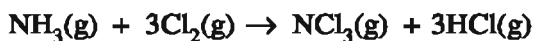
- As it has very strong attraction towards hydrogen, it forms HCl by combination with dihydrogen gas or compounds containing hydrogen.



- In the reaction of chlorine gas with excess amount of ammonia, ammonium chloride and dinitrogen gas are formed. If proportion of dichlorine gas is more in this reaction, nitrogen trichloride (explosive substance) is obtained.



(excess)



(excess)

- It gives mixture of chloride and hypochlorite by reaction with cold and dilute alkali, while it gives chloride and chlorate by reaction with hot and concentrated alkali.



(Cold and diluted))



(Hot and concentrated)

- It forms bleaching powder by reaction with slaked lime.



The composition of bleaching powder is $\text{Ca}(\text{OCl})_2 \cdot \text{CaCl}_2 \cdot \text{Ca}(\text{OH})_2 \cdot 2\text{H}_2\text{O}$.

- Dichlorine gas reacts with saturated hydrocarbons in presence of sunlight and gives substituted product but reacts with unsaturated hydrocarbons giving addition product.

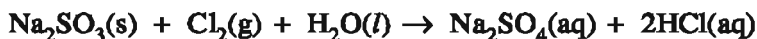


Methane Dichlorine gas Chloromethane



Ethene Dichlorine gas 1,2-Dichloroethane

- If chlorine water is kept for a long time, it loses its yellow colour because of formation of HCl and HOCl. The hypochlorous acid (HOCl) formed this way gives nascent oxygen which is responsible for its oxidation and bleaching property.

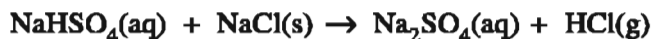
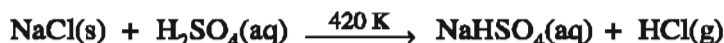


(3) Uses :

- Dichlorine gas is used for bleaching the wood pulp used in preparation of paper and jute.
- Chlorine gas is useful in extraction of gold and platinum, and preparation of medicines, dyes and organic compounds.
- It is used in preparation of poisonous gases like phosgene (COCl_2), tear gas (CCl_3NO_2) and mustard gas [$\text{ClCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$].

5.9.2 Preparation of Hydrogen Chloride Gas, Properties and Uses :

(1) Preparation : Hydrogen chloride can be prepared in the laboratory by reaction between sodium chloride and concentrated sulphuric acid.



By passing this HCl gas from concentrated sulphuric acid, it becomes dry.

(2) Properties :

(i) Physical properties :

- It is colourless gas with pungent smell.
- It is converted into colourless liquid (b.p.189 K) and in white crystalline solid substance (f.p. 159 K).
- It is highly soluble in water.

(ii) Chemical properties :

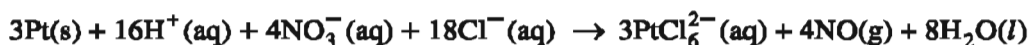
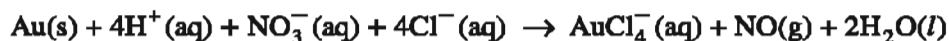
- The aqueous solution of hydrogen chloride is called hydrochloric acid.
- As hydrogen chloride is completely ionised in water, it acts as a strong acid.



- Hydrochloric acid gives white fumes of NH_4Cl by reaction with ammonia gas.



- For dissolving noble metals like gold, platinum etc. mixture of three parts of HCl and one part of HNO_3 (which is called aquaregia) is used.



- It decomposes salts of weak acid.



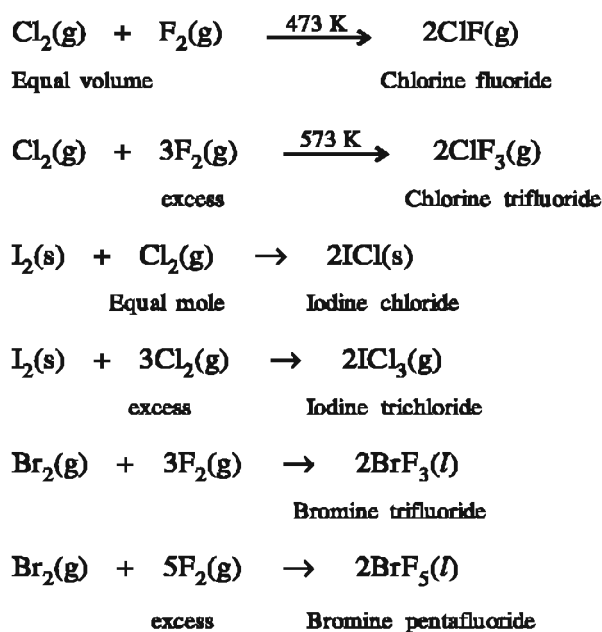
(iii) Uses :

- Hydrogen chloride gas; is useful in the production of glucose and ammonium chloride.
- It is useful as a reagent in laboratory.

5.10 Preparation, Properties and Uses of Interhalogen Compounds

When two different halogen elements react with each other and form the compounds, they are called **interhalogen compounds** e.g. XX' , XX'_3 , XX'_5 and XX'_7 compounds, where X = halogen elements with bigger size, X' = halogen elements with smaller size.

(1) Preparation : Interhalogen compounds are obtained by direct reaction of halogen elements with each other.



(2) Properties : Some properties of Interhalogen compounds are given in table 5.10.

Table 5.10 Some Properties of Interhalogen Compounds

Type	Formula	Physical state and colour	Structure (shape)
XX'	ClF	colourless gas	—
	BrF	pale brown gas	—
	IF	detected spectroscopically	—
	BrCl	gas	—
	ICl	ruby red solid (α -form)	—
		brown red solid (β -form)	—
	IBr	black solid	—

XX'_3	ClF_3	colourless gas	Bent T-shaped
	BrF_3	yellow green liquid	Bent T-shaped
	IF_3	yellow powder	Bent T-shaped
	ICl_3	orange solid	Bent T-shaped
XX'_5	IF_5	colourless gas but solid below 77 K	Square pyramidal
	BrF_5	colourless liquid	Square pyramidal
	ClF_5	colourless liquid	Square pyramidal
XX'_7	IF_7	colourless gas	Pentagonal bipyramidal

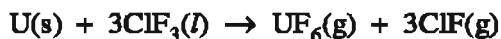
(i) Physical properties : Most of the interhalogen compounds are in volatile solid or liquid form. Some compounds are in gaseous form. (Table 5.10).

(ii) Chemical properties : Generally interhalogen compounds are more reactive than their corresponding halogen elements (Except fluorine) because the $X-X'$ bond in interhalogen compounds is relatively weak in comparison to $X-X$ bond. By hydrolysis of interhalogen compounds halide ion is formed from smaller size from them and hypohalite (for XX'), halite (for XX'_3), halate (for XX'_5) and perhalate (for XX'_7) ions are formed from bigger size halogen.



(3) Uses :

- Interhalogen compounds are used as non-aqueous solvent.
- They are very good fluorinating reagents.
- ClF_3 and BrF_3 are used to obtain U^{235} for concentration of UF_6 .



5.11 Oxoacid Compounds of Halogen Elements

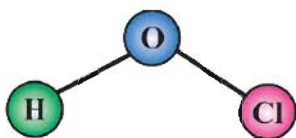
Fluorine forms only one oxoacid because of smaller size and more electronegativity of fluorine element. HOF is called fluoric (I) acid or hypofluorous acid. Other halogen elements form oxoacid compounds in more number. Most of the compounds cannot be separated in pure form. They are stable as aqueous solutions or in the form of salts. The oxoacid compounds of halogen elements are shown in table 5.11.

Table 5.11 Oxoacid Compounds of halogens

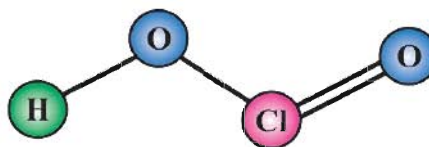
Halic (I) acid (Hypohalous acid)	HOF (Hypoflourous acid)	HOCl (Hypochlorous acid)	HOBr (Hypobromous acid)	HOI (Hypoiodous acid)
Halic (II) acid (Halous acid)	–	HOClO (Chlorous acid)	–	–
Halic (V) acid (Halic acid)	–	HOClO ₂ (Chloric acid)	HOBrO ₂ (Bromic acid)	HOIO ₂ (Iodic acid)
Halic (VII) acid (Perhalic acid)	–	HOClO ₃ (Perchloric acid)	HOBrO ₃ (Perbromic acid)	HOIO ₃ (Periodic acid)

The strength of oxoacids of halogens increases with the increase in oxidation state of halogen e.g. HClO is a very weak acid, in which oxidation state of Cl element is (+1). HClO₄ is a very strong acid in which oxidation state of Cl element is (+7).

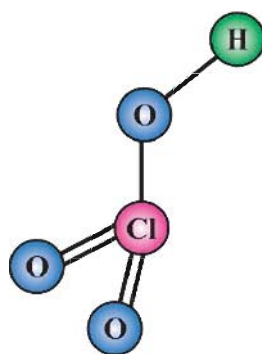
Here we will have structures of some of the oxoacids which are shown below :



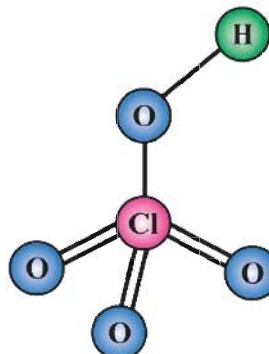
Hypochlorous acid



Chlorous acid



Chloric acid



Perchloric acid

5.12 Elements of Group 18

In this group six elements helium, neon, argon, krypton, xenon and radon are present. These elements are also known as, '**Inert gases**' or '**Noble gases**'. These elements are not considered as metals or non metals. All these elements are in gaseous form at the room temperature and are chemically inert. Hence they form very few compounds. The atomic and physical properties of the elements of this group are shown in table 5.12.

Table 5.12 Atomic and Physical Properties of group 18 Elements

Property	He	Ne	Ar	Kr	Xe	Rn
Atomic number	2	10	18	36	54	86
Atomic mass (g mol ⁻¹)	4.00	20.18	39.95	83.80	131.30	222.00
Electronic configuration	1s ²	[He]2s ² 2p ⁶	[Ne]3s ² 3p ⁶	[Ar]3d ¹⁰ 4s ² 4p ⁶	[Kr]4d ¹⁰ 5s ² 5p ⁶	[Xe]4f ¹⁴ 5d ¹⁰ 6s ² 6p ⁶
Ionisation enthalpy (Δ _i H) (kJ mol ⁻¹)	2372	2080	1520	1351	1170	1037
Electron gain enthalpy (kJ mol ⁻¹)	48	116	96	96	77	68
Atomic radius (pm)	120	160	190	200	220	–
Melting point (K)	–	24.6	83.8	115.9	161.3	202
Boiling Point (K)	4.2	27.1	87.2	119.7	165.0	211
Density (g cm ⁻³) (298 K)	1.8×10 ⁻⁴	9.0×10 ⁻⁴	1.8×10 ⁻³	3.7×10 ⁻³	5.9×10 ⁻³	9.7×10 ⁻³

5.12.1 Occurrence, Electronic Configuration, Oxidation States :

Electronic configuration : Except helium (1s²) the elements of group 18 have their electronic configuration in valence orbits is ns²np⁶. Except helium, all the elements have outermost orbit completely filled with electrons. Hence, these elements are chemically inert.

Occurrence : All the noble gases except radon are available from atmosphere. Helium is obtained mostly in nature. It is available from natural gas. Argon is 1% by volume in dry air.

Oxidation state : Xe possesses +2, +4, +6, or +8 oxidation states in its compounds.

5.12.2 Periodicity in Physical and Chemical Properties :

(1) Periodicity in physical properties : On the basis of table 5.12 it can be said that general tendency of increase in the atomic size, decrease in ionisation enthalpy with increase in atomic number in elements of group-18 is observed.

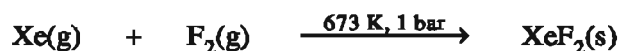
(i) Atomic radii : As we go down in the group from above, the atomic radii increases with increase in atomic number.

(ii) Ionisation enthalpy : Very high values of ionisation enthalpy because of stable electronic configuration of group 18 is observed. As we go down in the group the value of ionisation enthalpy decreases with increase in atomic number.

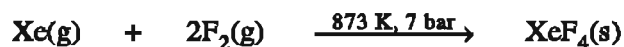
(iii) Electron gain enthalpy : Because of the stable electronic configuration of the elements of this group, they have no tendency to accept the electrons. Hence, the values of the electron gain enthalpy of these elements is more positive.

5.13 Xenon-Fluorine Compounds

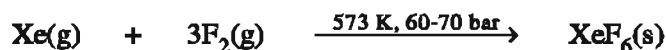
Xenon element forms three compounds with fluorine viz. XeF_2 , XeF_4 and XeF_6 . To obtain these compounds, xenon is to be reacted with fluorine under definite conditions.



excess

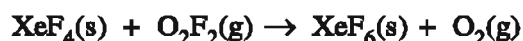


1:5 proportion



1:20 proportion

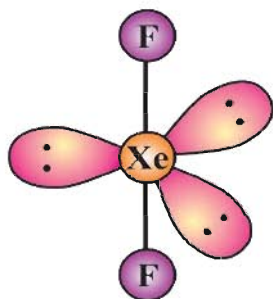
By reaction of XeF_4 and O_2F_2 at 143 K temperature, XeF_6 is obtained.



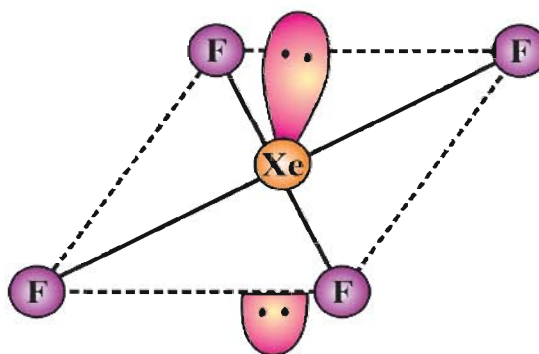
XeF_2 , XeF_4 , XeF_6 are colourless crystalline solid substances. They sublime easily at 298 K temperature. They are strong fluorinating agents. In very small amount of water they get hydrolysed e.g.



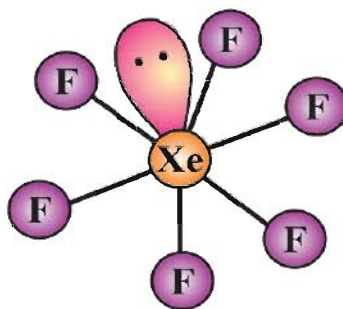
The structures of some important xenon fluorine compounds are shown below :



XeF_2
(Linear)



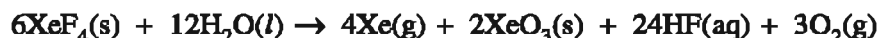
XeF_4
(Square planar)



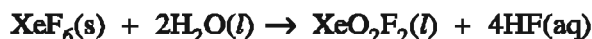
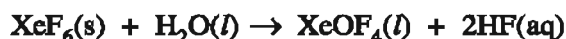
XeF_6
(Distorted octahedral)

5.14 Xenon-Oxygen Compounds

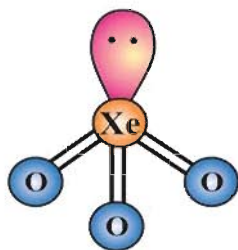
Xenon trioxide XeO_3 is formed by hydrolysis of XeF_4 and XeF_6 with water.



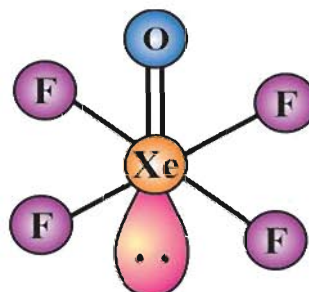
Because of partial hydrolysis of XeF_6 oxyfluoride compounds of Xenon XeOF_4 and XeO_2F_2 are formed.



XeO_3 is a colourless explosive solid substance. It possesses trigonal pyramidal structure. XeOF_4 is a colourless volatile liquid. It possesses square pyramidal structure. The structure of XeO_3 and XeOF_4 are shown below :



XeO_3 Trigonal pyramidal



XeOF_4 Square pyramidal

SUMMARY

The elements of groups 13 to 18 in the periodic table are known as p-block elements. The general electronic configuration of these elements is ns^2np^{1-6} . We have studied about the elements of groups 15, 16, 17 and 18 in this unit.

General introduction of elements of groups 15, 16, 17, 18

	group 15	group 16	group 17	group 18
Common name/ Identification	Nitrogen group	Chalogens or Oxygen group	Halogen Group	Noble Gas Group
Electronic configuration of valence shell	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
Oxidation state	N -3, to +5	O -2, -1, +1, +2	F -1	Ne -
	P, As -3, +3, +5	S, Se, Te -2, +2, +4, +6	Cl, Br, I -1, +1, +3, +5, +7	Xe +2, +4, +6, +8
	Sb, Bi +3, +5	Po +2, +4	- -	- -

The periodicity in properties of elements of groups 15,16,17,18.

Atomic radius, metallic character ↓				18
	15	16	17	He
	2p N	O	F	Ne
	3p P	S	Cl	Ar
	4p As	Se	Br	Kr
	5p Sb	Te	I	Xe
	6p Bi	Po	At	Rn
	Atomic radius, metallic character ←			
	↑ Electronegativity, Ionisation enthalpy			

The first element of group 15, differs in many aspects from the other elements in the group. The reason for which is its smaller size, the capacity of formation of $p\pi-p\pi$ triple bond between, nitrogen atoms and the nonavailability of d-orbitals. As we go down from above in the group, variations are found in properties. Dinitrogen (N_2) can be prepared in the laboratory as well as on commercial level. The oxides of nitrogen element are N_2O , NO , N_2O_3 , N_2O_4 and N_2O_5 which possess resonance forms. Ammonia and nitric acid are compounds of

nitrogen. Phosphorus element exists as P_4 molecule. It has many allotropes. It forms hydrides, halides and oxoacid compounds.

Polonium element of group 16 is radioactive. Oxygen forms metal oxides with metals. Ozone is a strong oxidising agent. Sulphur element possesses different allotropes. Out of these α and β allotropes are very important. Sulphur element combines with oxygen and forms oxide compounds like SO_2 and SO_3 . Out of the different oxoacids of sulphur, sulphuric acid is very important. It is called 'King of Chemicals.'

Astatine element of group 17 is radioactive. As these elements require one electron to have stable electronic configuration, they are very reactive. As a result of this, the elements of this group are not available in free state, but are available in the combined state as negative ions. The elements of this group form oxides, hydrogen halides, interhalogen compounds and oxoacid compounds.

Radon element of group 18 is radioactive. As the octet structure is complete in all the elements of this group they are chemically inert. Xenon element of this group, under specific reaction conditions combine with fluorine and oxygen elements and form fluoride and oxide compounds.

EXERCISE

1. Select the proper choice from the given multiple choices :

- How many groups are there in p-block element ?
(A) 3 (B) 4 (C) 5 (D) 6
- What is the molecular formula of chile salt petre ?
(A) KNO_3 (B) $NaNO_3$ (C) $Ca(NO_3)_2$ (D) $Ba(NO_3)_2$
- For the presence of which of the following ions, ring test is useful ?
(A) NO^- (B) NO_3^- (C) NO_2 (D) N_2O

- (4) Which of the following groups of four elements is called chalcogens ?
- (A) Nitrogen, phosphorus, arsenic and antimony
(B) Oxygen, sulphur, selenium and tellurium
(C) Fluorine, chlorine, bromine, iodine
(D) Helium, neon, argon, krypton.
- (5) Which of the following electronic configurations is the general electronic configuration of elements of group 16 ?
- (A) ns^2np^3 (B) ns^2np^4 (C) ns^2np^6 (D) ns^2np^5
- (6) Which of the following oxoacids of chlorine is most stable ?
- (A) $HClO_3$ (B) $HClO$ (C) $HClO_4$ (D) $HClO_2$
- (7) Which of the following orders with reference to stability is correct ?
- (A) $HF > HBr > HCl > HI$ (B) $HI < HCl < HBr < HF$
(C) $HF > HCl > HBr > HI$ (D) $HF > HI > HCl > HBr$
- (8) Which of the following is the interhalogen compound ?
- (A) XeF_4 (B) IF_7 (C) $NaCl$ (D) CaF_2
- (9) What is the molecular formula of oleum ?
- (A) H_2SO_3 (B) H_2SO_5 (C) $H_2S_2O_7$ (D) $H_2S_2O_8$
- (10) In which of the following oxides of nitrogen, the oxidation state of nitrogen element is (+4) ?
- (A) N_2O_3 (B) N_2O_4 (C) N_2O_5 (D) N_2O

2. Write the answers of following questions in short :

- (1) Mention the important allotropes of phosphorus.
- (2) Mention the oxidation state of underlined elements in the following compounds.
- (i) \underline{Cl}_2O (ii) $\underline{Cl}O_2$ (iii) $K\underline{Br}O_3$ (iv) $Na\underline{Cl}O_4$
- (3) Draw resonance formulas of NO_2 .
- (4) Write molecular formula of four oxoacids of sulphur element.
- (5) Mention the name and molecular formula of the oxoacid of fluorine element.
- (6) Write reaction for preparation of phosphorus trichloride.

- (7) Mention two uses of sulphur dioxide gas.
- (8) Which allotrope of phosphorus is stored in water ?
- (9) Mention the transition temperature for the two allotropes of sulphur-rhombic and monoclinic.
- (10) Write molecular formula of polymetaphosphoric acid.

3. Write answers of the following :

- (1) The values of ionisation enthalpy of elements of group 15 are more than the values of ionisation enthalpy of the group 14 in the same period, why ?
- (2) Write two chemical properties of ammonia gas.
- (3) Write ring test for the detection of nitrate ion.
- (4) Mention the interconversion of sulphur allotropes.
- (5) What is meant by interhalogen compounds ? Mention its types and give one example of each.
- (6) Write reaction of chlorine gas with ammonia gas.
- (7) Write two examples of oxide compounds of phosphorus with water.
- (8) Write two examples of each of xenon-fluorine and xenon-oxygen compounds.
- (9) Mention oxidation states of elements of group 16.
- (10) Write two reactions of preparation of dioxygen gas.

4. Give answers of the following in detail :

- (1) Discuss the reactions of elements in group 15 with hydrogen element, oxygen element, halogen elements and metallic elements.
- (2) Explain the anomalous behaviour of nitrogen element from other elements of group 15.
- (3) Discuss preparation, properties and uses of nitric acid.
- (4) Write a short note on 'oxides of nitrogen'.
- (5) Discuss preparation, properties and uses of dioxygen gas.
- (6) Discuss the industrial production of sulphuric acid by contact process.
- (7) Write names, molecular formulas and structural formulas of four oxoacids of sulphur.
- (8) Discuss chemical properties of hydrogen chloride.
- (9) Write preparation and properties of phosphorus.
- (10) Discuss preparation, properties and uses of ozone gas.



Unit

6

Haloalkane and Haloarene Compounds

6.1 Introduction

Amongst the elements included in the periodic table, maximum number of compounds are of carbon. If tetravalency of carbon element is satisfied by hydrogen then the compounds formed are called hydrocarbons. If the hydrogen in the compounds of hydrocarbons is substituted by one or more halogen functional group ($X = F, Cl, Br, I$), then the compounds obtained are called halogen containing organic compounds. These compounds are also called organic halides.

By substitution of hydrogen atom in hydrocarbons of alkane series (methane, ethane, propane) by halogen atom, the compounds obtained are called **haloalkanes (alkyl halides)**; while substitution of hydrogen atom by halogen atoms in the hydrocarbons of arene series are called **haloarenes (aryl halide)**. In haloalkane and haloarene compounds covalent bond ($C-X$) is formed between carbon and halogen. These compounds are not available in free form in nature, but are chemically synthesised. These compounds are useful for introducing alkyl or aryl group in other organic compounds. These compounds have unique importance as initial reactant or as initial raw material to obtain organic compounds in the form of product. In addition, haloalkane and haloarene compounds are good solvents. These compounds are useful in obtaining immunity against diseases in human body, physical growth and as enzyme secretion in biochemical reactions in hormone (iodine in thyroxine), substance used as anesthesia in surgery of the body (chloroform), in drugs for the remedy of diseases like typhoid, malaria. Haloalkane and haloarene compounds are very important in everyday life and in industries. We will study about preparation, physical and chemical properties and uses of haloalkane and haloarene compounds. In addition, we will have information about the effect of polyhalogen compounds on environment.

6.2 Classification

The classification of haloalkanes and haloarenes is carried out as follows :

(1) Classification on the basis of number of halogen atoms : On the basis of the number of same halogen element one, two, three or four or more combined with alkyl or aryl group, they are classified respectively as mono, di, tri, tetra or polyhalogen form. e.g., For haloalkane,

(i) $R-X$ mono haloalkane \rightarrow As only one halogen atom is present.

e.g., CH_3CH_2Cl monochloroethane \rightarrow as only one chlorine atom is present.

(ii) $R-X_2$ Dihaloalkane \rightarrow As there are two halogen atoms.

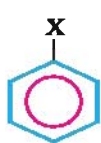
e.g., $\begin{array}{cc} CH_2 & - & CH_2 \\ | & & | \\ Br & & Br \end{array}$ 1,2-dibromo ethane \rightarrow as there are two bromine atoms.

(iii) $R-X_3$ Trihaloalkane \rightarrow As there are three halogen atoms.

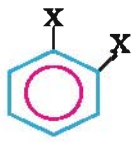
e.g., $\begin{array}{ccc} CH_2 & - & CH & - & CH_2 \\ | & & | & & | \\ Cl & & Cl & & Cl \end{array}$ 1, 2, 3-trichloropropane \rightarrow As there are three chlorine atoms.

In aromatic compounds, the classification can be carried out as follows on the basis of halogen atoms.

For haloarenes,



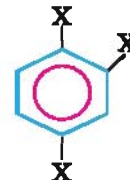
Monohalobenzene



or

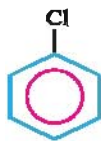


Dihalobenzene

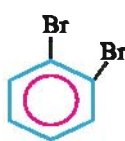


Trihalobenzene

e.g.,



Chlorobenzene

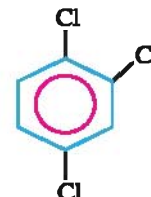


1,2-Dibromobenzene
(o-Dibromobenzene)

or



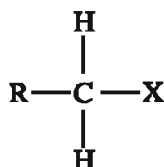
1,4-Dibromobenzene
(p-Dibromobenzene)



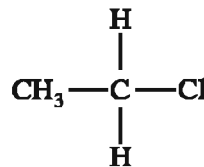
1,2,4-Trichlorobenzene

(2) Halogen attached to carbon possessing sp^3 hybridisation, in halogen containing organic compounds : In halogen containing organic compounds, halogen ($X = F, Cl, Br, I$) containing carbon is possessing sp^3 hybridisation, the compounds can be classified in three types as follows :

(a) Haloalkane or Alkyl halide : Halogen containing carbon which is sp^3 hybridised when attached to only one other carbon atom it is called **primary (1^0) alkyl halides**.

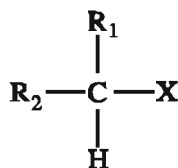


Primary (1^0) haloalkane
(Primary alkyl halide)

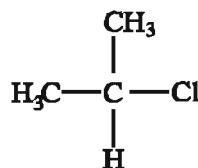


Primary (1^0) chloroethane.

Halogen containing carbon atom which is sp^3 hybridised when combine with other two carbon atoms, it is called **secondary (2^0) alkyl halide**.

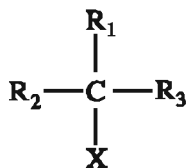


Secondary (2^0) haloalkane
(Secondary alkyl halide)

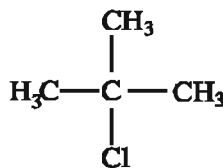


Secondary (2^0) 2-chloro propane

Halogen atom having carbon which is sp^3 hybridised when combine with other three carbon atoms, it is called **tertiary (3^0) alkyl halide**.



Tertiary (3^0) haloalkane
(Tertiary alkyl halide)

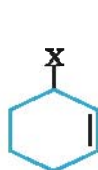


2-chloro-2-methyl propane
(Tertiary butyl chloride)

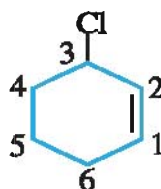
(b) Allylic halides : Halogen containing carbon atom which is sp^3 hybridised when combine with other carbon having double bond ($-\text{C}=\text{C}-$) then such compounds are called allylic halides.

e.g. (1) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{X}$ Allylic halide (3-haloprop-1-ene)

(2) $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{Cl}$ 1-Chlorobut-2-ene

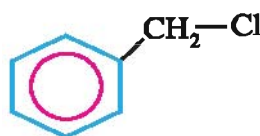
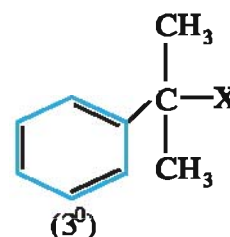
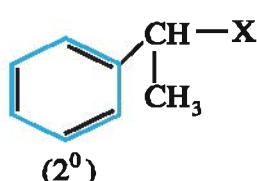
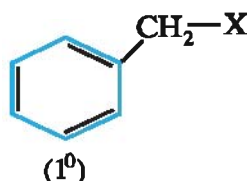


3-Halocyclohex-1-ene

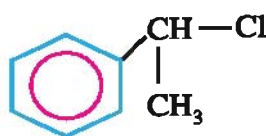


3-Chlorocyclohex-1-ene

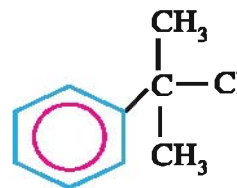
(c) Benzylic halide : Halogen containing carbon which is sp^3 hybridised when combine with carbon of benzene ring, then the compounds are called benzylic halides.



Benzyl chloride



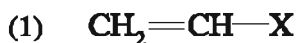
(1-Chloroethyl)benzene



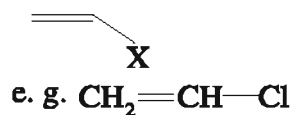
(1-Chloro-1-methylethyl)benzene

(3) Halogen attached to carbon possessing sp^2 hybridisation in halogen containing organic compounds : In halide compounds, carbon atom containing halogen ($X = F, Cl, Br, I$) possesses sp^2 hybridisation then the compounds can be classified in two types as follows :

(a) Vinyl halide : In this type of halide compounds halogen atom is combined with carbon atoms having ($-C=C-$) double bond carbon atom possessing sp^2 hybridisation.



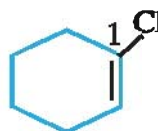
or



1-Chloro ethene (Vinyl chloride)

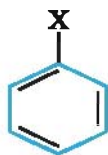


e.g.,

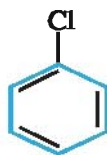


1-Chlorocyclo hex-1-ene

(b) Aryl halide : In this type of halide compounds halogen atoms are combined with sp^2 hybridised carbon atom of aromatic ring.



Halobenzene

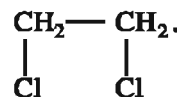


Chlorobenzene

6.3 Common and IUPAC Nomenclature of Haloalkane and Haloarene Compounds

For IUPAC nomenclature of haloalkane and haloarene compounds, the longest carbon chain is decided to which halogen atom is attached and the prefix halo is attached to the name of hydrocarbon. viz. for fluorine, chlorine, bromine, iodine; fluoro, chloro, bromo, iodo prefix are used respectively. For haloalkane containing three or more than three carbon atoms the least number showing the position of halogen is shown as prefix viz. 1-chloropropane ($\text{CH}_3\text{—CH}_2\text{—CH}_2\text{—Cl}$), 2-chloropropane ($\text{CH}_3\text{—CHCl—CH}_3$), etc.

If two, three, four or more same halogen atoms are present then the number showing the prefix di, tri, tetra etc. are used respectively viz 1,2-dichloro ethane



The common name of haloarene is aryl halide. For IUPAC nomenclature of haloarenes, after the corresponding halogen elements, the name of aromatic nucleus is joined after the name of corresponding prefix. e.g. chlorobenzene



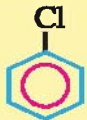
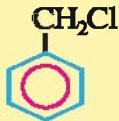
For dihalogen derivatives, o, m and p prefix are used in common nomenclature, but in IUPAC nomenclature, 1, 2; 1, 3 and 1, 4 are used. The classification of dihalo compounds containing only one type of halogen atoms, is made as geminal halide and vicinal halide. Geminal halide means both the halogen atoms are on one carbon only and in vicinal halide both the halogen atoms are combined with adjacent carbon atoms. In common nomenclature method, geminal dihalide is called alkylidene halide and vicinal halide is called alkylene dihalides; while in IUPAC nomenclature method, they are called dihaloalkanes.

e.g. (1) The common name of $\text{H}_3\text{C—CHCl}_2$ is ethylidene chloride while IUPAC name is 1,1-dichloro ethane.

(2) $\begin{array}{c} \text{CH}_2\text{—CH}_2 \\ | \quad | \\ \text{Cl} \quad \text{Cl} \end{array}$ Common name is Ethylene dichloride and IUPAC name is 1, 2-dichloro ethane.

Table 6.1 Common and IUPAC names of Haloalkane and Haloarene compounds

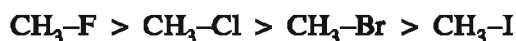
Structural Formula	IUPAC name	Common name
CH_3Cl	Chloromethane	Methyl chloride
$\text{CH}_3\text{CH}_2\text{Cl}$	Chloroethane	Ethyl chloride
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$	1-Chloropropane	n-Propyl chloride
$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_3 \\ \\ \text{Cl} \end{array}$	2-Chloropropane	Iso propyl chloride or secondary(2°) propylchloride
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{Br}$	1-Bromobutane	n-butyl bromide
$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{Br} \\ \\ \text{CH}_3 \end{array}$	1-Bromo 2-methylpropane	Iso butyl bromide
$\begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}_3 \\ \\ \text{Br} \end{array}$	2-Bromobutane	Secondary (2°) butyl bromide
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{Br} \\ \\ \text{CH}_3 \end{array}$	2-Bromo-2-methylpropane	Tert-butyl bromide
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_2-\text{Br} \\ \\ \text{CH}_3 \end{array}$	1-Bromo-2, 2-dimethyl propane	Neopentyl bromide
$\text{H}_2\text{C}=\text{CH}-\text{Cl}$	Chloroethene	Vinyl chloride
$\begin{array}{c} \text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CH}-\text{CH}_3 \\ \\ \text{Br} \end{array}$	4-Bromopent-2-ene	–
$\text{H}_2\text{C}=\text{CH}-\text{CH}_2-\text{Br}$	3-Bromopropene	Allyl bromide

	Chlorobenzene	Phenyl chloride
	(Chloromethyl)benzene	Benzyl chloride

6.4 Nature of C-X Bond

As the electronegativity of halogen atom is more than that of carbon atom, the bond between carbon and halogen (C-X) becomes polar. $\text{---}\overset{\delta+}{\text{C}}\text{---}\overset{\delta-}{\text{X}}$ as the electron pair of covalent bond is more attracted towards halogen nucleus having more electronegativity, partial negative electric charge (δ^-) on halogen atom and partial positive electric charge (δ^+) on the carbon atom is created.

The atomic sizes of halogens F, Cl, Br, and I present in haloalkane increases respectively, so the bond length of C-X increases successively and the bond enthalpy decreases successively.



The changes in the values of bond length, bond enthalpy and bond polarity as we move from C-F to C-I are given in table 6.2.

