1.THE SOLID STATE

Solids are substances having definite shape and definite volume. In solids, the particles are closely packed and the force of attraction between the particles is strong. So solids are rigid and incompressible.

Their constituent particles (atoms, molecules or ions) have fixed positions and can only vibrate about their mean positions.

Classification of solids

On the basis of orderly arrangement of particles, solids can be classified into two – i.e Crystalline solids and Amorphous solids.

1. Crystalline solids

In these solids, the constituent particles have a well ordered arrangement throughout the solid, i.e.,they have a long range order. They consist of a large number of small crystals. They have a definite geometrical shape, melting point and heat of fusion.

E.g.: Quartz, Diamond, Graphite, fullerene, NaCl, $CuSO_4.5H_2O$, ice, naphthalene, SiC etc.

2. Amorphous solids

In these solids, the ordered arrangement of constituent particles is only at some portions of the solid,i.e., they have only a short range order.

The structure of these solids is similar to that of liquids.

They haveno definite geometrical shape, melting point and heat of fusion.

E.g.:Plastic,Glass (quartzglass),Rubber,amorphous silica,coal, charcoal,coke,PVC etc.

Like liquids amorphous solids have a tendency to flow, though very slowly. Therefore, sometimes these are also called pseudo solids or super cooled liquids.

Glass panes fixed to windows or doors of old buildings are slightly thicker at the bottom than at the top. This is because the glass flows down very slowly and makes the bottom portion slightly thicker.

Amorphous solids on heating become crystalline at some temperature. Some glass objects from ancient civilizations are found to become milky in appearance due to some crystallization.

Anisotropic and isotropic substances:

Solids in which the physical properties like electrical conductance, refractive index etc are different when measured in different directions are said to be anisotropic in nature. This is due to the different arrangement of particles in different directions. Crystalline solids are anisotropic.

Solids in which the physical properties are same along any direction are said to be isotropic in nature.

This is due to the irregular arrangement of particles along different directions. Amorphous solids are isotropic.

Differences between Crystalline solids and Amorphous solids

Property	**Crystalline solids**	**Amorphous solids**
Shape	They have long range order.	They have short range order.
Melting point	They have definite melting point	They do not have definite melting point
Heat of fusion	They have a definite heat of fusion	They do not have definite heat of fusion
Compressibility	They are rigid and incompressible	These may not be compressed to any appreciable extent
Cutting with a sharp edged tool	They are given cleavage i.e. they break into two pieces with plane surfaces	They are given irregular cleavage i.e. they break into two pieces with irregular surface
Isotropy and Anisotropy	They are anisotropic	They are isotropic
Volume change	There is a sudden change in volume when it melts.	There is no sudden change in volume on melting.
Symmetry	These possess symmetry	These do not possess any symmetry.
Interfacial angles	These possess interfacial angles.	These do not possess interfacial angles.

Classification of Based on the nature of particles and binding force

On the basis of nature of particles and binding force between the particles, crystalline solids are classified into four types- molecular solids, ionic solids, metallic solids and covalent solids.

1.**Molecular Solids**:Here the constituent particles are molecules. These are further sub-divided into three:

i.Non-polar molecular solids: Here the constituent particles are either atoms like Ar, He etc. or non-polar molecules like H_2,Cl_2, I_2 etc and the binding force between the particles is London dispersion forces or weak van der Waal's forces.

These are soft solids and are non-conductors of electricity. They have low melting points and are usually liquid or gaseous state at room temperature and pressure.

ii.Polar molecular solids: Here the constituent particles are polar molecules like HCl, CO_2, SO_2 etc. and the binding force between the particles is relatively stronger dipole-dipole interactions. These are soft and non-conductors of electricity.

Their melting points are higher than those of non-polar molecular solids.

Most of them are gases or liquids at room temperature and pressure.

iii. Hydrogen bonded molecular solids: Here the constituent particles are molecules which contain atoms like H and F, O or N. The binding force between the particles is strong hydrogen bond. They are non-conductors of electricity and are volatile solids or soft solids at room temperature and pressure. E.g.:H_2O, NH_3 etc.

2. Ionic Solids: Here the constituent particles are ions and the binding force between the particles is strong electrostatic force of attraction (ionic bond). They are hard and brittle and have high m.p & b.p.

They are electrical insulators in the solid state, since the ions are not free to move about. But in the molten or solution state, the ions become free to move about and they conduct electricity. E.g.: NaCl, KCl, $CaCl_2$ etc.

3.Metallic Solids: They contain a large number of metal ions which are surrounded by a sea of electrons. The particles are held together by strong electrostatic force of attraction (metallic bond).

Due to the presence of a large number of free electrons, they are good conductors of heat and electricity, malleable and ductile and show metallic lustre. E.g. All metals

4.Covalent or Network Solids: Here the constituent particles are atoms and the binding force between the particles is strong covalent bond. They are very strong and brittle, have extremely high melting point and are electrical insulators.

E.g.Diamond, Silicon Carbide (SiC, commonly known as Carborundum),Quartz, Graphite etc.

Graphite has exceptional properties i.e., it is soft and good conductor of electricity. In graphite carbon atoms are arranged in different layers and each atom is covalently bonded to three adjacent carbon atoms. The fourth electron is free to move about between different layers.

So Graphite is a good conductor of electricity. The different layers are held together by weak van der Waal's force of attractions.

So each layer can slide over the other and hence it is soft and used as a good lubricant.

Crystal lattice

The regular three dimensional arrangements of constituent particles of a crystal in space is called crystal lattice or space lattice.

The important characteristics of a crystal lattice are:

(a) Each point in a lattice is called lattice point or lattice site.

(b) Each point in a crystal lattice represents one constituent particle which may be an atom, a molecule (group of atoms) or an ion.

(c) Lattice points are joined by straight lines to bring out the geometry of the lattice.

There are only **14** possible three dimensional lattices.

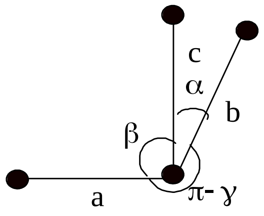
These are called **Bravais Lattices**.

Unit cell

A unit cell is the smallest repeating unit of a crystal lattice which, when repeated in three dimension we get a whole crystal. Or, it is the building block of a crystal.

A unit cell is characterised by its edge lengths (a, b and c) and angle between the edges – α (between b and c), β (between a and c) and γ (between a and c) and γ (between a and b).

Thus a unit cell is characterised by 6 parameters – a, b, c, α, β and γ.



Calculation of Number of atoms in a unit cell (z)

Unit cells are of two types:

(i) Primitive unit cell (ii) Centered unit cell

(i) Primitive unit cell or simple cubic unit cell (sc): In this unit cell the particles are present only at the corners.

Simple cubic unit cell or primitive unit cell has 8 corner atoms or 8 lattice points.

(ii) Centered unit cells: The unit cell which contains one or more constituent particles in addition to the corner particles is called centered unit cell.

Centered unit cells are of three types.

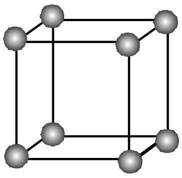
- Body centered unit cell.
- Face centered unit cell
- End centered unit cell

1.Body centered unit cell (bcc): – It contains 8 corner particles and one particle at its body centre. Body centred cubic unit cell has 9 lattice points.

2.Face centered unit cell (fcc):- It contains 8 corner particles and one particle each at the center of each face. FCC contains 14 lattice points.

3.End centered unit cell: It contains 8 corner particles and one particle each at the center of any two opposite faces. End centred unit cell has 10 lattice points.

Number of particles in primitive unit cell or simple cubic unit cell.



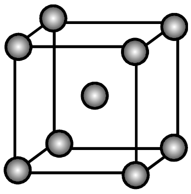
Simple cubic unit cell contains 8 corner particles.

Each corner particle is shared to eight unit cells.

The contribution of corner particle is $\frac{1}{8}$.

number of particles in the unit cell of simple cubic lattice $= 8 \times \frac{1}{8} = 1$

Number of particles in the unit cell of body centered cubic lattice (bcc).



Body Centered (I)

Body centered cubic lattice (bcc) contains 8 corner particles and one particle at the center of the body.

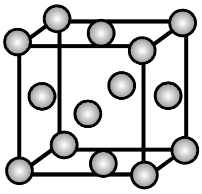
The contribution of corner atom to the unit cell is $\frac{1}{8}$.

The particle present at the body centre is not shared by other unit cell.

So, The contribution of body centre atom to the unit cell is 1.

Number of particles in the unit cell of bcc $= \left(8 \times \frac{1}{8}\right) + (1 \times 1)$ = 1 + 1 = **2**

Number of particles in the unit cell of face centered cubic lattice (fcc).



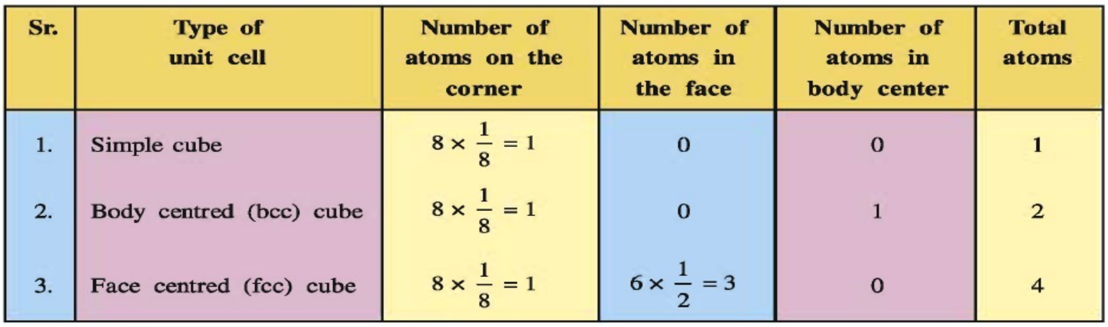
Face Centered (F)

fcc unit cell contains 8 corner atoms and 6 atoms at the faces.

The contribution of corner atom to the unit cell is 1/8.

The contribution of the atom at the face is 1/2.

Number of particles in the unit cell of fcc $= \left(8 \times \frac{1}{8}\right) + \left(6 \times \frac{1}{2}\right)$ = 1 + 3 = **4**



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

Seven types of crystal systems and their possible variations

Crystal System	Bravais Lattices	Parameters of Unit Cell		Example
		Intercepts	Interfacial angle	
1. Cubic	Primitive, Face Centered, Body Centered = 3	a = b = c	$\alpha = \beta = \gamma = 90^\circ$	Pb,Hg,Ag,Au Diamond, NaCl, ZnS
2. Orthorhombic	Primitive, Face Centered, Body Centered, End	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	KNO_2, K_2SO_4

	Centered = 4			
3. Tetragonal	Primitive, Body Centered =2	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	TiO_2,SnO_2
4. Monoclinic	Primitive, End Centered = 2	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ$, $\beta \neq 90^\circ$	$CaSO_4$,$2H_2O$
5. Triclinic	Primitive = 1	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^0$	$K_2Cr_2O_7$, $CuSO_45H_2O$
6. Hexagonal	Primitive = 1	$a = b \neq c$	$\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$	Mg, SiO_2, Zn, Cd
7. hombohedral	Primitive = 1	$a = b = c$	$\alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	As, Sb, Bi, $CaCO_3$
Total = 14				

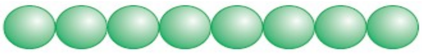
Close packing in solids

In solids the particles are closely packed. In close packed structures the particles are considered as hard spheres.

Solids are three dimensional and the 3 dimensional structure can be obtained by the following three steps:

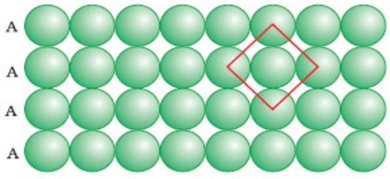
1.Close packing in One Dimensions

Here the spheres are arranged in a row touching each other. In this arrangement each sphere is in contact with 2 adjacent spheres. Therefore,
co-ordination number of each sphere is 2.



2.Close packing in Two Dimensions

Here the spheres are arranged in two directions – length-wise and breadth-wise. This can be done in two different ways.



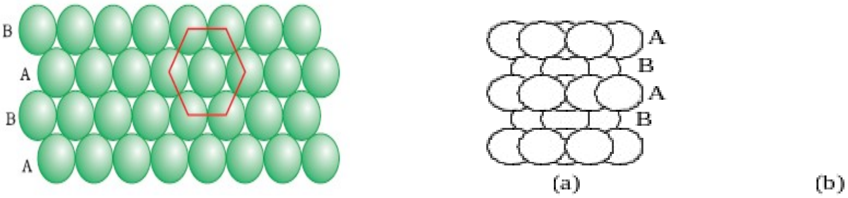
i.Square close packing: Here the spheres of second row are placed exactly above those of the first row. In this arrangement, each sphere is in contact with four adjacent spheres. So the co-ordination number of each sphere is 4.

When we join the centres of these spheres, we get a square. So this close packing is called square close packing in two dimensions.

ii.Hexagonal close packing: Here the spheres of the second row are placed in the depressions of the first row, the spheres of the third row are placed in the depressions of the second row and so on.

In this arrangement, each sphere is in contact with six adjacent spheres. So the co-ordination number of each sphere is 6.

When we join the centres of these spheres, we get a hexagon. So this close packing is called hexagonal close packing in two dimensions.



Hexagonal close packing is more efficient than square close packing in two dimensions. This is because in Hexagonal close packing maximum space is occupied by spheres.

3.Close packing in Three Dimensions

Here the particles are arranged in layers. This can be possible in two ways.

i.Three dimensional close packing from two dimensional square close-packed layers:

Here the spheres of the second layer are placed exactly above those of the first layer. In this arrangement spheres of both the layers are perfectly aligned horizontally as well as vertically.

The spheres of the third layer are placed exactly above those of the second layer and so on.

If the arrangement of the spheres in the first layer is denoted as ‘A’, all the layers are of ‘A’ type. So this arrangement forms AAA….. type pattern.

The lattice thus generated is the simple cubic lattice and its unit cell is the primitive cubic unit cell.

ii.Three dimensional close packing from two dimensional hexagonal close-packed layers:

Here the first layer is arranged as hexagonal manner. The second layer is placed above the depressions of the first layer.

On placing the second layer there arises two types of voids (vacant spaces) above the second layer – tetrahedral voids and octahedral voids.

Thus when we place the third layer over the second there are two possibilities:

Covering tetrahedral voids: Here the spheres of the third layer are placed above the tetrahedral voids of the second layer.

In this arrangement, the spheres of the third layer are vertically above those of the first layer, i.e. the first layer and the third layer are identical.

If we call the first layer as ‘A’ and the second layer as ‘B’, then the third layer will be ‘A’, the fourth layer will be ‘B’ and so on.

This will form the pattern ABAB…… This type of close packing is called **Hexagonal close packing (hcp) in three dimensions**.

This type of arrangement is found in metals like Mg, Zn etc.

Covering octahedral voids: Here the spheres of the third layer are placed above the octahedral voids of the second layer.

In this arrangement, the third layer is different from the first or the second layer.

But the spheres of the fourth layer are vertically above those of the first layer, i.e. the first layer and the fourth layer are identical.

If we call the first layer as ‘A’, the second layer as ‘B’, and the third layer as ‘C’, then the fourth layer will be ‘A’, the fifth layer will be ‘B’ and so on.

This will form the pattern ABCABC……This type of close packing is called **Cubic close packing (ccp) or face-centred cubic(fcc) packing in three dimensions**.

This type of arrangement is found in metals like Cu, Ag etc.

In both hcp and ccp 74% of the available space is occupied by spheres. So both are equally efficient.

Co-ordination Number

In a close packed arrangement the number of nearest neighbours with which a given sphere is in contact is called the co-ordination number of that sphere.

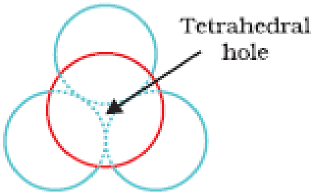
In both hcp and ccp each sphere is in contact with 12 adjacent spheres.

Thus the co-ordination number in both hcp and ccp is 12.

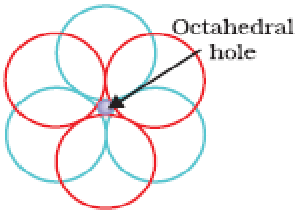
Interstitial voids

The vacant space in close packed arrangement is called voids. These are of two types- tetrahedral voids and octahedral voids.

Tetrahedral void: A void surrounded by four spheres in tetrahedral position is called tetrahedral void. In a close packed arrangement the number of tetrahedral voids is double the number of spheres, i.e. there are two tetrahedral voids per sphere.



Octahedral voids: A void surrounded by six spheres in octahedral position is called octahedral void. In a close packed arrangement the number of octahedral voids is equal to the number of spheres, i.e. there is only one octahedral void per sphere.



If there are N close packed spheres,

The number of tetrahedral voids = 2N and

The number of octahedral voids = N

Packing Efficiency

The percentage of the total space occupied by spheres (particles) is called packing efficiency.

$$\text{Packing Efficiency} = \frac{\text{Volume occupied by all the spheres in the unit cell} \times 100}{\text{volume of the unit cell}} \%$$

Packing fraction (P.F.): It is defined as ratio of the volume of the unit cell that is occupied by spheres of the unit cell to the total volume of the unit cell. Let radius of the atom in the packing = r

Edge length of the cube = a

Volume of the cube V = a^3

Volume of the atom (spherical) $v = \frac{4}{3}\pi r^3$, then packing density $= \frac{vZ}{V} = \frac{\frac{4}{3}\pi r^3 Z}{a^3}$

Density of the unit cell : It is defined as the ratio of mass per unit cell to the total volume of unit cell.

$$Density\ of\ \ unit\ cell(\rho) = \frac{\text{mass of unit cell}}{\text{volume of unit cell}}$$

$$\rho = \frac{\text{Number of particles } \times \text{mass of each particle}}{\text{volume of the unit cell}} \quad or \quad \frac{Z \times M}{a^3 \times N_0}$$

Where Z = Number of particles per unit cell,

M = Atomic mass or molecular mass,

$N_0 =$ Avogadro number $(6.023 \times 10^{23} mol^{-1})$

$a =$ Edge length of the unit cell= $a\ pm = a \times 10^{-10} cm$,

$a^3 =$ volume of the unit cell i.e. $\rho = \frac{Z \times M}{a^3 \times N_0 \times 10^{-30}} g/cm^3$

The density of the substance is same as the density of the unit cell.

Numerical problems

1. An element having atomic mass 60 has face centred cubic unit cell. The edge length of the unit cell is 400 pm. Find the density of the unit cell.

$d=\frac{zM}{a^3N_A}$ In fcc, z = 4 $d=\frac{4\ \text{atoms}\times 60\ \text{g mol}^{-1}}{(400\times 10^{-10}\ \text{cm})^3\times(6{\cdot}023\times 10^{23}\ \text{atoms mol}^{-1})}$ = 6.226 g cm^{-3}

2. Metallic iron crystallizes in a particular type of cubic unit cell. The unit cell edge length is 287 pm. The density of iron is 7.87 g cm^{-3}. How many iron atoms are there within one unit cell and name the type of crystal lattice.

$d=\frac{zM}{a^3N_A}$ $z=\frac{d\,a^3N_A}{M}=\frac{(7{\cdot}87\ \text{g cm}^{-3})\,(287\times 10^{-10}\ \text{cm})^3\times 6{\cdot}023\times 10^{23}\ \text{atoms mol}^{-1}}{55{\cdot}845\,\text{g mol}^{-1}}$ z = 2 atoms

So, the type of crystal lattice is BCC

3. Lead crystallises with fcc unit cell and has a density of 11.35 g cm^{-3}. Calculate the radius of lead atom. (Atomic mass of Pb = 207 g mol^{-1})

We know that $d=\frac{zM}{a^3N_A}$ $a^3=\frac{zM}{dN_A}$ $a^3=\frac{4\times 207\ \text{g mol}^{-1}}{11{\cdot}35\ \text{g cm}^{-3}\times 6{\cdot}023\times 10^{23}\,\text{mol}^{-1}}$

$a^3=121{\cdot}12\times 10^{-24}$ a = $(121{\cdot}12\times 10^{-24})^{1/3}$ Let x = $(121.12)^{1/3}$

$\log\ x=\frac{1}{3}\log(121{\cdot}12)$ $=\frac{1}{3}\times 2{\cdot}0831$ = 0.964

x = Antilog (0.694) x = 4.943

a = 4.943 × 10^{-8} cm In fcc $r=\frac{a}{2\sqrt{2}}$ $=\frac{494{\cdot}3\ \text{pm}}{2\sqrt{2}}=174{\cdot}787\ \text{pm}$

4. Metallic iron crystallizes in a particular type of cubic unit cell. The unit cell edge length is 287 pm. The density of iron is 7.87 g cm^{-3}. How many iron atoms are there within one unit cell and name the type of crystal lattice.