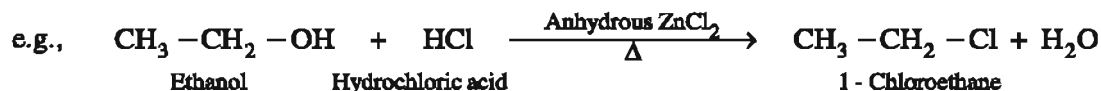
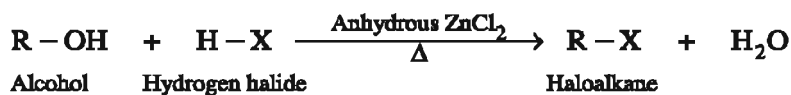
Table 6.2 Values of bond length, bond enthalpy and bond polarity of some alkyl halide compounds

Bond	Bond length (pm)	Bond enthalpy (kJ mol ⁻¹)	Polarity of bond (Debye)
CH ₃ —F	139	452	1.847
CH ₃ —Cl	178	351	1.860
CH ₃ —Br	193	293	1.830
CH ₃ —I	214	234	1.636

6.5 Preparation of Haloalkane and Haloarene Compounds

(1) From Alcohol : The method of formation of haloalkane from alcohol is simple. Haloalkane is obtained by substitution of hydroxyl group —OH of alcohol by halogen. Some reactions of preparation of haloalkane from alcohol are as follows :

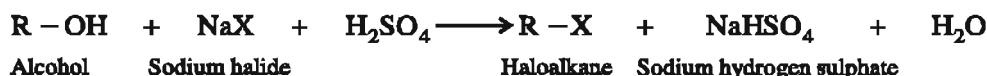
(a) Haloalkane is obtained by passing dry hydrogen halide gas from alcohol in presence of anhydrous zinc chloride or by heating alcohol and concentrated hydrogen halide at high temperature.



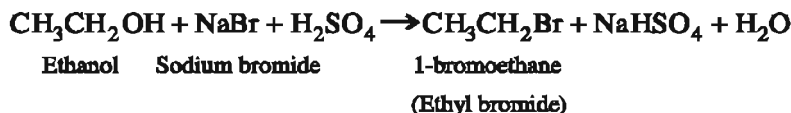
By reaction of ethanol with hydrochloric acid in presence of anhydrous zinc chloride at high temperature, molecule of water is liberated and chloroethane is obtained. Haloalkane is obtained by the above method from primary and secondary alcohols but haloalkane is obtained by mixing tertiary alcohol with concentrated HCl in presence of anhydrous ZnCl_2 at room temperature. The order of reactivity of alcohol with haloacid is $3^\circ > 2^\circ > 1^\circ$. On the basis of this reaction primary, secondary and tertiary alcohol can be identified by a test known as **Lucas test**.

For preparation of aryl halide, this method cannot be used because oxygen of the hydroxyl group in phenol is attached to carbon having double bond of benzene ring. Carbon-oxygen bond possesses partial double bond characteristic, which is very strong so it is difficult to break.

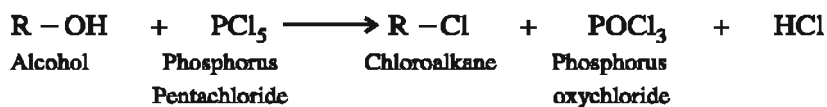
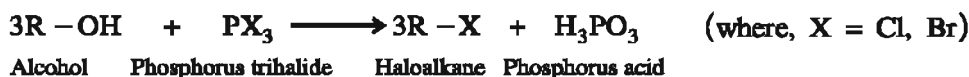
(b) Haloalkane is obtained by reaction of alcohol with sodium halide and concentrated sulphuric acid.



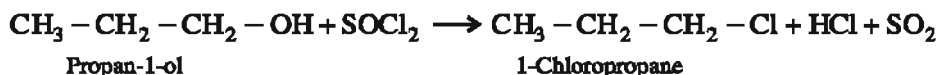
e.g., Bromoethane is obtained by reaction of ethanol with sodium bromide and concentrated H_2SO_4 .



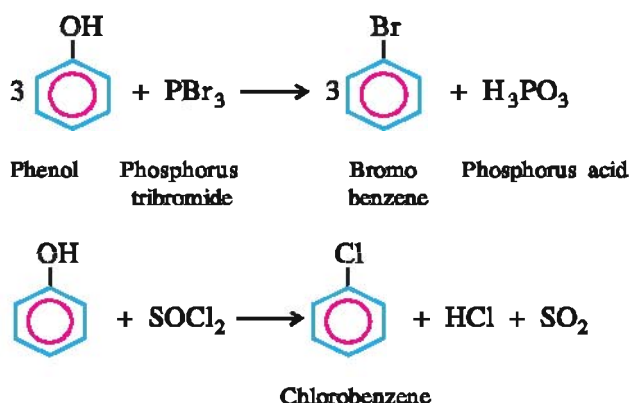
(c) Haloalkane is obtained by reaction of alcohol with halides of phosphorus. By this reaction, high purity and more quantity of haloalkanes are obtained.



(d) Haloalkane is obtained by reaction of alcohol with thionyl chloride.



(e) To prepare haloarene from phenol; phenol is reacted with reactants like PBr_3 or SOCl_2 .

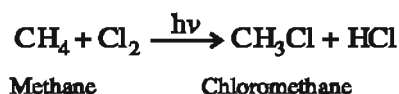


The products bromobenzene and chlorobenzene obtained by above two reactions are in very less proportion.

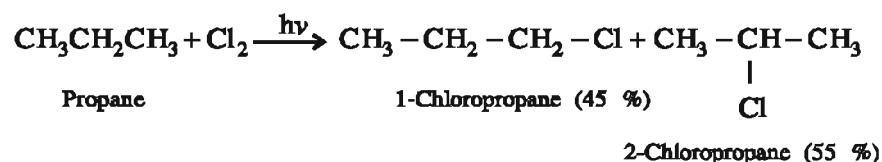
(2) From Hydrocarbon :

(a) **Free radical halogenation :** Haloalkane is obtained by substitution reaction of alkane compound with free radical X obtained by homolytic fission of dihalogen. e.g.,

(i) Chloromethane is obtained by doing reaction of methane with dichlorine gas in presence of ultraviolet light.

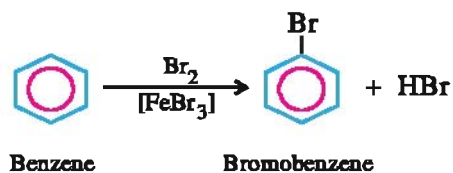


(ii) Mixture of isomers of chloropropane is obtained by halogenation reaction of propane with dichlorine gas in presence of ultraviolet light.

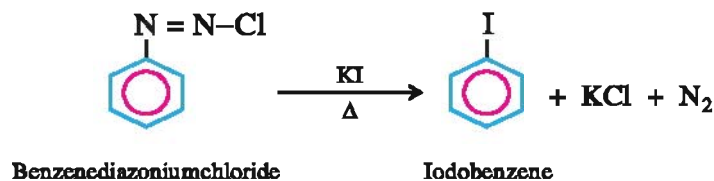


(b) **By electrophilic substitution :** In the chlorination or bromination reaction of benzene and toluene, first of all dihalogen gas (Cl_2 or Br_2) react with catalyst Fe or FeX_3 and gives electrophilic ion X^+ (Lewis acid). It is called electrophilic reagent. H^+ attached to carbon having π electron cloud of benzene is removed and X^+ enters in its place so electrophilic substitution reaction takes place.

Bromobenzene is obtained by bromination reaction of benzene with Br_2 at 303 to 313 K temperature in presence of FeBr_3 catalyst.

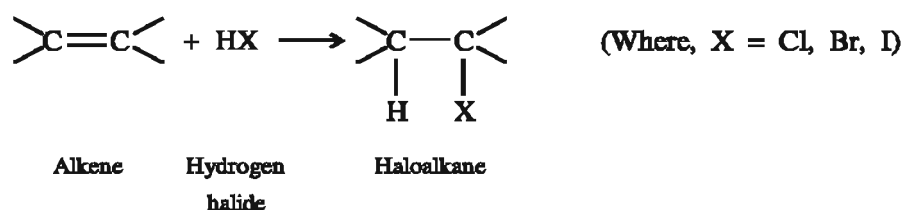


Iodobenzene is obtained by reaction of freshly prepared benzenediazoniumchloride with potassium iodide at higher temperature.

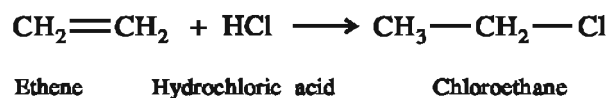


(d) From Alkenes :

(i) Addition reaction with hydrogen halide : In the reaction of alkene with hydrogen halide (HX) the π -bond between carbon-carbon atoms breaks and addition reaction takes place such that H is attached to one carbon and X to the other carbon. This reaction is called **hydrohalogenation**.

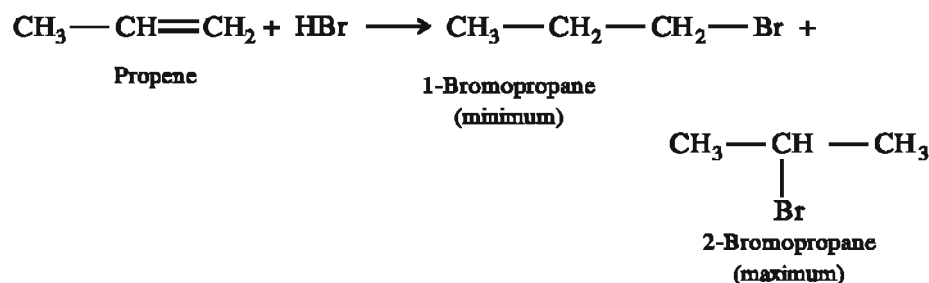


e.g., Chloroethane is obtained by reaction of ethane with hydrochloric acid.

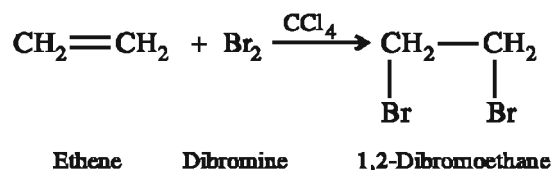


Two isomers of bromo propane are obtained by addition reaction of propene with hydrobromic acid.

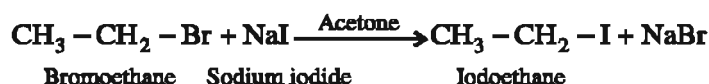
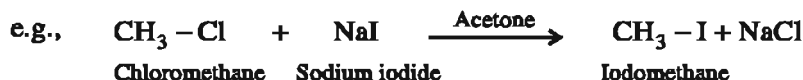
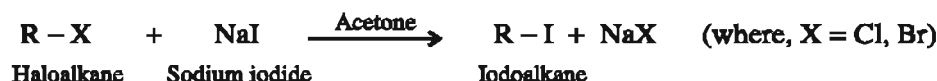
According to Markonikov's rule, the product 2-bromopropane is obtained in maximum proportion (see Std-11, Semester II, Unit 6 Hydrocarbons)



(ii) Addition reaction with dihalogen gas : Dihalogen containing alkane is obtained by addition of both the atoms of dihalogen molecule to an alkene and addition reaction occurs by breaking of π bond of ethylenic double bond. This reaction is called **halogenation reaction** e.g. 1,2-dibromoethane is obtained by addition reaction of ethene with solution of bromine prepared in CCl_4 .



(4) **By halogen exchange :** Iodoalkane is obtained by the reaction of bromoalkane or chloroalkane with solution of sodium iodide prepared in dry acetone. This reaction is known as **Finkelstein reaction**.



By reaction of bromomethane or chloromethane with metallic fluorides like AgF, Hg₂F₂, CoF₂ or SbF₃ fluoromethane is obtained. This reaction is called **Swartz reaction**.

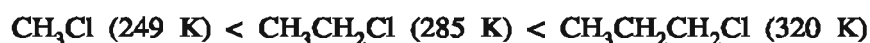


6.6. Physical Properties

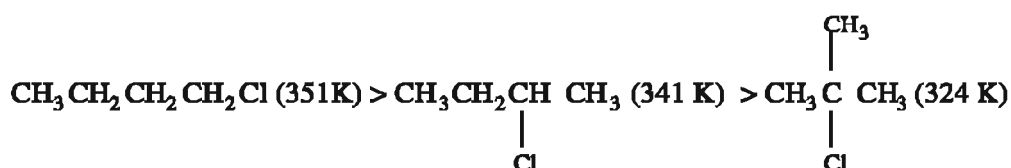
- Pure haloalkane compounds are colourless.
- Bromide and iodide compounds are coloured in presence of light.
- Volatile halide compounds possess sweet smell.
- Halides having one, two or three carbon atoms are in gaseous state at normal temperature while halides having more than three carbon atoms are in liquid or solid state.
- In haloalkane and haloarene compounds $\text{>C}^{\delta+}-\text{X}^{\delta-}$ being polar, inter-molecular forces (van der Waals) increases. As a result, the boiling points of haloalkanes are higher than their corresponding alkanes.



- As the number of carbon atoms increases in monohaloalkanes, there is increase in their boiling points. e.g.,



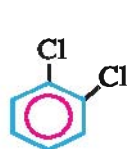
- There is decrease in boiling points of isomeric haloalkanes having equal number of carbon atoms and equal halogen atom, as we move from primary (1^o) to secondary (2^o) and secondary (2^o) to tertiary (3^o). e.g.,



- The boiling points decrease in the following order as the halogen atoms change in haloalkane containing similar alkyl group.



- The boiling points of haloarene compounds are high because of the presence of strong bond because of short C–X bond length in haloarene compounds than haloalkane compounds.
- In dihaloarene compounds, there is much less difference in the boiling points of (1,2) ortho, (1,3) meta and (1,4) para isomers.



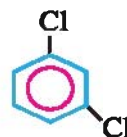
453 K

1,2-Dichloro benzene



448 K

1,4-Dichloro benzene



446 K

1,3-Dichloro benzene

- The densities of polychloroalkane, bromoalkane and iodoalkane are more than density of water and the density increases as the number of carbon atoms or halogen atoms or the atomic mass of halogen atom increases.

Table 6.3 Densities of some Haloalkanes (298 K)

Compound	Density gml ⁻¹	Compound	Density gml ⁻¹
n-C ₃ H ₇ Cl	0.89	CH ₂ Cl ₂	1.336
n-C ₃ H ₇ Br	1.335	CHCl ₃	1.489
n-C ₃ H ₇ I	1.747	CCl ₄	1.595

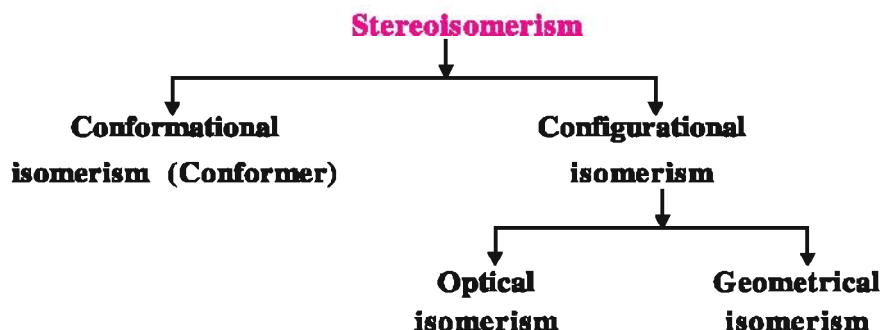
Haloalkane compounds are sparingly soluble in water, while they are soluble in organic solvents like acetone, ethanol.

To understand chemical properties of haloalkanes, some concepts of stereochemistry should be understood.

6.7 D, L (Relative configuration) and R,S (Absolute configuration) Nomenclature

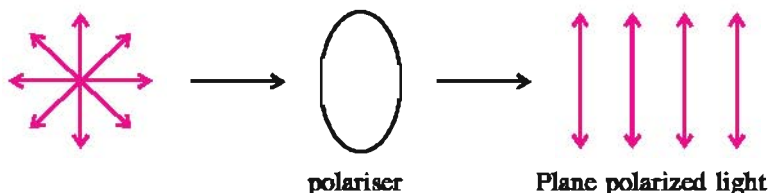
The branch of organic chemistry in which the study of three dimensional structure is carried out is called **stereochemistry**. Isomerism is the basic property in stereochemistry. Mainly two types of isomerism are there : (1) Structural isomerism and (2) Stereoisomerism

You have studied about structural isomerism in standard 11, Semester-I. The classification of stereoisomerism is as follows :



To understand optical isomerism, it is necessary to study the terms like plane polarised light, optical activity, chirality connected with it.

(1) Plane polarised light : There are seven colours in a white light. The light consisting the different wavelengths is vibrating in each possible plane. When such a light is passed through Nichol prism or polaroid, then the electromagnetic vibrations in the emerging light are found to be in the same plane. Such a light is called **polarised light**.



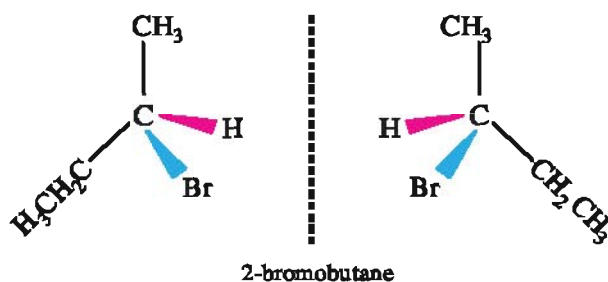
(2) Optical activity : The substance which has the capacity to rotate the plane of polarised light, is called **optically active substance**. Certain optically active substances which rotate the plane of polarised light towards left hand side are called **levo rotatory**. They are expressed by ***l* or (-)** symbol. The substances which rotate the plane of polarised light towards right hand side are called **dextro rotatory substance**. They are expressed by ***d* or (+)** symbol.

(3) Chirality : The main reason for optical activity is molecular asymmetry. There must be minimum one chiral carbon in each optically active compound. The carbon whose all the four valencies are satisfied by four different groups, is called **asymmetric carbon**. The substances whose images can not be superimposed are called **chiral substances**. This property is called **chirality** e.g., the hand or foot, and English **alphabets like B, C, D, E** etc.

The substances which can be superimposed on their images, are called **achiral substances**. e.g., spoon, and English **alphabets like A, H, I, M** etc.

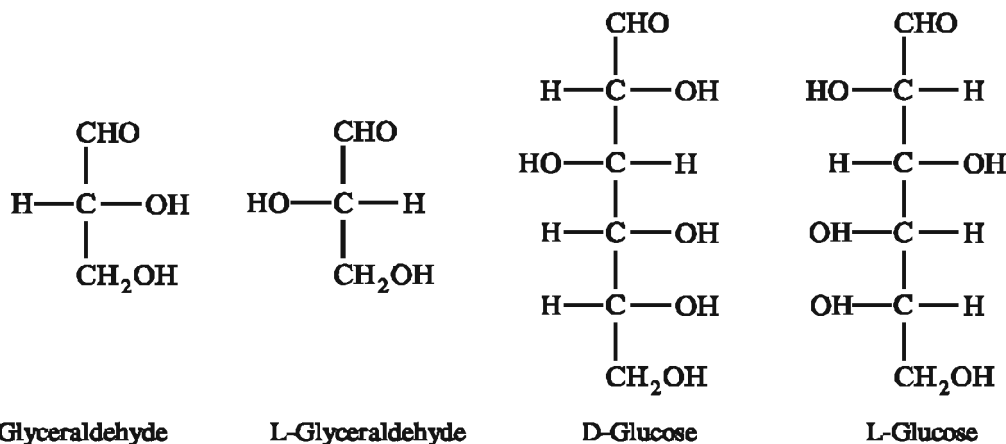
If one chiral carbon is present in a compound, then the following enantiomers are obtained which cannot be superimposed on one another.

e.g. 2-Bromobutane is a chiral molecule. It gives following two enantiomers which can not be superimposed on each other.



D and L configuration (Relative configuration) :

D and L terms are generally used to explain configuration of carbohydrates and amino acids. In the Fischer structure, if the -OH group is attached to the right hand side of the chiral carbon present at the end of the chain, then **D-configuration** and if attached on the left hand side, it is called **L-configuration**. In amino acids, D and L configurations are determined from the position of -NH_2 group e.g.,



Here, it is necessary to note that there is no direct relation of D with d and of L with l; that is compound having D-configuration can be of d or l type. Similarly compound having L-configuration can be of d or l type. e.g., D-Glyceraldehyde and D-Lactic acid are found experimentally to be d(+) and l(-).



D- or L-configuration of the compound are determined theoretically; while d or l configuration is determined experimentally with the help of polarimeter. D- and L-configurations of one substance are enantiomers.

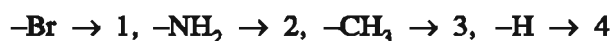
R-S Nomenclature (Absolute configuration) : For the identifications of chiral compounds having asymmetric carbon R, S nomenclature method is well-known.

This R, S nomenclature method was proposed by Cahn, Ingold and Prelog. In this method the configurations are expressed as **R** (Latin word Rectus = right) and **S** (Latin word Sinister = left).

For this nomenclature, all the four groups attached with asymmetric carbon are given sequence order (1,2,3,4). For this methods two steps are used.

Step-1 : To determine sequence order of group attached with asymmetric carbon :

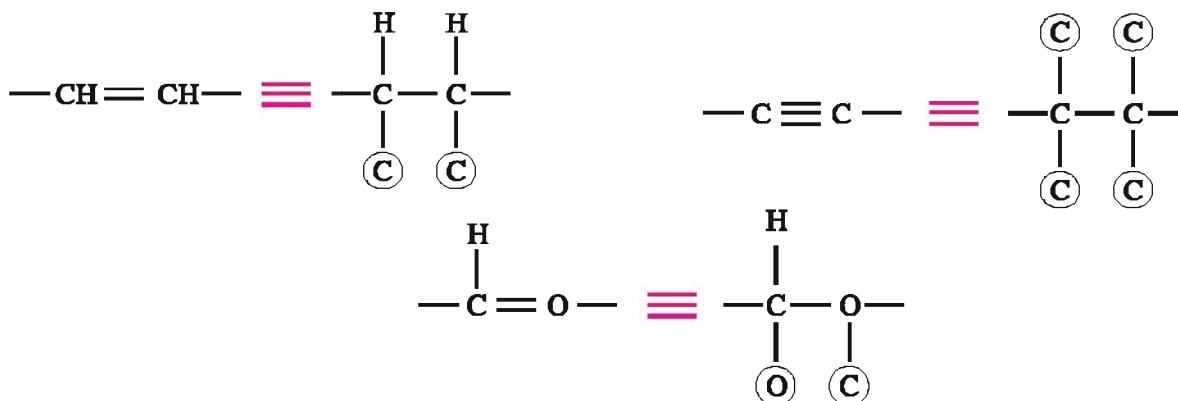
(1) To determine sequence order, the atomic number of first atom or group attached to an asymmetric carbon is taken into consideration. The atom whose atomic number is the highest will receive first sequence e.g., $-\text{H}$, $-\text{NH}_2$, $-\text{CH}_3$, $-\text{Br}$ are attached then sequence order is given as follows.



(2) If two isotopes are combined with asymmetric carbon atom, then the sequence number is given to isotope having more atomic mass in comparison to isotope having less atomic mass. e.g., H, Br, C, D (deuterium) atoms are attached with asymmetric carbon atom, then sequence order is given as 1,2,3, and 4 respectively to Br, C, D and H.

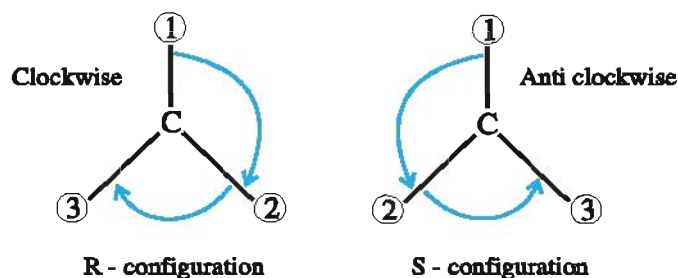
(3) If the first atom of two groups attached to asymmetric carbon atom, is same, then the atomic number of the second atom of the group is taken into consideration. e.g. If $-\text{CH}_2\text{NH}_2$, $-\text{CH}_3$, $-\text{CH}_2\text{OH}$, $-\text{CH}_2\text{CH}_3$ groups are attached to asymmetric carbon atom, then the sequence number 1,2,3,4 are given to $-\text{CH}_2\text{OH}$, $-\text{CH}_2\text{NH}_2$, $-\text{CH}_2\text{CH}_3$ and $-\text{CH}_3$ respectively.

(4) In giving sequence number to groups having double bond or triple bond, imaginary atoms are assumed to be attached to each π bond after breaking them.

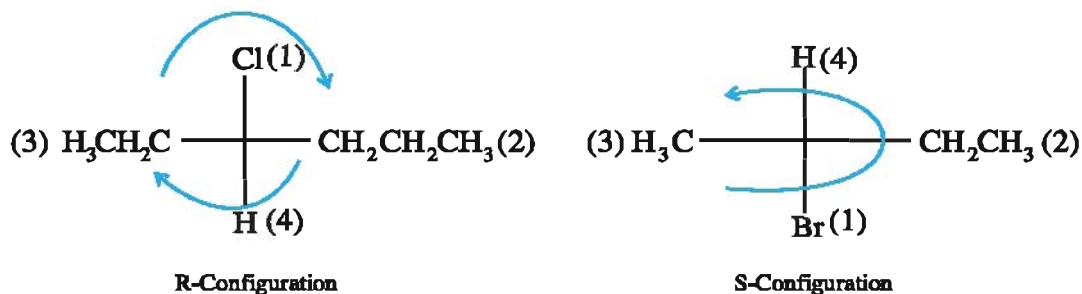


On the basis of the above sequence rules, the order of some important groups can be shown as follows : $-\text{I} > -\text{Br} > -\text{Cl} > -\text{SO}_3\text{H} > -\text{SH} > -\text{F} > -\text{OCOR} > -\text{OR} > -\text{OH} > -\text{NO}_2 > -\text{NR}_2 > -\text{NHR} > -\text{COOR} > -\text{COOH} > -\text{COR} > -\text{CHO} > -\text{CH}_2\text{OH} > -\text{CN} > -\text{CH}_3 > -\text{D} > -\text{H}$

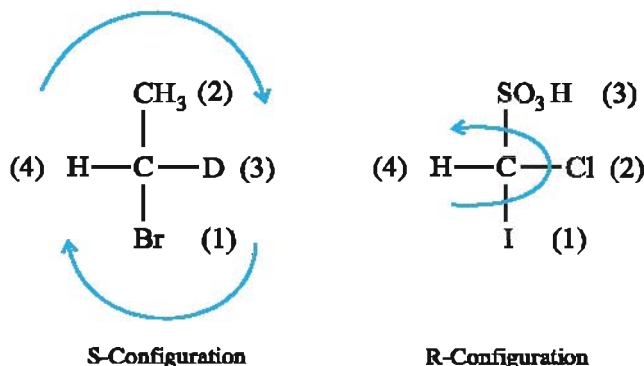
Step-2 To determine R and S configuration : After determination of selection of sequence number according to step 1, in the three dimensional structure, the group having lowest sequence number i.e. group number 4 is placed away from the observer. Then, the molecule is observed such that, the group having minimum sequence goes on opposite side. Then the increasing order of the remaining three groups (1, 2 and 3) is in clockwise direction (right hand side), then configuration of isomer is considered as R but if this sequence is in anticlockwise direction (left side) then it is considered as S-configuration.



According to the rules discussed above, the three dimensional, structure is to be assumed, which is difficult. Generally, showing chiral compounds in two dimension Fischer structure is more convenient. In the Fischer structure, the group showing lowest sequence number (4) is placed in vertical line and $1 \rightarrow 2 \rightarrow 3$ are in clockwise direction then it is R and if it is anticlockwise direction it is considered as S-configuration.



In Fischer structure if group showing sequence number (4) is in horizontal line, then the configuration of the compound is determined as above is opposite to that configuration. i.e. in such cases if $1 \rightarrow 2 \rightarrow 3$ is in clockwise direction then S and if in anticlockwise direction then R-configuration is considered. This explanation was given by Epling in 1982. e.g.,



6.8. Chemical Properties (Chemical Reactions)

6.8.1 Reactions of haloalkane compounds :

(1) Nucleophilic substitution reactions : As polar bond $C^{\delta+}-X^{\delta-}$ is present in haloalkane compounds, nucleophilic reagents ($:Nu^-$) are attracted by partially positively charged carbon atoms and substitutes halogen. Nucleophilic ions which are Lewis bases are called **nucleophilic reagents**.

The substitution reactions that take place through them are called **nucleophilic substitution reactions**. In short it is called **SN reaction**.



Some of the nucleophilic reagents are as follows :

$:\text{OH}^-$, $:\text{OR}^-$, $:\text{X}^-$, $:\text{CN}^-$, RCOO^- , $:\text{SH}^-$, $:\text{NH}_2^-$, $^- \text{O}-\ddot{\text{N}}=\text{O}$ etc. Which are Lewis bases also.

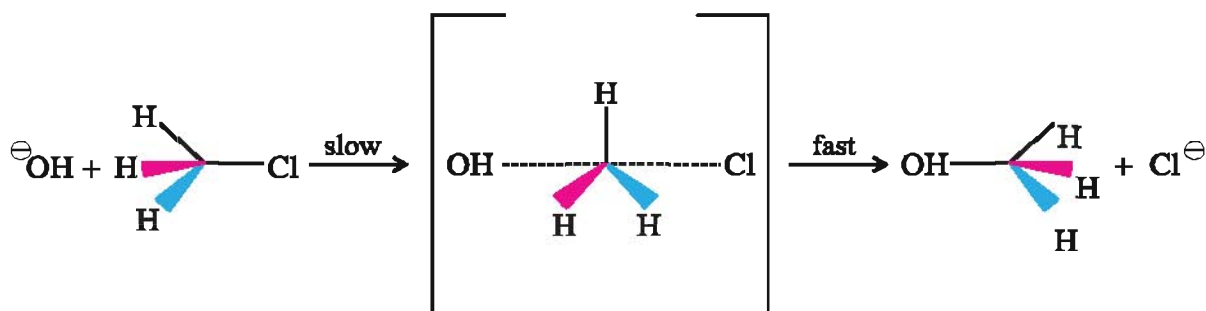
Nucleophilic reagents like cyanide and nitrite possess two nucleophilic centres. The structure of cyanide group is expressed in two ways. Cyanide group reacts as nucleophilic reagent in two different methods, In one of them carbon acts as a nucleophilic reagent. So that $(-\text{C}\equiv\text{N})$ becomes nucleophilic ion and alkyl cynde product is obtained; while in second structures, nitrogen acts as a nucleophilic reagent; so isocyanide product is obtained by $(:\text{C}=\text{N}^-)$ nucleophilic ion.

In the same way, in the nucleophilic ion nitrite ($\text{O}^- - \ddot{\text{N}}=\text{O}$) alkyl nitrite product is obtained but when nitrogen atom combines nitroalkane compound is obtained.

The reaction mechanism of nucleophilic substitution is classified in two ways as follows :

(a) Bimolecular Nucleophilic Substitution (SN^2) reaction : The reaction of chloromethane (CH_3Cl) with hydroxide ion ($:\text{OH}^-$) is second order nucleophilic substitution reaction. According to the principle of chemical kinetics, the order of reaction depends on the concentrations of both the reactants and so it is second order reaction.

We will understand by following example.



For Information only

In the above reaction the bond shown by dark shading is outside the plane. Bond shown by light shading is on the rear side of plane. While bond shown by straight line is in the plane of paper.

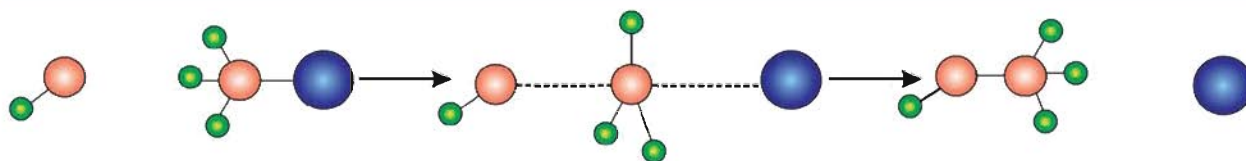


Fig. 6.2

Green dots indicate the entering hydroxyl group.

Blue sphere is the removing halide ion.

In 1937, scientist Edward Davies Hughes and Sir Christopher Ingold proposed the reaction mechanism of SN^2 reaction which can be studied from below :

Bimolecular Nucleophilic substitution reaction is called **SN^2 reaction**.

SN^2 reaction is the bimolecular reaction occurring between substrate (S) and nucleophilic reagent ($:\text{Nu}^-$). SN^2 reaction occurs in only one step without formation of intermediate product. In this reaction the substrate (reactant) does not undergo heterolytic fission. Carbon taking part in this reaction possesses sp^3 hybridisation; but at transition state it possesses sp^2 hybridisation. In transition state, the bonds are partially formed and broken. During the first step in the presence of released group Cl^- , nucleophilic reagent OH^- reacts with substrate and transition state is obtained. Thus, in transition state, both reagent and substrate combine.

At the transition state, the bond with Cl^- becomes weak and the formation of bond of nucleophilic OH^- starts. At this time, all the three hydrogen atoms with carbon are arranged in one plane only. As both the nucleophile OH^- and the group that is released, being negative, the nucleophile always combines in the direction totally opposite to the releasing group. The spatial arrangement of the obtained product is totally in opposite direction of the spatial arrangement of reactant. This means that, inverted product from substrate as a result of SN^2 reaction, is observed which is shown in fig 6.2.

The rate of SN^2 reaction depends on concentrations of both substrate and nucleophilic reagent.

Rate of reaction = $K [\text{S}]^1 [\text{Nu}^-]^1$ where S = substrate

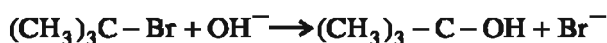
Nu^- = Nucleophilic reagent.

Hence, SN^2 reaction is a second order reaction. Thus, in rate determining step, when nucleophile reacts on carbon having less electron density, the rate controlling is done by both reacting agent and reagent in transition state; such substitution reactions are called bimolecular nucleophilic substitution (SN^2) reaction..

(b) Unimolecular Nucleophilic Substitution (SN^1) Reaction : SN^1 (unimolecular nucleophilic substitution) reaction takes place in two steps. In SN^1 reaction, firstly heterolytic fission of substrate takes place and carbocation (carbonium ion) is formed. The energy required to break C–X bond in the formation of carbocation is obtained from polar solvents like water, alcohol, acetic acid. In second step, nucleophile is attached to carbocation.

Tertiary butyl alcohol is obtained as product by reaction of tertiary butyl bromide with hydroxide ion.

This reaction is first order reaction from chemical kinetics point of view.



Tertiarybutyl bromide

Tertiarybutylalcohol

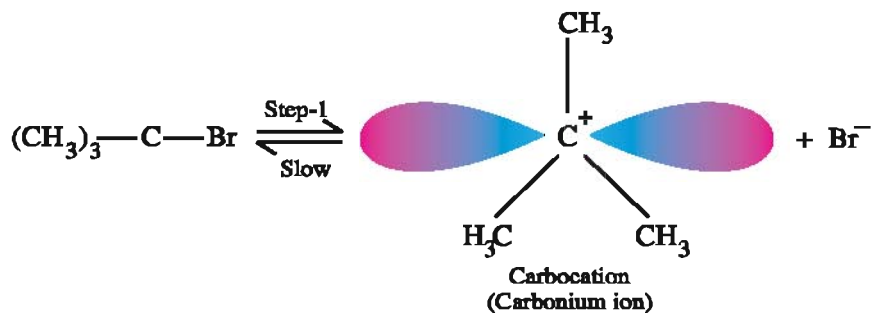
The order of this reaction depends only on the concentration of substrate and so it is a first order reaction.

$$\therefore \text{Rate of reaction} \propto [(\text{CH}_3)_3\text{C}-\text{Br}]$$

$$= K [(\text{CH}_3)_3\text{C}-\text{Br}]$$

The reaction mechanism of this reaction is in two steps as shown below :

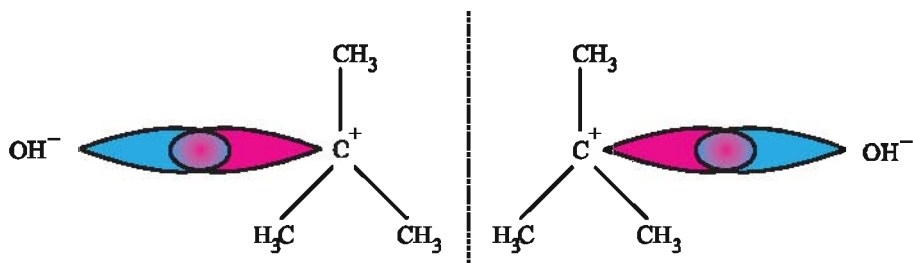
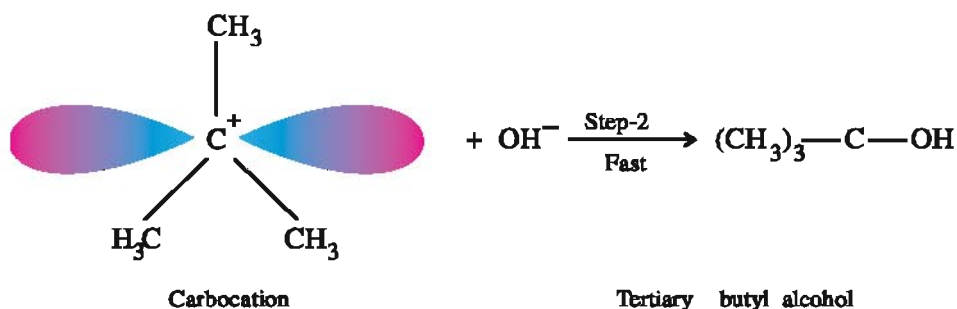
Step-1 :



The polar C-Br bond breaks slowly and carbocation and bromide ion are formed. As this step is slow, it is rate determining step.

Step-2 :

Nucleophilic reagent completes the substitution reaction by attacking the carbocation.



Mirror image

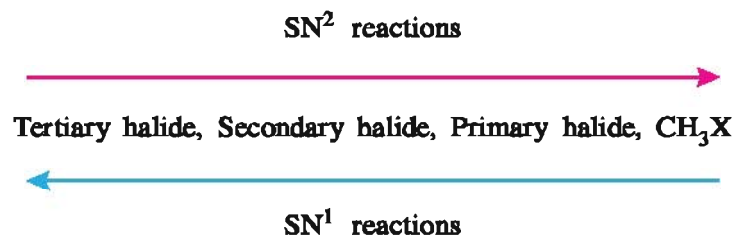
As shown above, the nucleophilic reagent (OH^-) can attack carbocation from both the sides, they will be mirror image of each other. In the above example substrate tertiary butylbromide is not optically active, hence the obtained product is optically inactive. If haloalkane substrate is optically active (e.g., secondarybutyl bromide) then product obtained will be optically active. As nucleophilic reagent OH^- can attack carbocation from both the sides, equal proportion of dextro and levorotatory optically active isomer which forms a **racemic mixture**.

In this second step of reaction carbocation readily combines with nucleophilic reagent (OH^-) and gives the product. Hence, the rate of reaction of SN^1 reaction does not depend at all on the concentration of nucleophilic reagent but it depends on the concentration of substrate.

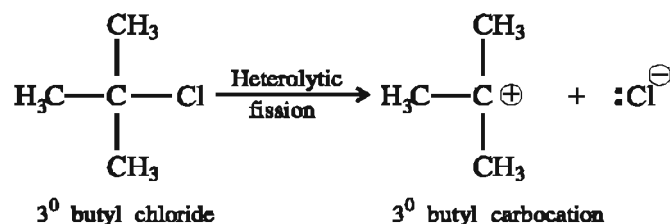
Rate of reaction = $K[\text{S}]^1$ where S = substrate. Thus, SN^1 reaction is a first order reaction.

The rate of SN^1 reaction depends on concentration of substrate, easy formation of carbocation and stability of carbocation. In SN^1 reaction weak nucleophilic reagent also reacts easily. As the stability of carbocation is more, the rate of SN^1 reaction will be fast. As stable carbocation is formed on tertiary carbon SN^1 reaction becomes easy; while SN^2 reaction is difficult.

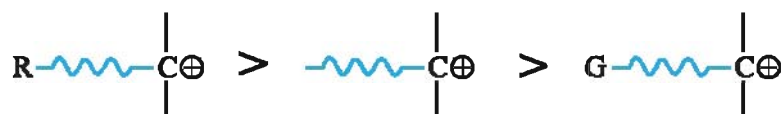
The order of case of SN^1 and SN^2 reactions in alkyl halides is as follows :



Stability of carbocation : 3° -butyl carbocation is obtained as intermediate by heterolytic fission of C-Cl bond during nucleophilic substitution of 3° -butylchloride as follows :



The stability of carbocation increases because of distribution of positive charge on carbon, any factor which tends to distribute the positive charge of carbon having deficiency of electron and the positive charge is equally distributed on the remaining part of ion must increase the stability of carbocation. Hence, if electron donating group is attached with carbocation, the stability increases. As contrast to this if electron attracting group combines with carbo cation, the stability decreases.

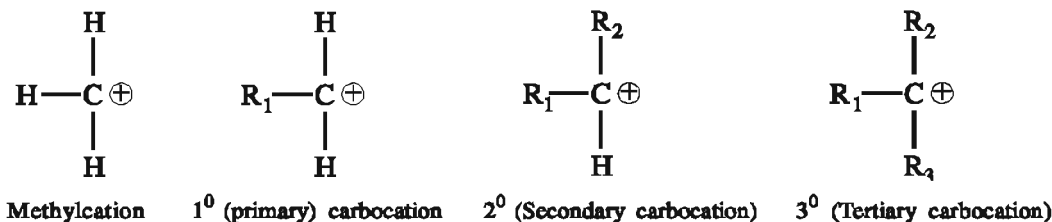


R = electron donating group

G = electron accepting group

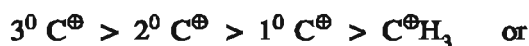
The alkyl group attached with carbon atom having positive charge possesses electron releasing inductive effect (I). Hence, the carbon to which alkyl group is attached the effect of positive charge of carbon will be less. Hence, alkyl group will be partially positively charged. The stability of carbocation will increase because of distribution of this positive charge.

e.g.,



Tertiary carbocation possesses maximum stability because three alkyl groups are attached to it; while two alkyl groups are attached with secondary carbocation. It possesses more stability than primary carbocation. The stability of the carbocation with which no alkyl group is attached has minimum stability.

Thus, the order of stability of carbocation can be shown as below :



Tertiary $\text{C}^{\oplus} >$ Secondary $\text{C}^{\oplus} >$ Primary $\text{C}^{\oplus} > \text{C}^{\oplus}\text{H}_3$. The rate of reaction depends on the stability of the carbocation obtained.

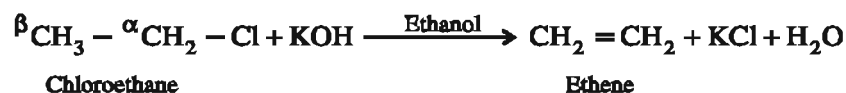
The stability of carbocation decreases if electron attracting atom or group is attached with carbocation having electron deficiency.

Resonance is also an important factor in deciding the stability of carbocation. The resonance structure can be drawn if electron pair deficient carbon is attached with unsaturated system in which positive charge is delocalized on the whole molecules.

The carbocation having possibility of resonance structure, is more than the carbocation having simple alkyl group; which can be made clear by the following example.

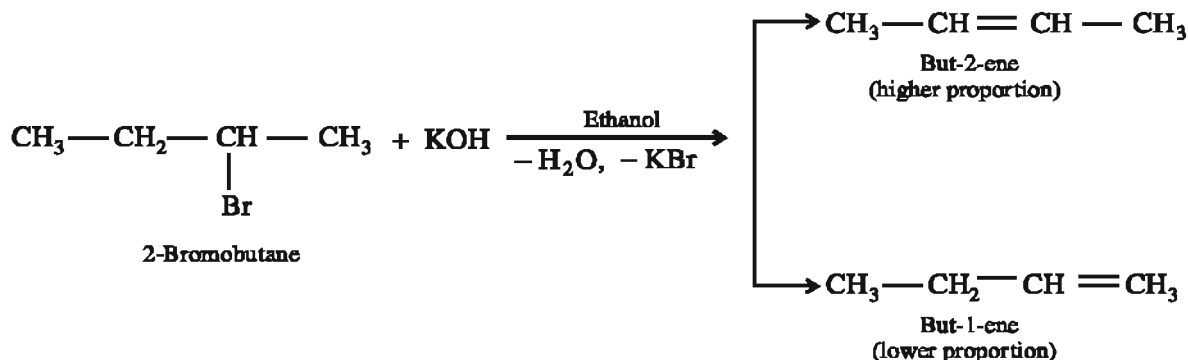


(2) Elimination Reactions : Alkene is formed by reaction of ethanolic solution of potassium hydroxide with haloalkanes containing hydrogen on β -carbon. Alkene compound is formed by formation of double bond between α and β -carbon atoms by releasing halogen atom of α -carbon atom and hydrogen atom of β -carbon atom of haloalkane. This reaction is called **β -elimination reaction**. This reaction is also called **dehydrohalogenation**.



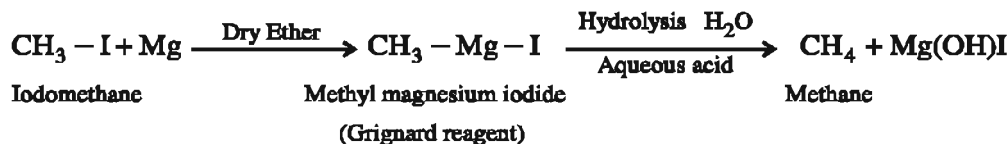
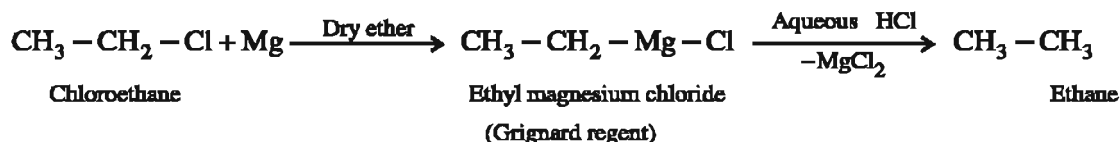
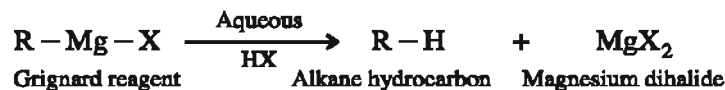
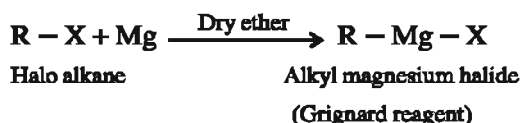
When there are more than one β -hydrogen in haloalkane, then more than one alkenes are obtained as product. Generally one product of alkene whose proportion is more is called major product and whose proportion is less called minor product.

In 1875, Russian scientist Alexander Zaitsev (it is also pronounced as Saytzeff) gave one formula. In dehydrohalogenation reaction, the alkene product having more number of alkyl groups attached to carbon atom containing double bond is obtained in higher proportion e.g.



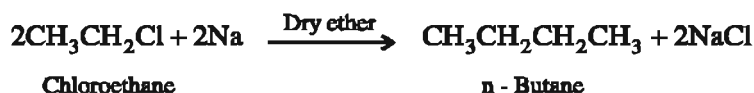
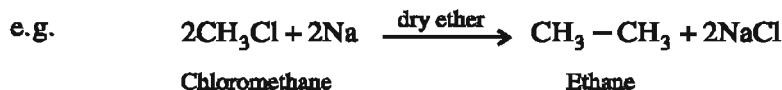
(3) Reactions with metals : By reaction of haloalkane with metals, chemical bond between carbon and metal are formed and the compounds obtained are known as organometallic compounds.

(a) Grignard reaction : In 1900, Victor Grignard discovered one important compound amongst organometallic compounds called alkyl magnesium halide. It became well known as **Grignard reagent RMgX**. Alkane is obtained by reaction of Grignard reagent with haloalkane.



(b) Wurtz Reaction : Alkane having double the number of carbon atoms compared to initial haloalkane is obtained by reaction of haloalkane with sodium metal in dry ether. This reaction is called **Wurtz reaction**.

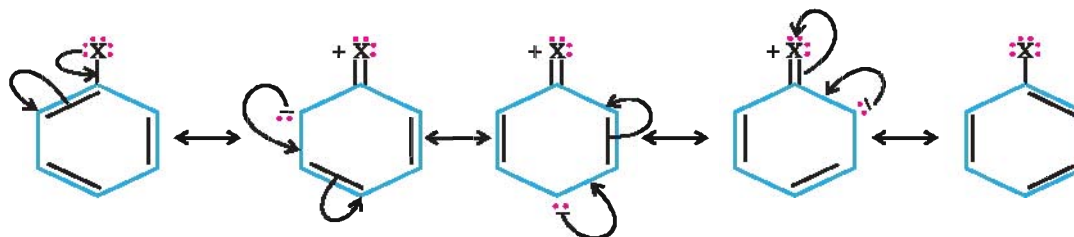




6.8.2 Reaction of Haloarene Compounds :

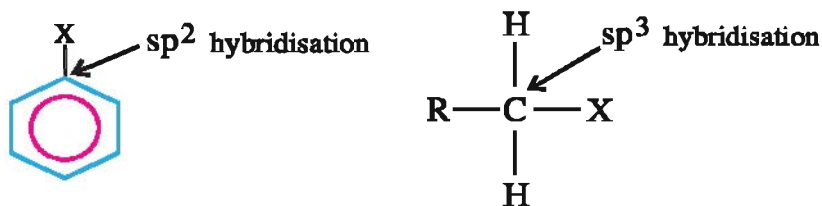
(1) Nucleophilic substitution reaction : The nucleophilic substitution reactions in haloarenes are not so easy as in haloalkanes. The reasons for nucleophilic substitution reactions in haloarene compounds being difficult are as under :

(i) Resonance effect : Halocation is formed because of electron pair on halogen atom in haloarene compound. The following resonance structures are possible for this cation.



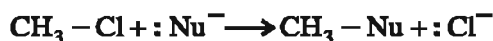
C-X bond becomes shorter due to resonance structures. As a result, carbon-halogen bond is stronger in haloarenes as compared to haloalkanes. Hence, strong reaction conditions are essential for nucleophilic substitution reaction in haloarenes e.g., The bond length of C-Cl in chlorobenzene is 169 pm which is less than the C-Cl bond length in chloromethane which is 177 pm. Hence, nucleophilic substitution reactions in chlorobenzene are difficult.

(ii) Difference in hybridisation of carbon atom in C-X bond : Carbon atom attached with halogen in haloarene compounds possesses sp^2 hybridisation while carbon atom attached with halogen in haloalkane compounds possesses sp^3 hybridisation.

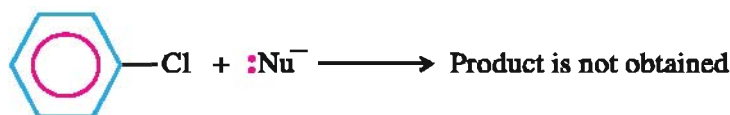


The carbon atom of haloarene, having sp^2 hybridisation possesses more electronegativity as compared to sp^3 hybridisation containing carbon atom in haloalkane; hence it attracts electron pair of C-X bond towards it. As a result the C-X bond length becomes shorter (169 pm). More energy will be required to break C-X bond which is shorter than C-X bond length in haloalkanes. As a result the reactivity of nucleophilic substitution of haloarene compounds is less in comparison to reactivity of haloalkane compounds.

(iii) Unstable phenyl cation : As phenyl cation is formed in haloarene compounds, generally self ionisation is not possible under general conditions. The resonance form of phenyl cation decreases the stability of self-ionisation reaction. Hence, $\text{S}_\text{N}1$ reaction is not possible in haloarene compounds.



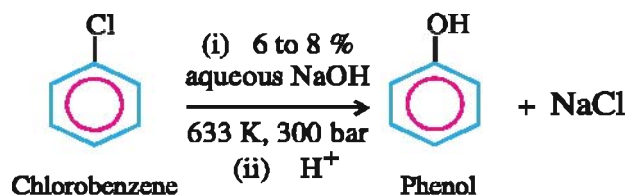
1-Chloromethane



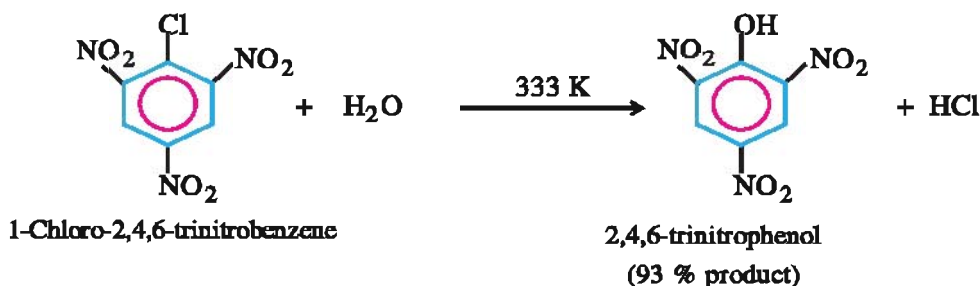
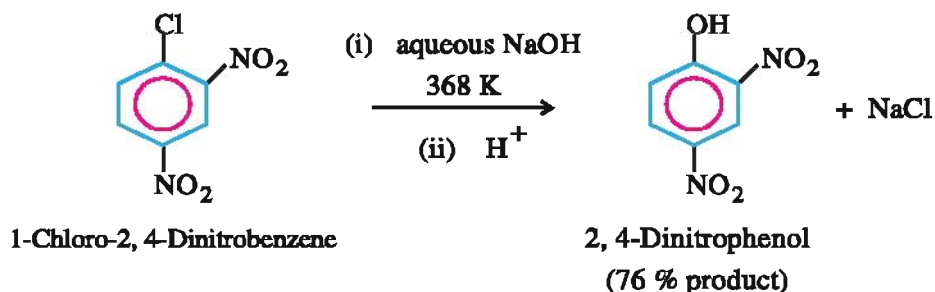
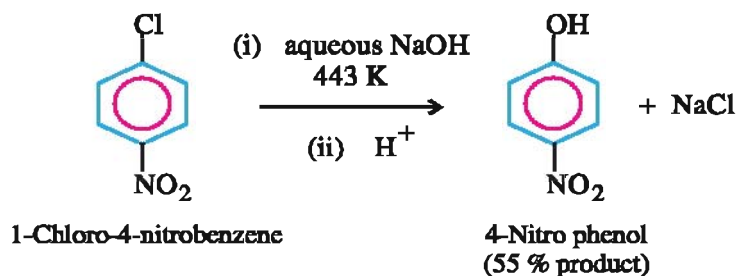
Chlorobenzene

Reactions : The nucleophilic substitution reactions in haloarenes under, strong conditions are as follows :

(i) Substitution by OH^- group : Phenol is formed by reaction of chlorobenzene with 6 to 8% aqueous NaOH at 633 K temperature and 300 bar pressure. This process called **Dow process**.

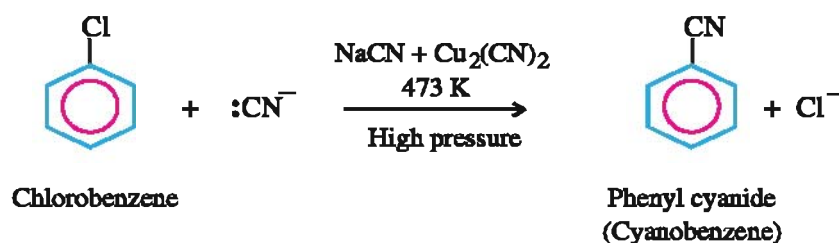


(ii) Substitution of Cl atom by OH^- group in presence of electron attracting group ($-\text{NO}_2$):



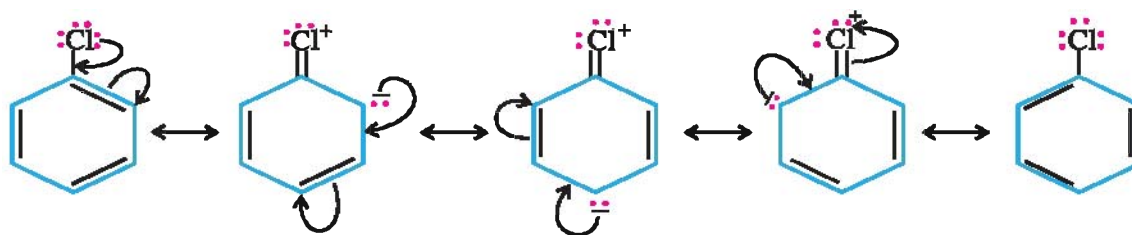
If the electron attracting group ($-\text{NO}_2$) is attached in ortho or para position of chlorobenzene, then in strong reaction conditions like high temperature about 443 K chloride (Cl^-) is substituted by ($:\text{OH}^-$) group and 55% product is obtained. If the electron attracting group ($-\text{NO}_2$) are in both ortho and para positions, then substitution of (Cl^-) by ($:\text{OH}^-$) group takes place at high temperature like 368 K and 76 % product is obtained. But, when electron attracting group ($-\text{NO}_2$) attached to two ortho and one para positions i.e. at all the three places, then by heating at 333 K temperature, chloride (Cl^-) is substituted easily by ($:\text{OH}^-$) group and about 93 % 2,4,6 trinitrophenol (TNP) product is obtained.

(iii) Substitution by $:\text{CN}^-$ group : Phenyl cyanide is formed by reaction of chlorobenzene with NaCN in presence of $\text{Cu}_2(\text{CN})_2$ at 473 K temperature.



(2) Electrophilic substitution reactions : In haloarene compounds inspite of halogen group producing ortho-para directing effect, it decreases reactivity of benzene nucleus. Hence, halogen groups differ from other ortho-para directing group.

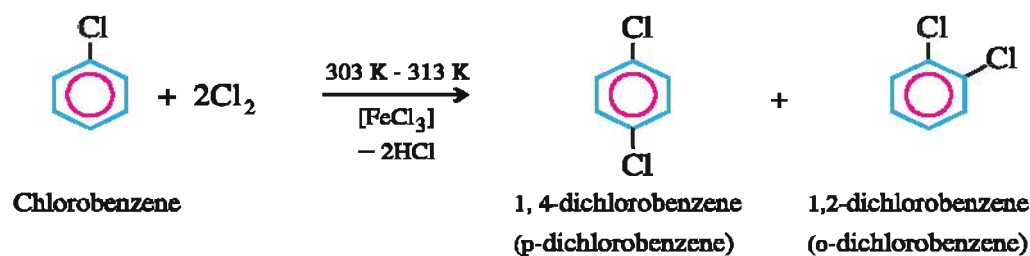
Negative inductive effect ($-\text{I}$ effect) is produced in chlorobenzene because of electronegative chlorine in chlorobenzene. The possibility of resonance structures increase because of non-bonding electron pairs on chlorine atom; which can be seen from the following structures :



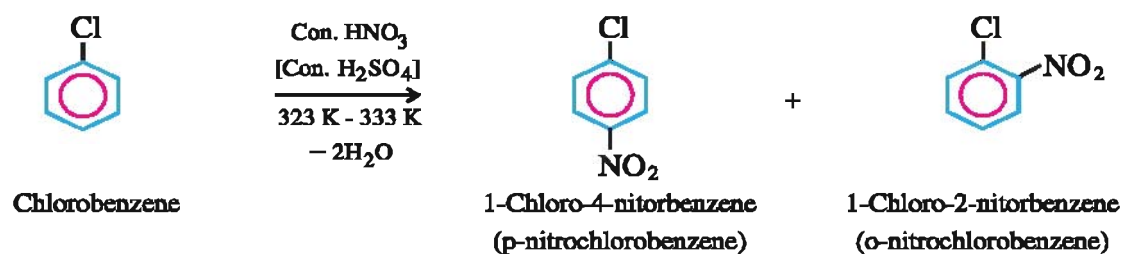
Because of resonance, the electron density of ortho and para positions, increases more than meta position. Because of negative inductive effect ($-\text{I}$) of chlorine, attracts electron from phenyl nucleus. As a result the negative inductive effect ($-\text{I}$) increases more than the resonance. Because of this benzene ring tries to be inert. Hence electrophilic substitution in haloarene compounds by chlorine are slow. In relation to benzene, in chlorobenzene, strong reaction conditions are necessary.

Certain electrophilic substitution reactions found in chlorobenzene such as halogenation, nitration, sulphonation and Friedel-Crafts reaction are shown below :

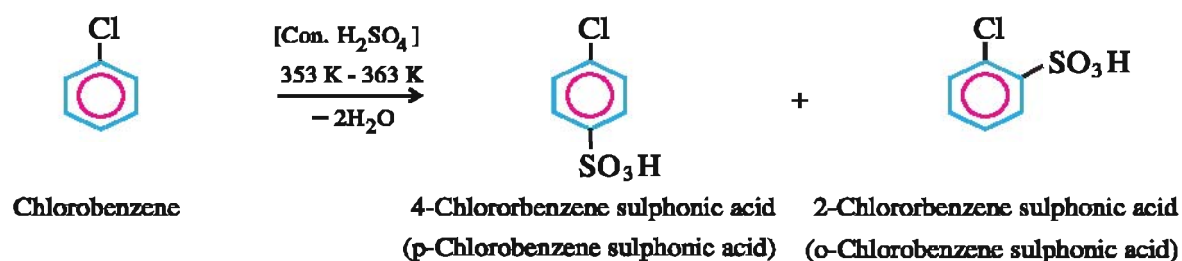
(a) Chlorination :



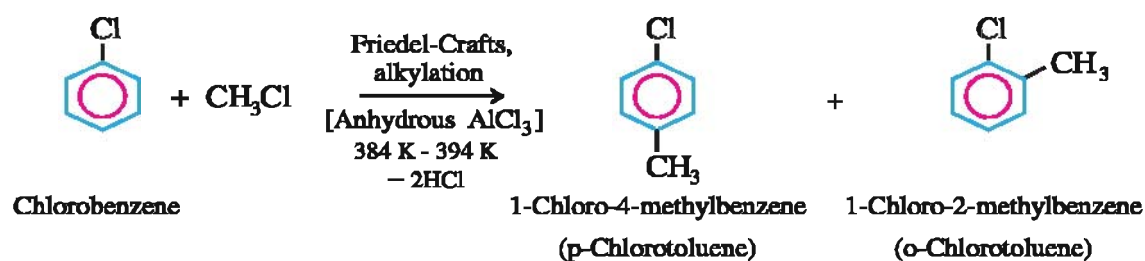
(b) Nitration :



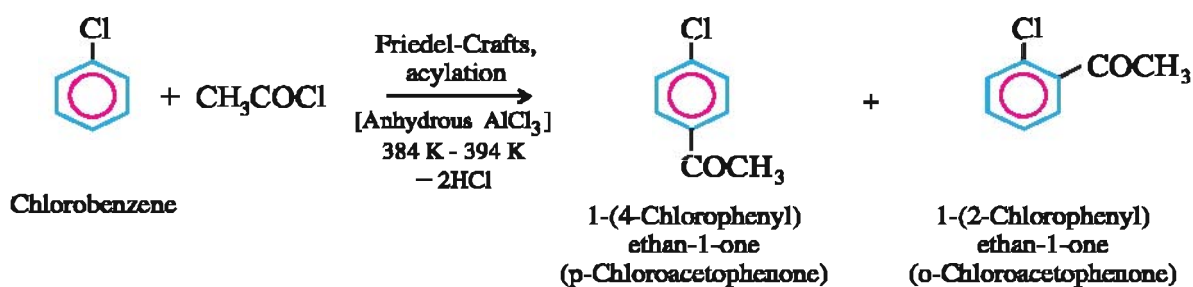
(c) Sulphonation :



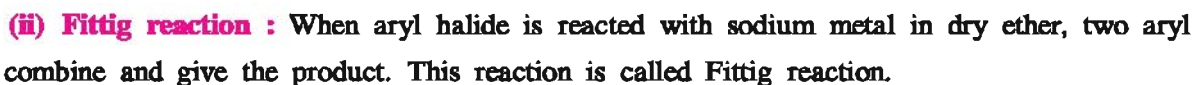
(d) Friedel-Crafts Alkylation :



(e) Friedel-Crafts Acylation :



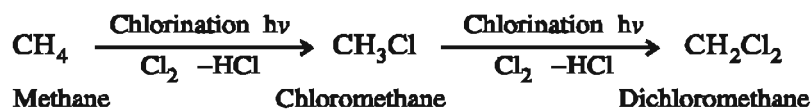
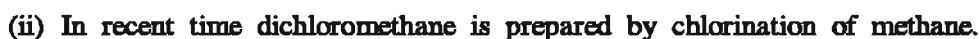
(i) Wurtz-Fittig reaction : Toluene is obtained by reaction of mixture of chlorobenzene and chloride with sodium metal in dry ether. This reaction is called Wurtz-Fittig reaction.



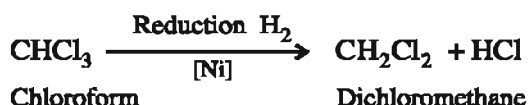
(1) Dichloromethane –CH₂Cl₂ (Methylene chloride) :

Preparation :

(i) Dichloromethane is formed by reduction of chloroform (CHCl_3) in presence of $\text{Zn} + \text{HCl}$.



(iii) Dichloromethane is obtained by reduction of chloroform.



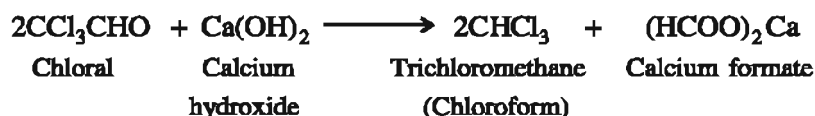
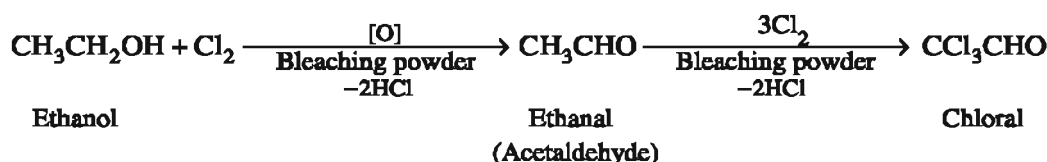
Properties and Uses :

- Dichloromethane is a colourless liquid.
- Its boiling point is 313 K.
- It is useful as solvent in industries. Mostly it is used as solvent in the production of chemicals used in removal of colour. It is harmful to nervous system. If it comes in direct contact of eye it damages the cornea.
- In addition, if it comes in direct contact of skin, red rashes are formed.

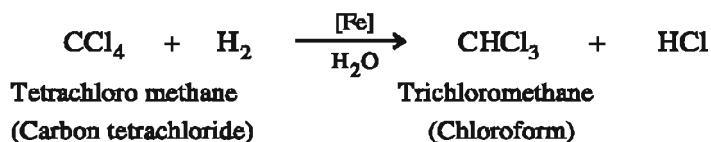
(2) Trichloromethane CHCl_3 (Chloroform)

Preparation :

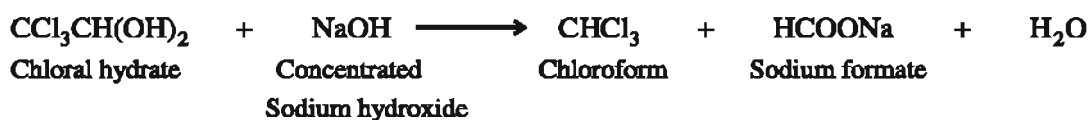
(i) Chloroform is obtained by reaction of ethanol with dichlorine gas in presence of bleaching powder.



(ii) Chloroform is formed by partial reduction of carbon tetrachloride with the help of water in the presence of iron.



(iii) Pure chloroform is obtained by reaction of chloral hydrate with concentrated alkali.



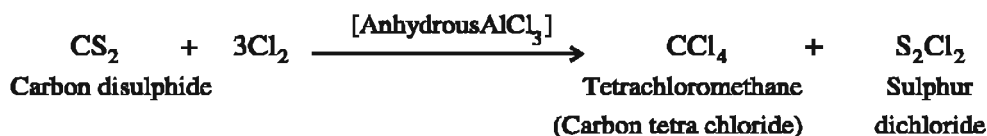
Properties and uses :

- Chloroform is a colourless liquid.
- Its boiling point is 334 K.

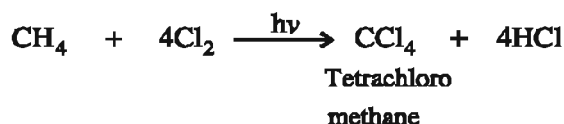
- Its vapour is combustible.
- It possesses sweet smell.
- It is soluble in alcohol and ether.
- If kept open in air, poisonous substance carbonyl chloride (COCl_2) is formed which is known as phosgene.
- Chloroform used as anesthetic should not be converted to phosgene and so alcohol is added to it.
- Chloroform is used as solvent. In addition, it is used as anesthetic for making patient unconscious during operation.

(3) Tetrachloromethane : CCl_4 (Carbon tetrachloride) :

(i) Tetrachloromethane is formed by reaction of carbon disulphide with dichlorine gas in presence of anhydrous AlCl_3 as catalyst.



(ii) Tetrachloro methane is formed by chlorination of methane.



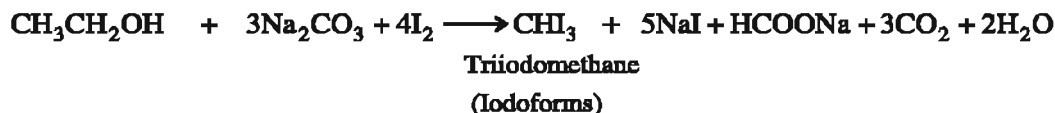
Properties and uses :

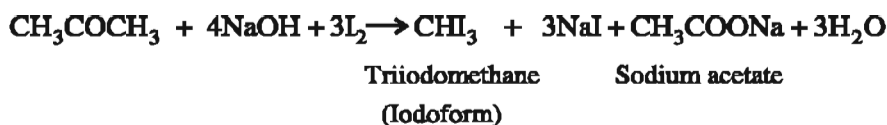
- Carbon tetrachloride is a colourless, fragrant liquid heavier than water.
- It is insoluble in water; but is soluble in ethanol and ether.
- Its boiling point is 350 K.
- CCl_4 is used under the name of pyrene for extinguishing the fire in substances like oil, fat and petrol because its vapour is not combustible.

It is stable at higher temperature (about 773 K). When it comes in contact with water at high temperature, poisonous substance phosgene is formed. Hence, care is to be taken while extinguishing the fire. It is useful as solvent in industry and drycleaning.