$d=\frac{zM}{a^3N_A}$

$z=\frac{d\,a^3N_A}{M}=\frac{(7{\cdot}87\ \text{g cm}^{-3})\,(287\times 10^{-10}\ \text{cm})^3\times 6{\cdot}023\times 10^{23}\ \text{atoms mol}^{-1}}{55{\cdot}845\,\text{g mol}^{-1}}$

5. **An element having atomic mass 63.1gram/mole,has FCC unit cell. The edge length of the unit cell is 3.608×10^8cm.Calculate the density of the unit cell.**

(N_o= 6.023×10^{23})

Density of unit cell

$$(d)=\frac{Z\times M}{a^3\times N_0}=\frac{4atoms\times 63.1gram/mole}{(3.608\times 10^{-8})cm^3\times 6.023\times 10^{23}atom/mole}=8.92g/cm^3$$

6. **If a metal with atomic mass 209 crystallizes in a simple cubic lattice, what is the edge length of its unit cell. (given d = 91.5kg m^{-3})**

Density of unit cell $(d)=\frac{Z\times M}{a^3\times N_0}$

$$a^3=\frac{Z\times M}{d\times N_0}=\frac{1\times 209}{91.5\times 10^{-3}\times 6.023\times 10^{23}}=3.34\times 10^{-6}cm$$

7. **Silver forms FCC lattice and X-ray studies of its crystals show that the edge length of unit cell is 408.6pm.calculate the density of silver.(atomic mass of silver is 107.9u).**

Density of unit cell $(d)=\frac{Z\times M}{a^3\times N_0}=\frac{4\times 107.9}{(4.08\times 10^{-24})^3\times 6.023\times 10^{23}}=10.56g/cm^3$

8. **Gold(atomic radius=0.144nm)crystallizesin a face centered unit cell. What is the length of the side of the cell?**

For FCC the edge length and radius of sphere arerelated by the equation,

$r=0.144nm \quad a=2\sqrt{2}r$

$$=2\sqrt{2}\times 0.144nm=2\times 1.414\times 0.144=0.40723nm$$

9. **X- ray diffraction studies show that copper crystallizes in an fcc unit cell with cell edge of 3.6×10^{-8}cm. In a separate experiment, copperis determined to have a density of 8.92g/cm^3,calculate the atomic mass of copper.**

$$d=\frac{zM}{a^3N_A}$$

$$M=\frac{da^3N_A}{Z}=\frac{8.92\times(3.6)^3\times 10^{-24}\times 6.022\times 10^{23}}{4}=62.6525\ u$$

10. **The edge of fcc unit cell of platinum is 392 pm and density is 21.5 /cm^3,calculate the Avogadro number.**

$$d=\frac{zM}{a^3N_A}$$

$$N_A=\frac{zM}{a^3d}=\frac{4\times 195.08}{21.5\times(3.92)^3\times 10^{-24}}=6.025\times 10^{23}$$

11. **A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of sodium chloride?**

$$d = \frac{zM}{a^3 N_A}$$

$$= \frac{4 \times 58.5}{(5.64)^3 \times 10^{-24} \times 6.022 \times 10^{23}} = 2.165\ g / cm^3$$

12. A body centered cubic element having density 10.3 g/cm^3, has a edge length of 314pm. Calculate the atomic mass of the element. (Avogadro's number= 6.023×10^{23}/mol)

$$d = \frac{zM}{a^3 N_A}$$

$$M = \frac{d \times a^3 \times N_A}{z}$$

$$= \frac{10.3 \times (3.14)^3 \times 10^{-24} \times 6.022 \times 10^{23}}{4} = 96.01u$$

13. Calcium metal crystallizes in a face centered cubic lattice with edge length of 0.556nm. Calculate the density of the metal. (Atomic mass of calcium = 40g/mol and Avogadro number= 6.022 × 10^{23}mol^{-1})

$$d = \frac{zM}{a^3 N_A}$$

$$= \frac{4 \times 40}{(5.56)^3 \times 10^{-24} \times 6.022 \times 10^{23}} = 1.54\ g / cm^3$$

14. Copper crystallizes into afcc lattice with edge length 3.61 x10^{-8}cm.Calculate the density of the of the crystal (Atomic mass of copper =63.5g/mol and Avogadro number= 6.022 ×10^{23}mol^{-1}).

$$d = \frac{zM}{a^3 N_A}$$

$$= \frac{4 \times 63.5}{(3.61)^3 \times 10^{-24} \times 6.022 \times 10^{23}} = 8.9\ g / cm^3$$

15. Silver crystallizes in a face centered cubic structure. If the edge length is 4.077×10^{8} cm and density is 10.5 g/cm^3, calculate the atomic mass of silver.

$$d = \frac{zM}{a^3 N_A}$$

$$M = \frac{d \times a^3 \times N_A}{Z}$$

$$= \frac{10.5 \times (4.077)^3 \times 10^{-24}}{4} = 107.09\ u$$

16. The density of Li atoms is 0.53g/cm^3.The edge length of Li is 3.5 A^0. Find out the number of Li atoms in a unit cell (N_A=6.022×10^{23}/mol & M= 6.94)

$$d = \frac{zM}{a^3 N_A}$$

$$Z = \frac{d \times a^3 \times N_A}{M}$$

$$= \frac{0.53 \times (3.5)^3 \times 10^{-24} \times 6.022 \times 10^{23}}{6.94} = 2$$

The number of lithium atoms in unit cell is 2

17. An element with molar mass 2.7 × 10^{-2} kg/mol forms a cubic unit cell with edge length 405pm. If its densityis 2.7 × 10^3 kg/m^3, what is the nature of the cubic unit cell.

$$d = \frac{zM}{a^3 N_A}$$

$$Z = \frac{a^3 \times d \times N_A}{M}$$

$$= \frac{2.7 \times 10^3 \times (405)^3 \times 10^{-27} \times 6.022 \times 10^{23}}{2.7 \times 10^{-2}} = 4$$

Since there are 4 atoms of the element present per unit cell. Hence, the cubic unit cell must be face centered or cubic close packed structure (ccp)

18. Niobium crystallises in body-centered cubic structure. If density is 8.55g/cm^3, calculate atomic radius of niobium, given that its atomic mass is 93 u.

$$d = \frac{zM}{a^3 N_A}$$

$$a^3 = \frac{zM}{d N_A} = \frac{2 \times 93}{8.55 \times 6.022 \times 10^{23}} = 36.1 \times 10^6$$

19.

$$For\ BCC \quad r = \frac{\sqrt{3}}{4} a$$

$$r = \frac{\sqrt{3}}{4} \times 330 = 143 pm$$

20. An element has a body-centered cubic (bcc) structure with cell edge of 288pm. The density of the element is 7.2 g/cm^3. How many atoms are present in 208g of the element?

$$d = \frac{zM}{a^3 N_A}$$

$$M = \frac{a^3 \times d \times N_A}{Z}$$

$$= \frac{7.2 \times (2.88)^3 \times 10^{-24} \times 6.022 \times 10^{23}}{2} = 51.78\ u$$

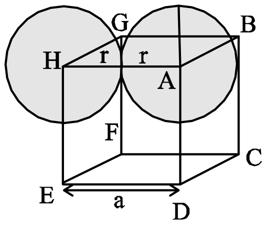
51.78 g (1mole) contains 6.022 $\times 10^{23}$ atoms.

Therefore 208g contains 4.01 $\times$ 6.022 x10^{23} = 24.187 $\times 10^{23}$ atoms.

Calculation of Packing Efficiency

1.Calculation of the packing efficiency in simple cubic unit cell (sc).

The number of atoms per unit cell in simple cube is only one. Each atom is considered as one sphere.



So, the volume of one atom (one sphere) = $\frac{4}{3}\pi r^3$.

Let the edge length of the cube be ‘a’ and the radius of each atom be r’.

In simple cube, the edge length of the cube (a) and the radius of each atom (r) are related as a = 2r Total volume of the cubic unit cell = $a^3 = (2r)^3 = 8r^3$

$$\text{Packing efficiency} = \frac{\text{Volume of one atom}}{\text{Volume of the unit cell}} \times 100\% \qquad \text{Packing efficiency} = \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100 = \frac{\pi}{6} \times 100 = 52.4\%$$

The vacant space available in simple cube = 100 – 52.4 = 47.6%

So, packing fraction in simple cube is 0.524 and fraction of vacant space available is 0.476.

2. Calculation of the packing efficiency in body centered cubic lattice or bcc structure.

The number of atoms per unit cell in bcc structures is two. Each atom is considered as one sphere. So, the volume of two atoms (two spheres) = 2 × $\frac{4}{3}\pi r^3$

From the figure 1.14 it is clear that there are three spheres touching each other along the body diagonal.

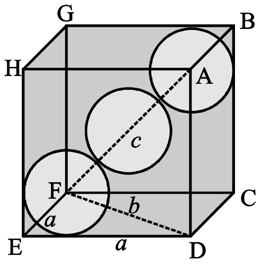
Let a be the edge length of the cube and r be the radius of the sphere. The body diagonal AF = c and face diagonal FD = b, then AF = c = 4r In Δ EFD,

$FD^2 = EF^2 + ED^2$

$b^2 = a^2 + a^2 = 2a^2 \qquad b = \sqrt{2}\ a$

Now in Δ AFD $\qquad AF^2 = AD^2 + FD^2$

$c^2 = a^2 + b^2 = a^2 + 2a^2 = 3a^2 \qquad c = \sqrt{3}\ a$



But c = 4r Therefore, $\sqrt{3}$ a = 4r a = $\frac{4r}{\sqrt{3}}$

Volume of the unit cell = a^3 = $\left(\frac{4r}{\sqrt{3}}\right)^3$

Therefore, $\text{Packing efficiency} = \frac{\text{Volume of two atoms (two spheres) in unit cell}}{\text{Volume of the unit cell}} \times 100$

$$\text{Packing efficiency} = \frac{2 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} \times 100\% \qquad = \frac{\frac{8}{3}\pi r^3}{\frac{64r^3}{3\sqrt{3}}} \times 100\% \qquad = \frac{\sqrt{3}\pi}{8} \times 100 = 68\%$$

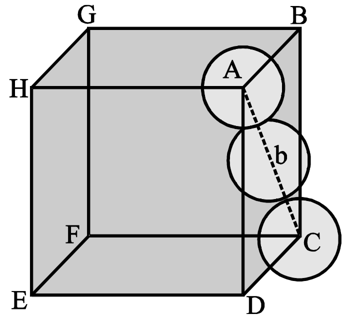
Therefore, 68% of unit cell is occupied by atoms and the rest 32% is empty space in bcc structures. The packing fraction in bcc structures = 0.68

The fraction of empty space in bcc structures = 0.32

3. Calculation of the packing efficiency in face centered cubic lattice or cubic close packing (ccp) structures.

The number of atoms per unit cell in fcc structures is four. Each atom is considered as one sphere. So, the volume of four atoms (four spheres) = 4 × $\frac{4}{3}\pi r^3$ = $\frac{16}{3}\pi r^3$

From this figure it is clear that there are three spheres touching each other along the face diagonal. Let a be the edge length of the cube and r be the radius of the sphere.



The face diagonal AC = b, then b = 4r.

In ABC, $AC^2 = BC^2 + AB^2$

b2 = $a^2 + a^2$ $b^2 = 2a^2$

b = $\sqrt{2}$ a = 4r $\sqrt{2}$ a = 4r

a = $\frac{4r}{\sqrt{2}}$ = $2\sqrt{2}\,r$

The volume of the cubic unit cell = $a^3 = (2\sqrt{2}\,r)^3$

Therefore, $\text{Packing efficiency} = \frac{\text{Volume of four atoms (four spheres) in unit cell}}{\text{Volume of the unit cell}} \times 100\%$

$$\text{Packing efficiency} = \frac{\frac{16}{3}\pi r^3}{(2\sqrt{2}\,r)^3} \times 100\ \% \qquad \text{Packing efficiency} = \frac{\frac{16}{3} \times \frac{22}{7} r^3}{8(\sqrt{2})^3\, r^3} \times 100\ \%$$

$$\text{Packing efficiency} = \frac{\frac{16}{3} \times \frac{22}{7}}{8(\sqrt{2})^3} \times 100\ \% = 74\%$$

Therefore, 74% of unit cell is occupied by atoms and the rest 26% is empty space in fcc structures . The packing fraction in fcc structures (ccp) = 0.74

The fraction of empty space in fcc structures (ccp) 0.26.

Note: The packing efficiency in hcp is same as in ccp. But the method of calculation is different.

Imperfections in solids (Crystal Defects)

The deviation from the regular orderly arrangement of particles of a solid is termed as **imperfections or crystal defects.**

The crystal defects are broadly classified into two – point defects and line defects. The imperfection around a point (an atom) in a crystalline substance, it is termed as **point defect**. The imperfection along a row is termed as **line defect**.

Point defects

Point defects can be classified into three types: Stoichiometric defects, Non-stoichiometric defects and Impurity defects.

1.Stoichiometric defects:

These are point defects which do not disturb the stoichiometry of the solid. They are also called intrinsic or thermodynamic defects, because these defects can also develop when a substance is heated.

These are of two types – vacancy defects and interstitial defects.

a.**Vacancy defect**: When some of the lattice sites are vacant, the crystal is said to have vacancy defect. This defect decreases the density of the solid.

b.**Interstitial defect**: When some constituent particles occupy an interstitial site, the crystal is said to have interstitial defect. This defect increases the density of the solid.

The above two types of defects are shown by non-ionic solids.

Ionic solids show two types of stoichiometric defects – **Schottky defect and Frenkel defect.**

i.Schottky defect: It is basically a vacancy defect. It arises due to the missing of equal number of anions and cations from the lattice site.

It is shown by ionic crystals in which the anionic and cationic sizes are almost equal. NaCl, KCl, CsCl, AgBr etc. show Schottky defect. Due to this defect the density of the solid decreases.

ii.Frenkel defect: It is a stoichiometric defect arising due to the misplacing of an ion (generally a cation) from the lattice site to the interstitial site. It is also called dislocation defect.

This type of defect is shown by ionic solids in which there is a large difference in the size of the ions.

E.g. ZnS, AgCl, AgBr, AgI etc. This defect does not change the density of the solid.

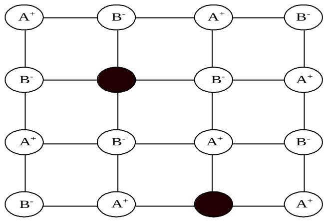


Fig. (a): Schottky Defect

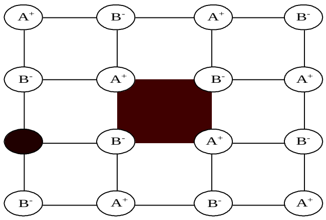


Fig. (b): Frenkel Defect

Difference between Schottkey defect and Frenkel defect:

Sl. No.	Schottky defect	Frenkel defect
1	It is missing of both cation and anion from the crystal lattice.	It is the dislocation of cation from its normal site to the interstial site.
2	Density decreases.	Density remains same.
3	It is found in ionic solids having high co-ordination number.	It is found in ionic solids having low co-ordination number.

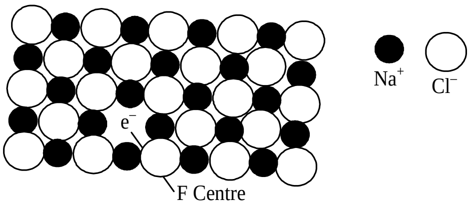
b)Non-Stoichiometric defects: These are point defects which change the stoichiometry of a solid. These defects are of two types:

i) Metal excess defect and ii) Metal deficiency defect

i) Metal excess Defect:

Here the number of cations is greater than the number of anions. This arises in two ways:

1.Metal excess defect due to anionic vacancies: Here some of the anions are missing from the lattice site. The electrical neutrality is maintained by occupying electrons in the anionic sites. These electrons are called **f-centres** because they give colour to the crystal.



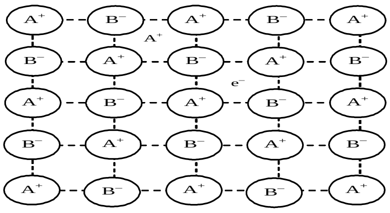
F-centre in a Sodium chloride crystal

This defect is shown by alkali metal halides. For example when NaCl is heated in an atmosphere of sodium vapour, some sodium atoms are deposited at the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combines with Na atom to form NaCl.

$$Na + Cl^- \longrightarrow NaCl + e-$$

The electron so formed diffuse into the crystal and occupies the anion vacancy. These electrons absorb light energy and get excited. As a result the crystal becomes yellow in colour. Similarly, excess of Li makes LiCl crystals pink and excess of K makes KCl crystals violet.

2.**Metal excess defect due to extra cations at interstitial sites**: Here some cations occupy the interstitial sites. The electrical neutrality is maintained by occupying some electrons in adjacent interstitial sites.



Metal excess defects caused by interstitial cations.

E.g. When ZnO crystals are heated, the white coloured crystals becomes yellow.

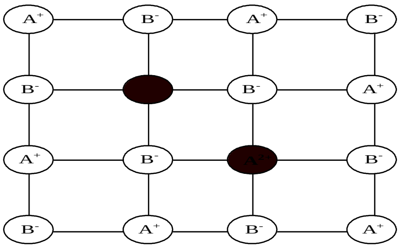
This is because on heating, the crystal loses oxygen as follows:

$$ZnO \longrightarrow Zn^{2+} + \frac{1}{2}O_2 + 2e^-$$

The Zn ions now move to the interstitial sites and the electrons to neighbouring interstitial sites.

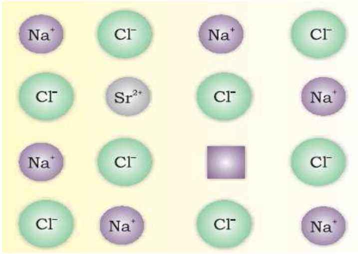
ii) **Metal deficiency Defect:**

Here the number of cations is smaller than the number of anions. This is mainly arises due to cation vacancies. This type of defect is commonly shown by transition metal compounds. E.g. FeO



Metal deficiency due to cation vacancy

c)Impurity Defects: It is the defect arising due to the presence of foreign particles in a crystal. For example if molten NaCl containing a little amount of SrCl2 is crystallised, some of the sites of Na^+ ions are occupied by Sr^{2+}. Each Sr^{2+} replaces two Na^+ ions. It occupies the site of one ion and the other site remains vacant. The cationic vacancies thus produced are equal to the number of Sr^{2+} ions. Another similar example is a solid solution of $CdCl_2$ and AgCl.



Properties of solids

1) Electrical properties: Based on the electrical conductivity, solids are classified into three types:

i.Conductors: They are solids which allow the passage of electricity through them. Their conductivity ranges from 10^4 to 10^7 $ohm^{-1}m^{-1}$.

Metals have conductivities in the order of 10^7 $ohm^{-1}m^{-1}$.

ii.Semi-conductors: They are solids which allow the passage of electricity only partially. Their conductivity ranges from 10^4 to 10^{-6} $ohm^{-1}m^{-1}$.

iii.Insulators: They are solids which do not allow the passage of electricity through them. Their conductivity ranges from 10^{-10} to 10^{-20} $ohm^{-1}m^{-1}$.

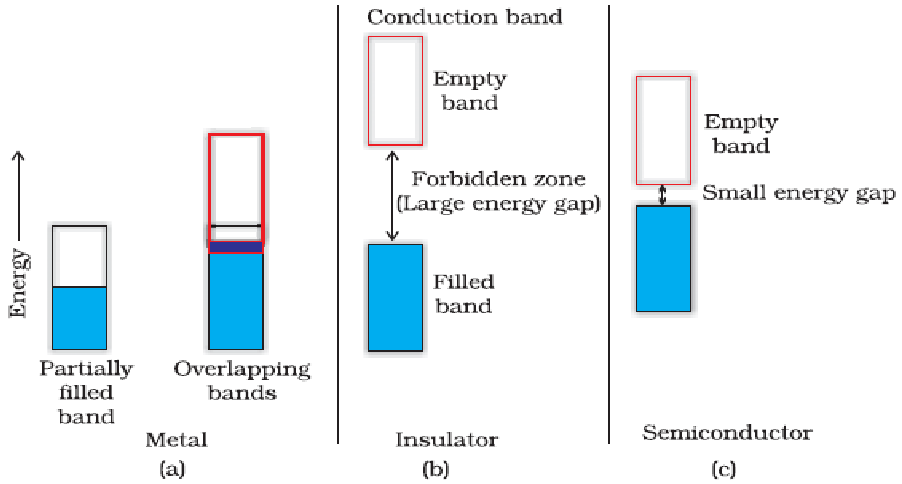
Conduction of Electricity in metals - Band Model

Metals conduct electricity in solid as well as in molten state. The conductivity of metals depends upon the number of valence electrons.

The atomic orbitals of metals combine to form molecular orbitals, which are so closely spaced that they form a band.

If this band is partially filled or it overlaps with a higher energy unoccupied conduction band, the electrons can flow easily under an applied electric field and the metal shows conductivity.

If the gap between filled valence band and the unoccupied conduction band is large the electrons cannot jump to it and such substances act as insulators.



Conduction of Electricity in semi-conductors

In the case of semiconductors, the gap between the valence band and the conduction band is small. So some electron may jump from valence band to conduction band and show some conductivity.

Their conductivity increases with rise in temperature, since more electrons can jump to the conduction band. Such semiconductors are also called intrinsic semiconductors. E.g.: Si, Ge etc.

The conductivity of intrinsic semiconductors is very low. Their conductivity can be increased by adding an appropriate impurity.

The process is called doping. Addition of impurities creates electronic defects in them. Such semiconductors are called extrinsic semiconductors.

Doping can be done by the addition of either electron rich impurity or electron deficit impurity.

a) Doping by electron rich impurity: When a group 14 (which contains 4 electrons in the valence shell) element like Si or Ge is doped with a group 15 element (which contains 5 electrons in the valence shell) like P or As, four electrons are used for the formation of covalent bonds and the fifth electron becomes free.

The presence of this delocalised electron increases the conductivity and hence silicon doped with electron rich impurities is called **n-type semiconductor**.

The semiconductor whose increased in conductivity is a result of ectron hole is called a p-type semiconductor.

When a crystal of group 14 elements suchas Si or Ge is doped with a group 13 element such as B, Al, or Ga , a p-type of semiconductor is generated.

b)Doping by electron deficient impurity:

When a group 14 (which contains 4 electrons in the valence shell) element like Si or Ge is doped with a group 13 element (which contains 3 electrons in the valence shell) like B, Al, or Ga, the three electrons are used for the formation of covalent bonds and the fourth valence electron is missing.

This creates an electron hole or electron vacancy. An electron from a neighbouring atom can come and fill the electron hole.

So the position of the hole is moved in the direction opposite to that of the electron has moved.

Under the influence of electric field, electrons would move towards the positively charged plate through electronic holes.

It would appear as if electron holes are positively charged. This type of semiconductors are called **p-type semiconductors**.

The semiconductor whose increased conductivity is a result of negatively-charged electrons is called an n-type semiconductor.

When the crystal of a group 14 element such as Si or Ge is doped with a group 15 element such as P or As, an n-type semiconductor is generated.

A large variety of solids which have lattices similar to Ge or Si have been prepared by the combination of groups 13&15 or 12&16. E.g. for 13and 15 group compounds are In,Sb, Al,P & Ga,As. They are used as semiconductors.

E.g. for 12 and 16 group compounds are ZnS, CdS, CdSe & HgTe.

Differences between n-type semiconductors and p-type semiconductors:

Sl. No.	n-type semiconductors	p-type semiconductors
1	They are obtained by doping pentavalent impurities (atoms).	They are obtained by doping trivalent impurity atoms.
2	Conduction is due to electrons.	Conduction is due to holes.
3	P, As, Sb, Bi are used for doping.	B, Al, Ga, In are used for doping.

2) Magnetic properties

Every solid has some magnetic properties associated with it due to the presence of electrons.

Each electron in an atom behaves like a tiny magnet. Electron being a charged particle and due to spin and orbital motions,has a permanent spin and orbital magnetic moment.

The magnitude of this magnetic moment is very small and is a measured in the unit called Bohr Magneton (μB). (1 μB = 9.27×10^{-24} Am^2 (amperemetre square)).

Based on the magnetic properties, solids can be classified into **five** types.

1.**Diamagnetic Substances**: These are weakly repelled by an external magnetic field. Diamagnetism arises due to the presence of only paired electrons.

Pairing of electrons cancels their magnetic moments and so they have no net magnetic moment. E.g.: H_2O, NaCl, Benzene (C_6H_6)

2.**Paramagnetic Substances**: They are weakly attracted by an external magnetic field. Paramagnetism is due to the presence of one or more unpaired electrons. They have a net magnetic moment.

They lose their magnetism in the absence of external magnetic field. So they are temporary magnets. Eg: O_2, Cu^{2+}, Fe^{3+}, Cr^{3+} etc.

3.**Ferromagnetic Substances**: They are very strongly attracted by a magnetic field and can be permanently magnetised.

In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called domains.

In the absence of an external magnetic field, these domains are randomly oriented. When the substance is placed in a magnetic field, all the domains get oriented in the direction of the magnetic field and a strong magnetic effect is produced.

This ordering of domains do not change even when the externalmagnetic field is removed and so they become permanent magnets.

Eg: Fe, Co, Ni, Gd (Gadolinium), CrO_2 etc.

4.Anti-ferromagnetic Substances: Here the domains are oppositively oriented and cancel each other. So they have no net magnetic moment. Eg: MnO

5.Ferrimagnetic Substances: Here the domains are arranged in opposite directions but in unequal numbers. So they have a net magnetic moment.

Eg: Fe_3O_4 (magnetite) and ferrites like $MgFe_2O_4$, $ZnFe_2O_4$ etc

$$\underset{\text{ferromagnetism}}{\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow} \qquad \underset{\text{Anti- ferromagnetism}}{\uparrow\downarrow\uparrow\downarrow\uparrow\downarrow\uparrow} \qquad \underset{\text{Ferrimagnetism}}{\uparrow\downarrow\downarrow\uparrow\downarrow\downarrow\uparrow}$$

UNIT 2

Solutions

A solution is a homogenous mixture of two or more substances, the composition of which may vary within limits. “A solution is a special kind of mixture in which substances are intermixed so intimately that they can not be observed as separate components”. The dispersed phase or the substance which is to be dissolved is called solute, while the dispersion medium in which the solute is dispersed to get a homogenous mixture is called the solvent. A solution is termed as binary, ternary and quartenary if it consists of two, three and four components respectively.

Types of solutions

Based on the physical state of the solvent, binary solutions are classified as

(1)Gaseous solutions (2)Liquid solutions (3) Solid solutions

Gaseous solutions: The solutions in which the solvent is gas and solute is either solid, liquid or a gas are called gaseous solutions.

Liquid solutions: The solutions in which the solvent is liquid and the solute is either a solid, liquid or a gas are called liquid so0lutions.

Solid solutions: The solutions in which the solvent is solid and the solute is either a solid, liquid or a gas, are called solid solutions.