(4) Triiodomethane CHI_3 (Iodoform) :

Preparation : Iodoform is formed by the reaction of alcohol containing CH_3CHOH -group or acetone with iodine and solution of sodium carbonate or dilute NaOH solution.



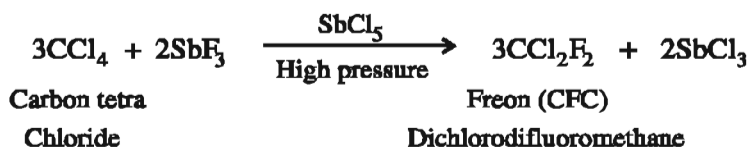


Properties and Uses :

- Iodoform is light yellow coloured crystalline, smell processing substance.
- Its melting point is 392 K. It is insoluble in water but dissolves in organic liquids like ethanol, ether etc.
- As iodine is liberated from iodoform, it is useful as antiseptic in medicines.

(5) Dichlorodifluoro methane (CCl_2F_2) Freon (Chlorofluorocarbon) :

Preparation : Chlorofluoro carbon is prepared by reaction between carbon tetrachloride and antimony trifluoride at high pressure in presence of antimony pentachloride.



These compounds have got a long series in which CCl_2F_2 is known as freon 12.

Properties and Uses :

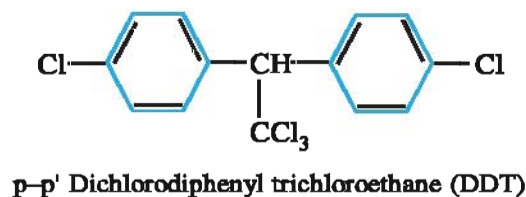
- Freon is a colourless, odourless gas.
- Its boiling point is 243 K.
- Metal does not corrode because of its effect.

It is more used in refrigerator and air conditioner. Freons CCl_2F_2 and $\text{C}_2\text{Cl}_2\text{F}_4$ series are used in them. Fragrant substances are used in aerosol mixtures of insecticide substances. In this, Freon-22, CClF_3 , CCl_2F_2 , CCl_3F etc. are also useful.

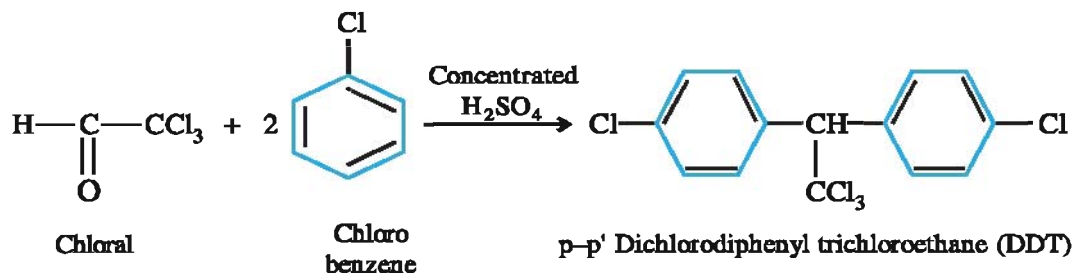
CFC is proved harmful to ozone layer.

(6) p-p' Dichlorodiphenyl trichloro ethane (DDT) :

Structural formula :



Preparation : DDT is formed by reaction of chloral and chlorobenzene in presence of concentrated sulphuric acid.



Properties and Uses :

- DDT is a white solid substance.
- It gives pungent smell of chlorine and the eyes get irritated, there is a possibility of cancer, if it enters the body.
- It is useful as household insecticides.

SUMMARY

The classification of haloalkane and haloarene compounds is made on the basis of one, two, three or more halogen atoms, respectively as mono, di, tri and polyform. They are classified into primary, secondary, and tertiary halides according to their characteristics combined with carbon with functional group halogen. In addition, the classification of halo compounds, halogen having carbon possessing sp^3 or sp^2 hybridisation as alkyl, allylic, benzylic, vinyl and aryl halide is also made.

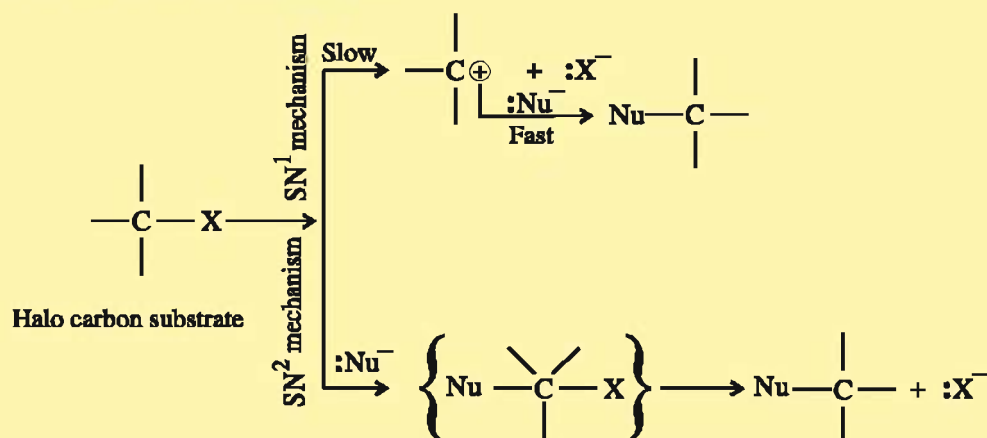
Prefix halo is used for IUPAC nomenclature of alkyl halide and aryl halide viz. for F, Cl, Br, I as fluoro, chloro, bromo, iodo respectively.

In these compounds, the electronegativity of halogen is more than that of carbon. $\text{C}^{\delta+}-\text{X}^{\delta-}$ bond becomes polar and partial positive charge on carbon and partial negative charge on halogen are produced.

Preparation of haloalkane compounds can be made by substitution of hydroxyl-OH group by halogen -X. Alkyl halides, or aryl halides can be prepared in the same way by halogenation from hydrocarbon, by electrophilic substitution in cyclic hydrocarbon, by addition reaction in alkene, by exchange of halogen etc.

In halocarbon compounds $\text{C}^{\delta+}-\text{X}^{\delta-}$ bond being polar, intermolecular attraction forces are more and so their boiling points are found to be higher in comparison to their corresponding hydrocarbons. As C-X bond length is shorter in haloarene than in haloalkane, their boiling points are higher. Halocarbon compounds are sparingly soluble in water but becomes soluble in organic solvents.

In alkyl halide because of the polarity of $C^{\delta+}-X^{\delta-}$ bond in alkyl halide, nucleophilic reagents ($:Nu^-$) are attracted by carbon having partial positive charge, they give nucleophilic substitution reactions. The reaction mechanism of these substitution reactions are classified in two parts in the form of SN^1 and SN^2 .



According to chemical kinetics principle, SN^1 is a first order reaction, while SN^2 is a second order reaction. The stability of carbocation depends on electron donating group, inductive effect (I) and resonance factor.

From stereochemistry point of view, because of the optical activity of chiral carbon produced from halocarbon compounds, racemic mixture is obtained in the form of product.

On the basis of chemical characteristics of haloalkane compounds, elimination reaction, Grignard reaction with metals, Wurtz reaction, different products can be obtained.

The reactions carried out by haloarene compounds viz. in nucleophilic substitution reactions, resonance effect, difference in hybridisation of C-X bond, effect of unstable phenyl cation, different products can be obtained.

Haloarene compounds give electrophilic substitution reactions. In addition, under strong reaction conditions gives nucleophilic reactions also.

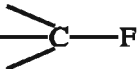
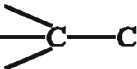
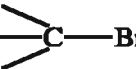
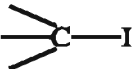
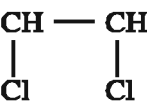
Phenol can be obtained by substitution of functional group $-X$ of haloarene by $-OH$ group. Similarly arylcyanide can be obtained by substitution of $-X$ by $-CN$. Electrophilic substitution reactions occurring in phenyl nucleus of haloarene, are more stable because of their resonance structures. In these reactions the ortho-para products of halogenation, nitration, sulphonation, Friedel-Crafts explains ortho-para directing effect of halogen functional group.

Haloarene with sodium metal gives different reactions like Wurtz, Fittig reaction.

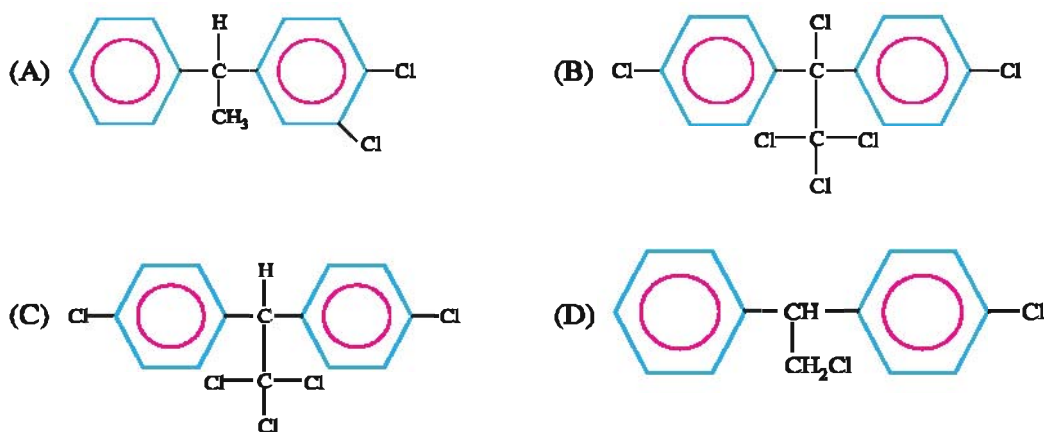
In certain important halocarbon compounds dichloromethane (CH_2Cl_2), trichloromethane (CHCl_3), Chloral (CCl_3CHO), tetrachloromethane (CCl_4), iodoform (CHI_3), freon, DDT etc. are included. Most of these compounds are not easily decomposed and so they are harmful to ozone layer; they are proved to be dangerous for environment.

EXERCISE

1. Select the proper choice from the given multiple choices :

- (1) In haloalkane bond is formed between carbon and halogen.
(A) Ionic (B) van der Waals (C) Covalent (D) Hydrogen
- (2) In haloarene compounds, halogen combines with carbon having which hybridisation ?
(A) sp^2 (B) sp^3 (C) sp (D) dsp^2
- (3) In haloalkane, carbon in C-X bond possesses which partial electric charge ?
(A) Chargeless (B) Positive (C) Negative (D) Anionic
- (4) Which of the following bonds is the strongest ?
(A)  (B)  (C)  (D) 
- (5) Which of the following is vinyl halide ?
(A) CH_2Cl_2 (B) $CH_2=CH-Cl$ (C) $CH\equiv C-Cl$ (D) 
- (6) What is B in $R-OH + PX_5 \rightarrow R-X + B + HX$?
(A) $HPOX_3$ (B) H_3PO_3 (C) POX_3 (D) H_3PO_2
- (7) Which catalyst is used in preparation of bromobenzene by bromination of benzene ?
(A) $FeBr_3$ (B) HBr (C) $AlBr_3$ (D) Br_2
- (8) By which name the reaction $CH_3-Br + Ag-F \rightarrow CH_3F + AgBr$ is known ?
(A) Grignard (B) Wurtz (C) Fittig (D) Swartz
- (9) What are nucleophilic reagents according to Lewis theory ?
(A) Acid (B) Base (C) Neutral molecules (D) Positive ions
- (10) On which of the following factors the stability of carbocation depends ?
(A) Resonance (B) Temperature (C) Transition state (D) Reaction rate

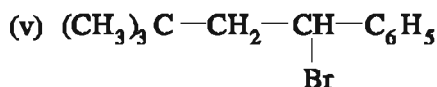
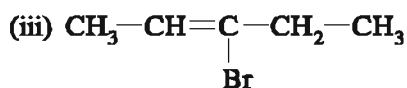
- (11) What is called an optically active substance ?
- (A) Which reflects polarised light
- (B) Which rotates the plane of polarised light
- (C) Which increases rate of polarised light
- (D) Which absorbs polarised light
- (12) Arrange giving the sequence order to Br, Cl, F and H combined with asymmetric carbon.
- (A) H, Cl, Br, F (B) H, Cl, F, Br (C) Br, Cl, F, H (D) H, F, Br, Cl
- (13) $2\text{C}_6\text{H}_5\text{-X} + 2\text{Na} \xrightarrow{\text{Dry ether}} \text{A} + 2\text{NaX}$. What will be the product A obtained in the reaction ?
- (A) $\text{C}_6\text{H}_5\text{Cl}$ (B) $\text{C}_{12}\text{H}_{10}$ (C) $\text{C}_6\text{H}_5\text{-C}_6\text{H}_5$ (D) $\text{C}_6\text{H}_5\text{Na}$
- (14) Which is the structural formula of DDT ?



- (15) Which substance is inflammable ?
- (A) DDT (B) Freon (C) CH_4 (D) CHCl_3

2. Answer the following questions in short :

- (1) Write IUPAC names of the following substances.
- (i) $(\text{CH}_3)_2\text{CH}-\text{CH}(\text{Cl})-\text{CH}_3$ (ii) $\text{CH}_3-\text{CH}(\text{CH}_3)-\text{CH}(\text{CH}_3)-\text{Cl}$
- (iii) $\text{CH}_3-\text{C}(\text{C}_2\text{H}_5)_2-\text{CH}_2-\text{Cl}$ (iv) $\text{CH}_3-\text{C}(\text{ClC}_2\text{H}_5)-\text{CH}_2-\text{Br}$
- (v) $\text{Cl}-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_2-\text{Cl}$
- (2) Classify the following compounds in the form as alkyl, allylic, benzylic, vinyl or aryl halide.
- (i) $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$ (ii) $\text{CH}_3-\text{CH}=\text{CH}-\text{Cl}$



(3) Write the structural formulas of the following :

(i) 2-bromo-3 methyl pentane

(ii) 1-chloro-4-methyl cyclohexane

(iii) 1, 4-dichlorobut-2-ene

(iv) 1-chloro-4-secondary butyl-2-methyl benzene

(4) Give examples of 1° , 2° , 3° haloalkanes.

(5) Give reason for polarity of C-X bond in haloalkane.

(6) Give examples of 1° , 2° , 3° benzyl halide.

(7) What is meant by chirality ?

(8) In haloalkanes intermolecular attraction forces are more than those in alkanes ? Why ?

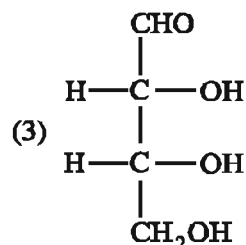
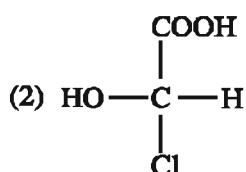
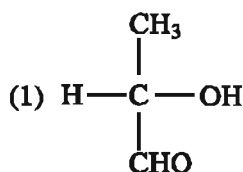
(9) What is called SN^1 reaction ?

(10) Why SN^2 reaction is called bimolecular substitution reaction ?

(11) Which poisonous substance is formed by keeping chloroform open in air ?

(12) On which factor, the stability of carbocation depends ?

(13) Mention D or L configurations in following compounds :



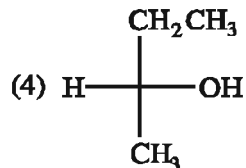
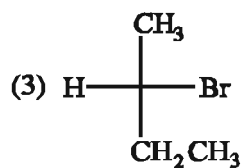
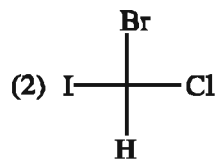
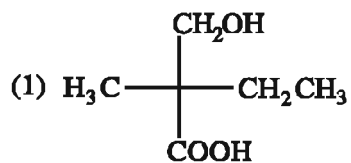
3. Write answers of the following questions :

- (1) Mention the classification of haloalkanes on the basis of number of halogen atoms giving suitable examples.
- (2) Explain the reaction for preparation of haloalkane from alcohol giving reaction equation.
- (3) Describe Zaitsev's formula giving suitable example.
- (4) Give only equations of substitution reaction in haloarenes by OH^- group.
- (5) Write preparation of methylene chloride.
- (6) Mention properties of dichloromethane.
- (7) Is 2, 3-dibromobutane optically active ?
- (8) Explain the factors affecting the rate of reaction in SN^1 and SN^2 reactions.
- (9) Write physical properties and uses of chloroform.
- (10) Write a note on resonance effect in the nucleophilic substitution reaction of haloarenes.

4. Give answers of the following questions in detail :

- (1) Explain classification of haloalkane and haloarene compounds on the basis of number of halogen atoms.
- (2) Write a note on C-X bond.
- (3) Write a note on β -elimination reaction in haloalkane.
- (4) Give following electrophilic reactions :
 - (i) Chlorination (ii) Nitration (iii) Sulphonation
 - (iv) Friedel-Crafts acylation (v) Friedel-Crafts alkylation
- (5) Explain in detail Fittig reaction of haloarene.
- (6) Explain in detail SN^1 reaction.
- (7) Write a note on SN^2 reaction.
- (8) Mention preparation, properties and uses of tetrachloromethane.
- (9) Give preparation of iodoform and its importance in medical field.
- (10) Mention types of freon and explain freon as coolant.

- (11) Explain stability of carbocation.
- (12) Explain the two steps to determine R-S nomenclature.
- (13) Explain D-L nomenclature.
- (14) Write a note about any three polyhalogen compounds.
- (15) Mention R or S configuration of following compounds :



Unit

7

Alcohol, Phenol and Ether Compounds

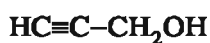
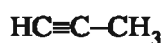
7.1 Introduction

We have learnt earlier that when one or more hydrogen atoms of a hydrocarbon, are substituted by another atom or a group of atoms (functional group) then new organic compounds are formed. When the hydrogen atom attached to saturated carbon of hydrocarbon, is substituted by hydroxyl group ($-OH$) then alcohol is formed.

e.g.,

Hydrocarbon

Alcohol



Thus, the general formula of alcohol is $R-OH$; where R = alkyl group or alkenyl or alkynyl or arylalkyl group. If the hydrogen atom attached to the carbon atom of an aromatic, is substituted by hydroxyl group then phenol is formed.

e.g.,

Hydrocarbon



Phenol



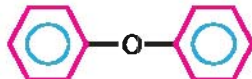
Thus, **the general formula of phenol is $\text{Ar}-\text{OH}$** ; where Ar = aryl group. If the hydrogen atom of hydroxyl group of alcohol or phenol, is substituted by alkyl or alkenyl or alkynyl or aryl group then ether is formed.

e.g.,

Alcohol/Phenol



Ether



Thus, **the general formula of ether is $\text{R}_1/\text{Ar}_1-\text{O}-\text{R}_2/\text{Ar}_2$** ; where R_1 and R_2 = alkyl or alkenyl or alkynyl group and Ar_1 and Ar_2 = aryl group.

Alcohols and ethers have same general formula $\text{C}_n\text{H}_{2n+2}\text{O}$ but due to different functional groups, they are called functional group isomers. For example, ethanol and methoxymethane have same molecular formula $\text{C}_2\text{H}_6\text{O}$ but their structural formula $\text{CH}_3\text{CH}_2\text{OH}$ and CH_3OCH_3 possess different functional groups.

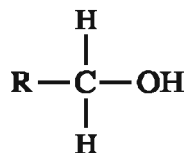
7.2 Classification of Alcohols

The classification of alcohols is carried out in three types depending on the carbon which has been attached to the hydroxyl group in structure of alcohol, viz (1) Primary (1°) alcohol, (2) Secondary (2°) alcohol and (3) Tertiary (3°) alcohol.

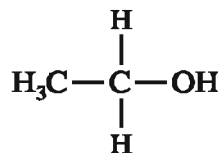
(1) Primary (1°) alcohol : Alcohol, in which the hydroxyl group is attached to primary carbon is called primary (1°) alcohol.

(2) Secondary (2°) alcohol : Alcohol, in which the hydroxyl group is attached to secondary carbon is called secondary (2°) alcohol.

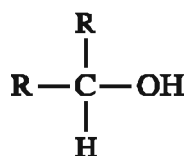
(3) Tertiary (3°) alcohol : Alcohol, in which the hydroxyl group is attached to tertiary carbon is called tertiary (3°) alcohol.



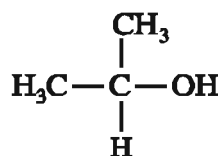
Primary (1°) alcohol.



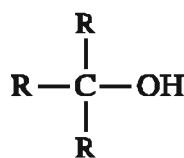
Primary (1°) alcohol.



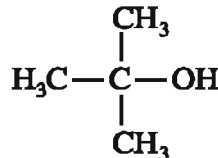
Secondary (2°) alcohol.



Secondary (2°) alcohol.



Tertiary (3°) alcohol.



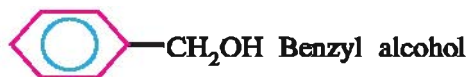
Tertiary (3°) alcohol.

7.3 Nomenclature of Alcohols

Common name : For the common name of alcohols, the **alcohol**, word is added after the name of hydrocarbon group which is attached to the $-\text{OH}$ group.

e.g., CH_3OH Methyl alcohol

$\text{CH}_3\text{CH}_2\text{OH}$ Ethyl alcohol



IUPAC name :

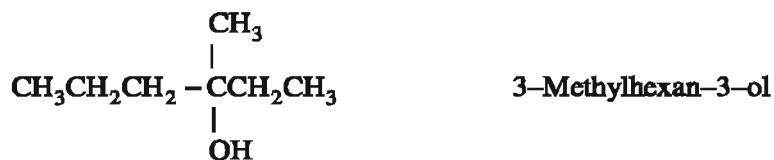
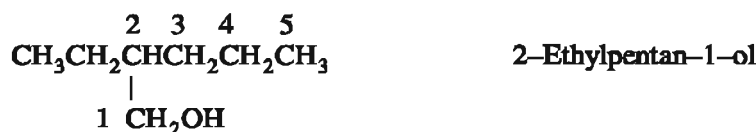
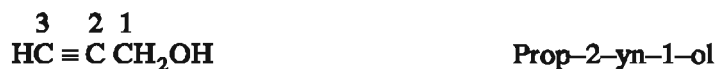
(1) In alcohol, the longest carbon chain of hydrocarbon containing hydroxyl group is selected. Then dropping the last letter 'e' from the name of hydrocarbon, the suffix 'ol' is added. For example, by dropping 'e' from methane and adding the suffix 'ol', the derived name will be **methan + ol = methanol** and in that manner from ethane, **ethan + ol = ethanol** is derived.

e.g., CH_3OH Methanol

$\text{CH}_3\text{CH}_2\text{OH}$ Ethanol

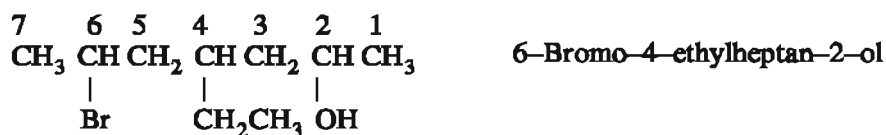
(2) In alcohols containing more than two carbon atoms the smallest number for location of the position of hydroxyl group is placed before the suffix 'ol'.

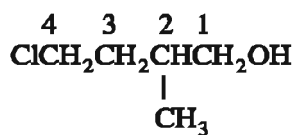
e.g.,



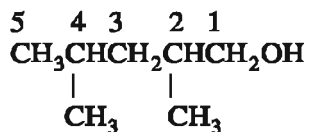
(3) If more than one substituents are present in alcohol molecule then in nomenclature they are presented in alphabetical order.

e.g.,





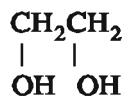
4-Chloro-2-methylbutan-1-ol



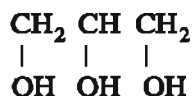
2, 4-Dimethylpentan-1-ol

(4) If alcohols containing more than one hydroxyl groups, the di, tri.....etc. prefix for two, three.... etc. number of hydroxyl groups respectively, are written before the suffix 'ol'. Here last alphabate 'e' is not removed from name of hydrocarbon.

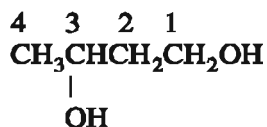
e.g.,



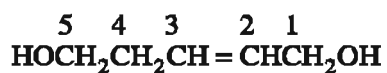
Ethane-1,2-diol



Propane-1,2,3-triol



Butane-1,3-diol



Pent-2-ene-1,5-diol

(5) In alcohols the hydroxyl group attached to the carbon of cyclic system is given the first number.

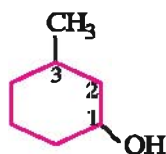
e.g.,



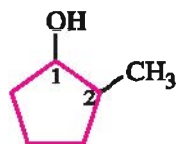
Cyclopentanol



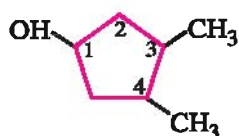
Cyclohexanol



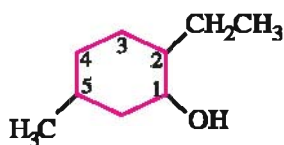
3-Methylcyclohexanol



2-Methylcyclopentanol



3,4-Dimethylcyclopentanol



2-Ethyl-5-methylcyclohexanol

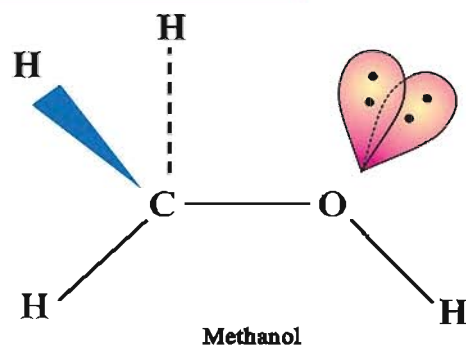
The structural formula, IUPAC name, common name, their type and boiling point of some alcohol molecules are presented in table 7.1.

Table 7.1 Alcohol compounds

Structural formula	IUPAC name	Common name	Type	Boiling point (K)
CH_3OH	Methanol	Methyl alcohol	1^0	338
$\text{CH}_3\text{CH}_2\text{OH}$	Ethanol	Ethyl alcohol	1^0	351
$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$	Propan-1-ol	n-Propyl alcohol	1^0	370
$\begin{array}{c} \text{CH}_3\text{CHCH}_3 \\ \\ \text{OH} \end{array}$	Propan-2-ol	Isopropyl alcohol	2^0	355
$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$	Butan-1-ol	n-Butyl alcohol	1^0	390
$\begin{array}{c} \text{CH}_3\text{CHCH}_2\text{OH} \\ \\ \text{CH}_3 \end{array}$	2-Methylpropan-1-ol	Isobutyl alcohol	1^0	381

$\begin{array}{c} \text{CH}_3\text{CH}_2\text{CHCH}_3 \\ \\ \text{OH} \end{array}$	Butan-2-ol	Secondary butyl alcohol	2 ^o	373
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\ \\ \text{OH} \end{array}$	2-Methylpropan-2-ol	Tertiary butyl alcohol	3 ^o	356
$\begin{array}{c} \text{CH}_2\text{CH}_2 \\ \quad \\ \text{OH} \quad \text{OH} \end{array}$	Ethane-1,2-diol	Ethylene glycol	1 ^o 1 ^o	471
$\begin{array}{c} \text{CH}_2 \quad \text{CH} \quad \text{CH}_2 \\ \quad \quad \\ \text{OH} \quad \text{OH} \quad \text{OH} \end{array}$	Propane-1,2,3-triol	Glycerol (Glycerine)	1 ^o 2 ^o 1 ^o	563
	Phenylmethanol	Benzyl alcohol	1 ^o	478

7.4 Electronic Structure of Alcohols



C-O and O-H

σ -bond

C and O

sp^3 hybridisation

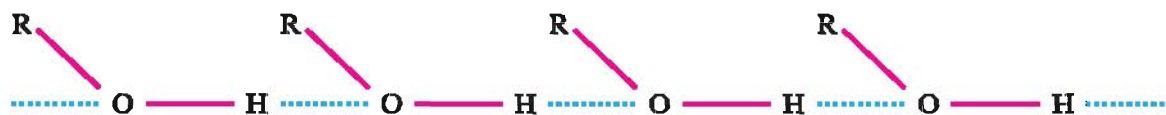
C-O-H angle

108.5^o

7.5 Physical Properties of Alcohols

In alcohol compounds, the electronegativity of oxygen atom (3.5) of hydroxyl group is higher than the electronegativity of hydrogen atom (2.1). Due to this, it induces partial negative charge (δ^-) on oxygen atom and partial positive charge (δ^+) on hydrogen atom. So $\text{O}^{\delta-}-\text{H}^{\delta+}$ bond becomes polar and in liquid alcohols intermolecular hydrogen bond is formed, as a result intermolecular

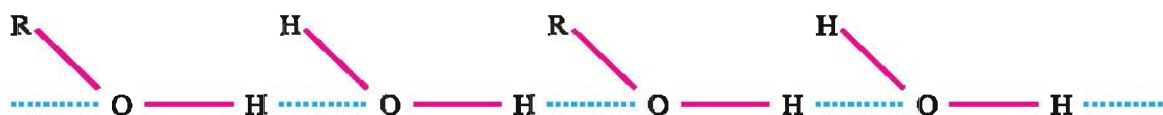
attraction increases. The higher energy is required to break these attraction forces. If there are more attractive forces in the molecules of liquid alcohol, then more thermal energy is required to break and to convert it in gaseous forms. So the values of boiling point increase. This type of hydrogen bond is not formed in alkanes because the polar bond is absent in them. Therefore **the boiling points of alcohols are higher than those of alkanes having approximately equal molecular mass.** e.g., boiling point of ethanol (molecular mass = 46 gram mole⁻¹, b.p. = 351 K) is higher than that of propane (molecular mass = 44 gram mole⁻¹, b.p. = 231 K) and boiling point of propanol (molecular mass = 60 gram mole⁻¹, b.p. = 370 K) is higher than that of butane (molecular mass = 58 gram mole⁻¹, b.p. = 273 K).



Intermolecular hydrogen bond between alcohol molecules

In linear series of primary alcohols, the boiling point increases gradually as the number of carbon atoms increases; because increasing with the number of carbon, intermolecular distance is decreased, as a result intermolecular attraction forces increase. e.g., while going from methanol to butan-1-ol, the boiling point gradually increases (Table 7.1), as compared to primary (1^o) alcohols containing three or more than three carbon atoms and with the same molecular formula, in secondary (2^o) alcohol and as compared to secondary (2^o) alcohol, in tertiary (3^o) alcohols having more branched chains. As a result it decreases the area of surface and decreases the intermolecular attraction with increase in intermolecular distance. Therefore **among alcohols containing same molecular formula, secondary alcohol has lower boiling point than primary alcohol and tertiary alcohol has lower boiling point than secondary alcohol.** This is due to decrease in the intermolecular attraction. e.g., boiling point of propan-2-ol (secondary) (b.p. 355 K) is lower than that of propan-1-ol (primary) (b.p. 370 K) and alcohols having molecular formula C₄H₉OH have three isomers butan-1-ol (primary) (b.p. 390 K), butan-2-ol (secondary) (b.p. 373 K) and 2-methyl propan-2-ol (tertiary) (b.p. 356 K) whose boiling points are decreasing respectively.

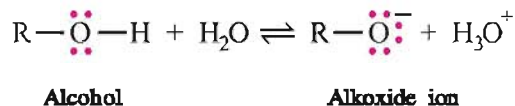
In aqueous solution of alcohols, the intermolecular attraction between them increases due to the formation of hydrogen bond between polar molecule water and polar molecule alcohol. Therefore, lower molecular mass containing methanol and ethanol are more soluble in water. As the number of carbon atoms of hydrocarbon group in alcohol increases, the molecular masses also increase; as a result solubility in water decreases, because of formation of hydrogen bond cannot be possible with an increase in length of chain.



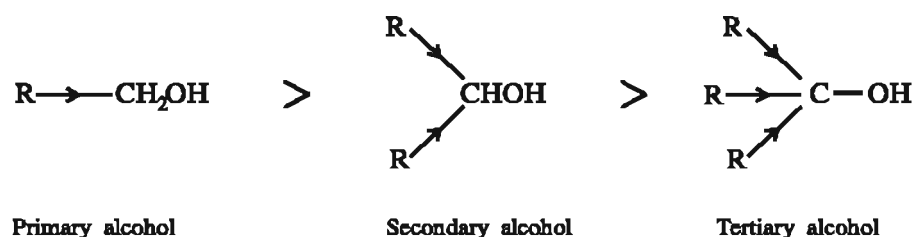
Intermolecular hydrogen bond between alcohol and water molecules

As we studied earlier, there is formation of hydrogen bond between two molecules of alcohol and the alcohol and water molecules. This results in the **increase in the boiling point and solubility in water with increase in number of hydroxyl groups in alcohols.** For example, boiling points and solubilities in water of ethanol (b.p. 351 K), ethane-1,2-diol (b.p. 471 K) and propane-1,2,3-triol (b.p. 563 K) increase gradually.

Acidity of Alcohols : Aqueous solution of alcohols possess slight acidic property due to polar O—H bond present in them. Alcohols have acidic property similar to that of water. Most of alcohols (except methanol) are less acidic than water.



In alcohol compounds, an electron releasing group—R(—CH₃, —C₂H₅) increases the electron density of O—H bond, so results in decrease of the polarity of O—H bond. As a result the acidic property decreases. Thus, the order of acidic strength of alcohol compounds is,

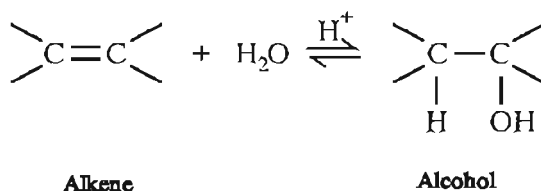


7.6 Preparation of Alcohols

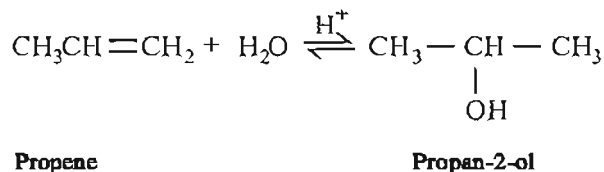
Alcohols can be prepared by different methods,

(1) Alcohol from alkene compounds :

(i) By acid catalysed hydration : Alkene compounds form alcohols by reaction with water in presence of acid catalyst.

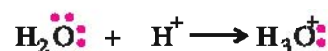


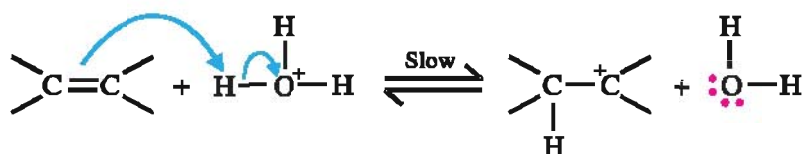
If unsymmetrical alkene is used as a starting material then the addition reaction follows the **Markonikov's rule** and give alcohols.



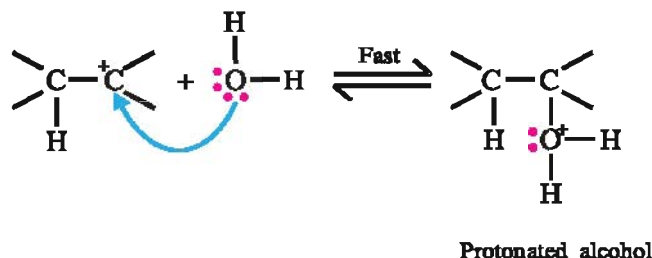
Mechanism :

Step-1 : Alkene molecule accepts a proton from aqueous acid H₃O⁺ and forms carbocation.

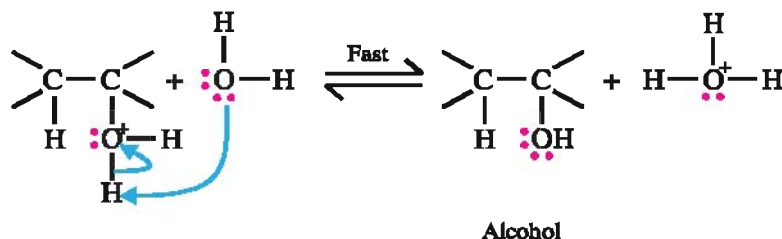




Step-2 : Nucleophilic reagent (water) attacks on carbocation and forms protonated alcohol.



Step-3 : Proton is removed and an alcohol is formed



Note : Concept about drawing of Curved Arrow (↷) : It is easy to understand the transfer of electrons by curved arrow (↷ or ↶) in the mechanism of reaction. This curved arrow is always drawn away from more electron containing (generally negatively charged) species towards a less electron containing (generally positively charged) species. The arrow starts from the electron source (electron pair or bond). It does not start from an atom. This curved arrow does not indicate the transfer of an atom.

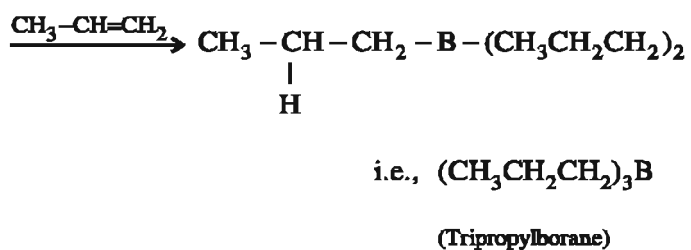
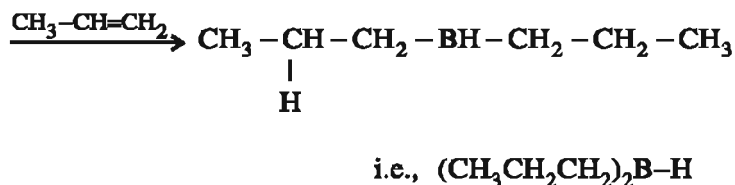
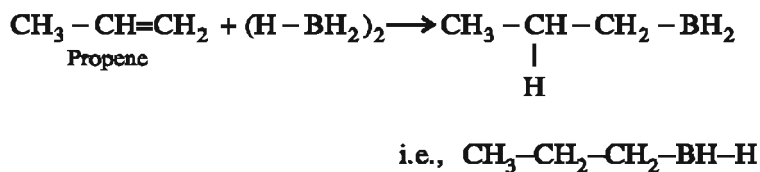
(ii) By hydroboration-oxidation : For the preparation of alcohol in laboratory, the indirect addition of water in alkene compounds can be achieved in presence of diborane (BH_3)₂. Diborane reacts with alkenes to give trialkylborane as addition product, which is called hydroboration reaction. Trialkylborane is oxidised to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.



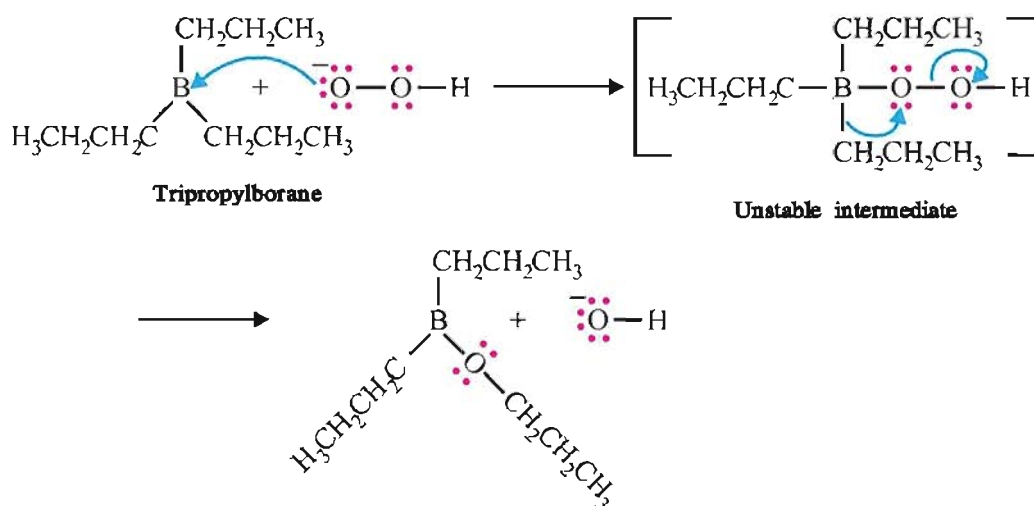
Mechanism :

Step-1 : Alk-1-ene like propene reacts with diborane and forms trialkylborane. It is the result of addition of boron hydride to double bond of three molecules of alk-1-ene. This hydroboration reaction follows the **anti-Markonikov rule**. So, boron atom gets attached to the carbon atom

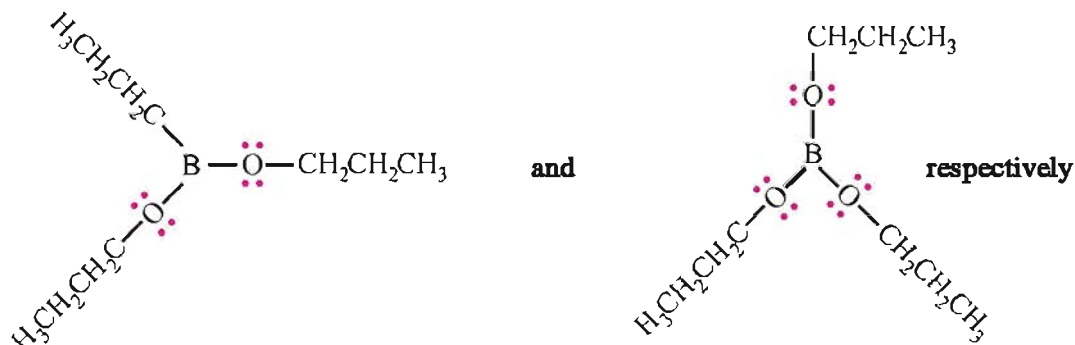
involved in double bond in alkene with more hydrogen atoms and hydrogen gets attached to the carbon atom with fewer hydrogen atoms.



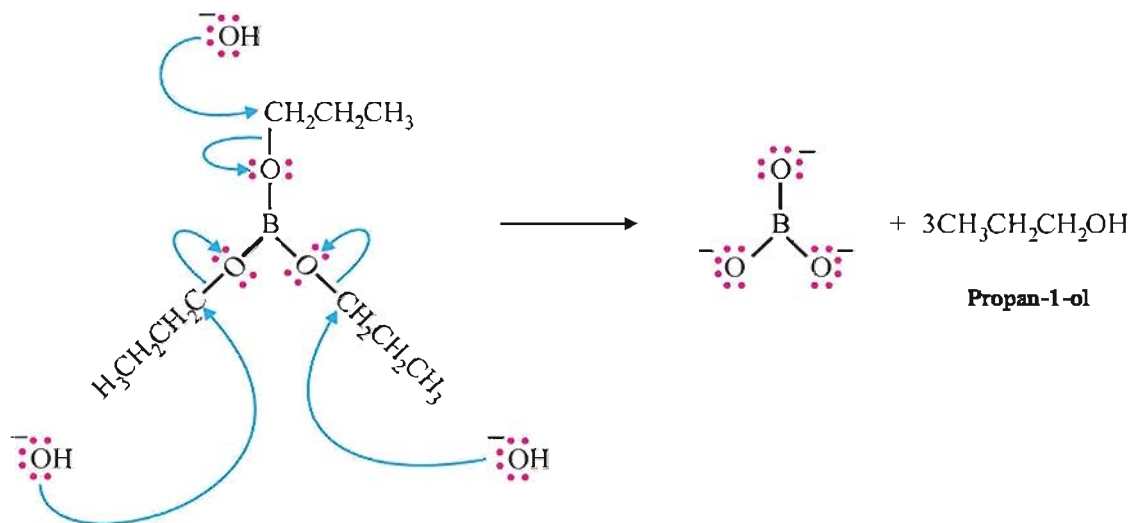
Step-2 : Tripropyl borane is oxidised to tripropyl borate by of hydrogen peroxide.



Two times repetition of this reaction forms

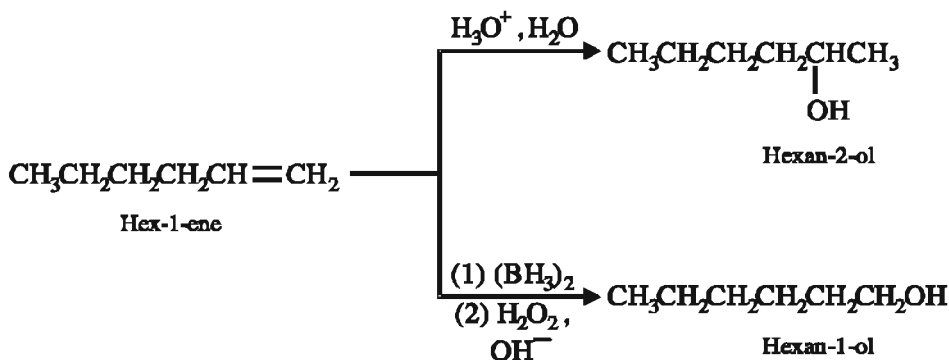


Step-3 : The hydrolysis of tripropylborate forms three molecules of propan-1-ol and borate ion in basic medium.



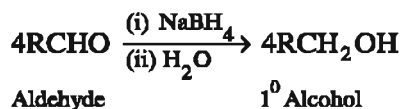
Thus, during the preparation of alcohols by acid catalysed hydration, the -OH group gets attached to the carbon atom involved in double bond of alkene, with fewer hydrogen atoms. In contrast to this, during the preparation of alcohols by hydroboration-oxidation, the -OH group gets attached to the carbon atom involved in double bond of alkene with more hydrogen atoms.

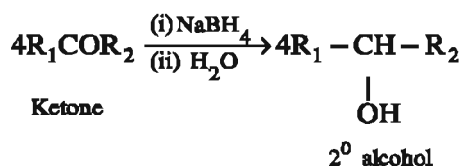
e.g.,



(2) Alcohols from carbonyl compounds :

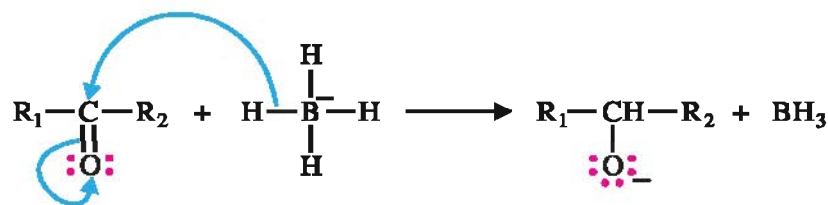
(i) By reduction of aldehydes and ketones : Alcohols can be obtained by reduction of aldehydes and ketones with sodium borohydride (NaBH_4) or lithium aluminium hydride (LiAlH_4). Reduction of aldehyde gives 1° alcohol and reduction of ketone gives 2° alcohol.



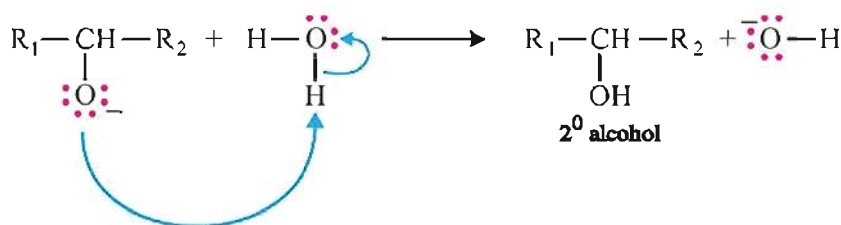


Mechanism :

Step-1 : Hydride ion ($:H^-$) of sodium borohydride reagent combines with carbonyl carbon and forms alkoxide ion.

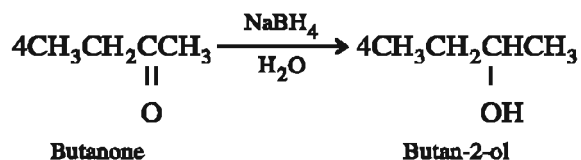
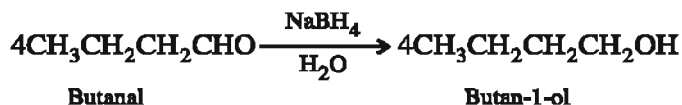


Step-2 : Alkoxide ion reacts with water and forms alcohol.

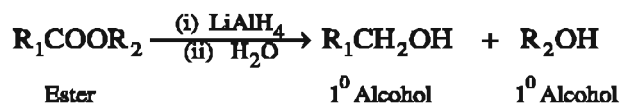
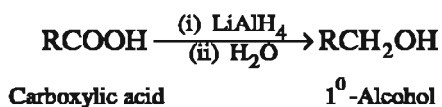


If the reaction is repeated three times more then as a result four moles of ketone form four moles of 2° alcohols. For this 1 mole of sodium borohydride is consumed.

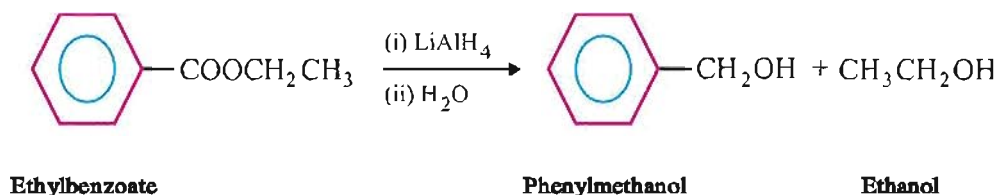
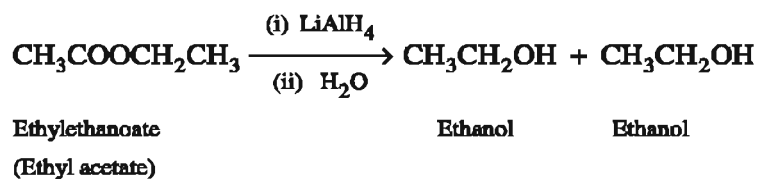
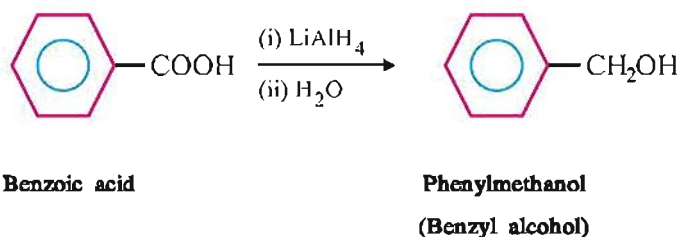
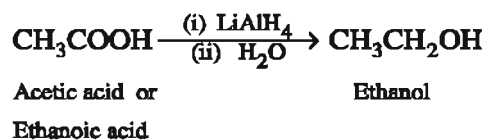
In this mechanism, putting the H instead of R_2 the mechanism of formation of alcohols by reduction of aldehyde can be understood.



(ii) By reduction of carboxylic acids or esters : Reduction of carboxylic acids and esters is achieved by use of strong reducing agent like lithium aluminium hydride and primary alcohols can be obtained.

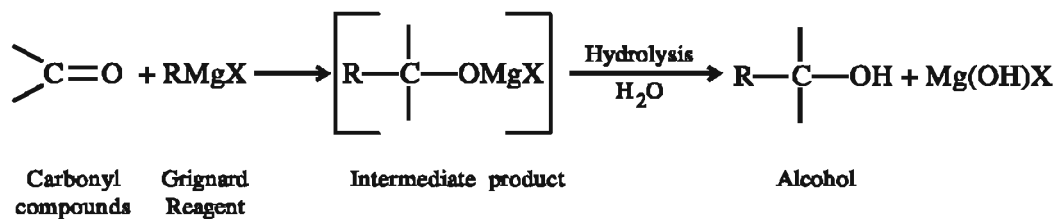


e.g.,

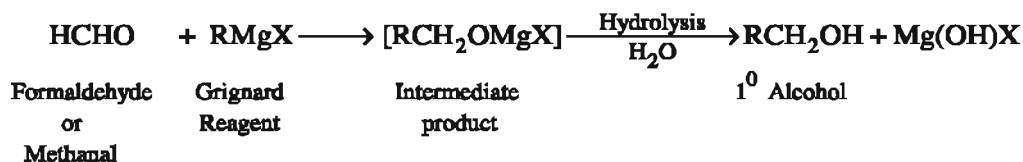


(3) Alcohols by Grignard reagents :

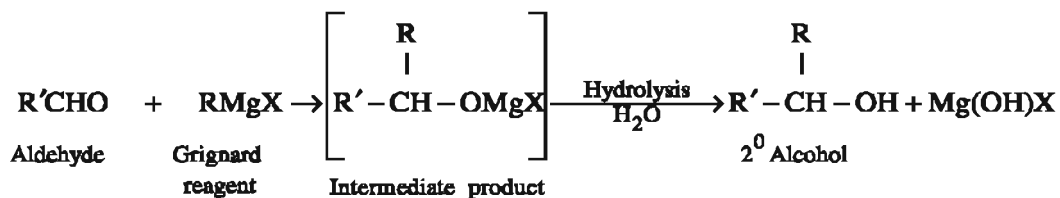
If Grignard reagents are added to carbonyl compounds then 1° , 2° and 3° alcohols are formed.



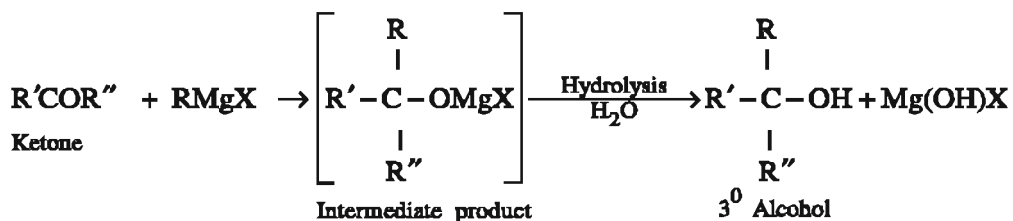
(i) Grignard reagent reacts with formaldehyde and gives 1^o alcohol.



(ii) Grignard reagent reacts with aldehyde compounds except formaldehyde and forms 2^o alcohols.

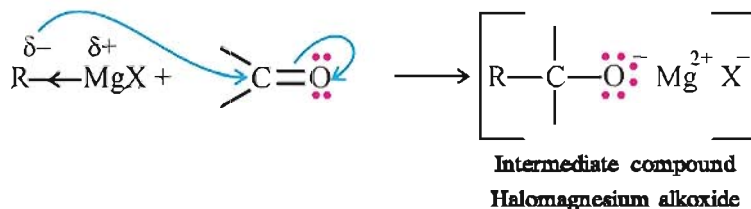


(iii) Grignard reagent reacts with ketone compounds and forms 3^o alcohols.

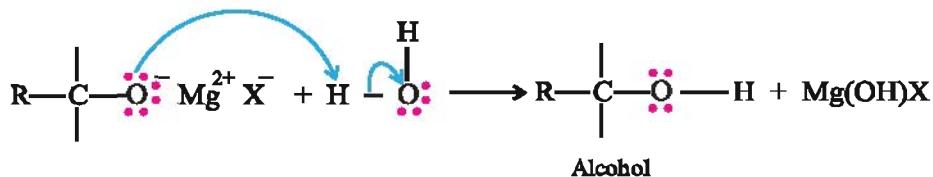


Mechanism :

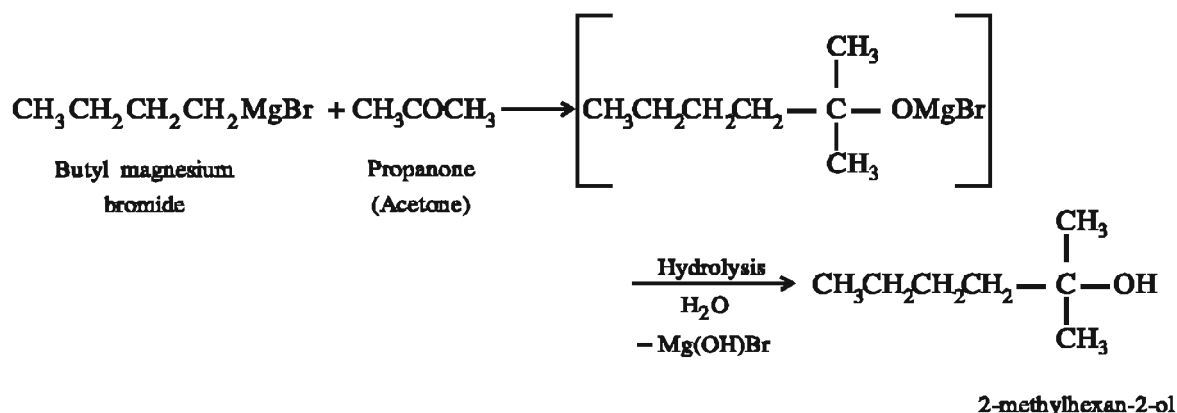
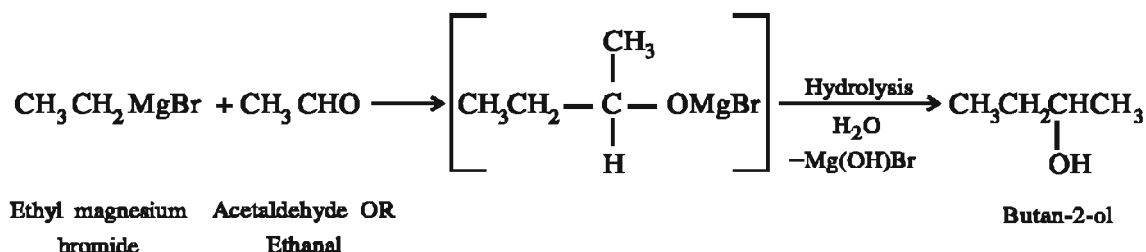
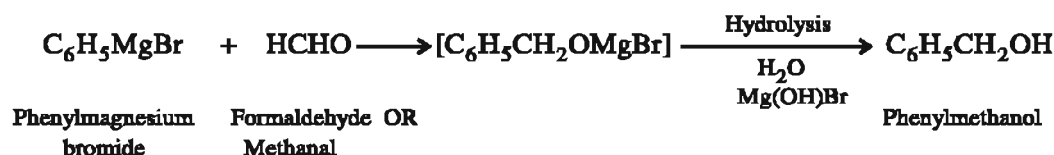
Step-1 : Grignard reagent is added to carbonyl compound and it forms intermediate compound. In Grignard reagent RMgX, the electronegativity (2.5) of carbon atom in R is higher than electronegativity (1.2) of magnesium atom and as a result the common electron pair of bond R-Mg is more attracted towards R, due to this partial negative charge on R and partial positive charge on Mg atom are induced.



Step-2 : Intermediate product reacts with water and forms alcohol.

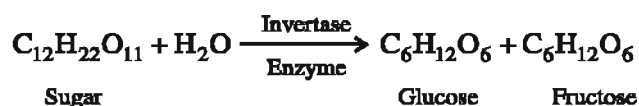


Examples of alcohols formed by Grignard reagent

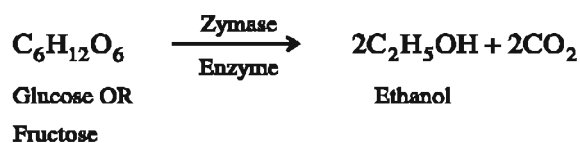


(4) Preparation of alcohol by fermentation method :

Fermentation method is most useful for preparation of ethanol. This method is extensively used for industrial production of ethanol. Sugar present in molasses is fermented by enzyme invertase, as a result glucose and fructose are formed.



Glucose and fructose are fermented by enzyme zymase found in yeast; due to this ethanol and carbon dioxide gas are formed.



Distillation of final solution produces an azeotropic mixture of 95% ethanol and 5% water i.e. only one component $\text{C}_2\text{H}_5\text{OH} \cdot \text{H}_2\text{O}$ is produced. Pure ethanol is obtained by membrane technology.

Pure ethanol is a colourless liquid. Its boiling point is 351 K. It is used as a solvent in paint industry. It is also used in preparation of a number of organic compounds.

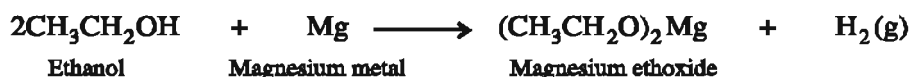
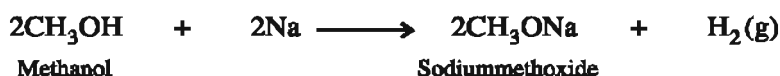
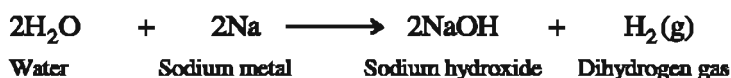
7.7 Chemical Reactions of Alcohols

There are two types of reactions in alcohols. Looking to the structure R–O–H in some reactions O–H bond is broken and in others R–O bond is broken. These reactions form different types of compounds.

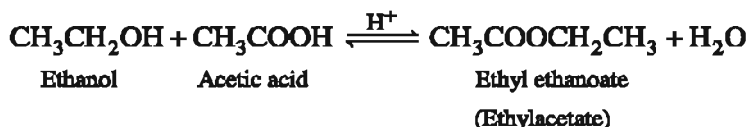
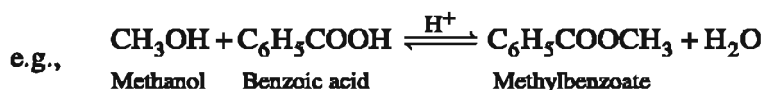
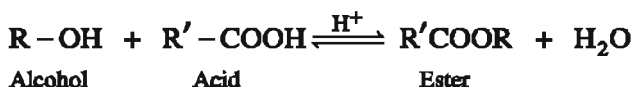
(1) Reactions involving cleavage of O–H bond :

(i) Reaction of alcohol with active metals : Like water, alcohols react with Li, Na, K, Mg, Al and other active metals to liberate dihydrogen gas and form metal alkoxides. These metal alkoxides act as stronger base than sodium hydroxide.

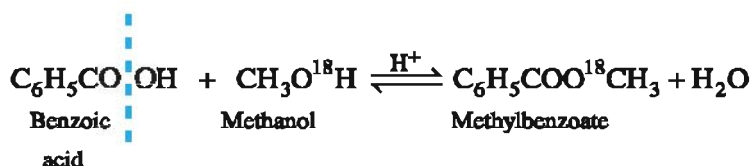
e.g.,



(ii) Reaction of alcohol with acids : Alcohols react with carboxylic acids in presence of acid catalyst to form esters through a condensation reaction. It is called **esterification**.

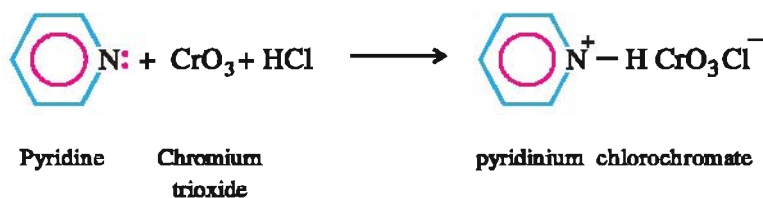
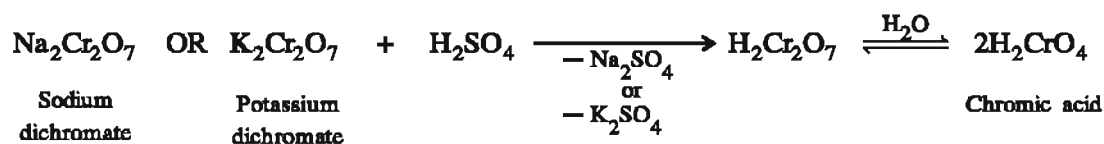


When benzoic acid reacts with methanol that has been labelled with radioactive O^{18} , the labelled O^{18} appears in the ester product. It is indicated that during the esterification the aggregate water molecule is removed as OH^- is removed from acid molecule and H^+ is removed from alcohol molecule.

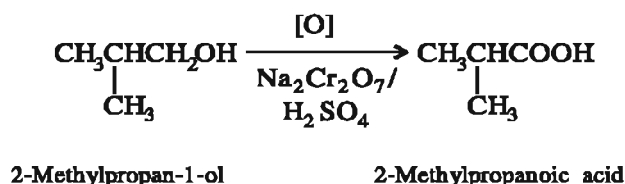
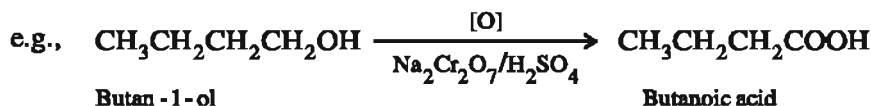
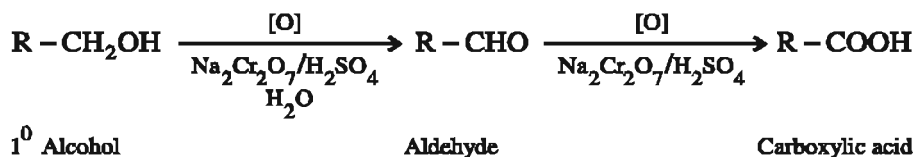


(iii) Oxidation of alcohols : During the oxidation of alcohols, one or more hydrogen atoms are lost from the carbon bearing the –OH group. The products obtained by oxidation of alcohols depend upon

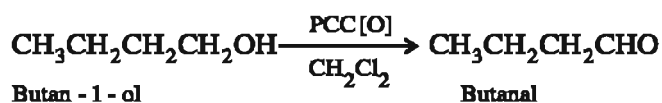
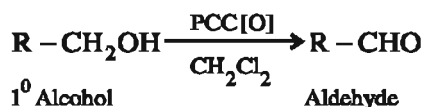
the type of alcohols and reagents. The reagents most commonly used as oxidising agents for the oxidation of alcohols are **chromic acid (H_2CrO_4)** or **potassium permanganate (KMnO_4)** or **pyridinium chlorochromate (PCC)**.

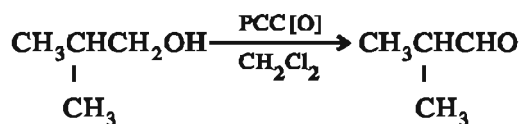


The primary alcohol is oxidised by KMnO_4 or H_2CrO_4 initially to an aldehyde. However, this aldehyde is very difficult to obtain as product because this aldehyde is more easily oxidised than the alcohol and so is converted rapidly to the carboxylic acid. Thus, **the normal product of oxidation of 1° alcohol with a strong oxidizing agent like KMnO_4 or H_2CrO_4 is a carboxylic acid.**



1° alcohol is oxidised by mild oxidizing agent like pyridinium chloro-chromate (PCC) and aldehyde is formed. Then after oxidation of aldehyde does not occur. This reaction is carried out in an anhydrous solvent such as dichloromethane (CH_2Cl_2).

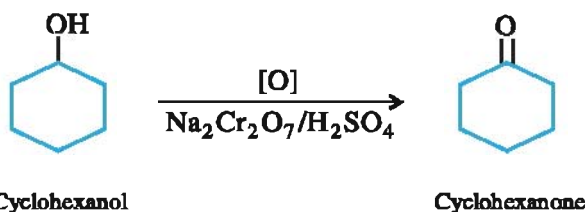
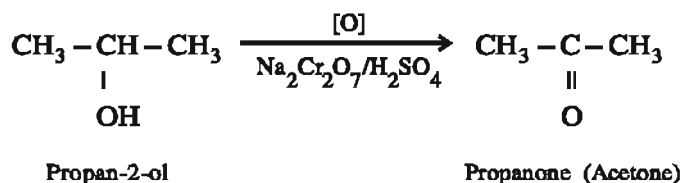
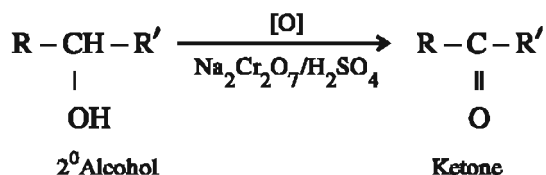




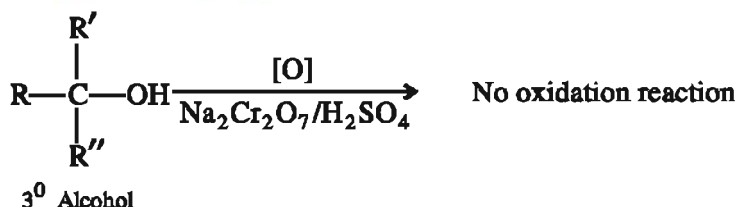
2-Methylpropan-1-ol

2-Methylpropanal

2° Alcohols are oxidised by H_2CrO_4 or KMnO_4 and form ketones.

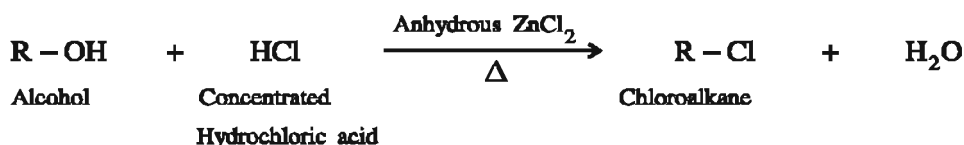


In 3° alcohols, the carbon bearing the $-\text{OH}$ group has no hydrogen, so they are not oxidized by strong oxidizing agents.



(2) Reactions involving cleavage of C-O bond :

(i) Reaction of alcohol with halogen acid : Alcohol when heated with concentrated hydrochloric acid in presence of anhydrous zinc chloride gives chloro alkane. This reaction is fast with tertiary alcohols, slow with secondary alcohols and difficult with primary alcohols.

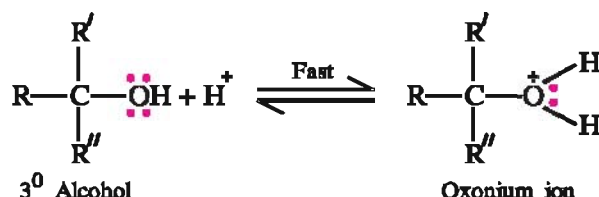


In laboratory primary, secondary and tertiary alcohols can be detected by this reaction and the method to do so is called **Lucas test**. In this test, a given sample of alcohol is mixed, shaken and

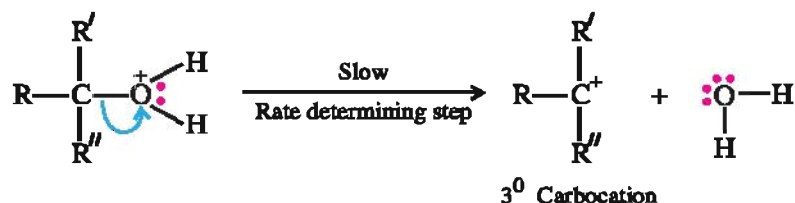
warmed slightly with anhydrous zinc chloride and concentrated hydrochloric acid and kept for some-time. If an oily drop appears in short time on the upper layer of the mixture, it must be 3^o alcohol, if it takes about five minutes to become milky, it must be 2^o alcohol; if mixture remains clear without any reaction, it must be 1^o alcohol. We will understand mechanism of reaction of tertiary alcohol with concentrated hydrochloric acid.