Different types of solutions and some examples

Types of solutions	Solute	Solvent	Common example
Gaseous Solutions	Gas Liquid Solid	Gas Gas Gas	Mixture of oxygen and nitrogen gases Chloroform in nitrogen gas Camphor in nitrogen gas
Liquid Solutions	Gas Liquid Solid	Liquid Liquid Liquid	Oxygen dissolved in water Ethanol dissolved in water Glucose dissolved water
Solid Solutions	Gas Liquid Solid	Solid Solid Solid	Solution of hydrogen in palladium Amalgam of mercury with sodium Copper dissolved in gold

Note: In aqueous solution water is the solvent.

Methods of expressing concentration of solutions

The concentration of a solution is the amount of a solute present in a given quantity of solvent or solution.

(a) Molarity (M) (b) Molality (m) (c) Mole fraction (x)

Molarity (M): Molarity of a solution is defined as the number of moles of the solute dissolved in one litre of the solution.

$$\text{Molarity} = \frac{\text{Number of moles of the solute}}{\text{Volume of the solution} \in \text{litre}}$$

If W_B gram of the solute of molar mass M_B is dissolved in V dm^3 of the solution, then the molarity is given by,

$$\text{Molarity} = \frac{W_B \times 1000}{M_B \times V}$$ Units: mol/L or mol/dm^3

- Molarity is most common way of representing the concentration of solution.
- Molarity is depend on temperature as, $\text{Molarity} \propto \frac{1}{\text{Temperature}}$

Advantages of molarity

✓ Stoichiometric calculations are simplified since the quantity of the solute is expressed in mole.

✓ Quantity of the solution is easily measured by volume rather than by mass.

Disadvantages of molarity

Molarity of a solution decreases with the increase in temperature since the volume of the solutions increases with the increase in temperature. Thus molarity is temperature dependent and cannot be used in experiments that involve temperature variations.

The exact amount of the solvent in a given volume of the solutions cannot be determined if the density of the solution is not known.

Molality (m): Molality of solution is defined as the number of moles of the solute dissolved in one kg of the solvent. Molality is denoted by ‘m’ and is calculated by the expression.

$$\text{Molality} = \frac{\text{Number of moles of the solute}}{\text{Mass of the solvent} \in kg}$$

If W_B gram of the solute of molar mass M_B is dissolved in W_A gram of the solvent, then molality is given by

$$\text{Molality} = \frac{W_B \times 1000}{W_A \times M_B}$$ Unit: mol/kg

Advantages of molality: Molality is temperature independent quantity. Therefore this unit can be conveniently used in experiments involving temperature variations

The exact mass of the solvent in given amount of the solution can be calculated easily.

Mole fraction(x): Mole fraction of a component in a solution is the ratio of number moles of that component to the total number of moles of all the components.

Let us consider a binary solution that contains n_A moles of solvent 'A' and n_B moles of the solute 'B'

Mole fraction of the solvent A is $x_A = \frac{n_A}{n_A + n_B}$

Mole fraction of the solute B is $x_B = \frac{n_B}{n_A + n_B}$

For a solution that contains a large number of components A, B,C,D,E……….I, mole fraction of component D is given by

$$x_D = \frac{n_D}{n_A + n_B + \ldots.. + n_I}$$

Sum of mole fraction of all the components in a solution is always equal to one i.e., $x_A + x_B = 1$

Mole fraction is defined to a component and not to the solution

Mole fraction has no unit

This unit is highly useful in the

- Calculation of partial pressure of a component gas in a solution of gases.
- Calculation of relative partial pressures of the vapour which is in equilibrium with the solution.

Mass percentage (w/w): Mass percentage of a solution is defined as the number of parts by mass of the solute dissolved in100 parts by mass of the solution.

Mass percentage = $\frac{Mass\ of\ the\ solute}{Mas\ of\ the\ solution} \times 100$

Note: Units of the two masses should be same

Volume percentage (v/v): Volume percentage of a solution is defined as the number of parts by volume of the solute dissolved in 100 parts by volume of the solution.

Volume percentage = $\frac{Volume\ of\ the\ solute}{Volume\ of\ the\ solution} \times 100$

Note: Units of the two volume unit be same.

This unit is more useful when both the solute and solvents are liquids.

Mass by volume percentage (w/v): Mass by volume percentage of a solution is defined as the number of parts by mass of the solute dissolved in 100 parts by volume of the solution.

Mass by volume percentage = $\frac{Mass\ of\ the\ solute}{Volume\ of\ the\ solution} \times 100$

In this case, generally gram and cm^3 are used as the units. Otherwise system of units should be same.

Parts per million (ppm): Parts per million of a solute is defined as the member of parts of solute dissolved in one million parts of the solution.

$$\text{Parts per million} = \frac{Number\ of\ parts\ of\ the\ solute}{Number\ of\ parts\ of\ the\ solution} \times 10^6$$

Note: The units of the parts of the solute and the solution should be same.

Parts per million are also expressed in w/w, v/v and w/v.

This unit is suitable when solutes are present in trace quantities.

Note:(I)Mass percentage, ppm, mole fraction, and molality are independent of temperature because mass is independent of temperature

(II) Molarity, volume percentage and mass by volume percentage depends on temperature because volume depends on temperature.

Solubility:

When a solute is mixed with a solvent, particles of the solute leave the solute phase and get mixed with the particles of the solvent phase. This process is known as dissolution. The solute is said to be dissolved in solvent.

Compounds like sugar, potassium nitrate, ammonium nitrate, etc., dissolve in water whereas they are insoluble in benzene or ether. Compounds like naphthalene, anthracene, diphenyl, etc., dissolve in solvents like benzene and ether but not in water. By these examples it may be broadly generalized that ‘Like dissolved like’. It means to say that polar solutes dissolve in polar solvents and non polar solutes dissolve in non polar solvents. Thus dissolution of a solute in a given solvent takes place when the nature of inter particle attractive forces in the solute and the solvent are same.

Solubility of a solid in a liquid:

Dissolution of a solute in a solvent is a reversible change. If dissolution is the forward change then crystallization is the backward change that takes place simultaneously.

When a large amount of solid solute is added to given amount of a solvent, initially dissolution of the solute takes place. But as the concentration of the solute particles in the solution phase increases, the back ward change, i.e., crystallization begins and its rate starts to increase. At one stage the rates of dissolution and crystallization become equal resulting in a dynamic equilibrium between the solid solute and the solute particle in the solution phase

$$\underset{\left(Solid\right)}{Solute}\ \overset{dissolution}{\text{¿}}\ \text{solute particles in solution}$$

Once the equilibrium is reached, the concentration of the solute particles in the solution remains constant. No more solute dissolves in the solvent. The solution thus formed is said to be saturated solution. A solution in which no more solute can be dissolved at the same temperature and pressure is called saturated solution. The amount of the solute present in a given quantity of the saturated solution at a given temperature and pressure is called solubility of the solute in the given solvent. A solution in which some more solute can be dissolved at the given temperature and pressure is called unsaturated solution.

Generally solubility is measured in mass percentage (w/w). Therefore, solubility of a solid solute in a given liquid solvent at a given temperature is the mass of the solute in gram dissolved in 100 grams of the saturated solution.

Effect of temperature on solubility of solid solute in a liquid solvent:

Since, solid solute and solvent particles in solution are in dynamic equilibrium, it follows Le-chatelier’s principle. According to this principle increase in temperature shifts the equilibrium towards endothermic change and decrease in temperature shifts the equilibrium towards the exothermic change.

Therefore, if the dissolution of a solute in a given solvent is endothermic then its solubility increases with the increase in temperature.

If the dissolution of a solute in a given solvent is exothermic, then the solubility of the solute decreases with increase in temperature.

Note: For exothermic dissolution, enthalpy solution, $\Delta_{sol} H < 0$ and for endothermic dissolution, enthalpy of solution $\Delta_{sol} H > 0$

Effect of pressure:

There is no significant effect of pressure on the solubility of a solid solute in a liquid solvent. This is because solids and liquids are highly incompressible and practically remain unaffected by changes in pressure.

Solubility of a gas in a liquid :

Gases dissolve in liquids to form liquid-gas solution. Example, carbon dioxide dissolves in water to form soda water. Water in wells, rivers, and sea contains dissolved air which is used by aquatic animals for their breathing.

Factors that influence solubility of gases in liquids:

The factors that influence the solubility of gases in liquids are

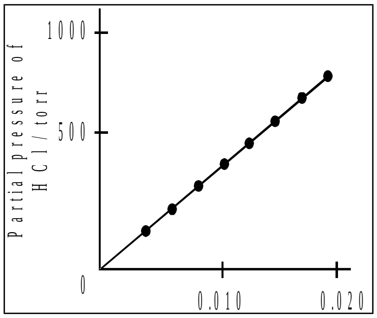
- The nature of the gas and solvent
- Nature of the solvent
- Temperature
- External pressure

The nature of gases and nature of solvents:

Non-polar gases are less soluble in polar solvents like water. For example, gases like, O_2, N_2, H_2 etc., which are non-polar are very less soluble in water which is a polar solvent at room temperature and pressure. But CO_2, HCl, NH_3 etc., being polar gases, are highly soluble in water under identical conditions.

Effect of temperature on the solubility of gases:

Generally solubility of all gases in liquids decreases with the increases in temperature. This is because of two reason ;



Generally dissolution of any gas in a liquid is exothermic. According to Le-Chatelier's principle, low temperature favours exothermic changes. That is why gases dissolve more at low temperatures and less at high temperatures in liquids.

Increase in temperature increases the kinetic energy of dissolved gas molecules. As a result, the gas molecules escape more from the solution phase by overcoming the attractive forces.

Note: Solubility of oxygen is more in cold water than in warm water. That is why aquatic speices are more comfortable in cold waters than in warm waters.

Effect of pressure:

The solubility of a gas in a liquid increases with the increase in its partial pressure above the liquid.

Henry's law:

This law gives the quantitative relationship between the solubility of a gas in a liquid and the partial pressure of the gas above the liquid at a given temperature. Henry's law states that "at constant temperature the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the solution".

If the solubility of a gas is in mole faction, the law can also be stated as " the partial pressure of the gas above the solution is directly proportional to the mole fraction of a gas in the solution".

i.e., p $\propto$x where p is partial pressure of the gas and x is solubility in mole fraction

$p = K_H x$ Here, K_H is called Henry's law constant.

$X = \frac{p}{K_H};$

Characteristics of Henry's law constant:

Higher is the value of K_H lower is the solubility of gas.

Different gases have different K_H values. Therefore K_H value depends on nature of the gas.

For example, K_H value. of CO_2 and O_2 in water at 20^0 C are respectively 1.67k bar and 457k bar. That is why CO_2 is about 28 times more soluble in water than oxygen at given temperature.

K_H value increases by increasing the temperature. This indicates that solubility of gases in liquid decreases by increasing temperature. This is because the dissolution of gas in liquid is an exothermic process.

Units of Henry's law constant are same as pressure.

Applications of Henry's law:

(a) Carbonated beverages:To increase the solubility of carbon dioxide in soda water and soft drinks, bottles are sealed under high pressure of CO_2.

(b) Deep sea diving:Oxygen cylinders used by sea divers (Scuba divers) are filled with air which is diluted with helium to minimize the solubility of nitrogen in the blood by decreasing its partial pressure to avoid the risk of 'bends'.

(Otherwise more nitrogen will be dissolved due to high pressure deep under sea water. When a sea diver comes back to the surface, the solubility of nitrogen again decreases and the dissolved gas is released, leading to the formation of nitrogen bubbles in the blood. This results in the blockage of capillaries and leads to a medical condition known as 'bends' or decompression sickness which causes acute pain).

(c) High altitude sickness:At high altitudes, partial pressure of oxygen is less than that at a ground level. This leads to low concentrations of oxygen in the blood and tissues of mountain climbers. Low-blood oxygen causes climbers to become weak and unable to think clearly. These are symptoms of anoxia.

Equilibrium vapour pressure of a liquid:

Consider a liquid taken in a closed container. The liquid being volatile, molecules of the liquid escape from the liquid phase and occupy the space above the liquid forming vapour phase.

But after some time molecules of the vapour phase also starts condensing into liquid.

Thus at one stage there will be a dynamic equilibrium between the vapour phase and the liquid when the rate of vapourisation becomes equal to that of condensation.

The pressure exerted by the molecules of the vapour phase on the liquid phase at equilibrium is called equilibrium vapour pressure.

For simplicity it is also called vapour pressure. At constant temperature, different liquids have different vapour pressures since they depend on nature of the liquids.

Vapour pressure of a solution of liquid in liquid:

The vapour phase of a binary solution placed in a closed vessel consists of vapours of both the components. The French chemist F.M Raoult (1886) gave quantitative relationship between the partial pressures of the components in the vapour phase and their mole fractions in the solution phase. This relationship is known as Raoult's law.

Raoult's law for a solution of two liquid components:

Raoult's law states that for a solution of volatile liquids, the partial pressure of each component in the vapour phase is directly proportional to the mole fractions of the respective components in the solution phase at a given temperature.

Let us consider a solution containing two volatile components A and B (that have measurable vapour pressures) in a closed container. The equilibrium is established between vapour phase and the liquid phase at constant temperature.

Let P_{total} be the total vapour pressure of the vapour phase about the solution and $p_A$and p_B be the partial vapour pressure of the two components A and B.

These partial pressures are related to the mole fractions $x_A \wedge x_B$ of the two components A and B respectively. According to Raoult's law for component A, $p_A \propto x_A$ or $p_A = p_A^0 x_A$

Where p_A^0 is the vapour pressure of the pure component A at the same temperature. Similarly, for component B $p_B \propto x_B$ or $p_B = P_B^0 X_B$

Where $p_B^0$is the vapour pressure of the pure component B at the same temperature.

According to Dalton’s law of partial pressures, the total pressure is the sum of the partial pressures of all components at the same temperature.

$$p_{total}=p_A+p_B \qquad \text{or} \qquad p_{total}=p_A^0 x_A+p_B^0 x_B$$

$$p_{total}=p_A^0\left(1-x_B\right)+p_B^0 x_B \qquad \text{or} \; p_{total}=p_A^0-p_A^0 x_B+\; p_B^0 x_B$$

$$p_{total}=p_A^0+\left(p_B^0-p_A^0\right)x_B$$

Total vapour pressure over the solution is directly proportional to the mole fraction of any one component ($x_A \vee x_B$¿.

Total vapour pressure of the vapour phase of the solutions varies linearly with the mole fraction of component B(orA).

Depending on the vapour pressures of the pure components A and B, total vapour pressure over the solution decreases or increases with the increase of the mole fraction of component A (or B).

The composition of vapour phase in equilibrium with the solution is determined by the partial pressures of the components. If $y_A \wedge y_B$are the mole fraction of the component A and B respectively in the vapour phase then, using Dalton’s law of partial pressures:

$$p_A=y_A\,p_{total} \qquad \text{or} \qquad p_B=y_B\times p_{total}$$

In general

$$p_i=y_i\,p_{total}$$

Raoult’s law as a special case of Henry’s law:

According Henry’s law “the partial pressure of the gas (p) in vapour phase is proportional to the mole fraction of the gas (x) in the solution i.e., $p=K_H x$

According to Raoult’s law “the partial pressure of each component of the solution is directly proportional to its mole faction present in the solution.

i.e., $p_i=p_i^0 x_i$

By comparing equations for Henry’s law and Raoult’s law, we can conclude that the partial pressure of volatile liquid or gas is directly proportional to its mole fraction in solution.

Only the difference is in their proportionality constants $K_H \wedge p_i^0$. Hence Raoult’s law is a special case of Henry’s law in which $K_H=p_i^0$.

Ideal and non- ideal solutions:

The binary solutions of the volatile liquids can be classified into two types. They are ideal and non-ideal solutions.

Ideal solutions:

A solution which obeys Raoult’s law at all concentration range of the components and temperature is called an ideal solution.

In ideal solutions,solvent(A)–solute (B) interactions are equal to solute (B)–solute(B)and solvent(A)–solvent(A)interactions.A perfectly ideal solution is rare but some solutions are nearly ideal in behaviour. A few examples are:

- Benzene and toluene
- Chlorobenzene and bromobenzene
- Carbon tetrachloride and silicon tetrachloride
- n-Hexane and n-heptane
- Ethylene bromide and ethylene chloride

Characteristics of Ideal solution

(i) It should obey Raoult's law, i.e., $P_A = P_A^0 X_A$ and $P_B = P_B^0 X_B$.

(ii) $\Delta H_{\text{mixing}} = 0$

(iii) $\Delta V_{\text{mixing}} = 0$

Non-ideal solutions:

A solution which does not obey Raoult's law at all concentration range of the components and temperature is called a non ideal solution.

The non ideal solutions are accompanied by change in enthalpy and volume during their formation i.e., $\Delta H_{mixing} \neq 0 \Delta V_{mixing} \neq 0$¿

In general, most of the solutions are non ideal and deviate from ideal behaviour.

It must be remembered that in non- ideal binary solution none of the components follows the Raoult's law. The non-ideal solutions are further classified into two categories. They are

1. Non-ideal solution showing positive deviation
2. Non ideal solution showing negative deviation

The causes for these deviations lie in the nature of interactions at the molecular level.

Non-ideal solution showing positive deviation:

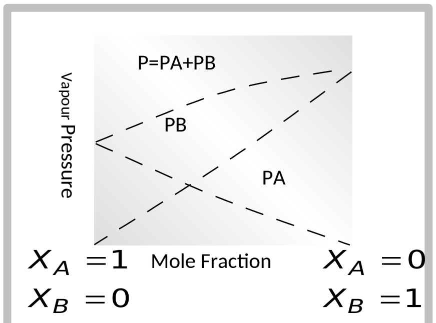
The solutions for which the total vapour pressure is higher than that expected from Raoult's law are called solutions with positive deviations.

For solutions with positive deviations from Raoult's law, partial vapour pressure of each component A and B is higher than that one that is calculated from Raoult's law for the same composition.

In these solutions, the intermolecular attractive forces between the solute-solvent molecules are weaker than those between the solute-solute, solvent-solvent interactions.

This means that in such solutions, molecules of A (or B) will find it easier to escape than in pure state. This will increases the vapour pressure and result in positive deviation.

Due to decrease in magnitude of intermolecular attractive forces, the molecules are loosely held and thus increasing intermolecular distances. Therefore formation of a non ideal solution is associated with increase in volume and absorption of energy.



Partial and total vapour pressure curves for solutions that show positive deviations fr

Characteristics:

$p_A > p_A^0 x_A$

$p_B > p_B^0 x_B$

$\Delta H_{mixing} = +ve$

$\Delta V_{mixing} = +ve\ i.e., (V_{solution} > V_A + V_B).$

Examples:

- Acetone + ethanol
- Water + ethanol
- Acetone + CS_2
- CCl_4 + toluene
- Water + methanol

Non-ideal solution showing negative deviation:

The solutions for which the total vapour pressure is lower than that of an ideal solution of same composition and temperature are called Solutions with negative deviations.

For solution with the negative deviation from Raoult's law, partial vapour pressure of each component A and B is lesser than the one that is calculated from Raoult's law for the same composition. So, the total vapour pressure of the solution is less than that of ideal solution of same composition

Boiling point of such a solution is relatively higher than the boiling points of A and B respectively.

In this case the intermolecular attractive forces between the solute-solvent molecules are stronger than those between the solute-solute and solvent-solvent molecules. This means that in such solutions, molecules of A (or B) will not find it easier to escape than in pure state. This will decrease the vapour pressure and result in negative deviation.

Characteristics:

$p_A < p_A^0 x_A$

$p_B < p_B^0 x_B$

$\Delta H_{mixing} = -ve$

$\Delta V_{mixing} = -ve\ i.e., (V_{solution} < V_A + V_B).$

Examples:

- Acetone +aniline
- H_2O + HNO_3
- Acetic acid + pyridine
- Acetone + chloroform

- Chloroform + diethylether
- Chloroform + benzene
- $CH_3OH + CH_3COOH$
- Water + HCl

Azeotropic Mixtures (or) constant Boiling Mixtures:

There are certain binary liquid mixture, which boil at constant temperature like a pure liquid such that both the components are distilled out simultaneously. The components of such mixtures cannot be separated during functional distillation. Such mixtures are named as Azotropic mixtures.

The mixture of liquids which boils at constant temperature and possess same composition for both liquid and vapour phases is named as azeotropic mixture.

Types of azeotropes:

Based on the relative values of boiling points of the components and the mixture, azeotrops are of 2 types:

1.Minimum boiling azeotropes: The azeotropic mixtures for which the boiling point is lower than the boiling points of both the component liquids are named as minimum boiling azeotropes.

Conditions for formation: Minimum boiling azeotropes are formed by non-ideal solutions with positive deviation. The composition of mixtures at which the vapour pressure is highest represents the azeotropic composition. Since the vapour pressure is highest, boiling point is minimum and hence is lower than both the components.

For example: a mixture of ethanol and water at a composition of 95.574% by mass of ethanol shows a constant boiling point of 351.1 K. This is lesser than both ethanol (b.p : 351.3 K) and water (b.p : 373 K).

2.Maximum boiling azeotropes:

The azeotropic mixtures for which the boiling point is higher than the boiling points of both the component liquids are named as maximum boiling azotropes.

Conditions for formation: Maximum boiling azeotropes are formed by non-ideal solutions with negative deviation. The composition of mixtures at which the vapour pressure is lowest represents the azeotropic composition. Since the vapour pressure is lowest, boiling point is maximum and hence is higher than both the components.

For example: a mixture of HNO_3 and water at a composition of 68% by mass of HNO_3 shows a constant boiling point of 393.5 K. This is greater than both HNO_3 (b.p : 359 K) and water (b.p : 373 K).

Table 2 : Differences between ideal and non-ideal solutions of two liquids:

Ideal solutions	Non-ideal solutions
Obey Raoult’s law at all range of concentration.	Do not obey Raoult’s law at all range of concentration.
$\Delta H_{mixing} = 0$(Neither heat is evolved nor absorbed during dissolution).	$\Delta H_{mixing} \neq 0$. (Either heat is evolved or absorbed during dissolution).
$\Delta V_{mixing} = 0$ (Volume of the solution is equal to the sum of volumes of the components).	$\Delta V_{mixing} \neq 0$ (Volume of the solution is not equal to the sum of volumes of the components).
$p_{total} = p_A^0 x_A + p_B^0 x_B$	$p_{total} \neq p_A^0 x_A + p_B^0 x_B$
The intermolecular attractive forces between A-A, B-B and A-B are same.	The intermolecular attractive forces between A-A, B-B and A-B are not same.

Differences between non ideal solution with positive and negative deviations:

Positive deviation from raoult’s law	Negative deviation from Raoult’s law
$\Delta H_{mixing} > 0$ (Heat is absorbed during dissolution.)	$\Delta H_{mixing} < 0$. Heat is evolved during dissolution
$\Delta V_{mixing} > 0$ (volume increases during dissolution.)	$\Delta H_{mixing} < 0$. Volume decreases during dissolution
$p_{total} > p_A^0 x_A + p_B^0 x_B$	$p_{total} > p_A^0 x_A + p_B^0 x_B$
Attractive force between A-B is weaker than A-A and B-B attractive forces.	Attractive force between A-B is stronger than A-A and B-B attractive forces.
Forms minimum boiling point azeotrope.	Forms maximum boiling point azeotrope.

Raoult’s Law for solution of solid in Liquid:

The French chemist F.M Raoult (1886) carried out a series of experiments to study the vapour pressure of a number of binary solutions. On the basis of results of the experiments, he proposed a generalisation called Raoult’s law which states that, the vapour pressure of a solution containing non volatile solute is directly proportional to the mole fraction of the solvent.

In case of a solution containing two components A (volatile solvent) and B(non volatile solute) the vapour pressure of solution is given as

$$P_A \alpha x_A \text{ Or } \qquad P_A = K x_A$$

Where K is proportionality constant

Colligative properties and determination of molecular masses:

The properties of dilute solutions of non volatile solutes which depend only on the number of particle of the solute relative to the total number of particles in the solution and not on the nature of the solute are called colligative properties. Thus, colligitive properties depend on the number of solute particles present, regardless of whether they are atoms, ions, or molecules.

The important colligative properties are:

1. Relative lowering of vapour-pressure of the solvent
2. Elevation of boiling-point of the solvent
3. Depression of freezing-point of the solvent
4. Osmotic pressure of the solution

1.Relative lowering of vapour pressure:

When a non volatile solute is dissolved in a volatile solvent, the vapour pressure of solvent decreases. So, the vapour pressure of solution is always lower than the vapour pressure of the pure solvent.

The difference in vapour pressures of pure solvent (p_A^0¿ and solution (p_A) is called lowering of vapour pressure (Δp¿

$$\Delta p = p_A^0 - p_A$$

The ratio of lowering of vapour pressure to the pure solvent is called relative lowering of vapour pressure.

Relative lowering of vapour pressure $= \frac{p_A^0 - p_A}{p_A^0}$

According to Raoult's law $\quad p_A = p_A^0 x_A$

$$p_A = p_A^0(1 - x_B) \quad \text{or} \quad p_A = p_A^0 - p_A^0 x_B$$

$$p_A^0 x_B = p_A^0 - p_A$$

$$\frac{p^0_{A-p_A}}{p_A^0} = x_B$$

So, "the relative lowering of vapour pressure of a solution containing non volatile solute is equal to mole fraction of solute". This is called Raoult's law of relative lowering of vapour pressure.

Thus relative lowering of vapour pressure depends only on the number of the solute particles and it is independent of their identity. Hence relative lowering of vapour pressure is a colligative property.

Mathematically, Raoult's law of relative of vapour pressure is

$$\frac{p^0_{A-p_A}}{p_A^0} = x_B = \frac{n_B}{n_A + n_B}$$

Calculation of molar mass of solute using relative lowering of vapour pressure:

The mole fraction of solute $x_B = \frac{n_B}{n_A + n_B}$

From Roult's Law, $\frac{p^0_{A-p_A}}{p_A^0} = \frac{n_B}{n_A + n_B}$

Here $n_A \wedge n_B$ are the number of moles of solvent and solute respectively present in the solution. For dilute solutions $n_B \ll n_A$, hence neglecting n_B in the denominator we have

$$\frac{p^0_{A-p_A}}{p^0_A} = \frac{n_B}{n_A} \qquad \text{or} \qquad \frac{p^0_{A-p_A}}{p^0_A} = \frac{w\,\square_B / M_B}{W_A / M_A}$$

$$\frac{p^0_{A-p_A}}{p^0_A} = \text{¿}\,\frac{w_B \times M_A}{w_A \times M_B} \qquad \text{or} \qquad M_B = \frac{w_B \times M_A \times p^0_A}{W_A \times \text{¿¿}}$$

Here W_A and w_B are the masses and $M_A \wedge M_B$are the molar masses of the solvent and solute respectively. Thus by determining the value of relative lowering of vapour pressure of a dilute solution of known concentration experimentally, the molar mass of the solute can be calculated

2.Elevation of boiling point:

Boiling point (T_b) of a liquid is the temperature at which its vapour pressure becomes equal to the external pressure. The vapour pressure of a non volatile solute is less than that of pure solvent. Therefore higher temperature is required to make the vapour pressure of the solution equal to the external pressure as shown in the graph. Hence, the boiling point of solution is more than that of pure solvent.

The difference in boiling points of the pure solvent and the solution is called the elevation in boiling point of solvent.

Let T^0_bbe the boiling point of pure solvent and $T_b$be the boiling point of solution.

The increase in the boiling point $\Delta T_b = T_b - T^0_b$ where $\Delta T_b$is known as elevation in boiling point.

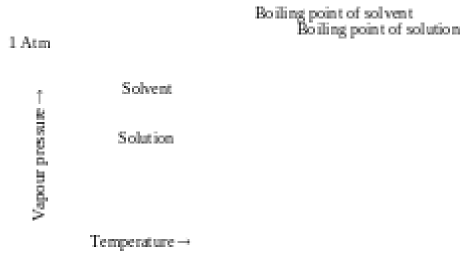
Experiments have shown that for dilute solutions, the elevation of boiling point (ΔT_b¿is directly proportional to the molal concentration of the solution. Thus $\Delta T_b \propto m$ or $\Delta T_b = K_b m$

Where m is the molality of the solution and K_b is the boiling point elevation constant or molal elevation constant or Ebullioscopic constant. Here molality is used because it is not affected by change in temperature.

When molality of solution, m=1, then $\Delta T_b = K_b$

Therefore, molal elevation constant of a solvent is defined as the elevation of boiling point caused by dissolving one mole of non volatile solute in one kg of solvent.

SI unit of the constant K_b is K Kg mol^{-1} and is specific for a given solvent.



Calculation of molar mass of the solute using elevation in boiling point:

Let W_B be the mass of the solute of molecular mass M_B dissolved in w_A gram of the solvent, then molality (m) of the solution is given by the equation:

$$m=\frac{w_B\times 1000}{M_B\times w_A}$$

Substituting the value of m in equation 1, we get, $\Delta T_b=K_b\times\frac{w_B\times 1000}{M_B\times w_A}$

The molar mass of the solute (M_B¿ is calculated using the equation,

$$M_B=\frac{K_b\times w_B\times 1000}{\Delta T_b\times w_A}$$

Thus, in order to determine M_B, molar mass of the solute, known mass of solute in a known mass of the solvent is taken and ΔT_b is determined for a known solvent whose K_b value is known.

The value of K_b depends upon the nature of the solvent and it can be determined using the formula:

$$K_b=\frac{R\times M_A\times T^2_{b_{solvent}}}{1000\times\Delta H_{vap}}$$

Where R = gas constant, M_A= molar mass of the solvent, $T_{b(solvent)}$= boiling pint of pure solvent, $\Delta H_{vap}=$¿the enthalpy of vapourisation.

3.Depression in freezing point:

Freezing point (T_f¿ of a liquid is the temperature at which the vapour pressure of the liquid becomes equal to that of its solid. The vapour pressure of the solution is less than that of pure solvent. Therefore, the vapour pressure of the solution becomes equal to that of solid solvent at lower temperature than that of pure solvent. Hence, the freezing point of the solution is less than that of the solvent as shown in the graph.

Let T_f^0 be the freezing point of the pure solvent and T_f be the freezing point of the solution. The depression in freezing point, $\Delta T_f=T_f^0-T_f$

So, depression of freezing point (ΔT_f¿ is the difference in the freezing point of the pure solvent and freezing point of solution.

Experiments have shown that for dilute solutions the depression of freezing point (ΔT_f¿ is directly proportional to the molal concentration of the solution. Thus

$$\Delta T_f \propto m \qquad \text{or} \qquad \Delta T_f = K_f m$$

Where m is the molality of the solution and K_f is the molal depression constant or freezing depression constant or cryoscopic constant.

When molality of solution, m = 1, then $\Delta T_f = K_f$

Therefore, molal depression constant of a solvent is defined as the depression in freezing point caused by dissolving one mole of non volatile solute in one kg of solvent.

SI unit of the constant K_b is Kkg mol^{-1} or Kmolal^{-1} and is specific for a given solvent.

Calculation of molar mass of a solute using depression in freezing point:

Let w_B be the mass of the solute of molecular mass M_B dissolved in w_A gram of the solvent, then molality (m) of the solution is given by the equation.

$$m = \frac{w_B \times 1000}{M_B \times w_A}$$

Substituting the value of m in equation 1, we get, $\Delta T_b = K_f \times \frac{w_B \times 1000}{M_B \times w_A}$

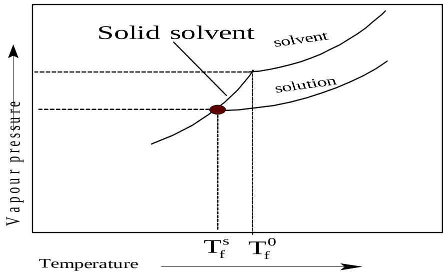
Therefore, the molar mass of the solute (M_B¿ can be determined according the equation, $M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A}$

Thus, in order to determine M_B, molar mass of the solute, known mass of the solute in a known mass of the solvent is taken and ΔT_f is determined experimentally for a solution whose K_f value is known.

The value of K_f depends upon the nature of the solvent and it can be determined using the formula:

$$K_f = \frac{R \times M_A \times T^2_{f(solvent)}}{1000 \times \Delta H_{fus}}$$

Where R= gas constant, M= molar mass of the solvent, $T_{f(solvent)}$= freezing point of pure solvent, ΔH_{fus}=¿ the enthalpy of fusion.



Osmosis:

A strong solution of sugar is taken in a thistle funnel, the mouth of which is covered with a piece of animal bladder or cellophane (semipermeable membrane). This is kept immersed in water taken in a beaker as shown in figure. It is observed that the level of the solution inside the stem of the thistle funnel starts raising. It must be due to the flow of solvent molecules (water) into the solution through the semi-permeable membrane. This phenomenon is known as osmosis.

The spontaneous movement of solvent molecules from the solution of lower concentration to the solution of higher concentration through semipermeable membrane is called osmosis.

Osmosis in natural processes:

- A raw mango placed in concentrated salt solution loses of water via osmosis and shrivel into pickle.
- Wilted flowers revive when placed in fresh water due to osmosis.
- A carrot that has become limp because of water loss, when placed in water, water will move into them through osmosis making it firm once again.
- When blood cells are placed in a solution containing more than 0.9% (mass/volume) of sodium chloride, blood cells shrink due to loss of water by osmosis.
- People taking a lot of salt or salty food experience water retention in tissue cells and intercellular spaces because of osmosis. The resulting puffiness or swelling is called edema.
- Water movement from soil into plant roots and subsequently into upper portion of the plant is partly due to osmosis.
- The preservation of meat by salting and of fruits by adding sugar against bacterial action through the process of osmosis, a bacterium on salted meat or candid fruit loss water, shrivels and dies.

Note: 0.9% sodium chloride in water is called saline solution.

4.Osmotic pressure:

Osmotic pressure of a solution is defined as the pressure to be applied on the solution of higher concentration just to stop osmosis.

Osmotic pressure is a colligative property because it depends on the number of moles of solute in the solution and not on the nature of the solute.

For dilute solutions, it has been found experimentally that osmotic pressure is proportional to the molarity of the solution at a given temperature T.

$\pi \propto C$ or $\pi = kC$

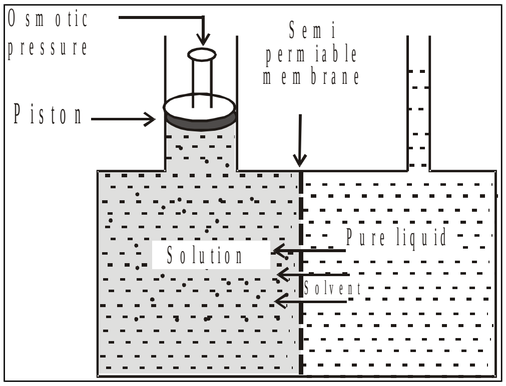
Where k is proportionally constant and is equal to RT where R is universal gas constant and T is the temperature in Kelvin. Therefore,

$\pi = CRT$ If n_B moles of solute is dissolved in V litres of the solution, C=$\frac{n_B}{V}$

$$\overset{\Rightarrow}{\square}\pi = \frac{n_B}{V}RT$$

If w_B grams of the solute of molar mass (M_B¿ is present in the solution, then $n_B = \frac{w_B}{M_B}$ $\overset{\Rightarrow}{\square}\pi = \frac{w_B RT}{M_B V}$

$$\overset{\Rightarrow}{\square}M_B = \frac{w_B RT}{\pi V}$$



Thus, by measuring the osmotic pressure of a solution of known concentration, molar mass of the solute can be calculated using the above equation.

Determination of molecular masses of solute by osmotic pressure measurements is highly useful in finding out the molecular masses of macromolecules like polymers, proteins, etc.

Isotonic, hypertonic and hypotonic solutions:

When such solutions are separated by semi-permeable membrane, no osmosis occurs. For example, the osmotic pressure of the fluid inside the blood cell is equivalent to that 0.9% (mass/volume) sodium chloride solution, called normal saline solution.

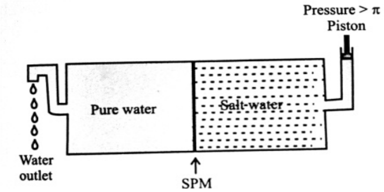
That is why normal saline solution is safe to inject intravenously because no osmosis takes place.

On the other hand, if we place the cells in a solution containing more than 0.9%(mass/volume) sodium chloride, water will flow out of the cell and they would shrink . Such a solution is named as hypertonic

A solution having higher osmotic pressure with respect other is called hypertonic solution. If the sodium chloride concentration is less than 0.9%(mass/volume), then water will flow into the cells if placed in this solution and they would swell.

The solution having lower osmotic pressure with respect other is called hypotonic solution.

Reverse osmosis and water purification:



When a solvent and a solution are separated by a semiprmeable membrane, osmosis occurs. However, if an external pressure, which is just equivalent to osmotic pressure is applied on solution side, no osmosis occurs. If the external pressure is greater than the osmotic pressure, then water will be forced to pass from solution to solvent side.

The process of reversing the direction of osmosis by applying the pressure higher than the osmotic pressure to the solution of higher concentration is called reverse osmosis. During reverse osmosis, the pure solvent flows out the solution through the semi-permeable membrane. Reverse osmosis is used in desalination of sea water. When pressure, more than osmotic pressure (30 atm at $25^{\circ}c$) is applied to the sea water, pure water is squeezed out of the sea water through the semi-permeable membrane as shown in figure.

A variety of membranes are used for reverse osmosis. Examples, Cellulose Tri-Acetate (CTA) membrane, Thin-Film-composite (TFC) membranes, etc.

Abnormal molar masses:

Molecular masses of solutes can be calculated by measuring any of the colligative properties of dilute solutions.

These methods are applicable only if

- The solution is dilute, so that Raoult's law is obeyed.
- The solute is non dissociable or non associable in the solution.

In case of solutes which either dissociate or associate in solutions, molecular masses of solutes determined by these methods will be abnormal.

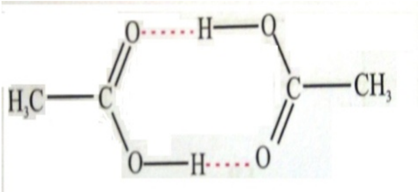
Association of solute molecules:

Certain solutions in solution are found to associate. This leads to decreases in the number of molecular particles in the solutions. Thus, it results in a decrease in the value of colligative properties.

$$\text{Molecular mass of solute} \propto \frac{1}{Colligative\ property}$$

Therefore, molecular masses determined, will be higher than the normal values for solutes which undergo association in solution.

Example: Acetic acid in benzene undergoes dimerization as indicated below.



Therefore, the molecular mass of acetic acid in benzene determined by collegative property method will be approximately double the actual value.

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

Dissociation of solute molecules:

Certain solutes in solution are found to dissociate into ions. This leads to the increase in the number of particles in the solutions. Thus, it results in a increases in the value of collegative properties.

$$\text{Molecular mass of solute} \propto \frac{1}{Colligative\ property}$$

Therefore, molecular mass determined, will be lower than the normal values for solutes which undergoes dissociation in solution.

Example: The molecular mass of NaCl in water determined by colligative property method will be approximately reduced to half the actual value due to dissociation. NaCl → Na^+ + cl^-

Van’t Hoff’s factor (i):

In 1886, Van’t Hoff introduced a factor ‘i’ called van’t Hoff’s factor, to express the extent of association or dissociation of solutes in solution. The van’t Hoff’s factor is a ratio of the normal molecular mass to the observed molecular mass of a solute.

$$i = \frac{Normal\ molecular\ mass}{Observed\ molecular\ mass} \quad \text{or} \quad i = \frac{Observed\ coligative\ property}{Calculated\ colligative\ property}$$

Consequently, introduction of the van’t Hoff’s factor modifies the equations for the colligative properties as:

Relative lowering of vapour pressure = $\frac{p_A^0 - p_A}{p_A^0} = i x_B$

Elevation of boiling point, $\Delta T_b = i K_b m$

Depression in freezing point, $\Delta T_f = i K_f m$

Osmotic pressure, $\pi = \frac{inRT}{V}$ or $\pi = iCRT$

From the value of ‘i’, it is possible to calculate degree of dissociation or association of substances.

$$\text{Degree of dissociation} = \frac{No.\ of\ moles\ of\ the\ substance\ dissociated}{Total\ no.\ of\ moles\ of\ the\ substance\ taken}$$

Suppose a molecule of an electrolyte give ‘n’ ions after dissociation. If we start with 1 mole of the solute, and $'\alpha'$ is the degree of dissociation, then at equilibrium.

No. of moles of solute left undissociated =1-α

No. of moles of ions formed = nα

Total no. of moles of particles = 1-$\alpha + n\alpha = 1 + (n-1)\alpha$

Van’t Hoff’s factor, $i = \frac{Total\ no.\ of\ moles\ of\ particles\ after\ dissociation}{No.\ of\ moles\ of\ particles\ before\ dissociation}$ ¿ $\frac{1+(n-1)\alpha}{1}$

Or Degree of dissolution, $\alpha = \frac{i-1}{n-1}$

Degree of Association:

It is defined as the fraction of total number of molecules which combine to form associated molecules.

Degree of association$=\frac{No.\,of\ moles\ of\ the\ substance\ associated}{Total\ no.\,of\ moles\ of\ the\ substance\ tasken}$

For example, suppose ‘n’ simple molecules of the solute associated to form the associated molecule A_n.

$nA \leftrightharpoons A_n$

If we start with 1 mole of simple molecule and α is the degree of association, then that at equilibrium

No. of moles of solute left unassociated ¿ $1-\alpha$

Total no. of moles after association¿ $1-\alpha+\frac{\alpha}{n}$

Van’t Hoff factor, $i=\frac{1-\alpha+\frac{\alpha}{n}}{1}$ ¿ $\frac{1+\alpha\left[\frac{1}{n}-1\right]}{1}$

(or) Degree of association, $\alpha=\frac{i-1}{\frac{1}{n}-1}$

One mark questions

1. What is binary solution?
   solution containing only two components is called binary solution. Example: salt solution (salt + water)
2. What is solid solution?
   A solution in which solid acts as a solvent is called solid solution.
3. What is liquid solution?
   A solution in which liquid acts as a solvent is called liquid solution.
4. What is gaseous solution?
   A solution in which gas acts as a solvent is called gaseous solution.
5. What is concentration?
   The amount of solute present in the given quantity of the solution is called concentration.
6. Name the units used to express concentrations.
   (i) Molarity (M) (ii) Molality (m) (iii) Mole fraction (x)
7. Among molarity and molality which is independent on temperature.
   Molality.
8. Define solubility.
   The maximum amount of a substance that can be dissolved in a specified amount of solvent at a specified temperature is called solubility.
9. What is the basic rule (principle) to decide the solubility of solute in solvent?
   “Like dissolves like”
10. What is dissolution?
    When a solute is added to the solvent, some solute dissolves and its concentration increases in solution. This process is called dissolution.
11. What is saturated solution?
    A solution in which no more solute can be dissolved at the same temperature and pressure is called a saturated solution.
12. What is unsaturated solution?
    A solution in which some more solute can be dissolved under the same temperature is called unsaturated solution.
13. What is the effect of pressure on solubility of solubility of solid in liquid?
    Pressure does not have any significant effect on solubility of solids in liquids.
14. What is the effect of temperature on the solubility of gas in liquid?
    Solubility of gas in liquid decreases when temperature is increased.
15. Solubility of gas in liquid decreases as temperature increases. Why?
    Because dissolution of gas in liquid is exothermic process.
16. Aquatic species are more comfortable in cold waters rather than in warm waters. Give reason.

Solubility of O_2 in cold water is more than warm water.

17. What is the significance of Henry's law constant?

The higher the value of K_H lower is the solubility.

18. At a given temperature and pressure nitrogen gas is more soluble in water than Helium gas. Which one of them has higher K_H value?

Helium.

19. What is vapour pressure?

The pressure exerted by the vapours above the liquid surface at constant temperature when they are in equilibrium with the liquid is called vapour pressure or saturated vapour pressure or equilibrium vapour pressure.

20. Write the mathematical form of Raoult's law for volatile solutes.

$P_{total} = p_A^o x_A + p_B^o x_B$

21. Name the types of azeotropes or azeotropic mixtures.

Azeotropic mixtures are of two types:

(i) Minimum boiling azeotropes (ii) Maximum boiling azeotropes.

22. What happens to the vapour pressure of the pure liquid when a non volatile solute is dissolved in it?

Vapour pressure decreases.

23. Write the mathematical form Raoult's law of relative lowering of vapour pressure.

$$\frac{p_A^o - P_A}{p_A^o} = \frac{n_B}{n_A + n_B}$$

24. What is boiling point?

The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called boiling point.

25. What happens to the boiling point of a liquid when a non volatile solute is dissolved in a pure solvent?

Boiling point increases.

26. Define Ebullioscopic constant or molal elevation constant.

It is the increase in the boiling point produced when one mole of non volatile solute is dissolved in 1 kg of a pure solvent.

27. What is the value of K_b for water?

0.52 K kg mol^{-1}.

28. What is the SI unit of K_b?

K kg mol^{-1}.

29. What is freezing point?

The temperature at which the vapour pressure of the liquid becomes equal to the vapour pressure of the solid is called freezing point.

30. What happens to the freezing point of a pure solvent when a non volatile solute is dissolved in it?

Freezing point decreases.

31. Give the relation between depression in freezing point and molality.

$\Delta T_f \propto m$ or $\Delta T_f = K_f \cdot m$

where K_f is called molal depression constant or cryoscopic constant.

32. Define cryoscopic constant or molal depression constant.

It is the decrease in the freezing point produced when one mole of non volatile solute is dissolved in one kg or 1000 g of a pure solvent.

33. What is the value of K_f for water?

$K_f = 1.86$ K kg mol^{-1} for water.

34. What is the SI unit of K_f?

K Kg mol^{-1}

35. What is osmosis?

The flow of solvent molecules from lower concentrated solution to higher concentrated solution through a semipermeable membrane is called osmosis.

36. What is semipermeable membrane?

A membrane which allows the movement of only solvent molecules through it but not the solute particles is called semipermeable membrane.

37. Give an example for natural semipermeable membrane.

Pig's bladder, animal membranes, vegetable membranes, skin, parchment paper etc.,

38. Give an example for synthetic or artificial semipermeable membrane.

Cellophane, cupric ferrocyanide coated on porous pot, $Cu_2[Fe(CN)_6]$.

39. What is osmotic pressure?

The external pressure applied on the concentrated solution to stop osmosis is called osmotic pressure. It is denoted by π.

40. On what factor does the colligative property value depends.

It depends on the number of solute particles but not on their nature.

41. Give reason: Osmotic pressure or elevation in boiling point or depression in freezing point or relative lowering of vapour pressure is a colligative property.

Because it depends only on the number of solute particles present in the solution but not on their nature.

42. Give Reason: To clear the snow covered roads and hilly areas salt is sprinkled.

When salt is sprinkled on the snow covered roads and hilly areas, snow starts melting due to depression in freezing point as a result formation of water takes place which helps to clear roads.

43. The osmotic pressure of NaCl solution is more than glucose solution.

NaCl solution contains more particles(2)than the glucose solution(1).

44. Which of the following has high osmotic pressure?

(i) Pure water (ii) 1 M glucose (iii) 1 M NaCl (iv) 1M $CaCl_2$

1M $CaCl_2$ due to 3 particles (1Ca^{2+} and 2Cl^-) in the solution.

45. Which of the following has high osmotic pressure?

(i) 0.1 M NaCl (ii) 0.2 M $CaCl_2$ (iii) 0.5 M Urea (iv) 1 M glucose

0.2M $CaCl_2$

46. Among pure water and sea water which has high boiling point and lowest freezing point.

Sea water.

47. Give reason:The freezing point of sea water is less than 0°C (of 273 K).

Due to dissolved salts.