Mechanism :

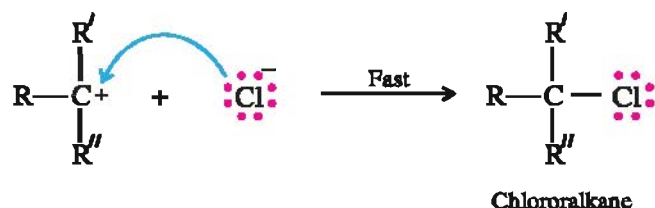
Step-1 : Tertiary alcohol is converted into an oxonium ion through protonation by H⁺ of acid. This step is fast.



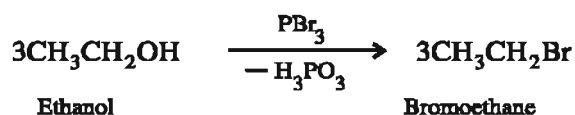
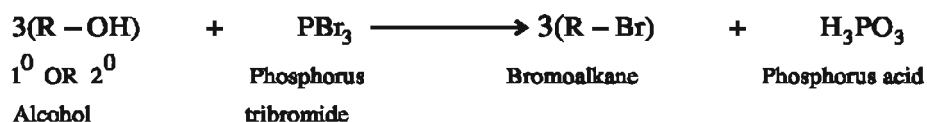
Step-2 : 3^o carbocation is formed by the loss of a water molecule from the oxonium ion. This step is slow so it is called the rate determining step.

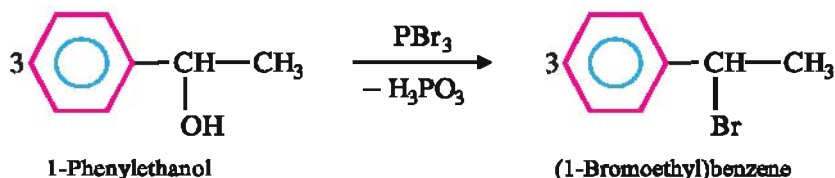
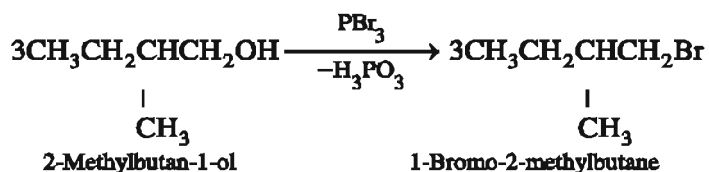


Step-3 : 3^o carbocation reacts with Cl⁻ rapidly and forms chloroalkane.



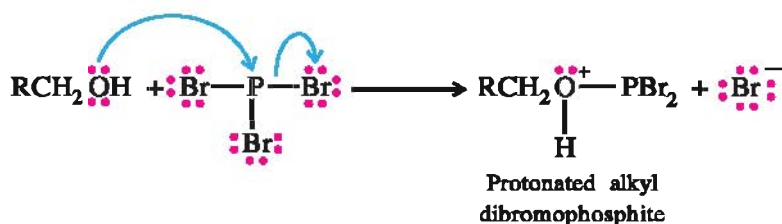
(ii) Reaction of alcohol with phosphorus tribromide : 1^o and 2^o alcohols react with phosphorus tribromide to form bromoalkane.



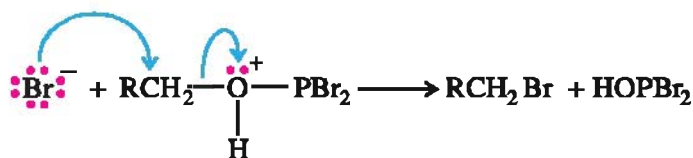


Mechanism :

Step-1 : Alcohol reacts with phosphorus tribromide and as a result intermediate compound alkyl dibromophosphite is formed.

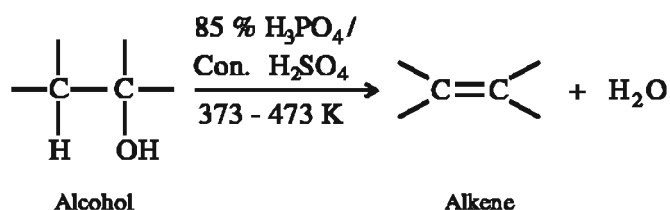


Step-2 : Bromide ion attacks on carbon atom and forms haloalkane.

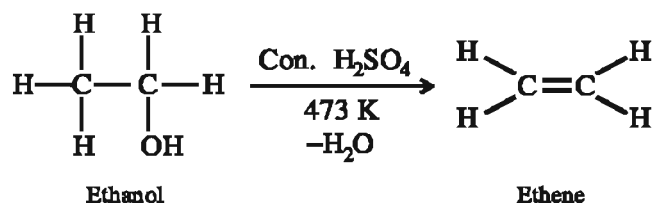


This HOPBr_2 reacts with other molecules of alcohol. Thus, at the end of the reaction three moles of haloalkanes are formed from three moles of alcohols. For this 1 mole of phosphorus tribromide is consumed.

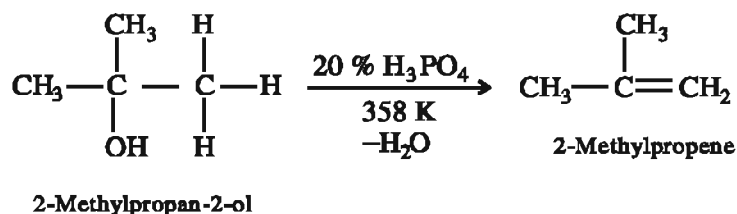
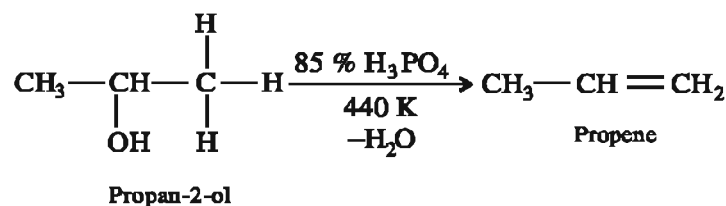
(iii) Dehydration of alcohols : An alkene is formed by elimination of a molecule of water from adjacent carbon atoms of an alcohol. **Elimination of a molecule of water is called dehydration.** In the laboratory, dehydration of alcohol is carried out by heating it in presence of 85 % phosphoric acid or concentrated sulphuric acid at 373 K to 473 K.



Ethanol (primary alcohol) is converted into ethene by heating it at 473 K.



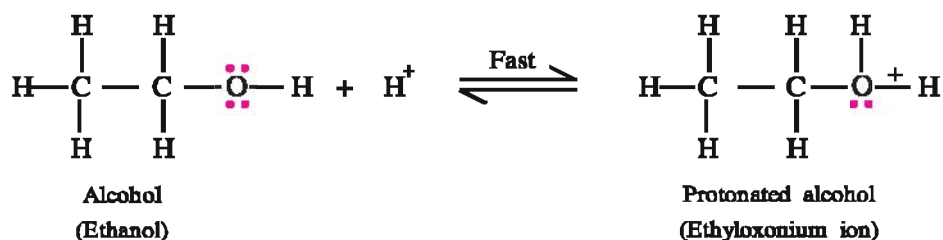
2° and 3° alcohols give dehydration reaction under milder conditions.



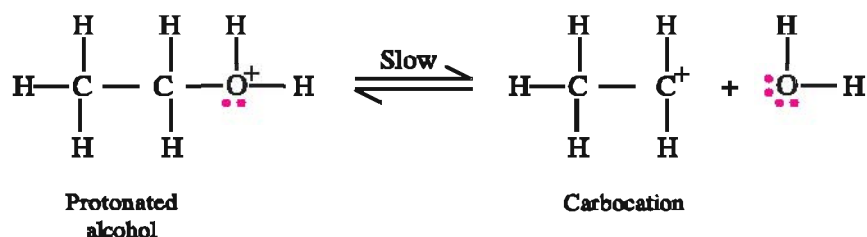
Thus, the order of ease of dehydration reaction of alcohols is 3° alcohol > 2° alcohol > 1° alcohol. Here we will understand mechanism of dehydration reaction of ethanol.

Mechanism :

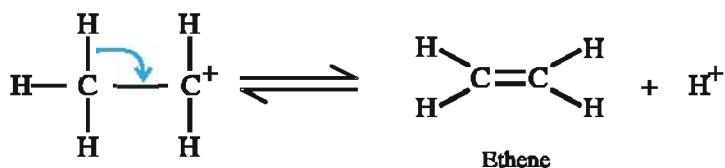
Step-1 : Ethanol is converted into ethyl oxonium ion through protonation by H⁺ of acid.



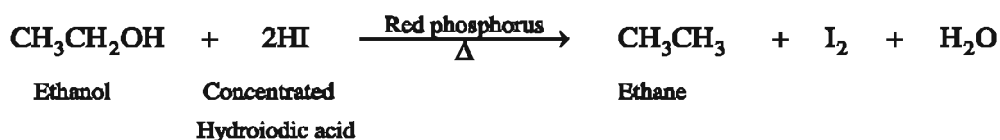
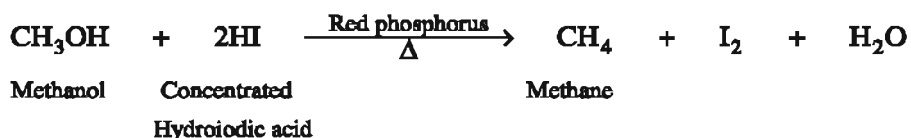
Step-2 : Carbocation is formed by the loss of a water molecule from the ethyloxonium ion. This step is slow so it is called rate determining step.



Step-3 : Ethene is formed by elimination of a proton from carbocation.




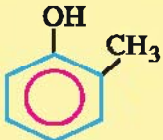
(iv) Reduction of alcohols : Reduction of alcohols by heating with red phosphorus and concentrated hydroiodic acid in a closed vessel give alkanes. By this reduction reaction, methanol gives methane and ethanol gives ethane.

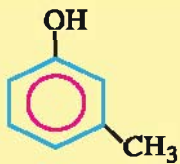

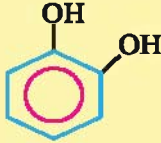
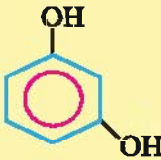

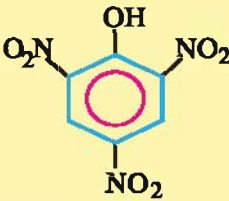
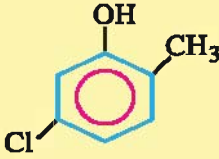


7.8 Nomenclature of Phenols

Phenol and some of its derivatives are known by their common names. e.g., Phenol, ortho-cresol, meta-cresol, para-cresol, catechol, resorcinol, hydroquinone, picric acid etc. The common names of phenol are also accepted as IUPAC names. For IUPAC nomenclature of phenol derivatives, to consider the phenol as parent hydrocarbon and mention the position of substituted other groups in aromatic ring. For this –OH group is attached to which carbon, the first number is given to it. Ortho (1, 2-disubstituted), meta (1,3-disubstituted), para (1,4-disubstituted) words are used to mention the position of substituted groups in common name. Substituted groups are written in alphabetical order. The structural formula, IUPAC name, common name of some phenol compounds are presented in table 7.2.

Table 7.2 Phenol compounds

Structural formula	IUPAC name	Common name
	Phenol	Phenol
	2-Methylphenol	o-Cresol

	3-Methylphenol	m-Cresol
	4-Methylphenol	p-Cresol
	Benzene -1, 2-diol	Catechol
	Benzene -1, 3-diol	Resorcinol
	Benzene -1, 4-diol	Hydroquinone (Quinol)
	2,4,6,- Trinitrophenol	Picric acid
	5-Chloro -2-methylphenol	—

7.9 Electronic Structure of Phenol

C–O and O–H

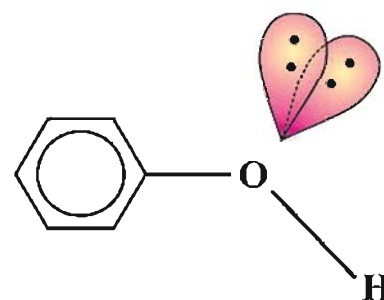
σ -bond

C sp^2 hybridisation

O sp^3 hybridisation

C–O–H angle

109°

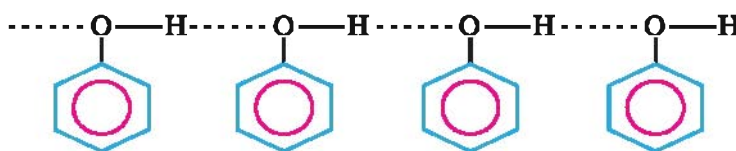


7.10 Physical Properties of Phenols

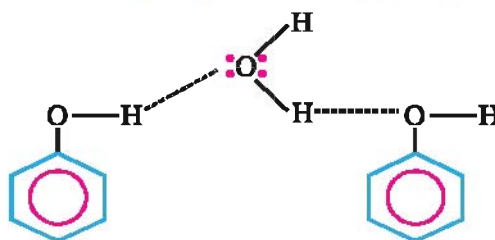
Phenol contains hydroxyl group, therefore in liquid state it forms intermolecular hydrogen bond with other molecule of phenol and with water molecule just like alcohols. Hence intermolecular attraction is increased. Due to this, phenol has higher boiling point and more solubility in water than toluene (arene compounds) and fluorobenzene (halo arene compounds) having approximately same molecular mass (table 7.3).

Table 7.3 Comparison of physical properties of phenol, arene and haloarene compounds (298 K)

Physical property	Compounds		
	Phenol	Toluene	Fluorobenzene
Molecular mass (gram mole ⁻¹)	94	92	96
Boiling point (K)	455	384	358
Solubility in water (Gram/100 ml)	8.2	0.05	0.2



Intermolecular hydrogen bond among the phenol molecules

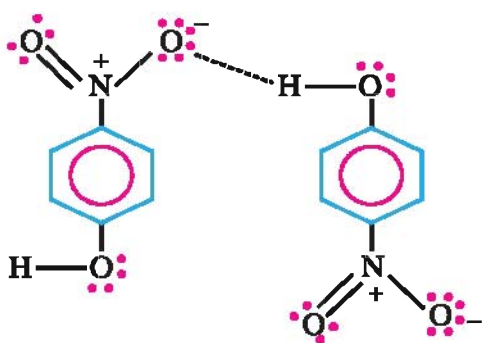


Intermolecular hydrogen bond between phenol and water molecules

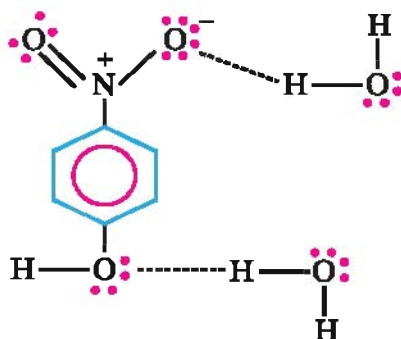
Some ortho substituted phenols like o-nitrophenol has lower melting point and less solubility in water than its m- and p- isomers (table 7.4), because m- and p- nitrophenol form intermolecular hydrogen bond with their other molecules and water molecule. But in o-nitrophenol the intramolecular hydrogen bond is formed. The hydrogen atom of hydroxyl group engaged in this bond cannot form intermolecular hydrogen bond with other molecule of o-nitrophenol and water molecule.

Table 7.4 Physical properties of isomers of nitrophenols (298 K)

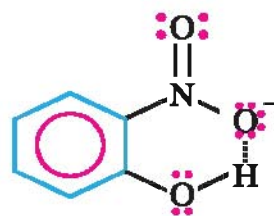
Compound	Physical properties	
	Melting point (K)	Solubility in water (gram/100 ml)
o-Nitrophenol	45	0.2
m-Nitrophenol	96	1.4
p-Nitrophenol	114	1.7



Intermolecular hydrogen bond among the p-nitrophenol molecules

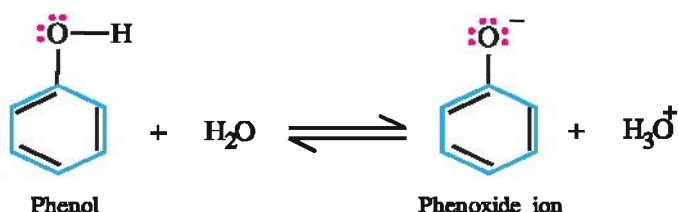


Intermolecular hydrogen bond between p-nitrophenol and water molecules

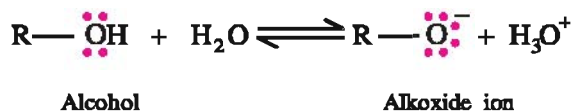


Intramolecular hydrogen bond in o-nitrophenol

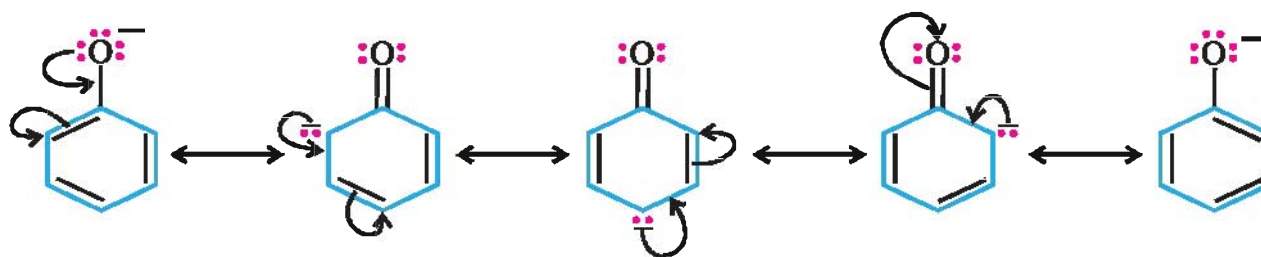
Acidity of phenol : Aqueous solution of phenol changes blue litmus paper into red. Moreover it is neutralised with solution of sodium hydroxide, but not with a solution of sodium carbonate. It indicates that phenol possesses weak acidic nature. Polar O–H bond present in phenol is responsible for acidity.



Here naturally a question will arise that which of the two from alcohol and phenol will have more acidity ? We will think about this. As we discussed previously the alkoxide ion is formed from alcohol.



In alkoxide the negative charge is localised on oxygen atom, that is its resonance forms are not possible. In phenoxide ion the negative charge on an oxygen atom becomes delocalised. Due to this more than one resonance forms of phenoxide ion are possible. Therefore stability of phenoxide ion is higher than that of alkoxide ion.

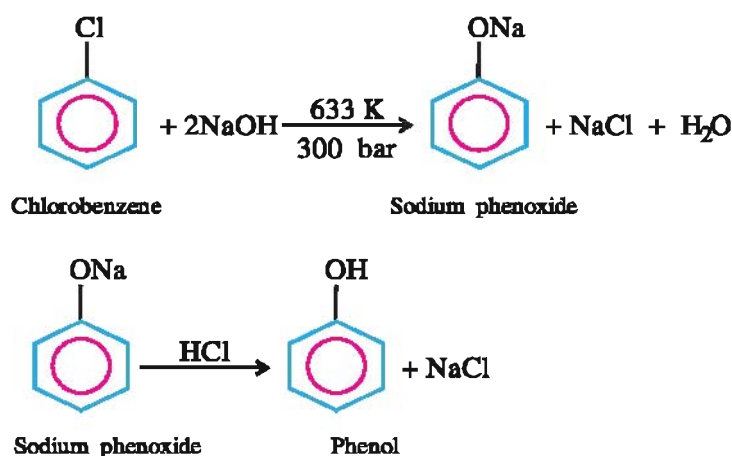


Due to higher stability of phenoxide ion, its reaction with H_3O^+ to form phenol means reverse reaction is less easy as compared to alkoxide ion. So, concentration of H_3O^+ is higher in aqueous solution of phenol than in aqueous solution of alcohol. Therefore **aqueous solution of phenol is more acidic than alcohol.**

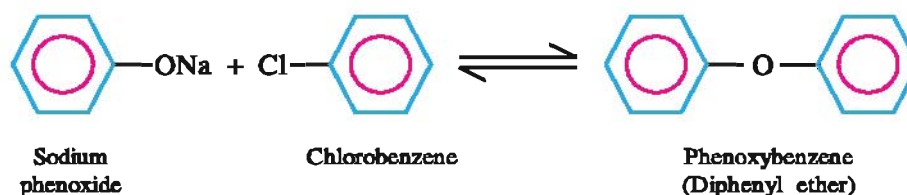
7.11 Preparation of Phenol

Phenol is most important chemical for industries. It is being used in manufacture of some dyes, drugs and polymer compounds. Phenol can be produced by different processes.

(1) Dow process : This process is used for industrial production of phenol. In this process a mixture of chlorobenzene and 6-8 % aqueous solution of sodium hydroxide is heated in a closed vessel at 300 bar pressure and 633 K as a result the sodium salt of phenol (sodium phenoxide) is produced as an intermediate product. Excess of chlorobenzene is removed from reaction mixture and acid is added into remaining solution to obtain phenol.

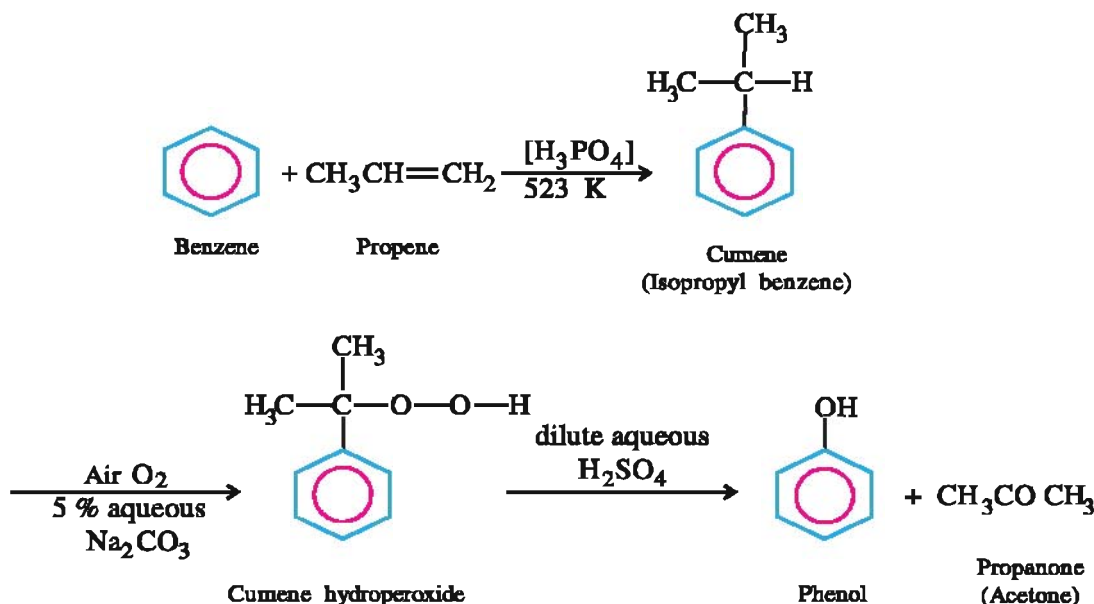


During this reaction sodium phenoxide and remaining chlorobenzene react with each other and produce phenoxybenzene (diphenyl ether) as a by-product. It decreases production of phenol. To overcome this difficulty, phenoxybenzene (diphenylether) is added into reaction mixture before carrying out reaction. Therefore according to principle of Le Chatelier the proportion of by-product is decreased, because following reaction occurs in reverse direction.

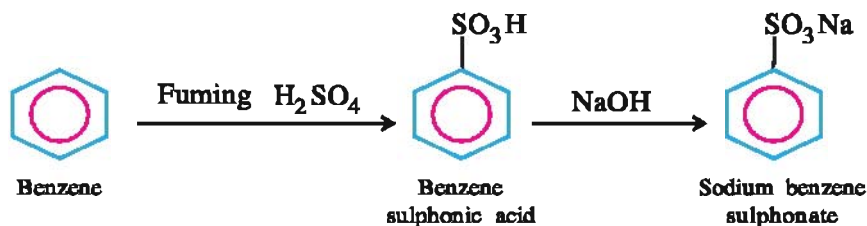


(2) Cumene Process : In this process a mixture of benzene and propene is heated at 523 K in a closed vessel in presence of phosphoric acid (H_3PO_4) catalyst to form cumene (isopropylbenzene). On passing air in a mixture of cumene and 5% aqueous sodium carbonate solution, cumene hydroperoxide is formed by oxidation. It is reacted with dilute sulphuric acid to form phenol and propanone (acetone). In this process propanone is obtained as a by-product. It is a useful solvent.

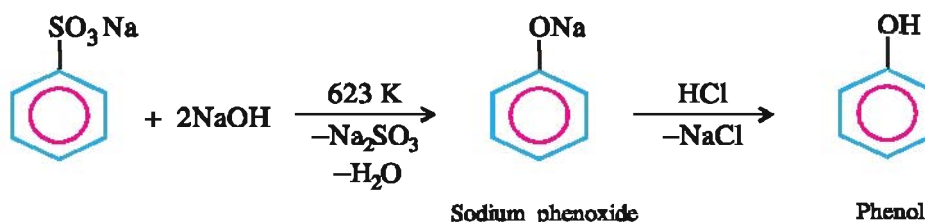
By this process highly pure phenol can be produced with less cost. Therefore most commonly this method is used for industrial production of phenol.



(3) Phenol from sodium benzene sulphonate : Benzene is reacted with fuming H_2SO_4 and then with NaOH gradually to form sodium benzene sulphonate.

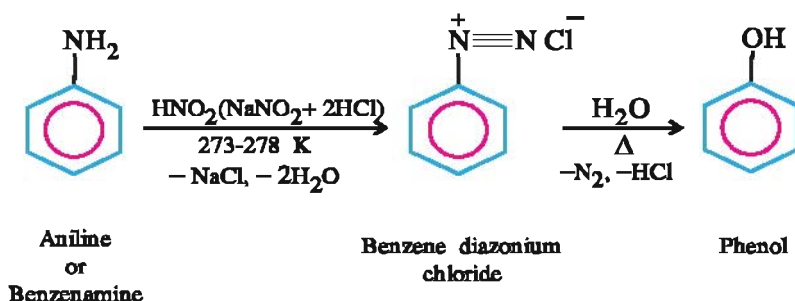


Sodium benzene sulphonate is melted with sodium hydroxide at 623 K temperature to obtain sodium phenoxide. It is reacted with acid and phenol is formed.



In 1890 this method was developed first of all in Germany for production of phenol.

(4) Phenol from diazonium salt : Aniline reacts with nitrous acid- HNO_2 ($\text{NaNO}_2 + \text{HCl}$) at lower temperature to form benzene diazonium chloride and heated it with water to form phenol.



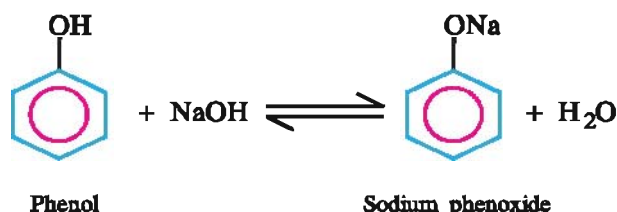
7.12 Chemical Reactions of Phenol

Two types of reactions are possible in phenol :

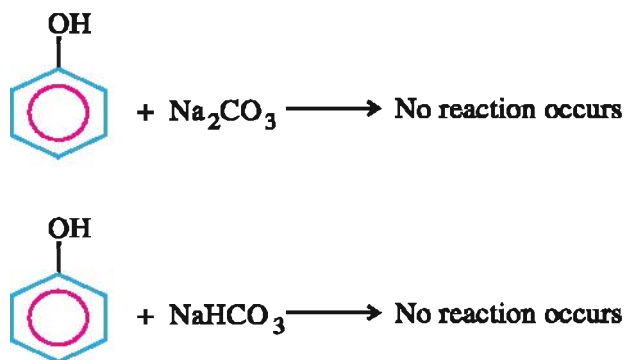
- (1) Reactions due to -OH group (2) Reaction occurring in aromatic ring

(1) Reactions due to -OH group :

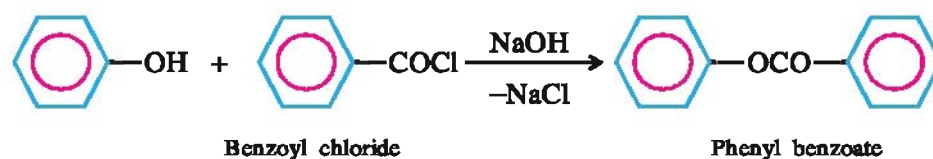
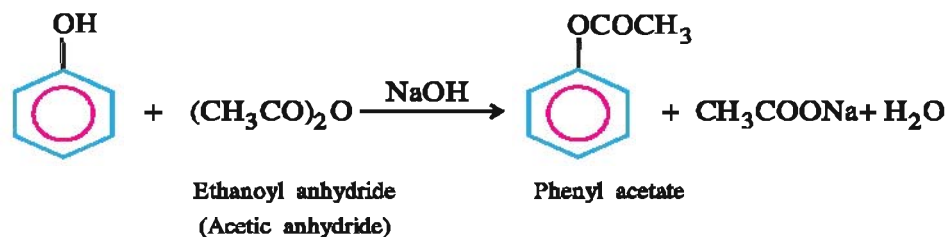
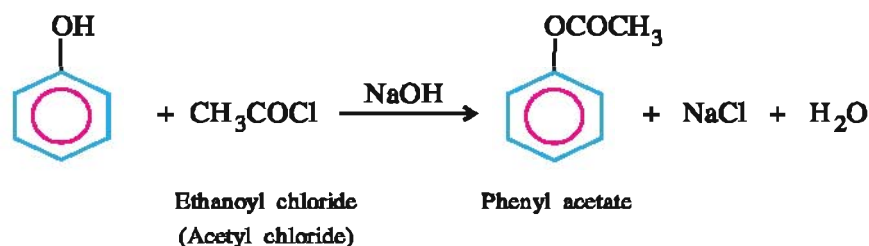
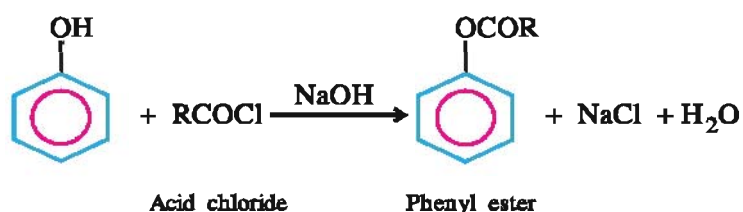
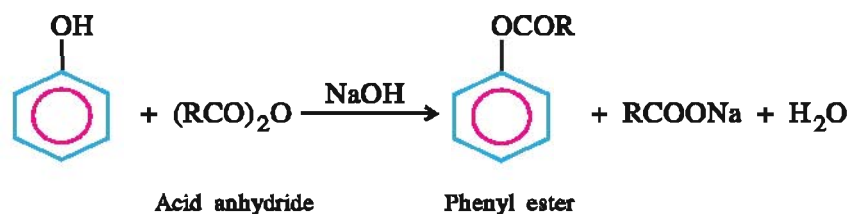
(i) Formation of salt : Reaction of phenol with aqueous sodium hydroxide forms salt and water.



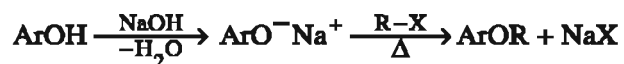
Phenol is weak acid so it does not give reaction with sodium carbonate and sodium hydrogen carbonate.



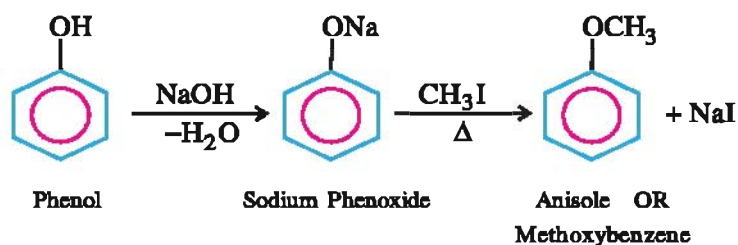
(ii) Formation of phenyl ester : Phenol forms phenyl ester through reaction with acid anhydride or acid chloride in alkaline medium.

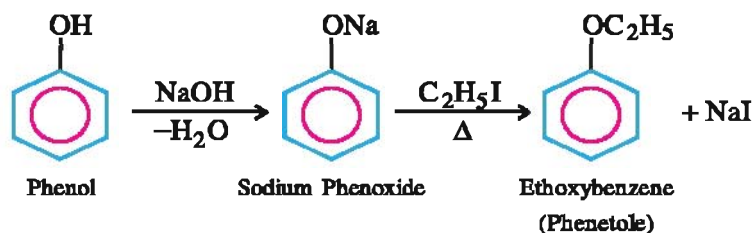


(iii) Formation of aryl ether : Heating the solution of phenol prepared in aqueous solution of sodium hydroxide, after addition of haloalkane it forms ether. This formation reaction of ether is called Williamson synthesis.

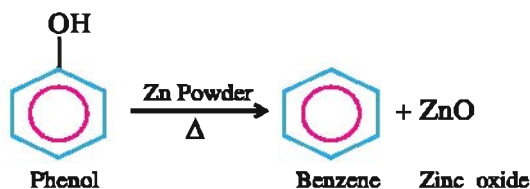


e.g.,





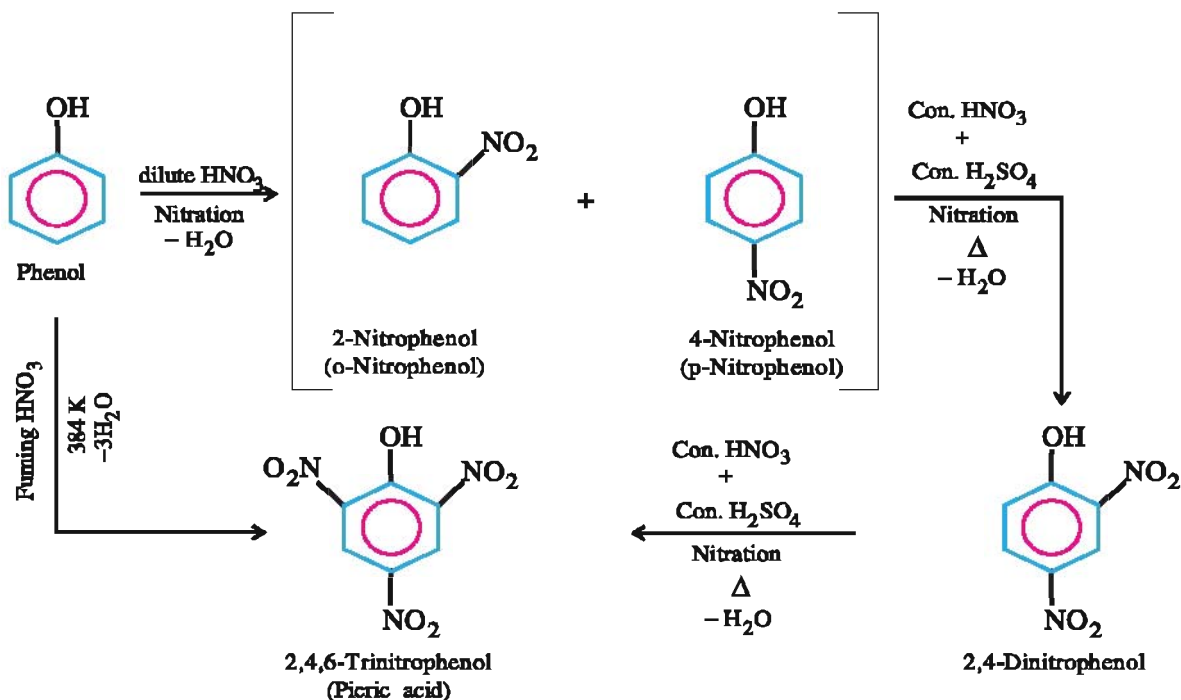
(iv) Formation of benzene : The mixture of aqueous phenol and zinc powder is heated. As a result benzene and zinc oxide are formed. In this reaction hydroxyl group attached to aromatic nucleus is eliminated.