48. Among pure water and sea water which has highest vapour pressure.

Pure water

49. Which of the following has lowest vapour pressure?
(i) Pure water (ii) 1 M urea (iii) 1 M NaCl (iv) 1 M $BaCl_2$
1M $BaCl_2$

50. Name the semipermeable membrane used in reverse osmosis.
Cellulose acetate.

51. Name the disease caused to the people living at high altitudes.
Anoxia

52. Name the disease caused to the sea divers if they carry nitrogen oxygen mixture or air.
Bends

Two mark questions

53. What is abnormal molar mass?
The molar mass determined by colligative properties is found to be lower or higher than the expected or normal molecular mass. Such a molecular mass is called abnormal molecular mass.

54. Define molarity (M)
The number of moles of solute dissolved in 1 litre (1 dm^3) of 1000 cm^3 of a solution is called molarity.Molarity is denoted by 'M'
Molarity is calculated by the equation,

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of the solution in litres}} \quad \text{or} \quad \text{Molarity} = \frac{W_B \times 1000\ \text{cm}^3}{M_B \times V}$$

The unit of molarity is mole / litre or mol L^{-1}.
Molarity changes with temperature because of expansion or contraction of liquid with temperature.

55. Define molality (m).
The number of moles of solute dissolved in one kg or 1000 g of a solvent is called molality. Molality is denoted by 'm'. Molality is calculated by the equation.

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of the solvent in kg}} = \frac{w_B \times 1000\text{g}}{M_B \times w_A}$$

Molality is independent of temperature because the mass of the solvent doesnot change with temperature. The unit of molality is mol / kg or mol kg^{-1}

56. Give two disadvantages of molarity.
(a) Molarity depends on temperature. So, this unit cannot be used in experiments that involve temperature variations.
(b) The exact amount of the solvent in a given volume of the solution cannot be determined if the density of the solution is not known.

57. Define mole fraction (x).
It is the ratio of number of moles of a particular component to the total number of moles of all the components in the solution. If n_2 moles of solute is present in 'n_1' moles of solvent, then

mole fraction of solute, $x_2 = \frac{n_2}{n_1 + n_2}$ mole fraction of solvent $x_1 = \frac{n_1}{n_1 + n_2}$

Sum of mole fractions of all components present in solution is equal to one i.e., $x_1 + x_2 = 1$

58. Define volume percentage. For which type of solutions this unit is useful?

Volume percentage of a solution is defined as the number of parts by volume of the solute dissolved in 100 parts by volume of the solution.

$$\text{Volume percentage} = \frac{\text{Volume of the solute}}{\text{Volume of the solution}} \times 100$$

Note: Units of the two volumes unit be same.

This unit is more useful when both the solute and solvents are liquids.

59. Define mass percentage (w/w)

Mass percentage of a solution is defined as the number of parts by mass of the solute dissolved in 100 parts by mass of the solution.

$$\text{Mass percentage} = \frac{\text{Mass of the solute}}{\text{Mass of the solution}} \times 100$$

Note: Units of the two masses should be same

60. Define mass by volume percentage. Give the expression to calculate the volume percentage for the given mass and volume of solute and solvent.

Mass by volume percentage of a solution is defined as the number of parts by mass of the solute dissolved in 100 parts by volume of the solution.

$$\text{Mass by volume percentage} = \frac{\text{Mass of the solute}}{\text{Volume of the solution}} \times 100$$

Note: In this case, generally gram and cm^3 are used as the units. Otherwise system of units should be same.

61. Define parts per million.

Parts per million of a solute is defined as the member of parts of solute dissolved in one million parts of the solution.

$$\text{Parts per million} = \frac{\text{Number of parts of the solute}}{\text{Number of parts of the solution}} \times 10^6$$

Note: The units of the parts of the solute and the solution should be same.

Parts per million are also expressed in w/w, v/v and w/v.

This unit is suitable when solutes are present in trace quantities.

(1) Mass percent, ppm, mole fraction and molality are independent on temperature because mass is independent on temperature

(2) Molarity, volume percent and mass by volume percent depends on temperature because volume depends on temperature.

62. What is the effect of temperature on solubility of solid in liquid?

(i) Solubility of solid in liquid increases as temperature increases if the dissolution process is endothermic ($\Delta H = +ve$).

(ii) Solubility of solid in liquid decreases as temperature increases if the dissolution process is exothermic ($\Delta H = -ve$)

63. State Henry’s law.

It states that, at constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas over the solution..

or

The partial presence of the gas in vapour phase (P) is directly proportional to the mole fraction of the gas in the solution.

i.e., $p = K_H x$

where K_H = Henry's law constant, x = mole fraction of the gas

p = Partial pressure of the gas in vapour phase.

64. What are isotonic solutions? Give an example.

Two solutions having the same osmotic pressure at a given temperature are called isotonic solutions.

Example: RBC (Red blood cells) is isotonic with 0.9% NaCl solution which is called normal saline. It is used in injections instead of distilled water.

65. What are hypertonic solutions?

The solutions whose osmotic pressure is higher than that of the given solution is called hypertonic solution.

Example: When RBC is placed in a sea water, water passes out of the cell due to osmosis and the cell shrinks.

66. What are hypotonic solutions?

The solutions whose osmotic pressure is lower than that of give solution are called hypotonic solutions.

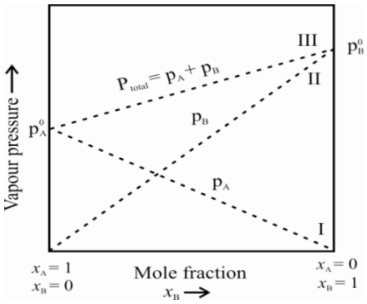
Example: When RBC is placed in hypotonic solution they swell and even burst due to the inflow of water.

67. What are ideal solutions? Give examples.

The solutions which obey Raoult's law at all concentrations are called ideal solutions.

68. Example: (i) Benzene and Toluene (ii) Ethyl bromide and ethyl iodide (iii) n-hexane and n-heptane

69. Draw the graph of vapour pressure against mole fraction for ideal solution.



70. What are non-ideal solutions give examples.

The solutions which do not obey Raoult's law at all concentrations are called non-ideal solutions.

Example: (i) HCl and water (ii) Ethyl alcohol and water.

71. Give any four conditions to form non-ideal solutions.

(i) They should not obey Raoult's law.

(ii) $\Delta V_{mix} \neq 0$

(iii) $\Delta H_{mix} \neq 0$

(iv) The forces of attraction between A and B molecules will be greater or lesser than that of A - A and B - B molecules.

72. Name the types of non-ideal solutions.

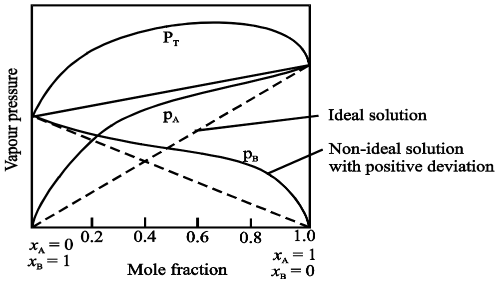
Non ideal solutions are of two types.

- Non ideal solution showing positive deviation from Raoult's law.
- Non ideal solution showing negative deviation from Raoult's law.

73. Which type of solutions show positive deviation?

If the vapour pressure of the solution is higher than that calculated from Raoult's law shows positive deviation. Example: (i) Ethyl alcohol and water, (ii) Chloroform and water, (iii) Methyl alcohol and water.

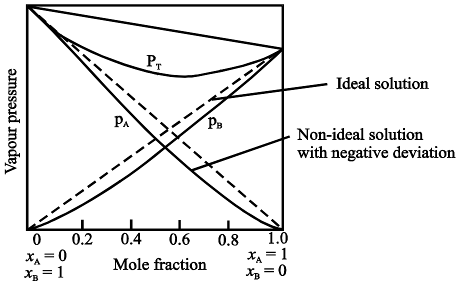
74. Draw the graph to show non ideal solutions with positive deviation from ideal behaviour.



75. Which type of solutions show negative deviation from Raoult's law?

If the vapour pressure of the solution is lower than that calculated by Raoult's law shows negative deviation from Raoult's law. Examples: HCl and water, HNO_3 and water, Chloroform and acetone

76. Draw the graph to show non ideal solutions with negative deviations.



77. What are azeotropes or azeotropic mixtures?

Binary liquid mixtures having the same composition in liquid and vapour phase and boil at a constant temperature are called azeotropic mixtures. Example: (i) 95.5% ethyl alcohol and 4.5% water (rectifiedspirit) (ii) 20.2% HCl and 79.8% water.

Note: In azeotropic mixtures the components cannot be separated by fractional distillation.

78. What are minimum boiling azeotropes? Give an example.

The solutions which show large positive deviation from Raoult's law are called minimum boiling azeotropes. They boil at lower temperature than the boiling point of the components.

Example: 95.5% Ethylalcohol and 4.5% water (rectified spirit). This mixture boils at 78.15°C (boiling point of water is 100°C and ethyl alcohol is 78.5°C.

79. What are maximum boiling azeotropes? Give an examples.

Solutions which shows the large negative deviations from Raoult's law are called maximum boiling azeotropes.

Example: (i) 20.2% HCl and 79.8% water. This mixture boils at 381.6 K which is higher than that of pure water (373 K) and HCl (188 K)

80. What are colligative properties?

The properties of dilute solutions depends only on the number of solute particles present in the dilute solution but not on their nature are called colligative properties.

81. Name the four colligative properties.

- Relative lowering of vapour pressure
- Elevation in boiling point or Ebuliscope or increase in boiling point.
- Depression in freezing point or Cryoscope or decrease in freezing point.
- Osmotic pressure.

82. Define lowering of vapour pressure.

When a non volatile solute is added in to the pure solvent, the vapour pressure of the solution decreases. It is the difference between the vapour pressure of the pure solvent and that of the solution.

Let p° be the vapour pressure of the pure solvent and p be the vapour pressure of the solution, then,

Lowering of vapour pressure $= p^\circ - p$

83. Define relative lowering of vapour pressure.

It is the ratio of lowering of vapour pressure to the vapour pressure of solvent.

$$\text{Relative lowering of vapour pressure} = \frac{p^0_A - p_A}{p^0_A}$$

84. State Raoult's law of relative lowering of vapour pressure.

It states that in a solution containing non volatile solute the relative lowering of vapour pressure is equal to the mole fraction of the solute in dilute solutions.

$$\frac{p^0_A - p_A}{p^0_A} = \frac{n_B}{n_A + n_B}$$

85. Define elevation in boiling point.

It is the difference between the boiling point of the solution and that of the pure solvent. i.e., $\Delta T_b = T_b - T^o_b$

where $\Delta T_b =$ elevation in boiling point, T_b = boiling point of the solution, $T^o_b =$ boiling point of the pure solvent.

86. Give the relation between elevation in boiling point and molality.

$\Delta T_b \propto m$ or $\Delta T_b = K_b \cdot m$

Where $\Delta T_b =$ elevation in boiling point, m = molality, K_b = molal elevation constant or ebullioscopic constant.

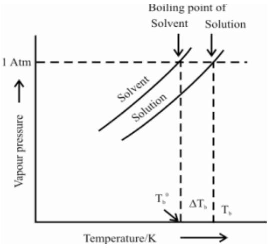
87. Give the relation to calculate molal elevation constant with respect to enthalpy of vapourisation.

$$K_b = \frac{R \times M_A \times T^2_{b\ (\text{solvent})}}{1000 \times \Delta H_{vap}}$$

where R = gas constant, M_B = molar mass of the solvent,

$T_{b(solvent)}$ = boiling point of pure solvent, ΔH_{vap} = the enthalpy of vapourisation.

88. Draw the graph of vapour pressure with temperature to show elevation in boiling point of solvent and solution.



89. Define depression in freezing point.

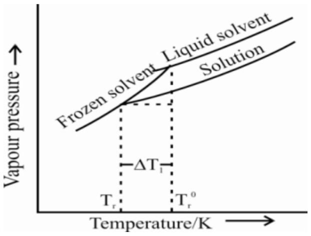
It is the difference between the freezing point of the pure solvent and that of the solution.

$\Delta T_f = T_f^o - T_f$ where ΔT_f depression in freezing point,

T_f^o = freezing point of the pure solvent.

T_f = freezing point of the solution.

90. Draw the graph of vapour pressure with temperature to show depression in freezing point of solvent and solution.



91. Derive the relation between depression in freezing point and the molecular mass of a solute.

We know that $\Delta T_f = K_f m$

where m is the molality of the solution and K_f is the molal depression constant or freezing point depression constant or cryoscopic constant.

But for the given mass of solute and solvent, molality is given by

$$m = \frac{w_B \times 1000}{M_B \times w_A} \quad \therefore \Delta T_f = K_f \left(\frac{w_B \times 1000}{M_B \times w_A} \right) \quad \because \Delta T_f = K_f \left(\frac{w_B \times 1000}{M_B \times w_A} \right)$$

or

$$M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A}.$$

92. Give the relation to calculate molar depression constant with respect to enthalpy of fusion.

$$R = \frac{R \times M_A \times T^2_{f\,(solvent)}}{1000 \times \Delta H_{fus}}$$

where R = universal gas constant

M_A = molecular mass of solvent

T_f = freezing point of solvent, ΔH_{fus} = Enthalpy of fusion.

93. What is reverse osmosis?

When a pressure larger than the osmotic pressure is applied on a concentrated solution, solvent flows from concentrated solution to dilute solution through a semi permeable membrane.

This phenomenon is called reverse osmosis. Reverse osmosis is used in the desalination of sea water to obtain fresh drinking water.

94. What is van't Hoff's factor?

It is the ratio of normal molar mass to the abnormal molar mass.

$i = \frac{\text{normal molar mass}}{\text{abnormal molar mass}}$ or $i = \frac{\text{observed colligative property}}{\text{calculated colligative property}}$

95. Give the significance of van't Hoff's factor.

- If i = 1, the solute doesn't undergo either dissociation or association.
- If i > 1, solute undergo dissociation.
- If i < 1 solute undergo association.

96. Write the colligative properties for solutes undergo dissociation or association.

- Elevation in boiling point, $\Delta T_b = i K_b m$
- Depression in freezing point, $\Delta T_f = i K_f m$
- Osmotic pressure $\pi = iCRT$
- Relative lowering of vapour pressure, $\frac{p^o - p}{p^o} = i x_2$

97. After removing the outer shell of two eggs in dilute HCl, one is placed in distilled water and the other is placed in a saturated solution of NaCl. What will you observe and why?

Egg in water swell and egg in NaCl solution shrinks because in water the solvent molecules enters into the egg cell (hypotonic). In NaCl solution egg shrinks because water flows out of the egg cell (hypertonic)

98. What do you expect to happen when RBC is placed in 1% NaCl solution and 0.5% NaCl solution.

In 1% NaCl solution RBC will shrink (hypertonic). In 0.5% NaCl solution RBC will swell and may even burst (hypotonic). The above phenomena is because RBC is isotonic 0.91% NaCl solution.

Three or four mark questions

99. Give any three applications of Henry's law.

(i) It is used in the preparation of carbonated beverages (To increase the solubility of CO_2 in soda water, soft drinks and in beer, the bottle is sealed under high pressure).

(ii) It is used by scuba or deep sea divers for respiration (To avoid bends and toxic effects of high concentration of nitrogen under deep sea).

(iii) It is used by mountain climbers for respiration. (At high altitudes the partial pressure of oxygen is less. The low concentration of oxygen in the blood and tissues causes climbers to become weak unable to think clearly which causes anoxia)

100. State Raoult's law of liquid solutions.

It states that in a solution of volatile liquids, the partial vapour pressure of each component is directly proportional to its mole fraction.

i.e., $p_A \propto x_1$ or $p_A = x_1 p_A^o$ Similarly $p_B = p_B^r x_B$

p_B = partial vapour pressure of solute in solution.

p_B^o = vapour pressure of pure solute. x_B = mole fraction of solute.

∴ Vapour pressure of solution $= p = p_A + p_B$ $= p_A^o x_A + p_B^o x_B$

where p_A^o = vapour pressure of the pure solvent,
x_A = mole fraction of the pure solvent, p_A = partial pressure of the pure solvent.

101. Give any four conditions to form ideal solutions.

(i) They should obey Raoult's law.
(ii) $\Delta V_{mix} = 0$, i.e., threshold be no change in volume on mixing.
(iii) $\Delta H_{mix} = 0$, i.e., there should be no change in enthalpy (heat) on mixing.
(iv) The forces of attraction between A and B (solvent and solute) molecules will be same as that of A - A (solvent – solvent) and B - B (Solute – solute) molecules.

102. Give differences between ideal and non-ideal solutions.

Sl.No.	Ideal solution	Non-ideal solution
1	They obey Raoult's law.	They do not obey Raoult's law.
2	$\Delta V_{mix} = 0$	$\Delta V_{mix} \neq 0$
3	$\Delta H_{mix} = 0$	$\Delta H_{mix} \neq 0$
4	The forces of attraction between A and B molecules will be same as that of A - A and B - B molecules.	The forces of attraction between A and B molecules will be greater or lesser than that of A - A and B - B molecules.

103. Give differences between solutions showing positive deviation and negative deviation from Raoult's law.

Sl. No.	Non ideal with positive deviation	Non ideal with negative deviation
1	$\Delta V_{mix} = +Ve$ (i.e., volume increases on mixing two components)	$\Delta V_{mix} = -ve$ (volume decreases on mixing two components)
2	$\Delta H_{mix} = +ve$ (heat is absorbed on mixing)	$\Delta H_{mix} = -ve$ (heat is liberated on mixing)
3	The vapour pressure is higher than that calculated from Raoult's law.	The vapour pressure is lower than that calculated from Raoult's law.
4	Forces of attraction between A and B molecules will be less than that of A - A and B - B molecules.	Forces of attraction between A and B molecules will be greater than that of A - A and B - B molecules.

104. Derive the relation to calculate is the molar mass or molecular mass or molecular weight using relative lowering of vapour pressure.

We know that from Raoult's law $\frac{p_A^o - p_A}{p_A^o} = \frac{n_B}{n_A + n_B}$

Here n_A and n_B are the number of moles of solvent and solute respectively present in the solution. For dilute solutions $n_B << n_A$, hence neglecting n_B in the denominator we have

$$\frac{p_A^o - p_A}{p_A^o} = \frac{n_B}{n_A} \qquad \frac{p_A^o - p_A}{p_A^o} = \frac{w_B/M_B}{w_A/M_A}$$

$$\frac{p_A^o - p_A}{p_A^o} = \frac{w_B \times M_A}{w_A \times M_B} \qquad M_B = \frac{w_B \times M_A \times p_A^o}{w_A \times (p_A^o - p_A)}$$

105. How is the molecular mass of a solute calculated by ebullioscopic method (elevation in boiling point).

We know that $\Delta T_b = K_b m$ ...(1)

Let w_B be the mass of the solute of molecular mass M_B dissolved in w_A gram of the solvent, then molality (m) of the solution is given by the equation:

$$m = \frac{w_B \times 1000}{M_B \times w_A}$$

Substituting the value of m in equation 1, we get, $\Delta T_b = K_b \times \frac{w_B \times 1000}{M_B \times w_A}$

The molar mass of the solute (M_B) is calculated using the equation,

$$M_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A}$$

Thus, in order to determine M_B, molar mass of the solute, known mass of solute in a known mass of the solvent is taken and ΔT_b is determined experimentally for a known solvent whose K_b value is known.

Derive the expression to calculate the molar mass of solute by osmotic pressure experiment. $\pi \propto C$

$\pi = CRT$ or $\pi = n_B CRT$ but $C = \frac{1}{V}$ and $n_B = \frac{w_B}{M_B}$

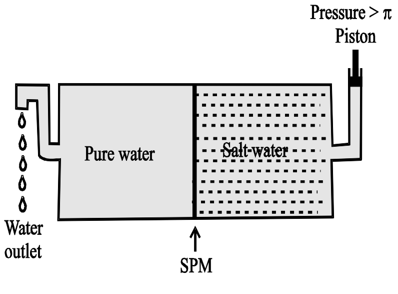
$\therefore \pi = \frac{w_B}{M_B} \times \frac{1}{V} RT$ $\therefore M_B = \frac{w_B RT}{\pi V}$

where R = solution constant whose value is same as that of gas constant. The above equation is used to calculate the molecular mass of a solute.

106. Explain the desalination of sea water (purification of water) by reverse osmosis.

The process of reversing the direction of osmosis by applying the pressure higher than the osmotic pressure to the solution of higher concentration is called reverse osmosis.

During reverse osmosis, the pure solvent flows out of the solution through the semi permeable membrane. Reverse osmosis is used in desalination of sea water.



When pressure, more than osmotic pressure (30 atm at 25^{o}C) is applied to the sea water, pure water is squeezed out of the sea water through the semipermeable membrane as shown in figure.

Worked out numerical problems

1. Calculate the molarity of a solution containing 5g of NaOH in 450 mL solution.

Molar mass of NaOH = M_B = 23 + 16 + 1 = 40 g mol^{-1}

Molarity = $\frac{w_B \times 1000}{M_B \times V} = \frac{5 \times 1000}{40 \times 450} = 0 \cdot 278 \text{ M}$.

2. Calculate the amount of benzoic acid [C_6H_5COOH] required for preparing 250 mL of 0.15 M solution in methanol

Molarity $= \frac{w_B \times 1000}{M_B \times V}$ $M_B = 6 \times 12 + 6 \times 1 + 2 \times 16 = 122 \text{ g mol}^{-1}$

$0 \cdot 15 = \frac{w_B \times 1000}{122 \times 250}$ $w_B = \frac{0 \cdot 15 \times 122 \times 250}{1000} = 4 \cdot 575 \text{ g}$.

3. Calculate molality of 2.5 g of ethanoic acid (CH_3COOH) in 75 g of benzene.

Molality $= \frac{w_B \times 1000}{M_B \times w_A}$ $w_B = 2 \cdot 5 \text{ g}, w_A = 75 \text{ g}$ $M_B = 2 \times 12 + 4 \times 1 + 2 \times 16 = 60 \text{ g mol}^{-1}$

Molality $= \frac{2 \cdot 5 \times 1000}{60 \times 75} = 0 \cdot 5556 \text{ m}$.

4. Calculate the mass of urea (NH_2CONH_2) required in making 2.5 kg of 0.25 molal aqueous solution

w_B = ?, $M_B = 2 \times 14 + 4 \times 1 + 12 + 16 = 60 \text{ g mol}^{-1}$, mass of solution = 25 kg = 2500 g

$m = 0 \cdot 25 \text{ molal}$ Mass of solute = moles of solute × molecular mass

$= 0 \cdot 25 \times 60 = 15 \text{ g}$

Mass of solvent, w_A = 2500 – 15 = 2485 g.

$\text{Molality} = \frac{w_B \times 1000}{M_B \times w_A}$ $0 \cdot 25 = \frac{w_B \times 1000}{60 \times 2485}$ $w_B = \frac{0 \cdot 25 \times 60 \times 2485}{1000}$ = 37.275 g

5. If the density of some lake water is 1.25 g mL^{-1} and contains 92 g of Na^{+} ions per kg of water. Calculate the molality of Na^{+} ion in the lake

$w_A = 1 \text{ kg water} = 1000 \text{ g}, M_B = \text{Atomic mass of Na} = 23 \text{ g mol}^{-1}, w_B = 92 \text{ g}$

Molality $= \frac{w_B \times 1000}{M_B \times w_A}$ $= \frac{92 \times 1000}{23 \times 1000}$ = 4 m

6. Calculate the mole fraction of ethylene glycol ($C_2H_6O_2$) in a solution containing 20% of $C_2H_6O_2$ by mass.

20% ethylene glycol means 20 g ethylene glycol present in 100g solution

$\therefore\ w_B = 20 \text{ g} \quad w_A = 100 - 20 = 80 \text{ g}$

$M_{C_2H_6O_2} = 62 \text{ g mol}^{-1}$, $M_{H_2O} = 18 \text{ g mol}^{-1}$

Number of moles of $C_2H_6O_2 = n_B = \frac{w_B}{M_B} = \frac{20}{62} = 0 \cdot 322 \text{ mol}$

Number of moles of $H_2O = n_A = \frac{w_A}{M_A} = \frac{80}{18} = 4 \cdot 444 \text{ mol}$

Mole fraction of ethylene glycol $= x_B = \frac{n_B}{n_A + n_B} = \frac{0 \cdot 322}{4 \cdot 444 + 0 \cdot 322} = 0 \cdot 0675$.