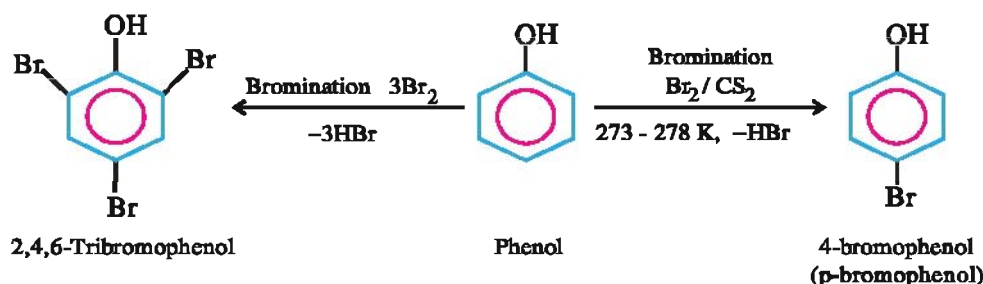
(2) Reactions occurring in aromatic ring :

(i) Electrophilic substitution reaction : The hydroxyl group of phenol being ortho-para directing, electrophilic substitution reaction like nitration and bromination of phenol give ortho-para derivatives.

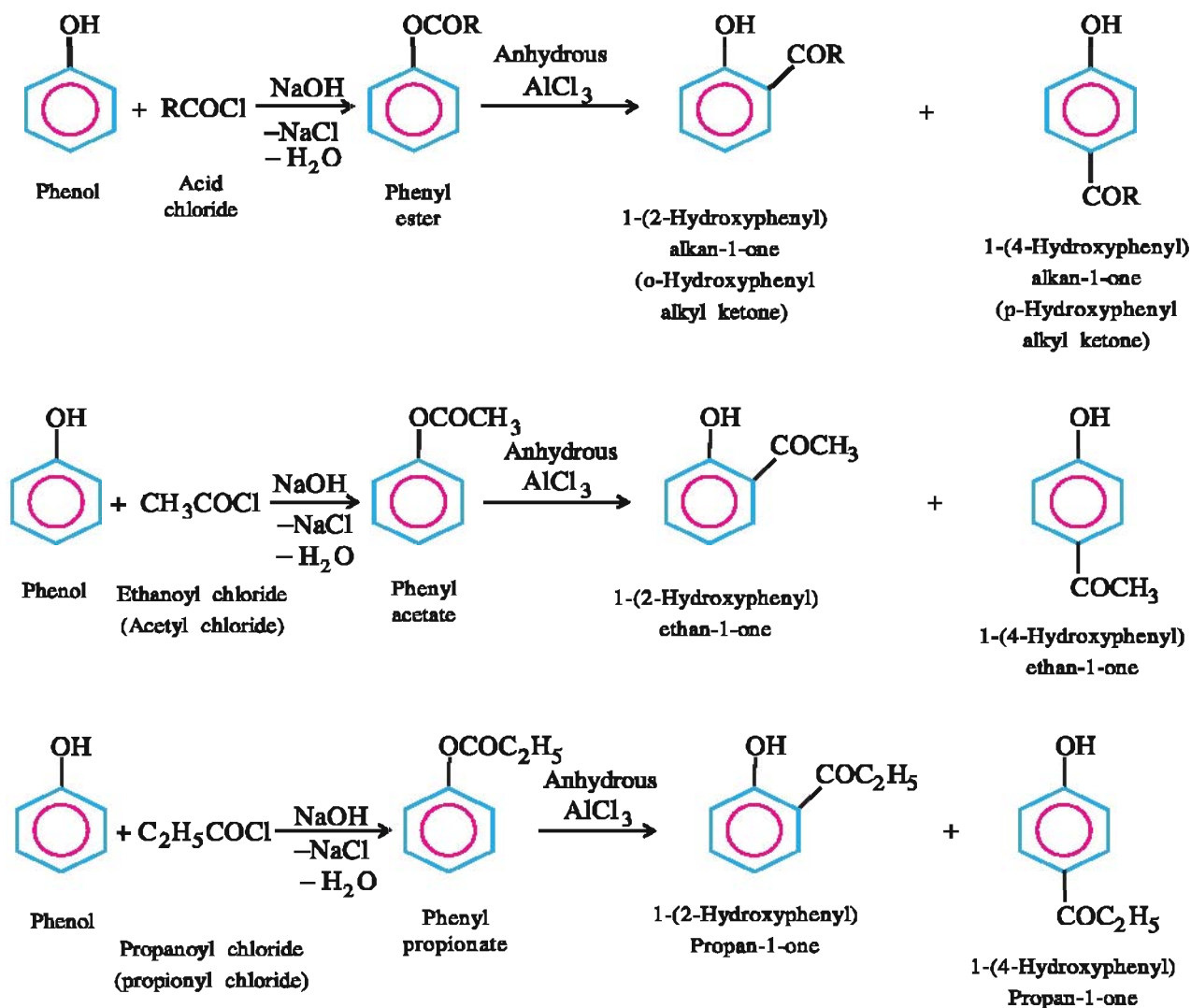
(A) Nitration of phenol : The chemical reaction between phenol and dilute nitric acid forms mixture of 2-nitrophenol (ortho-nitrophenol) and 4-nitrophenol (para-nitrophenol). It is called first nitration reaction. Second nitration of it occurs by heating with mixture of concentrated HNO_3 and concentrated H_2SO_4 to form 2,4-dinitrophenol and by third nitration 2,4,6-trinitrophenol (picric acid) is formed. Reaction of phenol with concentrated nitric acid also forms picric acid but product of this reaction is less.



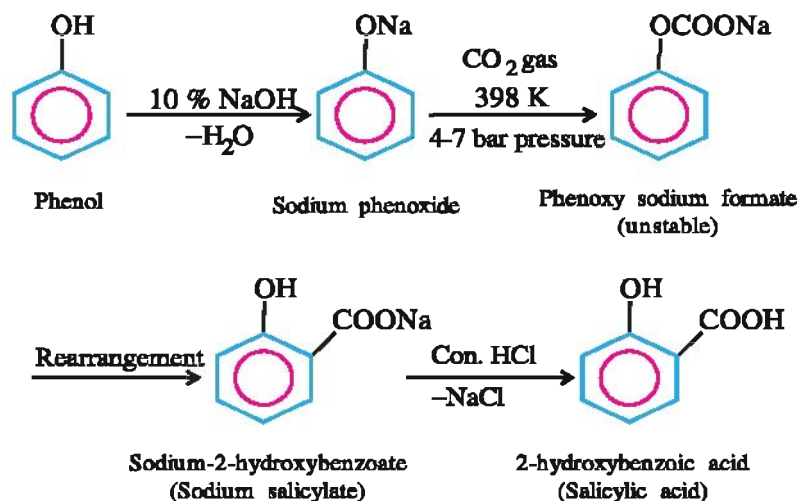
(B) Bromination of phenol : When bromine water is added to phenol at room temperature then white precipitates of 2,4,6-tribromophenol are formed. When the solution of bromine in carbon disulphide is added to phenol at 273 to 278 K temperature as a result 4-bromophenol is formed.



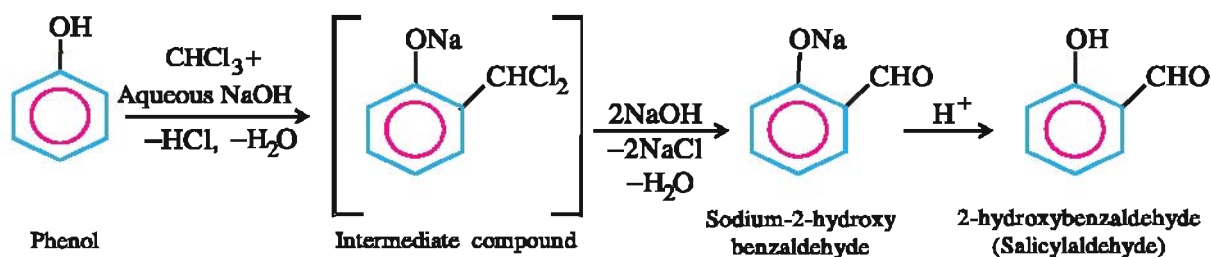
(ii) Fries Rearrangement : For preparation of phenolic ketone from phenol, phenol is reacted with acid chloride or acid anhydride and it forms phenylester. Reaction of this ester with anhydrous aluminium chloride is the resulting acylgroup ($-\text{COR}$) attached with phenolic oxygen is transferred at its ortho and para position in aromatic nucleus. This reaction is called Fries rearrangement.



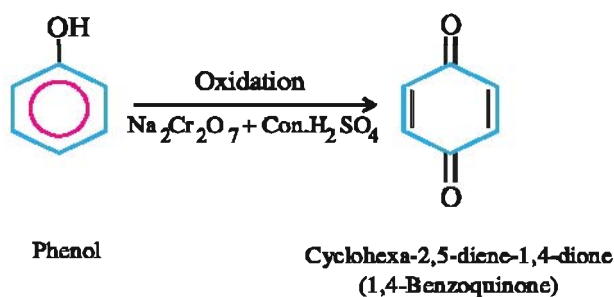
(iii) Kolbe-Schmitt Reaction : Phenol dissolved in 10% aqueous solution of sodium hydroxide, heated with carbon dioxide at 398 K temperature and 4 to 7 bar pressure in a closed vessel; unstable phenoxy sodium formate is formed in the first step which is converted to sodium-2-hydroxy benzoate (sodium salicylate) by rearrangement. After completion of reaction, acidification of the solution by concentrated hydrochloric acid gives white precipitate of 2-hydroxybenzoic acid (salicylic acid). 2-Hydroxybenzoic acid is used in the preparation of analgesic drugs like 2-Acetoxybenzoic acid (Aspirin) and Methyl-2-hydroxy benzoate (Methyl salicylate).





(iv) Reimer-Tiemann Reaction : Phenol is heated with trichloromethane (chloroform) in presence of aqueous sodium hydroxide solution, aldehyde group enters into aromatic ring. This reaction is called Reimer-Tiemann reaction. Substituted dichlorophenylmethane (benzal chloride) produced as an intermediate compound is hydrolysed in alkaline medium to produce 2-hydroxybenzaldehyde (salicylaldehyde).



(v) Oxidation of Phenol : Phenol is oxidized by chromic acid ($Na_2Cr_2O_7 + \text{Concentrated } H_2SO_4$) to produce 1, 4-benzoquinone.



7.13 Nomenclature of Ether Compounds

As we have studied in the beginning of this unit, general formula of ether is $R_1/Ar_1-O-R_2/Ar_2$ where R_1 and R_2 = alkyl or alkenyl or alkynyl group; Ar_1 and Ar_2 = aryl group. If both hydrocarbon groups attached to oxygen of ether compounds are same, then it is called **simple or symmetrical ether**. e.g., CH_3OCH_3 , $C_2H_5OC_2H_5$,  etc. If both hydrocarbon groups attached to oxygen of ether compounds are different then it is called **mixed or unsymmetrical ether**. e.g., $CH_3OCH_2CH_3$, $CH_3OCH_2CH_2CH_3$,  etc.






For common name of ethers, the names of two hydrocarbon groups are cited in alphabetical order and the word, 'ether' is added at the end. If both the hydrocarbon groups are the same, the prefix 'di' is added before the name of hydrocarbon group and word 'ether' added at the end (see table 7.5). **In IUPAC nomenclature of ethers, ether is mentioned as substituted hydrocarbon by alkoxy (RO-) or phenoxy (ArO-) group.** Alkoxy or phenoxy groups are named by removing the 'yl' from the end of name of alkyl or phenyl group and adding suffix 'oxy'. e.g., CH_3O -(methoxy), C_2H_5O -(ethoxy), -(phenoxy). Thus, IUPAC name of ether is written by adding the name of substituent alkoxy or phenoxy group as prefix before the name of hydrocarbon containing long chain of carbons attached to the oxygen of ether (see table 7.5).

Table 7.5 Ether compounds

Structural formula	IUPAC name	Common name	Type
CH_3-O-CH_3	Methoxymethane	Dimethyl ether	Symmetrical
$CH_3-O-CH_2CH_3$	Methoxyethane	Ethylmethyl ether	Unsymmetrical
$CH_3CH_2-O-CH_2CH_3$	Ethoxyethane	Diethyl ether	Symmetrical
CH_3O- 	Methoxybenzene or Anisole	Methyl phenyl ether (Anisole)	Unsymmetrical
CH_3CH_2O- 	Ethoxybenzene	Ethylphenyl ether (Phenetole)	Unsymmetrical
 -O- 	Phenoxybenzene	Diphenyl ether	Symmetrical
$H_2C=CHCH_2OCH_3$	3-Methoxy prop-1-ene	Methyl propenyl ether	Unsymmetrical
$HC\equiv CCH_2OCH_3$	3-Methoxy prop-1-yne	Methyl propynyl ether	Symmetrical
$CH_2=CH-O-CH=CH_2$	Ethenoxyethene	Divinyl ether	Symmetrical
$CH_3CH_2OCH(CH_3)CH_3$	2-Ethoxypropane	Ethyl isopropyl ether	Unsymmetrical

7.14 Electronic Structure of Ether

C—O

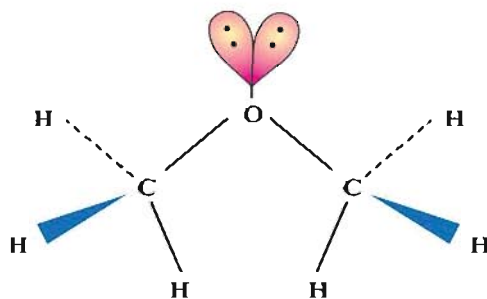
C and O

C—O—C angle

σ -bond

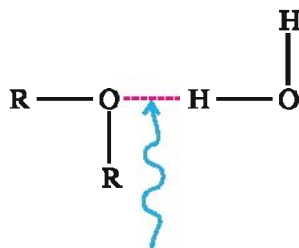
sp^3 hybridisation

111.7°



7.15 Physical Properties of Ether

For equal molecular mass containing alcohols and ethers, ethers have lower boiling points than alcohols, because in ethers, intermolecular hydrogen bonds are not present. e.g., Boiling point of methoxy-methane (molecular mass = 46 gram mole⁻¹, b.p. = 248 K) is lower than that of ethanol (molecular mass = 46 gram mole⁻¹, b.p. = 351 K) and boiling point of ethoxyethane (molecular mass = 74 gram mole⁻¹, b.p. = 308 K) is lower than that of butan-1-ol (molecular mass = 74 gram mole⁻¹, b.p. = 390 K). Like alcohol, ether forms intermolecular hydrogen bond with molecule of water. Therefore, solubilities of ethers in water are similar to those of alcohols with the same molecular mass. e.g., same molecular mass containing butan-1-ol and ethoxyethane have solubility in 100 g water is approximately 8 gram.



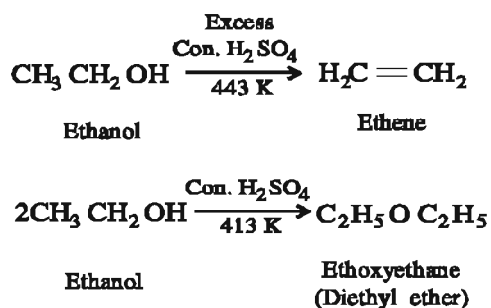
Intermolecular hydrogen bond

Intermolecular hydrogen bond between ether and water molecules

7.16 Preparation of Ethers

Mainly two methods are famous for preparation of ethers :

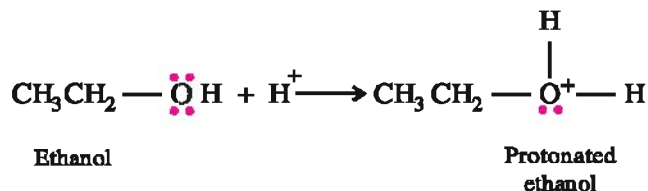
(1) By dehydration of alcohols : Dehydration of alcohols can be possible in presence of acid. Product of this reaction will be either alkene or ether. It depends on the reaction conditions. e.g., Dehydration of ethanol in presence of sulphuric acid gives ethene at 443 K temperature and ethoxyethane at 413 K temperature as a main product.



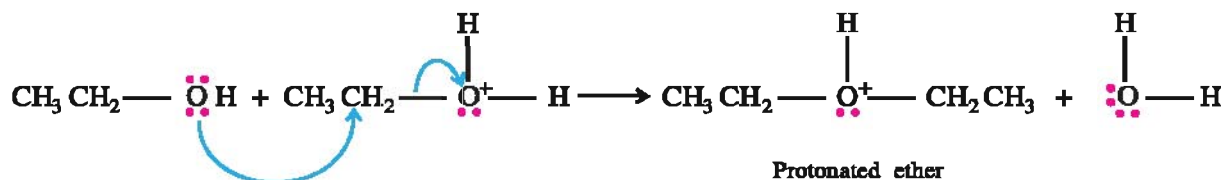
2 moles of ethanol and concentrated sulphuric acid are reacted at 413 K temperature; as a result obtained product ethoxyethane is in vapour form at temperature of reaction due to its lower boiling point 308 K. This vapour when cooled by passing through a water condenser gives liquid ether. In this reaction, if conditions are set in such a way that if ethanol is continuously added from one end so that liquid ethoxyethane is obtained continuously at the other end, the method is known as continuous etherification. Ether is produced industrially by this method.

Mechanism :

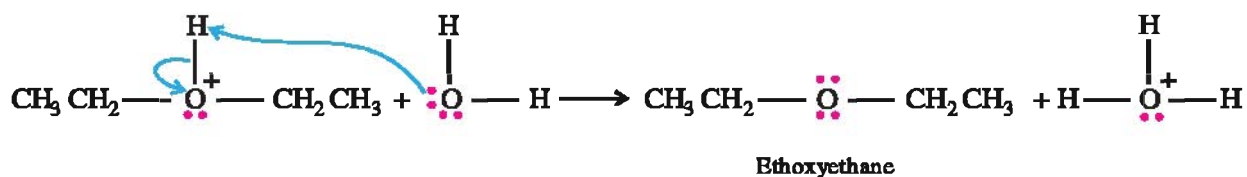
Step-1 : Alcohol accepts proton from the sulphuric acid to form protonated alcohol.



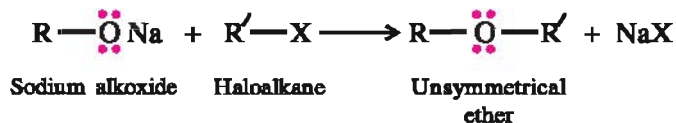
Step-2 : Second molecule of alcohol acts as nucleophilic reagent to attack on protonated alcohol.



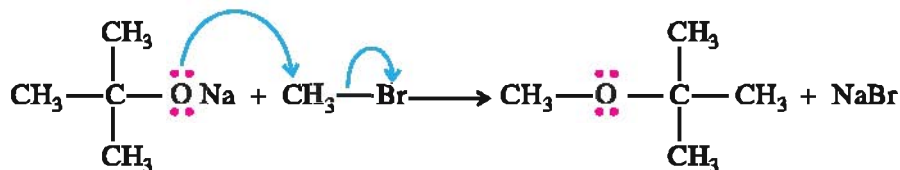
Step-3 : Ether is formed by elimination of proton from the protonated ether.



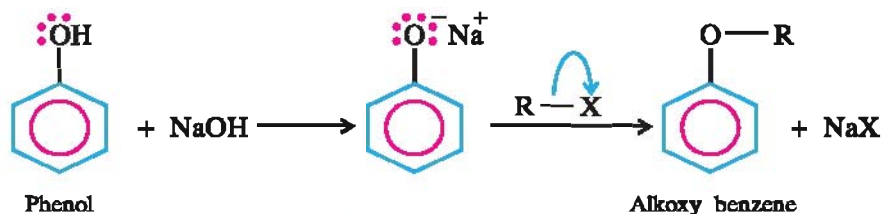
(2) By Williamson synthesis : English Chemist Alexander William Williamson discovered the nucleophilic substitution reaction for synthesis of unsymmetrical ethers. This reaction is called Williamson synthesis. This synthesis is bimolecular nucleophilic substitution ($\text{S}_{\text{N}}2$) reaction of sodium alkoxides and haloalkanes.



If -R is a secondary or tertiary alkyl group in sodium alkoxide then ether is also synthesised by this reaction.



Only primary haloalkane can synthesise ether easily. If secondary or tertiary haloalkane is used then elimination reaction occurs to form alkene. Therefore ether can be prepared also from phenol.



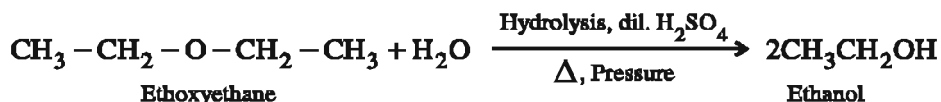
7.17 Chemical Reactions of Ether

Ether compounds having less chemical reactivity, they do not undergo oxidation and reduction. Moreover they do not react with active metals and base. However it gives some reactions with strong acids. Generally two types of reactions occur in ethers :

- (1) Reactions involving cleavage of C–O bond.
- (2) Electrophilic substitution reaction occurring in aromatic ring.

(1) Reactions involving cleavage of C–O bond :

(i) Reaction with dilute acid : A mixture of ethoxyethane (diethyl ether) and dilute sulphuric acid is heated in closed vessel under pressure; as a result two moles of ethanol are produced by hydrolysis.

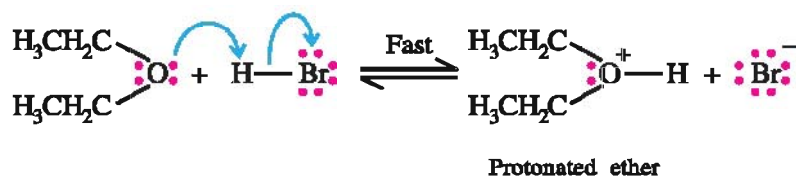


(ii) Reaction with hydrogen halide : If a mixture of ethoxyethane and two moles of concentrated hydro bromide is heated at high temperature, two moles of bromoethane are produced.



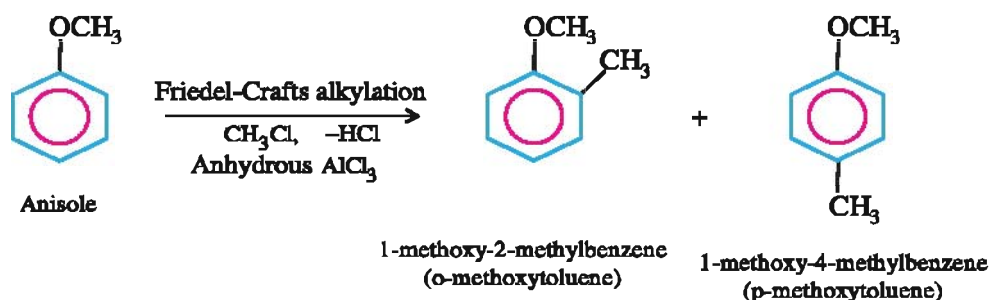
Mechanism :

Step-1 : Ethoxyethane is converted to protonated ether by accepting H^+ from hydrogen bromide.

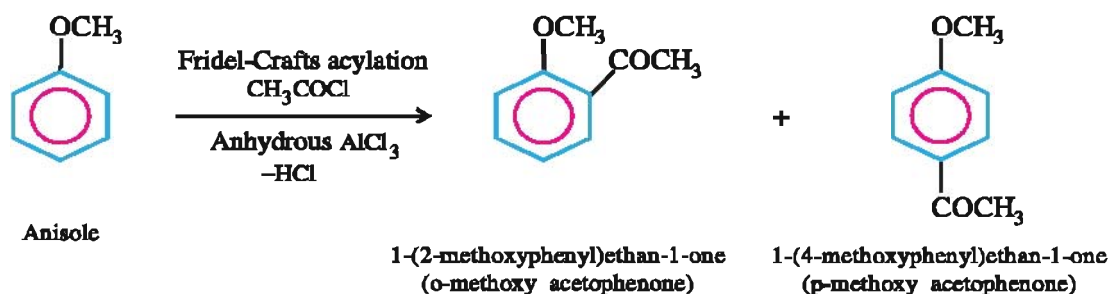


Step-2 : Bromide ion acts as nucleophilic reagent to attack on carbon of protonated ether. During this step one mole bromoethane (ethylbromide) and one mole of ethanol are formed.

(iii) Friedel-Crafts alkylation : Friedel-Crafts alkylation reaction of anisole with chloromethane (Methyl chloride) in presence of anhydrous aluminium chloride gives 1-methoxy-2-methylbenzene (o-methoxytoluene) and 1-methoxy-4-methylbenzene (p-methoxytoluene).

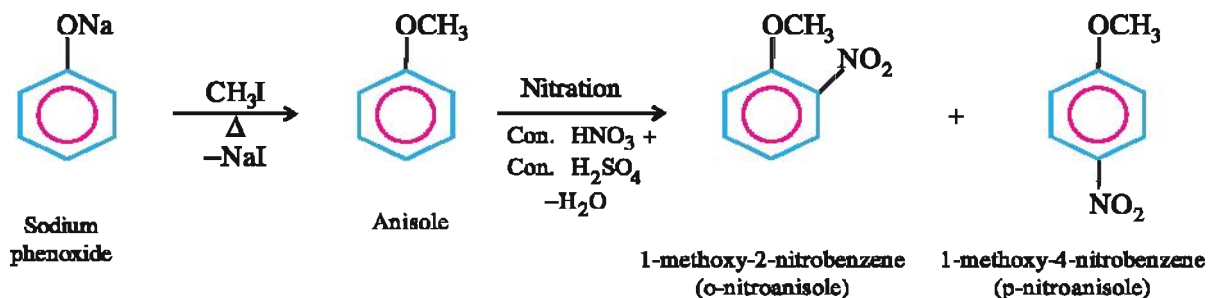


(iv) Friedel-Crafts acylation : Friedel-Crafts acylation reaction of anisole with ethanoyl chloride (acetyl chloride) in presence of anhydrous aluminium chloride gives 1-(2-methoxy phenyl) ethan-1-one (o-methoxy acetophenone) and 1-(4-methoxy phenyl) ethan-1-one (p-methoxy acetophenone).

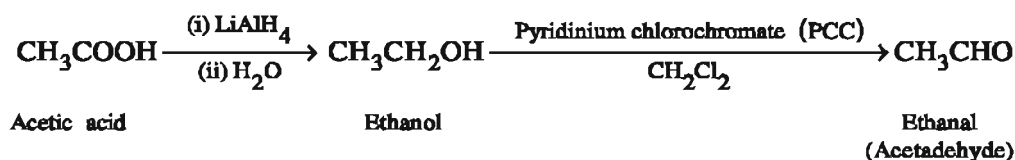


Some organic conversions :

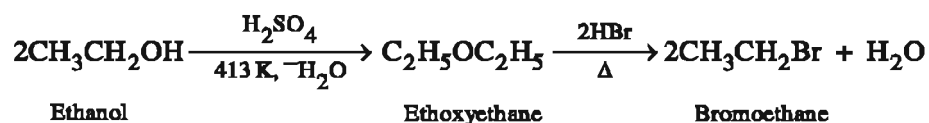
(1) 1-Methoxy-2-nitrobenzene and 1-methoxy-4-nitrobenzene from sodium phenoxide



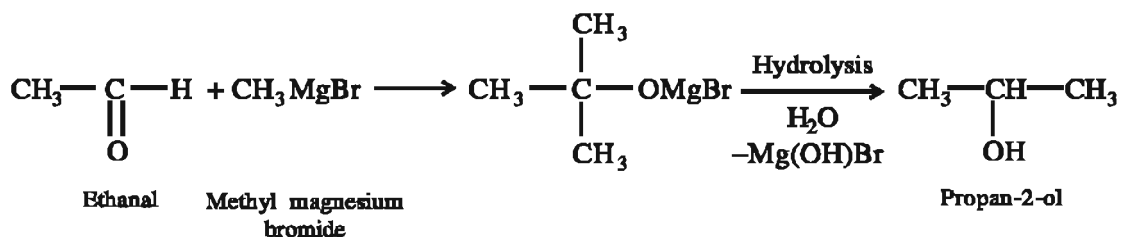
(2) Ethanal (acetaldehyde) from acetic acid



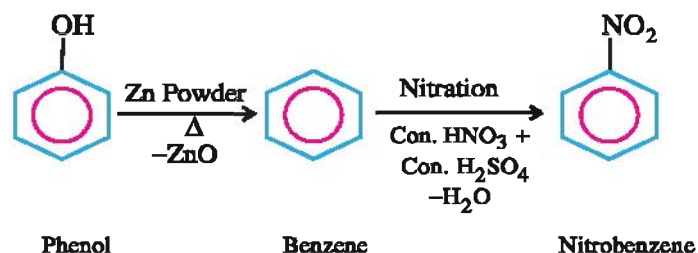
(3) Bromoethane from ethanol



(4) Propan-2-ol from ethanal

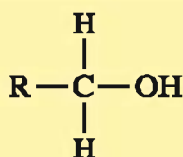


(5) Nitrobenzene from phenol

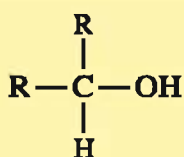


SUMMARY

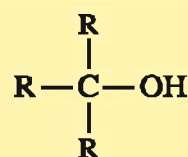
- Alcohol is formed when the hydrogen atom attached to saturated carbon of hydrocarbon is substituted by hydroxyl group (–OH). The general formula of alcohol is R–OH, where R = alkyl or alkenyl or alkynyl or arylalkyl.
- If the hydrogen atom attached to the carbon atom of an aromatic nucleus, is substituted by hydroxyl group then phenol is formed. The general formula of phenol is Ar–OH, where Ar = aryl group.
- If the hydrogen atom of hydroxyl group of alcohol or phenol, is substituted by alkyl or alkenyl or alkynyl or aryl group then ether is formed. The general formula of ether is R₁/Ar₁–O–R₂/Ar₂, where R₁ and R₂ alkyl or alkenyl or alkynyl group and Ar₁ and Ar₂ = aryl group.
- Alcohol, in which the hydroxyl group is attached to primary carbon is called primary alcohol, attached to secondary carbon is called secondary alcohol and attached to tertiary carbon is called tertiary alcohol.



Primary (1°) alcohol



Secondary (2°) alcohol



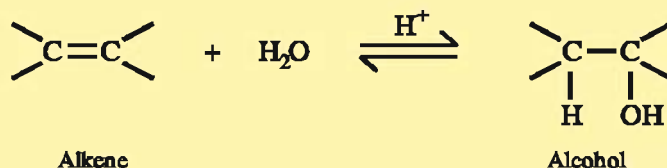
Tertiary (3°) alcohol

Physical Properties of Alcohols : The boiling points of alcohols are higher than those of alkanes having approximately equal molecular mass. In linear series of primary alcohols, the boiling point increases gradually as the number of carbon atoms increases. Among alcohols containing same molecular formula, secondary alcohol has lower boiling point than primary alcohol and tertiary alcohol has lower boiling point than secondary alcohol. In alcohol molecules, increase in the boiling point and solubility in water will increase with increase in number of hydroxyl groups.

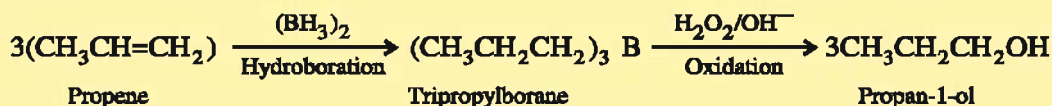
Preparation of Alcohols :

(1) Alcohol from alkene compounds

(i) By acid catalysed hydration

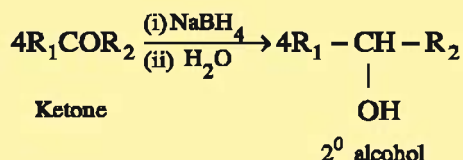
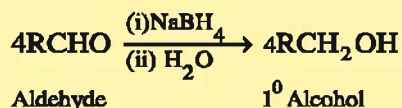


(ii) By hydroboration-oxidation

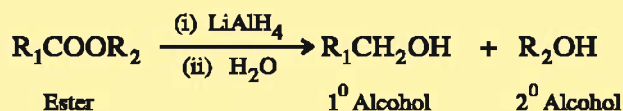
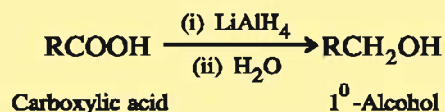


(2) Alcohols from carbonyl compounds

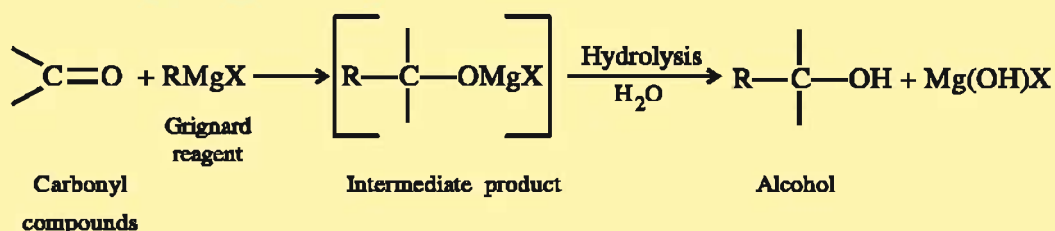
(i) By reduction of aldehydes and ketones



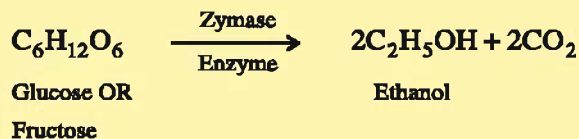
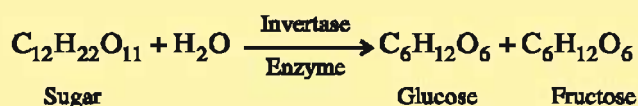
(ii) By reduction of carboxylic acids or esters



(3) Alcohols by Grignard reagents



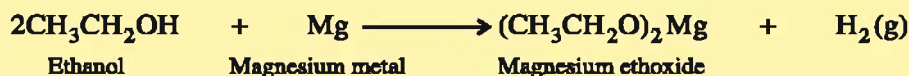
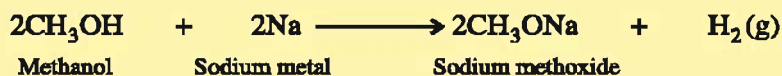
(4) By fermentation method



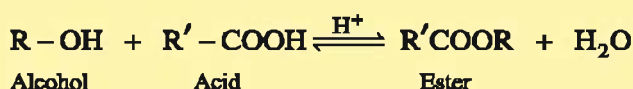
Chemical Reactions of Alcohols :

(1) Reactions involving cleavage of O-H group

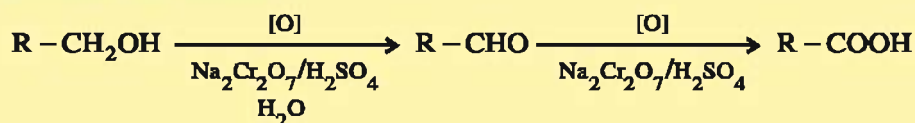
(i) Reaction of alcohol with active metals



(ii) Reaction with acids



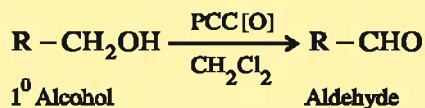
(iii) Oxidation of alcohols



1° Alcohol

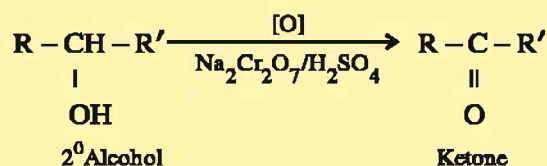
Aldehyde

Carboxylic acid



1° Alcohol

Aldehyde

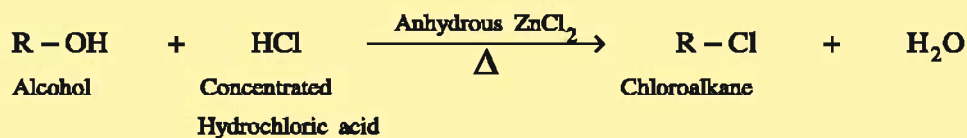


2° Alcohol

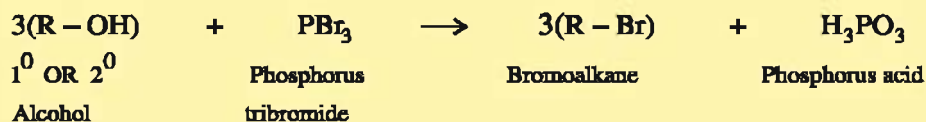
Ketone

(2) Reactions involving cleavage of C-O bond

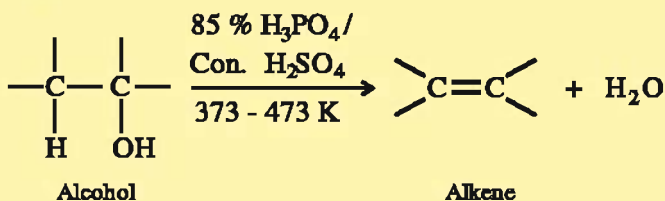
(i) Reaction with halogen acid (Lucas test)



(ii) Reaction with phosphorus tribromide



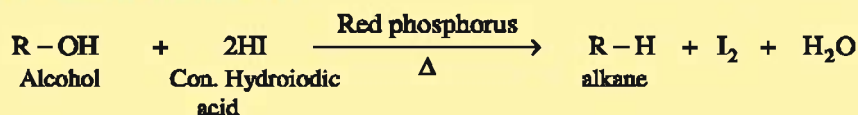
(iii) Dehydration of alcohols



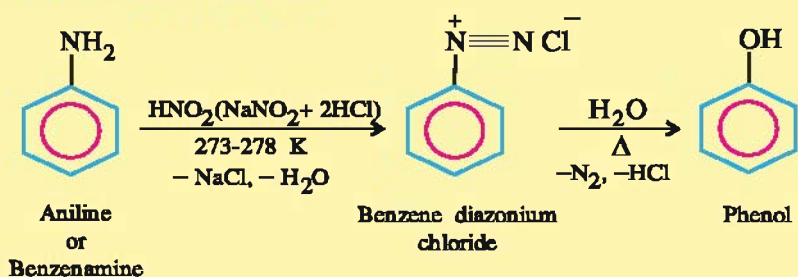
The order of ease of dehydration reaction of alcohols is

3° alcohol > 2° alcohol > 1° alcohol

(iv) Reduction of alcohol



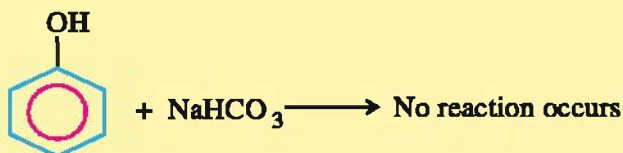
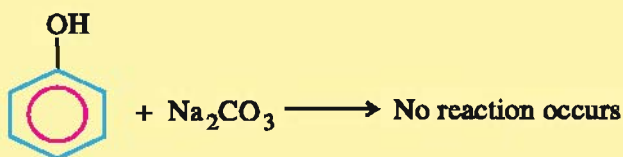
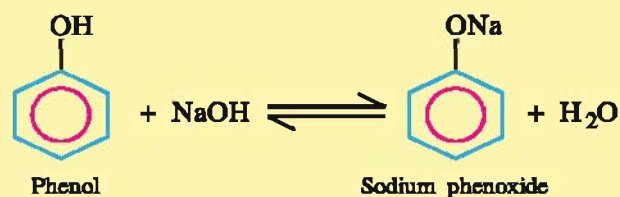
(4) From diazonium salt



Chemical Reactions of phenol :

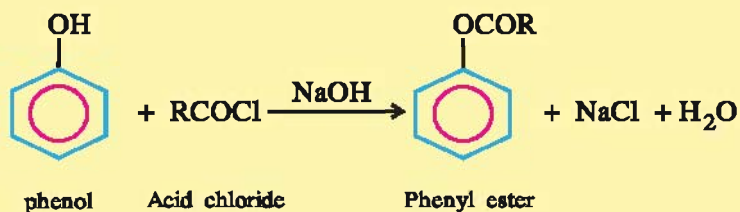
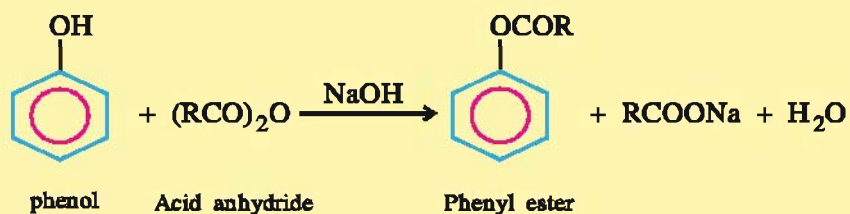
(1) Reactions due to $-\text{OH}$ group

(i) Formation of salt

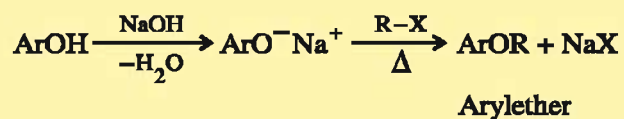


Thus, the nature of phenol is like weak acid.

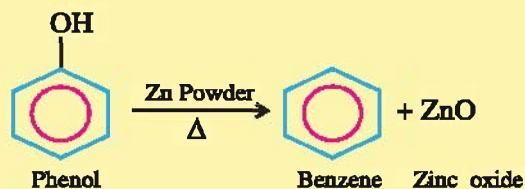
(ii) Formation of phenyl ester



(iii) Formation of aryl ether



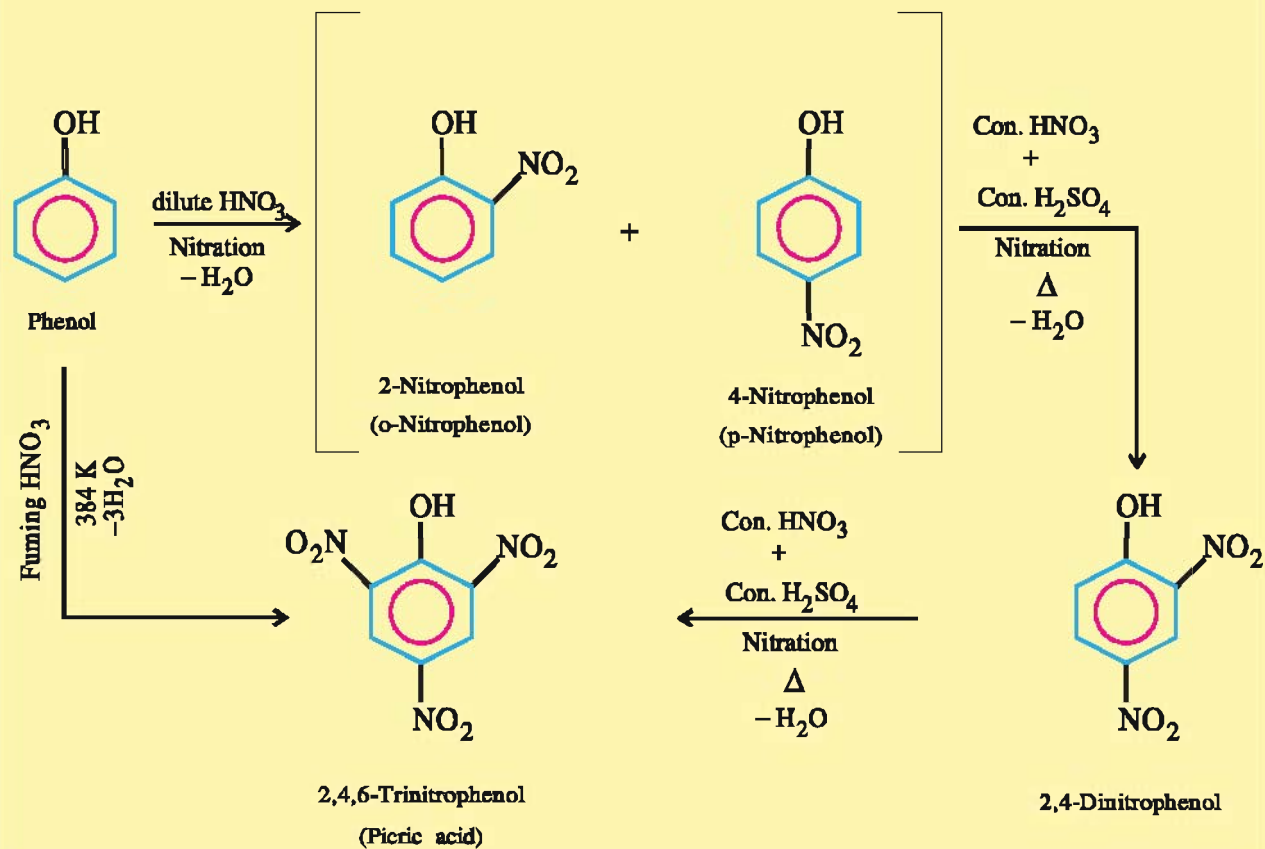
(iv) Formation of benzene



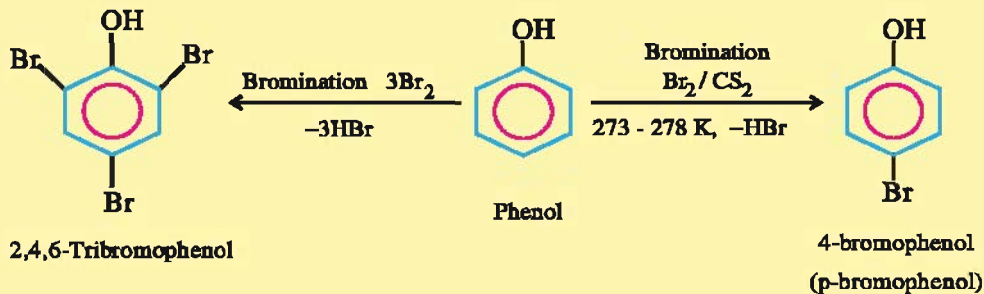
(2) Reactions occurring in aromatic ring

(i) Electrophilic substitution reaction

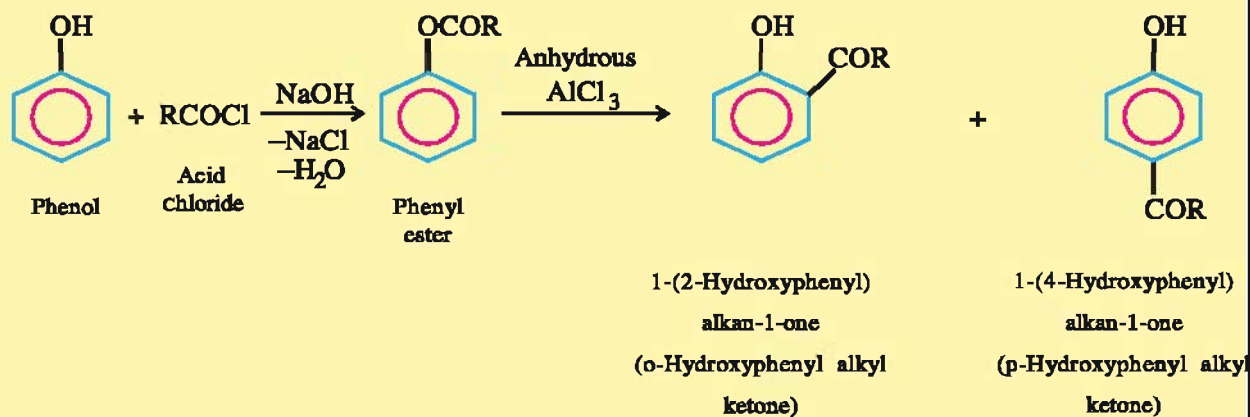
(A) Nitration of phenol



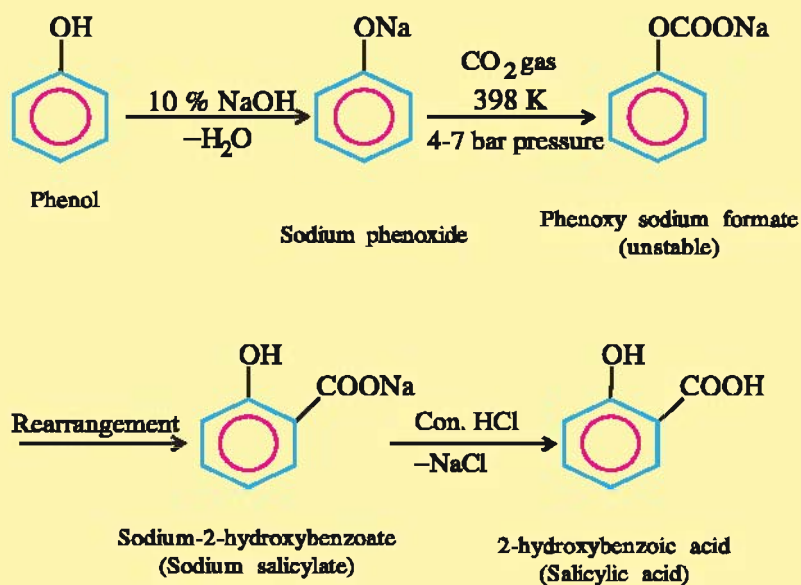
(B) Bromination of phenol

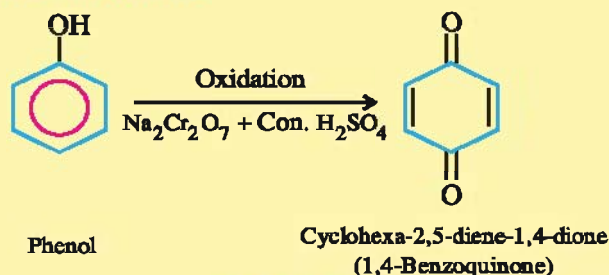
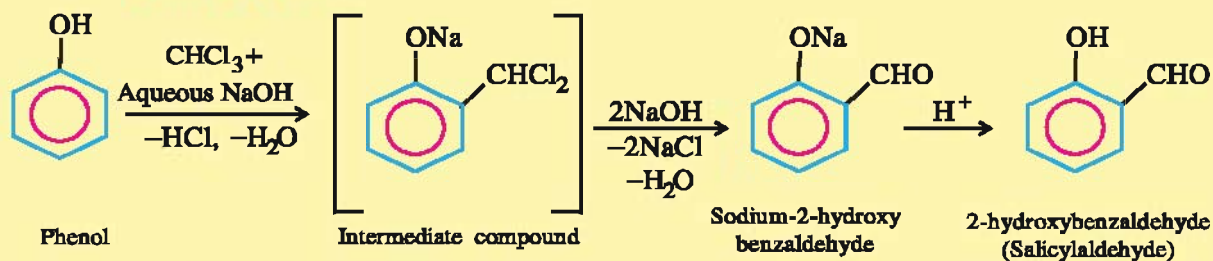


(ii) Fries Rearrangement



(iii) Kolbe-Schmitt Reaction

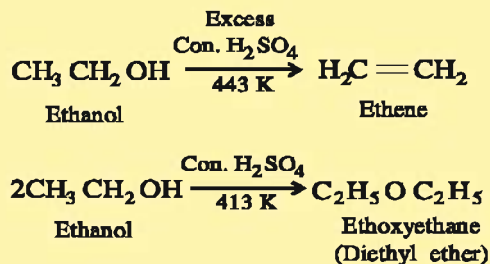




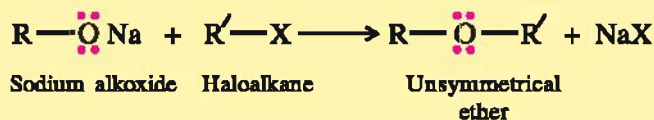
Physical Properties of Ether Compounds : For equal molecular mass containing alcohols and ethers, ethers have lower boiling points than alcohols., because in ethers, intermolecular hydrogen bonds are not present.

Preparation of Ether :

(1) By dehydration of alcohols



(2) By Williamson synthesis

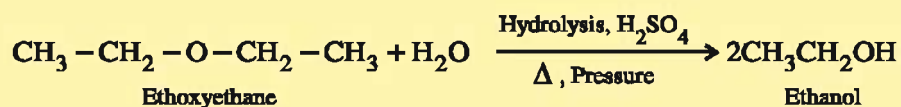


Only primary haloalkane can synthesise ether easily.

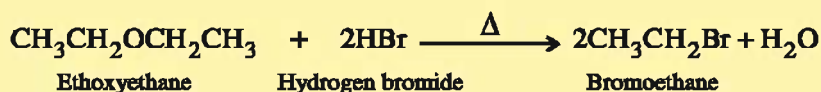
Chemical Reactions of Ethers :

(1) Reactions involving cleavage of C-O bond

(i) Reaction with dilute acid

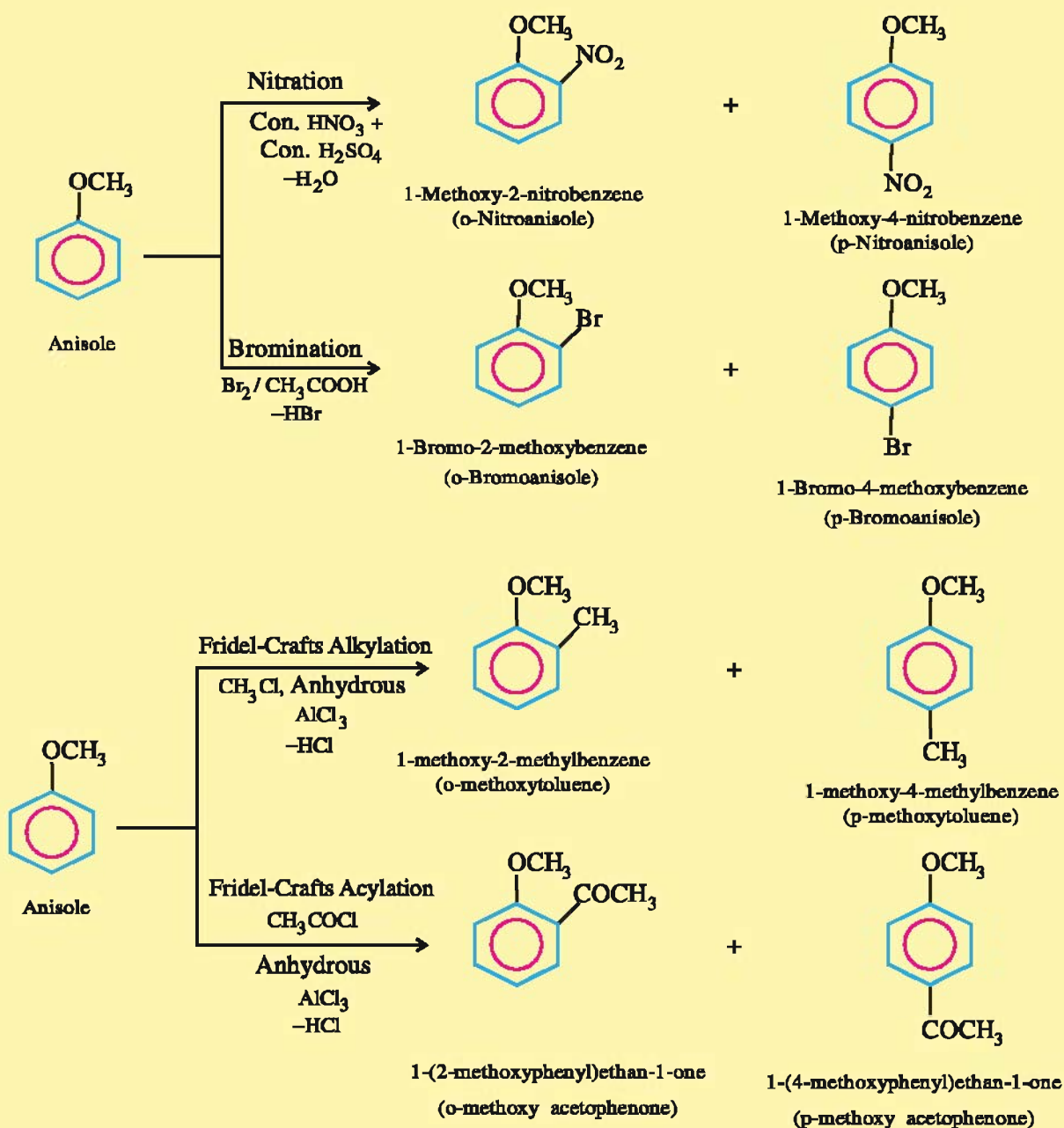


(ii) Reaction with hydrogen halide



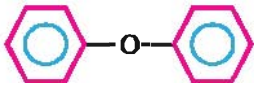
(2) Electrophilic substitution reaction occurring in aromatic ring

The -OR group of alkylaryl ether compounds being ortho-para directing, their electrophilic substitution reactions give mixture of ortho-para products.

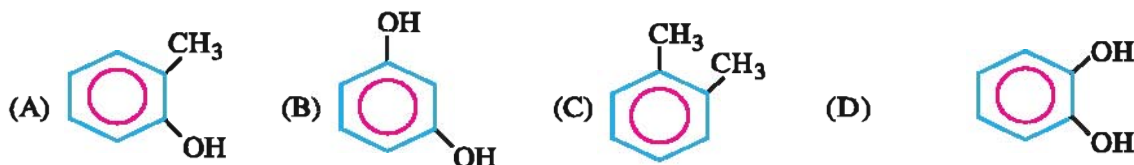


EXERCISE

1. Select the proper choice from the given multiple choices :

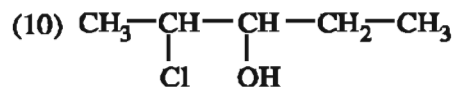
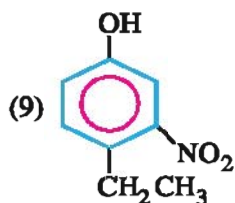
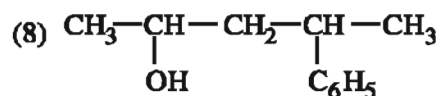
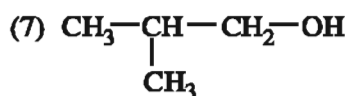
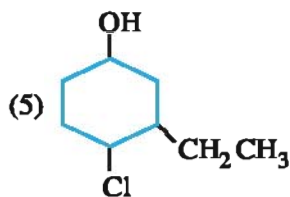
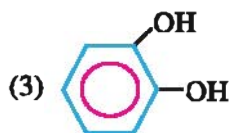
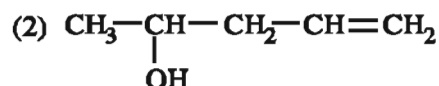
- (1) Which general formula is that of alcohol ?
(A) R_1-O-R_2 (B) $Ar-OH$ (C) $R-OH$ (D) Ar_1-O-Ar_2
- (2) Which formula is of tertiary alcohol ?
(A) CH_3OH (B) $(CH_3)_2CHOH$ (C) $(CH_3)_3COH$ (D) CH_3CH_2OH
- (3) Which order from the following is true for boiling points ?
(A) Chloroethane < ethane < ethanol (B) Ethane < chloroethane < ethanol
(C) Ethanol < ethane < chloroethane (D) Ethane > chloroethane > ethanol
- (4) Which substance from the following is a reducing agent ?
(A) Potassium permanganate (B) Lithium aluminium hydride
(C) Chromic acid (D) Pyridinium chloro chromate
- (5) Which substance from the following is unsymmetrical ether ?
(A)  (B) $C_2H_5-O-CH_2CH_3$
(C) $CH_3-O-C_2H_5$ (D) CH_3-O-CH_3
- (6) What will be formed after oxidation reaction of 2° alcohol with chromic acid ?
(A) Aldehyde (B) Ketone (C) Carboxylic acid (D) Ester
- (7) In which from the following intermolecular hydrogen bond is not present ?
(A) alcohol-alcohol (B) alcohol-water (C) ether-ether (D) ether-water
- (8) Which species from the following is nucleophilic reagent ?
(A) E (B) E^+ (C) E^- (D) $\overset{\cdot}{E}$
- (9) Which statement from the following is true ?
(A) During dehydration reaction H_2O molecule is added to reactant
(B) Lucas test is used for detection of ethers
(C) During esterification OH^- from acid molecule and H^+ from alcohol are removed.
(D) During esterification H^+ from acid molecule and OH^- from alcohol are removed.

(10) Which structural formula is of o-cresol ?



2. Answer the following question in short :

(A) Write IUPAC name of the following compounds :



(B) Mention the structures of the following IUPAC named compounds :

(1) 1-Ethoxy-3-methylpentane

(2) 2-Chloropentan-3-ol

(3) 3-Bromophenol

(4) 2-Nitrophenol

(5) Cyclohexane-1,2-diol

(6) 2-Isopropoxypentane

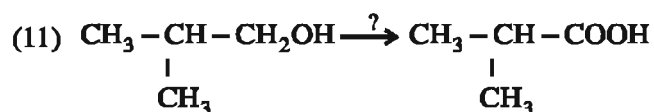
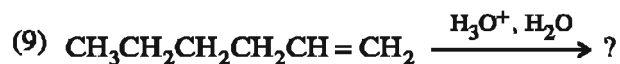
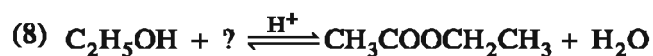
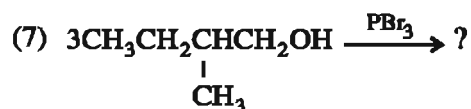
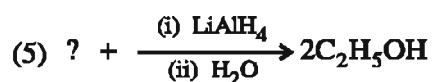
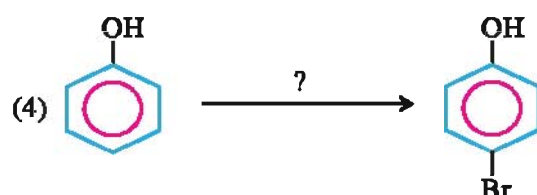
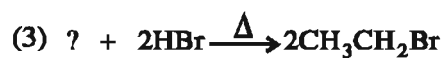
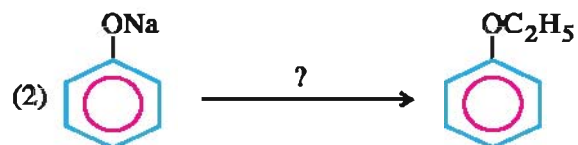
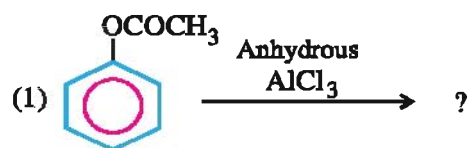
(7) 2,2-Dimethylpropan-1-ol

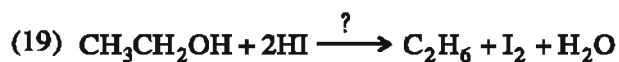
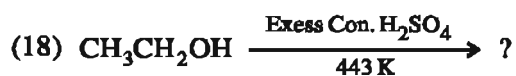
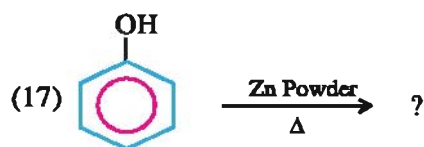
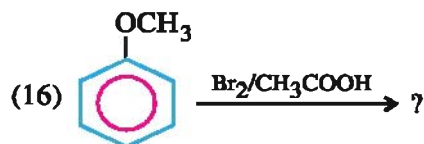
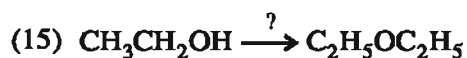
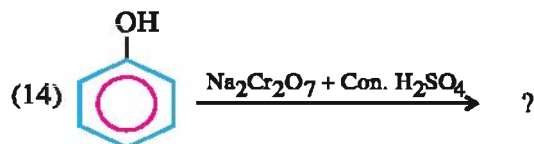
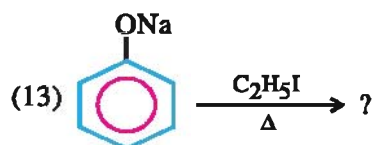
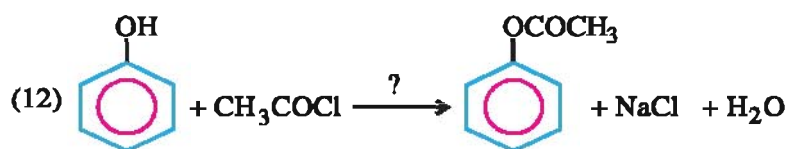
(8) 2,4-Dimethylpentan-1-ol

(9) 2,6-Dimethylphenol

(10) 1,2-Dimethoxyethane

(C) Complete the following chemical reactions :





3. Answer the following questions :

(A) Explain the following statements giving scientific reasons with example :

- (1) The boiling points of alcohols are higher than those of alkanes having equal molecular masses.
- (2) While going from primary to tertiary isomeric alcohols, their boiling points are decreasing.
- (3) Phenol has higher boiling point than toluene and fluorobenzene having approximately same molecular mass.

- (4) o-Nitrophenol has lower melting point and solubility in water than m-and p-nitrophenol.
- (5) Aqueous solution of phenol is more acidic than alcohol.
- (6) Ethers have lower boiling point than alcohols having same molecular mass.

(B) Write equation of chemical conversions for following organic compounds :

- (1) Acetone from propene
- (2) Propan-1-ol from propene
- (3) Hexan-2-ol from hex-1-ene
- (4) Butan-2-ol from acetaldehyde
- (5) Phenol from chlorobenzene
- (6) Phenol from aniline
- (7) Ethoxybenzene from phenol
- (8) 2, 4-Dinitro phenol from phenol
- (9) 2-Hydroxy benzoic acid from phenol
- (10) 2-Hydroxy benzaldehyde from phenol
- (11) 1-Methoxy-2-methylbenzene and 1-methoxy-4-methylbenzene from sodium phenoxide.
- (12) 1-(2-Hydroxyphenyl) propan-1-one and 1-(4-Hydroxyphenyl) propan-1-one from phenol

(C) Write chemical equations for the following reactions :

- (1) Oxidation reactions of primary, secondary and tertiary alcohols.
- (2) Reactions of ethanol with (i) Mg (ii) CH_3COOH (iii) PBr_3 (iv) HI.
- (3) Reactions of preparation for (i) phenyl acetate (ii) anisole (iii) benzene from phenol
- (4) Nitration and bromination reactions of phenol
- (5) Reactions of ethoxyethane with
 - (i) dilute H_2SO_4 (ii) concentrated HBr.
- (6) Nitration and bromination reactions of anisole.
- (7) Friedel-Crafts alkylation and acylation reactions of anisole

4. Answer the following questions in detail :

(A) Explain the following reactions with mechanism :

- (1) Preparation of alcohols from alkene compounds by acid catalysed hydration.
- (2) Preparation of alcohols from alkene compounds by hydroboration-oxidation.
- (3) Preparation of alcohols by reduction of aldehydes and ketones.
- (4) Preparation of alcohols from carbonyl compounds by Grignard reagent.
- (5) Reaction of tertiary alcohol with hydrochloric acid.
- (6) Reaction of alcohol with phosphorus tribromide.
- (7) Preparation of ethene by dehydration reaction of ethanol.
- (8) Preparation of ethers by dehydration reaction of alcohols.
- (9) $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3 + 2\text{HBr} \xrightarrow{\Delta} 2\text{CH}_3\text{CH}_2\text{Br} + \text{H}_2\text{O}$

(B) Write short notes on following :

- (1) Preparation of alcohols by fermentation method
- (2) Industrial production of phenol by Dow process and Cumene process
- (3) Lucas test
- (4) Fries rearrangement
- (5) Kolbe-Schmitt reaction
- (6) Reimer-Tiemann reaction
- (7) Williamson synthesis
- (8) Classification of alcohols and ethers

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Difference								
											1	2	3	4	5	6	7	8	9
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11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
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14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
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23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
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37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
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47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
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51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

LOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Difference								
											1	2	3	4	5	6	7	8	9
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7769	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9025	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Difference								
											1	2	3	4	5	6	7	8	9
.00	1000	1002	1005	1007	1009	1012	1014	1016	1019	1021	0	0	1	1	1	1	2	2	2
.01	1023	1026	1028	1030	1033	1035	1038	1040	1042	1045	0	0	1	1	1	1	2	2	2
.02	1047	1050	1052	1054	1057	1059	1062	1064	1067	1069	0	0	1	1	1	1	2	2	2
.03	1072	1074	1076	1079	1081	1084	1086	1089	1091	1094	0	0	1	1	1	1	2	2	2
.04	1096	1099	1102	1104	1107	1109	1112	1114	1117	1119	0	1	1	1	1	2	2	2	2
.05	1122	1125	1127	1130	1132	1135	1138	1140	1143	1146	0	1	1	1	1	2	2	2	2
.06	1148	1151	1153	1156	1159	1161	1164	1167	1169	1172	0	1	1	1	1	2	2	2	2
.07	1175	1178	1180	1183	1186	1189	1191	1194	1197	1199	0	1	1	1	1	2	2	2	2
.08	1202	1205	1208	1211	1213	1216	1219	1222	1225	1227	0	1	1	1	1	2	2	2	3
.09	1230	1233	1236	1239	1242	1245	1247	1250	1253	1256	0	1	1	1	1	2	2	2	3
.10	1259	1262	1265	1268	1271	1274	1276	1279	1282	1285	0	1	1	1	1	2	2	2	3
.11	1288	1291	1294	1297	1300	1303	1306	1309	1312	1315	0	1	1	1	2	2	2	3	3
.12	1318	1321	1324	1327	1330	1334	1337	1340	1343	1346	0	1	1	1	2	2	2	2	3
.13	1349	1352	1355	1358	1361	1365	1368	1371	1374	1377	0	1	1	1	2	2	2	3	3
.14	1380	1384	1387	1390	1393	1396	1400	1403	1406	1409	0	1	1	1	2	2	2	3	3
.15	1413	1416	1419	1422	1426	1429	1432	1435	1439	1442	0	1	1	1	2	2	2	3	3
.16	1445	1449	1452	1455	1459	1462	1466	1469	1472	1476	0	1	1	1	2	2	2	3	3
.17	1479	1483	1486	1489	1493	1496	1500	1503	1507	1510	0	1	1	1	2	2	2	3	3
.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	2	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	2	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	1	2	2	2	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	1	2	2	2	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	1	2	2	2	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	1	2	2	2	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	1	2	2	2	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	1	2	2	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	1	2	2	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	1	2	2	3	3	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	1	2	2	3	3	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	1	2	2	3	3	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	1	2	2	3	3	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	1	2	2	3	3	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	1	2	2	3	3	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2380	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9

ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	Mean Difference								
											1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6715	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	12	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	5	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20
	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9