7. Calculate the mole fraction of benzene in solution containing 30% by mass of it in carbon tetrachloride.

Molar mass of $C_6H_6 = 6 \times 12 + 6 \times 1 = 78 \text{ g mol}^{-1}$

Molar mass of $CCl_4 = 1 \times 12 + 4 \times 35 \cdot 5 = 154 \text{ g mol}^{-1}$

30% benzene by mass means 30 g benzene in 100 g solution

∴ Mass of benzene = 30 g Mass of CCl_4 = 100 – 30 = 70 g

$n_{C_6H_6} = \frac{30}{78} = 0\cdot385 \text{ mol}$ $n_{CCl_4} = \frac{70}{154} = 0\cdot454 \text{ mol}$

$x_{C_6H_6} = \frac{n_{C_6H_6}}{n_{C_6H_6} + n_{CCl_4}} = \frac{0\cdot385}{0\cdot385 + 0\cdot454} = 0\cdot459$.

8. Calculate (a) molality (b) molarity and (c) mole fraction of KI if the density of 20% (mass / mass) aqueous KI is 1.202 g mL^{-1}.

20% (w/w) aqueous KI solution means 20 g KI is present in 100 g of the solution.

Mass of KI = w_B = 20 g, Mass of water = w_A = 100 g – 20 g = 80 g

Volume of solution $= \frac{\text{mass of solution}}{\text{density of solution}}$

∴ Volume of solution $= V = \frac{100 \text{ g}}{1\cdot202} = 83\cdot1947 \text{ mL}$

Molar mass of KI = M_B = 16 g mol^{-1}, Molar mass of H_2O = M_A = 18 g mol^{-1}

Number of moles of KI $= n_B = \frac{20}{166} = 0\cdot12048 \text{ mol}$

Number of moles of water $= n_A = \frac{80}{18} = 4\cdot444 \text{ mol}$

(a)Calculation of molality of KI Molality $= \frac{w_B \times 1000}{M_B \times w_A} = \frac{20 \times 1000}{166 \times 80} = 1\cdot506 \text{ m}$

(b)Calculation of molarity of KI Molarity $= \frac{w_B \times 1000}{M_B \times V} = \frac{20 \times 1000}{166 \times 83\cdot1947} = 1\cdot448 \text{ M}$

(c)Calculation of mole fraction of KI $x_{KI} = \frac{n_B}{n_A + n_B} = \frac{0\cdot12048}{4\cdot444 + 0\cdot12048} = 0\cdot02639$.

9. If nitrogen gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolve in 1 litre of water? Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48 K bar.

According to Henry's law

$p = K_H x$ $x_{N_2} = \frac{p}{K_H} = \frac{0\cdot987 \text{ bar}}{76\cdot48 \times 10^3 \text{ bar}} = 1\cdot29 \times 10^{-5}$

$x_{N_2} = \frac{n_{N_2}}{n_{H_2O} + n_{N_2}}$ $n_{H_2O} = \frac{\text{Mass of 1L water}}{\text{Molecular mass}} = \frac{1000 \text{ g}}{18} = 55\cdot55 \text{ moles}$

$1\cdot29 \times 10^{-5} = \frac{n_{N_2}}{55\cdot55 + n_{N_2}}$ n_{N_2} in denominator is neglected as $n_{N_2} << 55\cdot55$

$\therefore 1\cdot29 \times 10^{-5} = \frac{n_{N_2}}{55\cdot5}$ $n_{N_2} = 55\cdot55 \times 1\cdot29 \times 10^{-5} = 71\cdot66 \times 10^{-5}$ moles

$\therefore n_{N_2} = 0\cdot716 \text{ m mol}$.

10. H_2S, a toxic gas with rotten egg smell, is used for the qualitative analysis. If the solubility of H_2S in water at STP is 0.195 m, calculate Henry's law constant.

Solubility of H_2S = 0.195 m = 0.195 mole in 1000g water

∴ Mass of water = 1000 g

Number of moles of water $= n_{H_2O} = \frac{1000}{18} = 55 \cdot 55$ moles

Mole fraction of $H_2S = x_{H_2S} = \frac{n_{H_2S}}{n_{H_2O} + n_{H_2S}} = \frac{0 \cdot 195}{55 \cdot 55 + 0 \cdot 195} = 0 \cdot 003498$

Pressure at STP = 0.987 bar

According to Henry's law $p = K_H x$

$$K_H = \frac{p}{x_{H_2S}} = \frac{0 \cdot 987}{0 \cdot 003498} = 282 \cdot 16 \text{ bar}$$

11. Henry's law constant for the molality of methane in benzene at 298 K is 4.27 × 10^5 mm Hg. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg.

According to Henry's law

$$p_{CH_4} = K_H x_{CH_4} \qquad x_{CH_4} = \frac{p_{CH_4}}{K_H} = \frac{760 \text{ mm Hg}}{4 \cdot 27 \times 10^5 \text{ mm Hg}} = 1 \cdot 78 \times 10^{-3}$$

Note: Mole fraction represents the solubility of methane in benzene.

12. Heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components are 105.2 kpa and 46.8 kpa respectively. What will be the vapour pressure of a mixture of 26g heptane and 35g of octane?

According to Raout's law

$p_{octane} = x_{octane} \times p^0_{octane}$ $\qquad$ $p_{heptane} = x_{heptane} \times p^0_{heptane}$

Molar mass of octane (C_8H_{18}) = 8 × 12 + 18 × 1 = 114 g mol^{-1}

Molar mass of heptane (C_7H_{16}) = 7 × 12 + 1 × 16 = 100 g mol^{-1}

Number moles of octane $= \frac{w}{M} = \frac{35}{114} = 0.31 \text{ mol}$

Number of moles of heptane $= \frac{w}{M} = \frac{26}{100} = 0.26 \text{ mol}$

Mole fraction of octane $= x_{octane} = \frac{n_{octane}}{n_{octane} + n_{heptane}} = \frac{0.31}{0.31 + 0.26} = 0.544$

$x_{heptane} = 1 - x_{octane} = 1 - 0.544 = 0.456$

p_{octane} = 0.544 × 46.8 kpa = 25.46 kpa

$p_{heptane}$ = 0.456 × 105.2 kpa = 47.97 k pa

Total vapour pressure $P_{total} = p_{octane} + p_{heptane}$ = 25.46 + 47.97 = 73.43 k pa

13. The vapour pressure of pure liquids A and B are 450 and 700 mm Hg respectively, at 350 K. Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg. Also find the composition of the vapour phase.

It is given that: $p^o_A = 450$ mm of Hg $\qquad p^o_B = 700$ mm of Hg $\qquad P_{total}$ = 600 mm of Hg

From Raoult's law, $p_A = p^o_A x_A$ and $p_B = p^o_B x_B$ $\qquad P_{total} = p_A + p_B$

$x_B = 1 - x_A$

$$P_{total} = p^o_A x_A + p^o_B (1 - x_A) \qquad P_{total} = p^o_A x_A + p^o_B - p^o_B x_A \qquad P_{total} = (p^o_A - p^o_B) x_A + p^o_B$$

100 = (450 – 700)x_A + 700

–100 = –250x_A $\quad x_A$ = 0.4

Therefore, x_B = 1 – x_A $\quad$ = 1 – 0.4 = 0.6

Now, $p_A = p_A^o x_A$ = 450 × 0.4 = 180 mm of Hg

$p_B = p_B^o x_B$ = 700 × 0.6 = 420 mm of Hg

Now, in the vapour phase: $\text{Mole fraction of A} = \frac{p_A}{p_A + p_B} = \frac{180}{180 + 420} = 0.3$

Mole fraction of B = 1– 0.3 = 0.7

14. The vapour pressure of water is 12.3 kpa at 300K. Calculate vapour pressure of 1 molal solution of non volatile solute in it.

According to the Raoult's law

$$\frac{p_A^0 - p_A}{p_A^0} = \frac{n_B}{n_B + n_A} \qquad \begin{pmatrix} A = H_2O \\ B = \text{solute} \end{pmatrix}$$

1 molal means 1 mole of non volatile solute present in 1000g H_2O

Molar mass of H_2O = 18 g mol^{-1}

Number of moles in $1000\text{g } H_2O = \frac{1000}{18} = 55.56$ moles.

Number of moles of solute = 1 mol.

$$\therefore \frac{12.3 - p_A}{12.3} = \frac{1}{1 + 55.56}$$

12.3 – p_A = 0.0177 × 12.3

p_A = 12.3 – 0.2177 = 12.08 k pa

15. Vapour pressure of water at 293 K is 17.535 mm Hg. Calculate the vapour pressure of water at 293 K when 25 g of glucose is dissolved in 450 g water

Molar mass of glucose ($C_6H_{12}O_6$) = 6 × 12 + 12 × 1 + 6 × 16 = 180 g mol^{-1}

Number of moles of glucose $= \frac{25\text{ g}}{180\text{ g mol}^{-1}} = 0.139$ mol

Number of moles of water $= \frac{450\text{g}}{18\text{ g mol}^{-1}} = 25$ mol

According to Raoult's law, $\frac{p_A^0 - p_A}{p_A^0} = \frac{n_B}{n_B + n_A}$

p_A^0 = Vapour pressure of water and p_A= Vapour pressure of solution

$$\frac{17.535 - p_A}{17.535} = \frac{0.139}{0.139 + 25} \qquad 17.535 - p_A = \frac{0.139 \times 17.535}{25.139}$$

17.535 – p_A = 0.097 $\qquad$ p_A = 17.535 – 0.097 = 17.44 mm Hg

16. Calculate the mass of a non–volatile solute (molar mass 40 g mol^{-1}) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.

Molecular mass of octane (C_8H_{18}) = M_A = 8 × 12 + 18 × 1 = 114 g mol^{-1}

Vapour pressure of octane after dissolving solute $= \frac{80p_A^o}{100} = 0.8p_A^o$

$$\frac{p_A^o - p_A}{p_A^o} = \frac{n_B}{n_A + n_B} \qquad n_B = \frac{w_B}{40}\text{ mol}, \qquad n_A = \frac{114}{114} = 1\text{ mol}$$

$$\therefore \frac{p_A^o - 0{\cdot}8p_A^o}{p_A^o} = \frac{\frac{w_B}{40}}{\left(\frac{w_B}{40}+1\right)} \quad ; \quad \frac{p_A^0 - 0{\cdot}8p_A^0}{p_A^0} = \frac{w_B}{w_B+40}$$

$$0{\cdot}2 = \frac{w_B}{w_B+40} \qquad \therefore w_B = 10\text{g}$$

17. The boiling point of a solution of 0.1050 g of a substance in 15.84 g of ether was found to be 0.1^{o}C higher than that of ether. What is the molecular weight of the substance? (K_b = 2.02 K kg mol^{-1})

$$M_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A} \qquad = \frac{2{\cdot}02 \times 0{\cdot}1050 \times 1000}{0{\cdot}1 \times 15{\cdot}84} = 133{\cdot}9 \text{ g mol}^{-1}$$

18. The molecular weight of an organic compound is 58 g mol^{-1}. Calculate the boiling point of a solution containing 24 g of the solute and 600 g of water. The boiling point of water = 100^{o}C. K_b for water = 0.52 K kg mol^{-1}.

$$\Delta T_b = \frac{K_b \times w_B \times 1000}{M_B \times w_A}$$

$$T_b - T_b^o = \frac{0{\cdot}52 \times 24 \times 1000}{58 \times 600} \qquad T_b = 0{\cdot}358 + T_b^o = 0{\cdot}358 + 100 = 100{\cdot}358^\circ\text{C}$$

19. Acetone boils at 56.38^{o}C and a solution of 1.41 grams of an organic compound in 20 g of acetone boils at 56.88^{o}C. If K_b for acetone is 1.67 K kg mol^{-1}. Calculate the mass of one mole of the organic solid.

$$M_B = \frac{w_B \times K_b \times 1000}{\Delta T_b \times w_A} \qquad \Delta T_b = T_b - T_b^o = 56{\cdot}88 - 56{\cdot}38 = 0{\cdot}5^\circ\text{C}$$

$$M_B = \frac{1{\cdot}41 \times 1{\cdot}67 \times 1000}{0{\cdot}5 \times 20} = 235{\cdot}47 \text{ g mol}^{-1}$$

20. In a cold climate, water gets frozen causing damage to the radiator of a car. Ethylene glycol is used as an antifreezing agent. Calculate the amount of ethylene glycol to be added to 4 kg of water to prevent it from freezing at –6^{o}Cp
(K_f for water = 1.85 K kg mol^{-1} molar mass of ethylene glycol = 62 g mol^{-1}).

$$\Delta T_f = \frac{K_f \times w_B \times 1000}{M_B \times w_A} \qquad 6 = \frac{1{\cdot}85 \times w_B \times 1000}{62 \times 4 \times 10^3} \qquad w_B = 804{\cdot}32 \text{ g}$$

21. Addition of 0.643 g of a compound to 50 mL of a liquid (density = 0.879 g/mL) lowers the freezing point from 5.51^{o}C to 5.03^{o}C. Calculate the molar mass of the compound. (K_f for benzene = 5.12 K kg mol^{-1}).

$$M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A} \qquad w_A = 50 \times 0{\cdot}879 = 43{\cdot}95\text{g} \quad (\because \text{ mass} = v \times d)$$

$$\Delta T_f = T_f^o - T_f = 5{\cdot}51 - 5{\cdot}03 = 0{\cdot}48^\circ\text{C} \qquad \therefore M_B = \frac{5{\cdot}12 \times 0{\cdot}643 \times 1000}{0{\cdot}48 \times 43{\cdot}95} = 156{\cdot}056 \text{ g mol}^{-1}$$

22. 45 g of ethylene glycol ($C_2H_6O_2$) is mixed with 600 g of water. Calculate (a) the freezing point depression and (b) the freezing point of the solution.
(K_f = 1.86 K kg mol^{-1})

Freezing point depression (ΔT_f) is given by $$\Delta T_f = \frac{K_f \times w_B \times 1000}{M_B \times w_A}$$

Molecular mass of ethylene glycol ($C_2H_6O_2$) = $2\times12+6\times1+2\times16$ = 62 g mol^{-1}.

$$\Delta T_f = \frac{1{\cdot}86\times45\times1000}{62\times600}$$

$\Delta T_f = 2{\cdot}25\,K$ $\qquad$ $\Delta T_f = T_f^0 - T_f$

$T_f^0 =$ freezing point of water = 273.15 K $\qquad$ $T_f =$ freezing point of solution

$T_f = T_f^0 - \Delta T_f$ $\qquad$ $= 273{\cdot}15 - 2{\cdot}25 = 270{\cdot}9\,K$.

23. 1.4 g acetone dissolved in 100 g benzene gave a solution which freezes at 277.12 K. Pure benzene freezes at 278.4 K. 2.8 g of a solute dissolved in 100 g benzene gave a solution which froze at 277.76 K. Calculate the molecular weight of solute.

$$K_f = \frac{\Delta T_f \times w_A \times M_B}{w_B \times 1000} \qquad \Delta T_f = T_f^o - T_f = 278{\cdot}4 - 277{\cdot}12 = 1{\cdot}28\,K$$

$$= \frac{1{\cdot}28\times100\times58}{1{\cdot}4\times1000} = 5{\cdot}3\,K\,kg\,mol^{-1} \qquad M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A} = \frac{5{\cdot}3\times2{\cdot}8\times1000}{0{\cdot}64\times100} = 231{\cdot}87$$ g mol^{-1}

24. The osmotic pressure of blood is 7.65 atm at 37^{o}C. How much glucose should be used per litre for an intravenous injection that is to have the same osmotic pressure as blood? (Molar mass of glucoses = 180 g mol^{-1})

$$M_B = \frac{w_B RT}{\pi V} \qquad w_B = \frac{M_B \pi V}{RT} \qquad = \frac{180\ g\ mol^{-1}\times7{\cdot}65\ atm\times1L}{0{\cdot}0821\ L\ atm\ mol^{-1}K^{-1}\times310\ K} = 54{\cdot}14\ g$$

25. What is the osmotic pressure of 0.05% urea solution in water at 20^{o}C? R = 0.0821 lit atm mol^{-1} K^{-1} molar mass of urea = 60 g mol^{-1}.
0.05% urea means 0.05 g urea present in 100 mL water.

$$\pi = \frac{w_B RT}{M_B V} \qquad = \frac{0{\cdot}05\times0{\cdot}0821\times293}{60\times0{\cdot}1\ L} \qquad (\because\ 100\ nL = 0{\cdot}1\ L) \qquad = 0{\cdot}2\ atm$$

26. 200 cm^3 of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressure of such a solution at 300 K is found to be 2.57 × 10^{-3} bar. Calculate the molar mass of the protein. (R = 0.083L bar mol^{-1} K^{-1})

$$M_B = \frac{w_B RT}{\pi V} \qquad V = 200\ cm^3 = 0{\cdot}2\ L$$

$$= \frac{1{\cdot}26\times0{\cdot}083\times300}{2{\cdot}57\times10^{-3}\times0{\cdot}2}$$ = 61039 g mol^{-1}.

27. Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185000 in 450 mL of water at 37^{o}C (R = 0.0821 L atm K^{-1} mol^{-1}).

$$\pi = \frac{w_B RT}{M_B V} \qquad V = 450\ mL = 0{\cdot}45L$$

$$= \frac{1\times0{\cdot}0821\times310}{185000\times0{\cdot}45} \qquad = 0{\cdot}00030572\ atm \qquad = 0{\cdot}00030572\times101325$$ = 30.9768 Pa.

Solutions

A solution is a homogenous mixture of two or more substances, the composition of which may vary within limits. "A solution is a special kind of mixture in which substances are intermixed so intimately that they can not be observed as separate components". The dispersed phase or the substance which is to be dissolved is called **solute**, while the dispersion medium in which the solute is dispersed to get a homogenous mixture is called the **solvent**. A solution is termed as binary, ternary and quartenary if it consists of two, three and four components respectively.

Solubility.

Solubility of as substance in the solvent is the measure of the capacity of the solute to dissolve in the solvent at a given temperature and pressure. "Solubility of a substance may be defined as the amount of solute dissolved in 100gms of a solvent to form a saturated solution at a given temperature". A **saturated solution** is a solution which contains at a given temperature as much solute as it can hold in presence of dissolving solvent. Any solution may contain less solute than would be necessary to saturate it. Such a solution is known as **unsaturated solution**. When the solution contains more solute than would be necessary to saturate it then it is termed as **supersaturated solution**. It is metastable.

$$Solubility = \frac{Weight\ of\ solute}{weigtht\ of\ solvent} \times 100$$

Types of solutions

Based on the physical state of the solvent, binary solutions are classified as

- Gaseous solutions
- Liquid solutions
- Solid solutions

- **Gaseous solutions:** The solutions in which the solvent is gas and solute is either solid, liquid or a gas are called gaseous solutions.

- **Liquid solutions:** The solutions in which the solvent is liquid and the solute is either a solid, liquid or a gas are called liquid so0lutions.

- **Solid solutions:** The solutions in which the solvent is solid and the solute is either a solid, liquid or a gas, are called solid solutions.

Different types of solutions and some examples

Types of solutions	Solute	Solvent	Common example
Gaseous Solutions	Gas Liquid Solid	Gas Gas Gas	Mixture of oxygen and nitrogen gases Chloroform in nitrogen gas Camphor in nitrogen gas
Liquid Solutions	Gas Liquid Solid	Liquid Liquid Liquid	Oxygen dissolved in water Ethanol dissolved in water Glucose dissolved water

Solid Solutions	Gas Liquid Solid	Solid Solid Solid	Solution of hydrogen in palladium Amalgam of mercury with sodium Copper dissolved in gold

Note: In aqueous solution water is the solvent.

Methods of expressing concentration of solutions

The concentration of a solution is the amount of a solute present in a given quantity of solvent or solution.

Units to express the concentration of solutions

Concentration of solutions is expressed in different units. Some of the common units are

(a) Molarity (M) (b) Molality (m) (c) Mole fraction (x)

- **Molarity (M):** Molarity of a solution is defined as **the number of moles of the solute dissolved in one litre of the solution.**

$$\text{Molarity} = \frac{\text{Number of moles of the solute}}{\text{Volume of the solution} \in \text{litre}}$$

If W_B gram of the solute of molar mass M_B is dissolved in V dm^3 of the solution, then the molarity is given by,

$$\text{Molarity} = \frac{W_B \times 1000}{M_B \times V}$$

Units: mol/L or mol/dm^3

For example, a molar $(1M)$ solution of sugar means a solution containing 1 mole of sugar (i.e., 342 g or 6.02×10^{23} molecules of it) per litre of the solution. Solutions in term of molarity generally expressed as,

$1M$ = Molar solution, $2M$ = Molarity is two, $\frac{M}{2}$ or 0.5 M = Semimolar solution,

$\frac{M}{10}$ or 0.1 M = Decimolar solution, $\frac{M}{100}$ or 0.01 M = Centimolar solution

$\frac{M}{1000}$ or 0.001 M = Millimolar solution

- Molarity is most common way of representing the concentration of solution.
- Molarity is depend on temperature as, $\text{Molarity} \propto \frac{1}{\text{Temperature}}$

Advantages of molarity

✓ Stoichiometric calculations are simplified since the quantity of the solute is expressed in mole.

✓ Quantity of the solution is easily measured by volume rather than by mass.

Disadvantages of molarity

- Molarity of a solution decreases with the increase in temperature since the volume of the solutions increases with the increase in temperature. Thus molarity is temperature dependent and cannot be used in experiments that involve temperature variations.
- The exact amount of the solvent in a given volume of the solutions cannot be determined if the density of the solution is not known.

- **Molality (m):** Molality of solution is defined as **the number of moles of the solute dissolved in one kg of the solvent.** Molality is denoted by 'm' and is calculated by the expression.

$$\text{Molality} = \frac{\textit{Number of moles of the solute}}{\textit{Mass of the solvent} \in kg}$$

If W_B gram of the solute of molar mass M_B is dissolved in W_A gram of the solvent, then

molality is given by

$$\text{Molality} = \frac{W_B \times 1000}{W_A \times M_B}$$

Unit: mol/kg

Advantages of molality

- Molality is temperature independent quantity. Therefore this unit can be conveniently used in experiments involving temperature variations
- The exact mass of the solvent in given amount of the solution can be calculated easily.

Mole fraction:

Mole fraction of a component in a solution is the ratio of number moles of that component to the total number of moles of all the components.

Let us consider a binary solution that contains n_A moles of solvent 'A' and n_B moles of the solute 'B'

Mole fraction of the solvent A is given by,

$$x_A = \frac{n_A}{n_A + n_B}$$

Mole fraction of the solute B is given by

$$x_B = \frac{n_B}{n_A + n_B}$$

For a solution that contains a large number of components A, B,C,D,E………I, mole fraction of component D is given by

$$x_D = \frac{n_D}{n_A + n_B + \ldots.. + n_I}$$

Mass percentage (w/w)

Mass percentage of a solution is defined as the **number of parts by mass of the solute dissolved in 100 parts by mass of the solution.**

$$\text{Mass percentage} = \frac{\text{Mass of the solute}}{\text{Mas of the solution}} \times 100$$

Note: Units of the two masses should be same

Volume percentage (v/v)

Volume percentage of a solution is defined as **the number of parts by volume of the solute dissolved in 100 parts by volume of the solution.**

$$\text{Volume percentage} = \frac{\text{Volume of the solute}}{\text{Volume of the solution}} \times 100$$

Note: Units of the two volume unit be same

This unit is more useful when both the solute and solvents are liquids.

Mass by volume percentage (w/v)

Mass by volume percentage of a solution is defined as **the number of parts by mass of the solute dissolved in 100 parts by volume of the solution.**

$$\text{Mass by volume percentage} = \frac{\text{Mass of the solute}}{\text{Volume of the solution}} \times 100$$

Note:

In this case, generally gram and cm^3 are used as the units. Otherwise system of units should be same.

Parts per million (ppm)

Parts per million of a solute is defined as **the member of parts of solute dissolved in one million parts of the solution.**

$$\text{Parts per million} = \frac{\text{Number of parts of the solute}}{\text{Number of parts of the solution}} \times 10^6$$

Note: The units of the parts of the solute and the solution should be same.

Parts per million are also expressed in w/w, v/v and w/v.

This unit is suitable when solutes are present in trace quantities.

Note: (I) Mass percentage, ppm, mole fraction, and molality are independent of temperature because mass is independent of temperature

(II) Molarity, volume percentage and mass by volume percentage depends on temperature because volume depends on temperature.

Solubility:

When a solute is mixed with a solvent, particles of the solute leave the solute phase and get mixed with the particles of the solvent phase. This process is known as **dissolution.** The solute is said to be dissolved in solvent.

Compounds like sugar, potassium nitrate, ammonium nitrate, etc., dissolve in water whereas they are insoluble in benzene or ether. Compounds like naphthalene, anthracene, diphenyl, etc., dissolve in solvents like benzene and ether but not in water. By these examples it may be broadly generalized that 'Like dissolved like'. It means to say that polar solutes dissolve in polar solvents and non polar solutes dissolve in non polar solvents. Thus dissolution of a solute in a given solvent takes place when the nature of inter particle attractive forces in the solute and the solvent are same.

Solubility of a solid in a liquid:

Dissolution of a solute in a solvent is a reversible change. If dissolution is the forward change then crystallization is the backward change that takes place simultaneously.

When a large amount of solid solute is added to given amount of a solvent, initially dissolution of the solute takes place. But as the concentration of the solute particles in the solution phase increases, the back ward change, i.e., crystallization begins and its rate starts to increase. At one stage the rates of dissolution and crystallization become equal resulting in a dynamic equilibrium between the solid solute and the solute particle in the solution phase

$$\underset{(Solid)}{Solute}\ \underset{¿}{dissolution}\text{solute particles in solution}$$

Once the equilibrium is reached, the concentration of the solute particles in the solution remains constant. No more solute dissolves in the solvent. The solution thus formed is said to be saturated solution. **A solution in which no more solute can be dissolved at the same temperature and pressure is called saturated solution. The amount of the solute present in a given quantity of the saturated solution at a given temperature and pressure is called solubility of the solute in the given solvent. A solution in which some more solute can be dissolved at the given temperature and pressure is called unsaturated solution.**

Generally solubility is measured in mass percentage (w/w). Therefore, solubility of a solid solute in a given liquid solvent at a given temperature is the mass of the solute in gram dissolved in 100 grams of the saturated solution.

Effect of temperature on solubility of solid solute in a liquid solvent :

Since, solid solute and solvent particles in solution are in dynamic equilibrium, it follows Le-chatelier's principle. According to this principle increase in temperature shifts the equilibrium towards endothermic change and decrease in temperature shifts the equilibrium towards the exothermic change.

Therefore, if the dissolution of a solute in a given solvent is endothermic then its solubility increases with the increase in temperature.

If the dissolution of a solute in a given solvent is exothermic, then the solubility of the solute decreases with increase in temperature.

Note: For exothermic dissolution, enthalpy solution, $\Delta_{sol} H < 0$ and for endothermic dissolution, enthalpy of solution$\Delta_{sol} H > 0$

Effect of pressure:

There is no significant effect of pressure on the solubility of a solid solute in a liquid solvent. This is because solids and liquids are highly incompressible and practically remain unaffected by changes in pressure.

Solubility of a gas in a liquid :

Gases dissolve in liquids to form liquid-gas solution. Example, carbon dioxide dissolves in water to form soda water. Water in wells, rivers, and sea contains dissolved air which is used by aquatic animals for their breathing.

Factors that influence solubility of gases in liquids:

The factors that influence the solubility of gases in liquids are

- The nature of the gas and solvent
- Nature of the solvent
- Temperature
- External pressure

The nature of gases and nature of solvents:

Non-polar gases are less soluble in polar solvents like water. For example, gases like, O_2, N_2, H_2 etc., which are non-polar are very less soluble in water which is a polar solvent at room temperature and pressure. But CO_2, HCl, NH_3 etc., being polar gases, are highly soluble in water under identical conditions.

Effect of temperature on the solubility of gases:

Generally solubility of all gases in liquids decreases with the increases in temperature. This is because of two reason ;

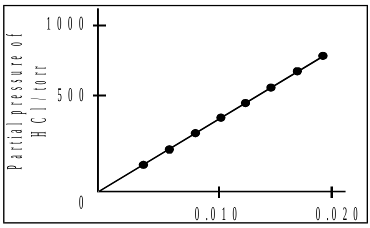
- ❖ Generally dissolution of any gas in a liquid is exothermic. According to Le-Chatelier's principle, low temperature favours exothermic changes. That is why gases dissolve more at low temperatures and less at high temperatures in liquids.
- ❖ Increase in temperature increases the kinetic energy of dissolved gas molecules. As a result, the gas molecules escape more from the solution phase by overcoming the attractive forces.

Note: Solubility of oxygen is more in cold water than in warm water. That is why aquatic speices are more comfortable in cold waters than in warm waters.

Effect of pressure:

The solubility of a gas in a liquid increases with the increase in its partial pressure above the liquid.

Henry's law:



This law gives the quantitative relationship between the solubility of a gas in a liquid and the partial pressure of the gas above the liquid at a given temperature. Henry's law states that **" at constant temperature the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the solution".** If the solubility of a gas is in mole faction, the law can also be stated as **" the partial pressure of the gas above the solution is directly proportional to the mole fraction of a gas in the solution".**

i.e., p $\propto$x where p is partial pressure of the gas and x is solubility in mole fraction

$p = K_H\, x$ Here, K_H is called Henry's law constant.

$X = \frac{p}{K_H};$

Characteristics of Henry's law constant:

- Higher is the value of K_H lower is the solubility of gas.
- Different gases have different K_H values. Therefore K_H value depends on nature of the gas.

For example, K_H value. of CO_2 and O_2 in water at 20^0 C are respectively 1.67k bar and 457k bar. That is why CO_2 is about 28 times more soluble in water than oxygen at given temperature.

- K_H value increases by increasing the temperature. This indicates that solubility of gases in liquid decreases by increasing temperature. This is because the dissolution of gas in liquid is an exothermic process.
- Units of Henry's law constant are same as pressure.

Applications of Henry's law :

(a) Carbonated beverages

- To increase the solubility of carbon dioxide in soda water and soft drinks, bottles are sealed under high pressure of CO_2.

(b) Deep sea diving

- Oxygen cylinders used by sea divers (Scuba divers) are filled with air which is diluted with helium to minimize the solubility of nitrogen in the blood by decreasing its partial pressure to avoid the risk of 'bends'.

(Otherwise more nitrogen will be dissolved due to high pressure deep under sea water. When a sea diver comes back to the surface, the solubility of nitrogen again decreases and the dissolved gas is released, leading to the formation of nitrogen bubbles in the blood. This results in the blockage of capillaries and leads to a medical condition known as 'bends' or decompression sickness which causes acute pain).

(c) High altitude sickness

- At high altitudes, partial pressure of oxygen is less than that at a ground level. This leads to low concentrations of oxygen in the blood and tissues of mountain climbers. Low-blood oxygen causes climbers to become weak and unable to think clearly. These are symptoms of anoxia.

Equilibrium vapour pressure of a liquid :

Consider a liquid taken in a closed container. The liquid being volatile, molecules of the liquid escape from the liquid phase and occupy the space above the liquid forming vapour phase. But after some time molecules of the vapour phase also starts condensing into liquid. Thus at one stage there will be a dynamic equilibrium between the vapour phase and the liquid when the rate of vapourisation becomes equal to that of condensation. **The pressure exerted by the molecules of the vapour phase on the liquid phase at equilibrium is called equilibrium vapour pressure.** For simplicity it is also called **vapour pressure.** At constant temperature, different liquids have different vapour pressures since they depend on nature of the liquids.

Vapour pressure of a solution of liquid in liquid :

The vapour phase of a binary solution placed in a closed vessel consists of vapours of both the components. The French chemist F.M Raoult (1886) gave quantitative relationship between the partial pressures of the components in the vapour phase and their mole fractions in the solution phase. This relationship is known as Raoult's law.

Raoult's law for a solution of two liquid components:

Raoult's law states **that for a solution of volatile liquids, the partial pressure of each component in the vapour phase is directly proportional to the mole fractions of the respective components in the solution phase at a given temperature.**

Let us consider a solution containing two volatile components A and B (that have measurable vapour pressures) in a closed container. The equilibrium is established between vapour phase and the liquid phase at constant temperature. Let P_{total} be the total vapour pressure of the vapour phase about the solution and $p_A$and p_B be the partial vapour pressure of the two components A and B. These partial pressures are related to the mole fractions $x_A \wedge x_B$ of the two components A and B respectively. According to Raoult's law for component A,

$$p_A \propto x_A$$

$$p_A = p_A^0 x_A$$

Where p_A^0 is the vapour pressure of the pure component A at the same temperature.

Similarly, for component B

$$p_B \propto x_B$$

$$p_B = P_B^0 X_B$$

Where p_B^0 is the vapour pressure of the pure component B at the same temperature.

According to Dalton's law of partial pressures, the total pressure is the sum of the partial pressures of all components at the same temperature.

$$p_{total} = p_A + p_B$$

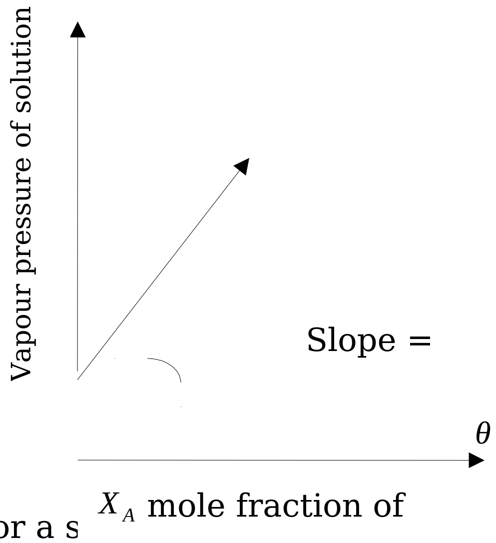
$$p_{total} = p_A^0 x_A + p_B^0 x_B$$

$$p_{total} = p_A^0 (1 - x_B) + p_B^0 x_B$$

$$p_{total} = p_A^0 - p_A^0 x_B + p_B^0 x_B$$

$$p_{total} = p_A^0 + (p_B^0 - p_A^0) x_B$$

$\tan\theta = P_A^o$



The plots of p_A and p_B verses the mole fractions $x_A \wedge x_B$ for a s temperature are linear graphs as shown

Following conclusions can be drawn from the above equations and graphs;

→ Total vapour pressure over the solution is directly proportional to the mole fraction of any one component ($x_A \vee x_B$¿.

→ Total vapour pressure of the vapour phase of the solutions varies linearly with the mole fraction of component B(or A).

→ Depending on the vapour pressures of the pure components A and B, total vapour pressure over the solution decreases or increases with the increase of the mole fraction of component A (or B).

The composition of vapour phase in equilibrium with the solution is determined by the partial pressures of the components. If $y_A \wedge y_B$ are the mole fraction of the component A and B respectively in the vapour phase then, using Dalton's law of partial pressures:

$$p_A = y_A p_{total}$$

$$p_B = y_B \times p_{total}$$

In general

$$p_i = y_i \, p_{total}$$

Raoult’s law as a special case of Henry’s law:

According Henry’s law “the partial pressure of the gas (p) in vapour phase is proportional to the mole fraction of the gas (x) in the solution i.e., $p = K_H x$

According to Raoult’s law “the partial pressure of each component of the solution is directly proportional to its mole faction present in the solution.

i.e., $p_i = p_i^0 x_i$

By comparing equations for Henry’s law and Raoult’s law, we can conclude that the partial pressure of volatile liquid or gas is directly proportional to its mole fraction in solution. Only the difference is in their proportionality constants $K_H \wedge p_i^0$. Hence Raoult’s law is a special case of Henry’s law in which $K_H = p_i^0$.

Ideal and non- ideal solutions:

The binary solutions of the volatile liquids can be classified into two types. They are ideal and non-ideal solutions.

Ideal solutions:

- **A solution which obeys Raoult’s law at all concentration range of the components and temperature is called an ideal solution.**
- In ideal solutions, solvent (A) – solute (B) interactions are equal to solute (B) – solute (B) and solvent (A) – solvent (A) interactions. A perfectly ideal solution is rare but some solutions are nearly ideal in behaviour. A few examples are:
  - Benzene and toluene
  - Chlorobenzene and bromobenzene
  - Carbon tetrachloride and silicon tetrachloride
  - n-Hexane and n-heptane
  - Ethylene bromide and ethylene chloride
  - Ethyl bromide and ethyl iodide.

Characteristics of Ideal solution

(i) It should obey Raoult’s law, i.e., $P_A = P_A^0 X_A$ and $P_B = P_B^0 X_B$.

(ii) $\Delta H_{\text{mixing}} = 0$

(iii) $\Delta V_{\text{mixing}} = 0$

Non-ideal solutions:

A solution which does not obey Raoult’s law at all concentration range of the components and temperature is called a non ideal solution.

- The non ideal solutions are accompanied by change in enthalpy and volume during their formation i.e., $\Delta H_{mixing} \neq 0 \Delta V_{mixing} \neq 0 ¿$
- In general, most of the solutions are non ideal and deviate from ideal behaviour. It must be remembered that in non- ideal binary solution none of the components follows the Raoult’s law. The non-ideal solutions are further classified into two categories. They are

I. Non-ideal solution showing positive deviation
II. Non ideal solution showing negative deviation

The causes for these deviations lie in the nature of interactions at the molecular level.

Non-ideal solution showing positive deviation:

- The solutions for which the total vapour pressure is higher than that expected from Raoult’s law are called **solutions with positive deviations.**
- For solutions with positive deviations from Raoult’s law, partial vapour pressure of each component A and B is higher than that one that is calculated from Raoult’s law for the same composition.
- In these solutions, the intermolecular attractive forces between the solute-solvent molecules are weaker than those between the solute-solute, solvent-solvent interactions.
- This means that in such solutions, molecules of A (or B) will find it easier to escape than in pure state. This will increases the vapour pressure and result in positive deviation.
- Due to decrease in magnitude of intermolecular attractive forces, the molecules are loosely held and thus increasing intermolecular distances. Therefore formation of a non ideal solution is associated with increase in volume and absorption of energy.

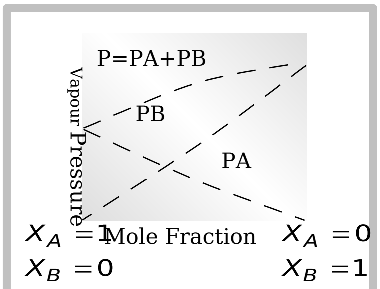
Characteristics:

$p_A > p_A^0 x_A$

$p_B > p_B^0 x_B$ and

$\Delta H_{mixing} = +ve$

$\Delta V_{mixing} = +ve\ i.e., \left(V_{solution} > V_A + V_B\right).$



Partial and total vapour pressure curves for solutions that show positive

Examples:

- Acetone + ethanol
- Water + ethanol
- Acetone + CS_2
- CCl_4 + toluene
- Water + methanol

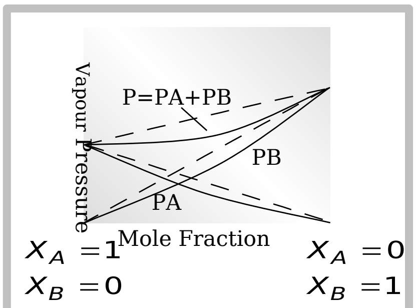
Non-ideal solution showing negative deviation:

- The solutions for which the total vapour pressure is lower than that of an ideal solution of same composition and temperature are called **Solutions with negative deviations.**
- For solution with the negative deviation from Raoult’s law, partial vapour pressure of each component A and B is lesser than the one that is calculated from Raoult’s law for the same composition. So, the total vapour pressure of the solution is less than that of ideal solution of same composition
- Boiling point of such a solution is relatively higher than the boiling points of A and B respectively.
- In this case the intermolecular attractive forces between the solute-solvent molecules are stronger than those between the solute-solute and solvent-

solvent molecules. This means that in such solutions, molecules of A (or B) will not find it easier to escape than in pure state. This will decrease the vapour pressure and result in negative deviation.

Characteristics:

$$p_A < p_A^0 x_A$$
$$p_B < p_B^0 x_B$$ and
$$\Delta H_{mixing} = -ve$$
$$\Delta V_{mixing} = -ve \; i.e., \left(V_{solution} < V_A + V_B\right).$$



A vapour pressure curve showing negative deviation (solid lines) from idea

Examples:

- Acetone +aniline
- H_2O + HNO_3
- Acetic acid + pyridine
- Acetone + chloroform
- Chloroform + diethylether
- Chloroform + benzene
- CH_3OH + CH_3COOH
- Water + HCl

Azeotropic Mixtures (or) constant Boiling Mixtures:

There are certain binary liquid mixture, which boil at constant temperature like a pure liquid such that both the components are distilled out simultaneously. The components of such mixtures cannot be separated during functional distillation. Such mixtures are named as Azotropic mixtures.

The mixture of liquids which boils at constant temperature and possess same composition for both liquid and vapour phases is named as azeotropic mixture.

Types of azeotropes:

Based on the relative values of boiling points of the components and the mixture, azeotrops are of 2 types:

i **Minimum boiling azeotropes:** The azeotropic mixtures for which the boiling point is lower than the boiling points of both the component liquids are named as minimum boiling azeotropes.

ii **Conditions for formation:** Minimum boiling azeotropes are formed by non-ideal solutions with positive deviation. The composition of mixtures at which the vapour pressure is highest represents the azeotropic composition. Since the vapour pressure is highest, boiling point is minimum and hence is lower than both the components.
For example: a mixture of ethanol and water at a composition of 95.574% by mass of ethanol shows a constant boiling point of 351.1 K. This is lesser than both ethanol (b.p : 351.3 K) and water (b.p : 373 K).

Components		Mass % of B	Boiling points (K)		
A	**B**		**A**	**B**	Azeotrope
H_2O	C_2H_5OH	95.57	373	351.3	351.1
H_2O	$C_2H_5CH_2OH$	71.69	373	370	350.72
$CHCl_3$	C_2H_5OH	67	334	351.3	332.3
$(CH_3)_2CO$	CS_2	6.8	329.25	320	312.2

iii Maximum boiling azeotropes:

The azeotropic mixtures for which the boiling point is higher than the boiling points of both the component liquids are named as maximum boiling azotropes.

Conditions for formation: Maximum boiling azeotropes are formed by non-ideal solutions with negative deviation. The composition of mixtures at which the vapour pressure is lowest represents the azeotropic composition. Since the vapour pressure is lowest, boiling point is maximum and hence is higher than both the components.
For example: a mixture of HNO_3 and water at a composition of 68% by mass of HNO_3 shows a constant boiling point of 393.5 K. This is greater than both HNO_3 (b.p : 359 K) and water (b.p : 373 K).

Components		Mass % of B	Boiling points (K)		
A	**B**		**A**	**B**	Azeotrope
H_2O	HCl	20.3	373	188	383
H_2O	HNO_3	58.0	373	359	393.5
H_2O	$HClO_4$	71.6	373	383	476

Table 2 : Differences between ideal and non-ideal solutions of two liquids :

Ideal solutions	**Non-ideal solutions**
➢ Obey Raoult's law at all range of concentration.	➢ Do not obey Raoult's law at all range of concentration.
➢ $\Delta H_{mixing}=0$(Neither heat is evolved nor absorbed during dissolution).	➢ $\Delta H_{mixing}\neq 0$. (Either heat is evolved or absorbed during dissolution).
➢ $\Delta V_{mixing}=0$ (Volume of the solution is equal to the sum of	➢ $\Delta V_{mixing}\neq 0$ (Volume of the solution is not equal to the

volumes of the components).	sum of volumes of the components).
➢ $p_{total} = p_A^0 x_A + p_B^0 x_B$	➢ $p_{total} \neq p_A^0 x_A + p_B^0 x_B$
➢ The intermolecular attractive forces between A-A, B-B and A-B are same.	➢ The intermolecular attractive forces between A-A, B-B and A-B are not same.

Table 3 : Differences between non ideal solution with positive and negative deviations:

Positive deviation from raoult's law	Negative deviation from Raoult's law
✓ $\Delta H_{mixing} > 0$ (Heat is absorbed during dissolution.)	✓ $\Delta H_{mixing} < 0$. Heat is evolved during dissolution
✓ $\Delta V_{mixing} > 0$ (volume increases during dissolution.)	✓ $\Delta H_{mixing} < 0$. Volume decreases during dissolution
✓ $p_{total} > p_A^0 x_A + p_B^0 x_B$	✓ $p_{total} > p_A^0 x_A + p_B^0 x_B$
✓ Attractive force between A-B is weaker than A-A and B-B attractive forces.	✓ Attractive force between A-B is stronger than A-A and B-B attractive forces.
✓ Forms minimum boiling point azeotrope.	✓ Forms maximum boiling point azeotrope.

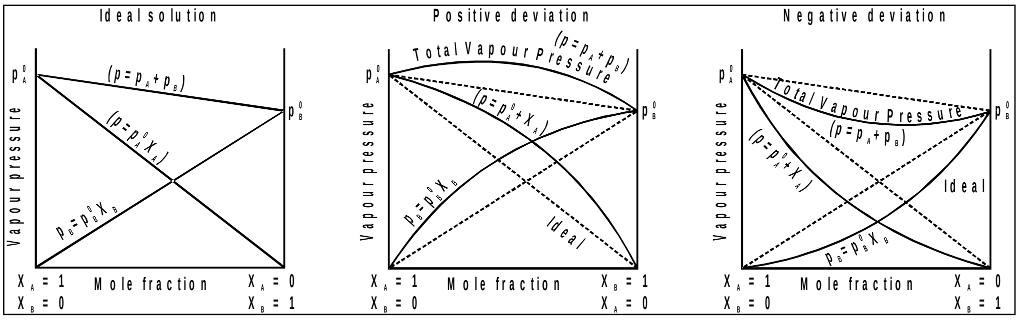


Table 4: Differences between Maximum and minimum Boiling azeotropic mixtures:

Maximum Boiling point	Minimum Boiling Point
Boiling point of mixture is higher than the boiling point of both components	Boiling point of mixture is lower than the boiling point of both components
This type of mixture is formed by solution showing negative deviation.	This type of mixture is formed by solution showing positive deviation.
Solute-solvent interactions are stronger than those between solute-solute and solvent-solvent interactions.	Solute-solvent interactions are weaker than those between solute-solute and solvent-solvent interactions.
Example: *HCl* andwater	Example: Alcohol and water

Raoult's Law for solution of solid in Liquid:

The French chemist F.M Raoult (1886) carried out a series of experiments to study the vapour pressure of a number of binary solutions. On the basis of results of the experiments, he proposed a generalisation called **Raoult's law** which states that, **the vapour pressure of a solution containing non volatile solute is directly proportional to the mole fraction of the solvent.**

In case of a solution containing two components A (volatile solvent) and B(non volatile solute) the vapour pressure of solution is given as

$P_A \alpha x_A$

Or $P_A = K x_A$

Where K is proportionality constant

Colligative properties and determination of molecular masses:

The properties of dilute solutions of non volatile solutes which depend only on the number of particle of the solute relative to the total number of particles in the solution and not on the nature of the solute are called colligative properties. Thus, colligitive properties depend on the number of solute particles present, regardless of whether they are atoms, ions, or molecules.

The important colligative properties are:

I. Relative lowering of vapour-pressure of the solvent
II. Elevation of boiling-point of the solvent
III. Depression of freezing-point of the solvent
IV. Osmotic pressure of the solution

Relative lowering of vapour pressure:

I. When a non volatile solute is dissolved in a volatile solvent, the vapour pressure of solvent decreases. So, the vapour pressure of solution is always lower than the vapour pressure of the pure solvent. The difference in vapour pressures of pure solvent (p_A^0¿ and solution (p_A) is called lowering of vapour pressure (Δp¿

$$\Delta p = p_A^0 - p_A$$

The ratio of lowering of vapour pressure to the pure solvent is called relative lowering of vapour pressure.

Relative lowering of vapour pressure $= \frac{p_A^0 - p_A}{p_A^0}$

The relative lowering of vapour pressure is prefferd to lowering of vapour pressure because it is

- Independent of temperature
- A dimensionless quantity
- Constant when equimolar amounts of different solutes are dissolved separately in the same solvent of same mass

According to Raoult's law

$$p_A = p_A^0 x_A$$

$$p_A = p_A^0(1 - x_B)$$

$$p_A = p_A^0 - p_A^0 x_B$$

$$p_A^0 x_B = p_A^0 - p_A$$

$$\frac{p^0_{A-p_A}}{p_A^0} = x_B$$

So, "**the relative lowering of vapour pressure of a solution containing non volatile solute is equal to mole fraction of solute".** This is called **Raoult's law of relative lowering of vapour pressure.** Thus relative lowering of vapour pressure depends only on the number of the solute particles and it is independent of their identity. Hence relative lowering of vapour pressure is a colligative property.

Mathematically, Raoult's law of relative of vapour pressure is $\frac{p^0_{A-p_A}}{p_A^0} = x_B = \frac{n_B}{n_A + n_B}$

Calculation of molar mass of solute using relative lowering of vapour pressure:

The mole fraction of solute $x_B = \frac{n_B}{n_A + n_B}$

From Roult's Law, $\frac{p^0_{A-p_A}}{p_A^0} = \frac{n_B}{n_A + n_B}$

Here $n_A \wedge n_B$ are the number of moles of solvent and solute respectively present in the solution. For dilute solutions $n_B \ll n_A$, hence neglecting n_B in the denominator we have

$$\frac{p^0_{A-p_A}}{p_A^0} = \frac{n_B}{n_A}$$

$$\frac{p^0_{A-p_A}}{p_A^0} = \frac{w\square_B / M_B}{W_A / M_A}$$

$$\frac{p^0_{A-p_A}}{p_A^0} = \text{¿}\,\frac{w_B \times M_A}{w_A \times M_B}$$

$$M_B = \frac{w_B \times M_A \times p_A^0}{W_A \times \text{¿¿}}$$

Here W_A and w_B are the masses and $M_A \wedge M_B$are the molar masses of the solvent and solute respectively. Thus by determining the value of relative lowering of vapour pressure of a dilute solution of known concentration experimentally, the molar mass of the solute can be calculated

Elevation of boiling point:

Boiling point (T_b) of a liquid is the temperature at which its vapour pressure becomes equal to the external pressure. The vapour pressure of a non volatile solute is less than that of pure solvent. Therefore higher temperature is required to make the vapour pressure of the solution equal to the external pressure as shown in the graph. Hence, the boiling point of solution is more than that of pure solvent.

The difference in boiling points of the pure solvent and the solution is called the elevation in boiling point of solvent.

Let T_b^0be the boiling point of pure solvent and $T_b$be the boiling point of solution.

The increase in the boiling point $\Delta T_b = T_b - T_b^0$ where $\Delta T_b$is known as elevation in boiling point.

Experiments have shown that for dilute solutions, the elevation of boiling point (ΔT_b¿is directly proportional to the molal concentration of the solution. Thus

$$\Delta T_b \propto m$$

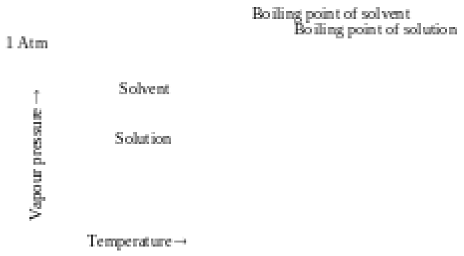
$$\Delta T_b = K_b m$$

Where m is the molality of the solution and K_b is the boiling point elevation constant or molal elevation constant or Ebullioscopic constant. Here molality is used because it is not affected by change in temperature.

When molality of solution, m=1, then $\Delta T_b = K_b$

Therefore, **molal elevation constant of a solvent is defined as the elevation of boiling point caused by dissolving one mole of non volatile solute in one kg of solvent.**

SI unit of the constant K_b is K Kg mol^{-1} **and is specific for a given solvent.**



Calculation of molar mass of the solute using elevation in boiling point:

Let W_B be the mass of the solute of molecular mass M_B dissolved in w_A gram of the solvent, then molality (m) of the solution is given by the equation:

$$m = \frac{w_B \times 1000}{M_B \times w_A}$$

Substituting the value of m in equation 1, we get,

$$\Delta T_b = K_b \times \frac{w_B \times 1000}{M_B \times w_A}$$

The molar mass of the solute (M_B¿ is calculated using the equation,

$$M_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A}$$

Thus, in order to determine M_B, molar mass of the solute, known mass of solute in a known mass of the solvent is taken and ΔT_b is determined for a known solvent whose K_b value is known.

The value of K_b depends upon the nature of the solvent and it can be determined using the formula:

$$K_b = \frac{R \times M_A \times T^2_{b_{solvent}}}{1000 \times \Delta H_{vap}}$$

Where R = gas constant, M_A= molar mass of the solvent, $T_{b(solvent)}$= boiling pint of pure solvent, $\Delta H_{vap}=$¿the enthalpy of vapourisation.

Depression in freezing point:

Freezing point (T_f¿ of a liquid is the temperature at which the vapour pressure of the liquid becomes equal to that of its solid. The vapour pressure of the solution is less than that of pure solvent. Therefore, the vapour pressure of the solution becomes equal to that of solid solvent at lower temperature than that of pure solvent. Hence, the freezing point of the solution is less than that of the solvent as shown in the graph.

Let T_f^0 be the freezing point of the pure solvent and T_f be the freezing point of the solution. The depression in freezing point, $\Delta T_f = T_f^0 - T_f$

So, **depression of freezing point (**ΔT_f¿ **is the difference in the freezing point of the pure solvent and freezing point of solution.**

Experiments have shown that for dilute solutions the depression of freezing point (ΔT_f¿ is directly proportional to the molal concentration of the solution. Thus

$$\Delta T_f \propto m$$

$$\Delta T_f = K_f m$$

Where m is the molality of the solution and K_f is the molal depression constant or freezing depression constant or cryoscopic constant.

When molality of solution, m = 1, then $\Delta T_f = K_f$

Therefore, **molal depression constant of a solvent is defined as the depression in freezing point caused by dissolving one mole of non volatile solute in one kg of solvent.**

SI unit of the constant K_b is **K kg mol^{-1}** or **K molal^{-1}** and is specific for a given solvent.

Calculation of molar mass of a solute using depression in freezing point:

Let w_B be the mass of the solute of molecular mass M_B dissolved in w_A gram of the solvent, then molality (m) of the solution is given by the equation.

$$m = \frac{w_B \times 1000}{M_B \times w_A}$$

Substituting the value of m in equation 1, we get,

$$\Delta T_b = K_f \times \frac{w_B \times 1000}{M_B \times w_A}$$

Therefore, the molar mass of the solute (M_B¿ can be determined according the equation,

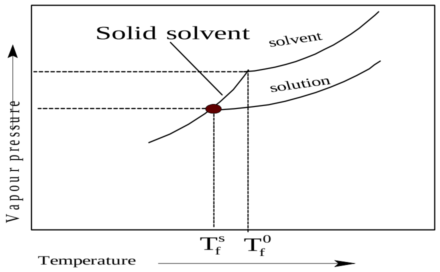
$$M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A}$$

Thus, in order to determine M_B, molar mass of the solute, known mass of the solute in a known mass of the solvent is taken and ΔT_f is determined experimentally for a solution whose K_f value is known.

The value of K_f depends upon the nature of the solvent and it can be determined using the formula:

$$K_f = \frac{R \times M_A \times T_{f(solvent)}^2}{1000 \times \Delta H_{fus}}$$

Where R= gas constant, M= molar mass of the solvent, $T_{f(solvent)}$= freezing point of pure solvent, ΔH_{fus}=¿ the enthalpy of fusion.



Osmosis:

A strong solution of sugar is taken in a thistle funnel, the mouth of which is covered with a piece of animal bladder or cellophane (semipermeable membrane). This is kept immersed in water taken in a beaker as shown in figure. It is observed that the level of the solution inside the stem of the thistle funnel starts raising. It must be due to the flow of solvent molecules (water) into the solution through the semi-permeable membrane. This phenomenon is known as osmosis.

The spontaneous movement of solvent molecules from the solution of lower concentration to the solution of higher concentration through semipermeable membrane is called osmosis.

Osmosis in natural processes:

- A raw mango placed in concentrated salt solution loses of water via osmosis and shrivel into pickle.
- Wilted flowers revive when placed in fresh water due to osmosis.
- A carrot that has become limp because of water loss, when placed in water, water will move into them through osmosis making it firm once again.
- When blood cells are placed in a solution containing more than 0.9% (mass/volume) of sodium chloride, blood cells shrink due to loss of water by osmosis.

- People taking a lot of salt or salty food experience water retention in tissue cells and intercellular spaces because of osmosis. The resulting puffiness or swelling is called edema.
- Water movement from soil into plant roots and subsequently into upper portion of the plant is partly due to osmosis.
- The preservation of meat by salting and of fruits by adding sugar against bacterial action through the process of osmosis, a bacterium on salted meat or candid fruit loss water, shrivels and dies.

Note: 0.9% sodium chloride in water is called **saline solution.**

Osmotic pressure:

- **Osmotic pressure of a solution is defined as the pressure to be applied on the solution of higher concentration just to stop osmosis.**
- Osmotic pressure is a colligative property because it depends on the number of moles of solute in the solution and not on the nature of the solute.
- For dilute solutions, it has been found experimentally that osmotic pressure is proportional to the molarity of the solution at a given temperature T.

$$\pi \propto C$$

$$\pi = kC$$

Where k is proportionally constant and is equal to RT where R is universal gas constant and T is the temperature in Kelvin. Therefore,

$$\pi = CRT$$

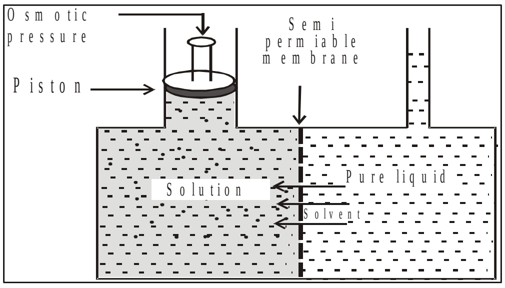
If n_B moles of solute is dissolved in V litres of the solution, C=$\frac{n_B}{V}$

$$\Rightarrow \pi = \frac{n_B}{V} RT$$

If w_B grams of the solute of molar mass (M_B¿ is present in the solution, then $n_B = \frac{w_B}{M_B}$

$$\Rightarrow \pi = \frac{w_B RT}{M_B V}$$

$$\Rightarrow M_B = \frac{w_B RT}{\pi V}$$



Thus, by measuring the osmotic pressure of a solution of known concentration, molar mass of the solute can be calculated using the above equation.

Determination of molecular masses of solute by osmotic pressure measurements is highly useful in finding out the molecular masses of macromolecules like polymers, proteins, etc.

Isotonic, hypertonic and hypotonic solutions:

- When such solutions are separated by semi-permeable membrane, no osmosis occurs. For example, the osmotic pressure of the fluid inside the blood cell is equivalent to that 0.9% (mass/volume) sodium chloride solution, called normal saline solution. That is why normal saline solution is safe to inject intravenously because no osmosis takes place.

For isotonic solutions, $\pi_1=\pi_2$ Primary Condition .....(i)

Also, $C_1=C_2$

or $\frac{n_1}{V_1}=\frac{n_2}{V_2}$ Secondary Conditions

or $\frac{w_1}{m_1V_1}=\frac{w_2}{m_2V_2}$ .....(ii)

Eq. (ii) holds good only for those solutes which neither possess the tendency to get associate nor dissociate in solution, e.g.,

(a) Urea and glucose are isotonic then, $\pi_1=\pi_2$ and $C_1=C_2$

(b) Urea and $\underset{(dissociate)}{NaCl}$ are isotonic then, $\pi_1=\pi_2$ but $C_1\neq C_2$

(c) Urea and $\underset{(associate)}{\text{Benzoic acid}}$ are isotonic then, $\pi_1=\pi_2$ but $C_1\neq C_2$

On the other hand, if we place the cells in a solution containing more than 0.9% (mass/volume) sodium chloride, water will flow out of the cell and they would shrink (Fig). Such a solution is named as hypertonic

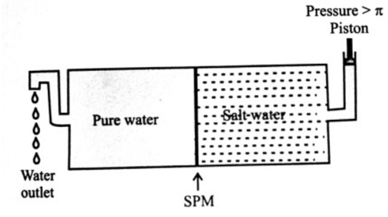
- **A solution having higher osmotic pressure with respect other is called hypertonic solution.** If the sodium chloride concentration is less than 0.9% (mass/volume), then water will flow into the cells if placed in this solution and they would swell (fig).
- **The solution having lower osmotic pressure with respect other is called hypotonic solution.**

Problems

1. What is the osmotic pressure of a solution containing $3.42\,g$of sucrose in 500 mL. Solution at $27\,℃$.
   (R = 0.0821 lit atm $mol^{-1}K^{-1}$ molar mass of sucrose = $342\,g\,mol^{-1}$¿ **(ANS:** $0.492\,atm$¿
2. The osmotic pressure of an aqueous solution of sucrose is 4.92 atm at $27\,℃$. What is the molarity of the solution? How many grams of sucrose were dissolved per 250 mL of the solution. (**ANS:** $17.1\,g$¿

Reverse osmosis and water purification:

When a solvent and a solution are separated by a semiprmeable membrane, osmosis occurs. However, if an external pressure, which is just equivalent to osmotic pressure is applied on solution side, no osmosis occurs. If the external pressure is greater than the osmotic pressure, then water will be forced to pass from solution to solvent side.



The process of reversing the direction of osmosis by applying the pressure higher than the osmotic pressure to the solution of higher concentration is called **reverse osmosis.** During reverse osmosis, the pure solvent flows out the solution through the semi-permeable membrane. Reverse osmosis is used in desalination of sea water. When pressure, more than osmotic pressure (30 atm at $25°C$) is applied to the sea water, pure water is squeezed out of the sea water through the semi-permeable membrane as shown in figure.

A variety of membranes are used for reverse osmosis. Examples, Cellulose Tri-Acetate (CTA) membrane, Thin-Film-composite (TFC) membranes, etc.

Abnormal molar masses:

Molecular masses of solutes can be calculated by measuring any of the colligative properties of dilute solutions.

These methods are applicable only if

- The solution is dilute, so that Raoult's law is obeyed.
- The solute is non dissociable or non associable in the solution.

In case of solutes which either dissociate or associate in solutions, molecular masses of solutes determined by these methods will be abnormal.

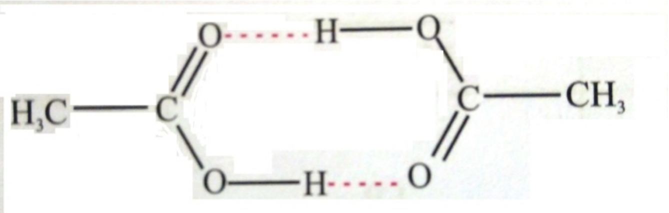
Association of solute molecules:

Certain solutions in solution are found to associate. This leads to decreases in the number of molecular particles in the solutions. Thus, it results in a decrease in the value of colligative properties.

$$\text{Molecular mass of solute} \propto \frac{1}{Colligative\ property}$$

Therefore, molecular masses determined, will be higher than the normal values for solutes which undergo association in solution.

Example: Acetic acid in benzene undergoes dimerization as indicated below.



Therefore, the molecular mass of acetic acid in benzene determined by collegative property method will be approximately double the actual value.

$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$

Dissociation of solute molecules:

Certain solutes in solution are found to dissociate into ions. This leads to the increase in the number of particles in the solutions. Thus, it results in a increases in the value of collegative properties.

$$\text{Molecular mass of solute} \propto \frac{1}{Colligative\ property}$$

Therefore, molecular mass determined, will be lower than the normal values for solutes which undergoes dissociation in solution.

Example: The molecular mass of NaCl in water determined by colligative property method will be approximately reduced to half the actual value due to dissociation.

$$NaCl \rightarrow Na^{+} + cl^{-}$$

Van't Hoff's factor (i):

In 1886, Van't Hoff introduced a factor 'i' called van't Hoff's factor, to express the extent of association or dissociation of solutes in solution. The van't Hoff's factor is a ratio of the normal molecular mass to the observed molecular mass of a solute.

$$i = \frac{Normal\ molecular\ mass}{Observed\ molecular\ mass} \quad \text{or} \quad i = \frac{Observed\ coligative\ property}{Calculated\ colligative\ property}$$

Consequently, introduction of the van't Hoff's factor modifies the equations for the colligative properties as:

Relative lowering of vapour pressure = $\frac{p_A^0 - p_A}{p_A^0} = i x_B$

Elevation of boiling point, $\Delta T_b = i K_b m$

Depression in freezing point, $\Delta T_f = i K_f m$

Osmotic pressure, $\pi = \frac{inRT}{V}$ or $\pi = iCRT$

From the value of 'i', it is possible to calculate degree of dissociation or association of substances.

Table 4 : Values of Van't Hoff factor:

Nature of substance	**Associable substance**	**non associable/ Non dissociable Substances**	**Dissociable substances (Electrolytes)**
Van't Hoff's factor	<1	1	>1

Table 5 : The van't Hoff's factor of 0.05 M electrolyte solutions at $25\,℃$:

Electrolyte	**i (Measured)**	**i (Calculated)**
Sucrose	1.0	1.0
HCl	1.9	2.0
NaCl	1.9	2.0
MgSO4	1.3	2.0
MgCl2	2.7	3.0
FeCl3	3.4	4.0

Degree of Dissociation:

It is defined as the fraction of total substance that undergoes dissociation into ions.

$$\text{Degree of dissociation} = \frac{No.\ of\ moles\ of\ the\ substance\ dissociated}{Total\ no.\ of\ moles\ of\ the\ substance\ taken}$$

Suppose a molecule of an electrolyte give ‘n’ ions after dissociation. If we start with 1 mole of the solute, and $'\alpha'$ is the degree of dissociation, then at equilibrium.

No. of moles of solute left undissociated =1-α
No. of moles of ions formed = nα
Total no. of moles of particles = 1-$\alpha + n\alpha = 1 + (n-1)\alpha$

Van’t Hoff’s factor, $i = \frac{Total\ no.\ of\ moles\ of\ particles\ after\ dissociation}{No.\ of\ moles\ of\ particles\ before\ dissociation}$

$$¿\frac{1+(n-1)\alpha}{1}$$

Or Degree of dissolution, $\alpha = \frac{i-1}{n-1}$

Degree of Association:

It is defined as the fraction of total number of molecules which combine to form associated molecules.

$$\text{Degree of association} = \frac{No.\ of\ moles\ of\ the\ substance\ associated}{Total\ no.\ of\ moles\ of\ the\ substance\ tasken}$$

For example, suppose ‘n’ simple molecules of the solute associated to form the associated molecule A_n.

$$nA \leftrightharpoons A_n$$

If we start with 1 mole of simple molecule and α is the degree of association, then that at equilibrium

No. of moles of solute left unassociated $¿1-\alpha$

Total no. of moles after association$¿1-\alpha+\frac{\alpha}{n}$

Van’t Hoff factor, $i = \frac{1-\alpha+\frac{\alpha}{n}}{1}$

$$¿\frac{1+\alpha\left[\frac{1}{n}-1\right]}{1}$$

(or) Degree of association, $\alpha = \frac{i-1}{\frac{1}{n}-1}$

SOLVED PROBLEMS

1. **How many grams of a dibasic acid are (mol. wt. 200) present in 100 ml of its aqueous solution to give decimolar strength?**

Molarity of solution = $\frac{1}{10}\text{mol/litre}$

Molarity = $\frac{\text{Mass of solute in gram}}{\text{GMM of solute} \times \text{Volume of solution in litre}}$

Mass of solute in grams = molarity × GMM of solute × $V_{(L)}$

$=\frac{1}{10}\times 200\times\frac{100}{1000}=2\text{ grams}$

2. **Calculate the quantity of sodium carbonate required to prepare 200ml of $\frac{M}{10}$ solution.**

Mass of solute in gram= molarity × GMM × $V_{(L)}$

$=\frac{1}{10}\times 106\times\frac{200}{1000}=2.12\text{g}$

3. **Vapour pressure of water at 300 K is 12.3 kPa. What will be the vapour pressure of one molal solution of non volatile solute in water at 300K?**

One molal solution means one mole of solute is present in 1 kg of water.

∴ moles of solute = 1

Moles of water = $\frac{1000}{18}=55.55$

Mole fraction of solvent i.e., water = $\frac{55.55}{56.55}=0.9823$

Vapour pressure of solution containing non volatile

Solute = vapour pressure of solvent × mole fraction of solvent = $P^0_{\text{solvent}}\times X_{\text{solvent}}$

= 12.3 × 0.9823 = 12.08 kPa

4. **Calculate the vapour pressure of a solution at 373K containing 3.42g of cane sugar in 36g of water.**

Moles of sugar = $\frac{3.42}{342}=0.01$

Moles of water = $\frac{36}{18}=2$

Vapour pressure of pure water at 373K is 760 mm of Hg

$\therefore\frac{P_0 - P_s}{P_0}=\frac{n}{n+N}$

Where P_0 → vapour pressure of pure solvent

P_s → vapour pressure of solution containing non-volatile solute.

n → moles of solute and N → moles of solvent

$\frac{P_0 - P_s}{P_0}=\frac{0.01}{0.01+2}=\frac{0.01}{2.01}$

or $\frac{P_0}{P_0}-\frac{P_s}{P_0}=\frac{1}{201}$ or $1-\frac{P_s}{P_0}=\frac{1}{201}$

$\frac{P_s}{P_0}=1-\frac{1}{201}=\frac{200}{201}$

$$P_s = P_0 \times \frac{200}{201} = 760 \times \frac{200}{201} = 756.22 \text{mm of Hg}$$

5. 9 g of glucose is dissolved in 90 g of water . Calculate the mole fraction of glucose and water

$$Mole\ fraction\ of\ water = \frac{n_1}{n_1 + n_2}$$

n_1 → number of moles of solvent

n_2 → number of moles of solute

$$mole\ fraction\ water(solvent) = \frac{number\ of\ moles\ of\ solvent}{number\ of\ moles\ of\ solvent + No.of\ moles\ of\ solute}$$

$$No.of\ moles\ of\ solvent(n_1) = \frac{mass\ in\ g}{molecular\ mass} = \frac{90}{18} = 5.$$

$$No.of\ moles\ of\ solute(n_2) = \frac{mass\ in\ g}{molecular\ mass} = \frac{9}{180} = 0.05$$

$$mole\ fraction\ of\ the\ solvent = \frac{n}{n_1 + n_2} = \frac{5}{5 + 0.05} = 0.999$$

$$solute = \frac{n_2}{n_1 + n_2} = \frac{0.05}{5 + 0.05} = 0.0099$$

2 moles of urea is dissolved is 8 moles of water . Calculate the mole fraction of urea and water in the solution

$$Mole\ fraction\ of\ solvent = \frac{n_1}{n_1 + n_2}$$

n_1 → number of moles of solvent = 8 moles

n_2 → number of moles of solute = 2

$$x_1 = \frac{8}{8 + 20} = 0.8$$

Mole fraction of solute $= \frac{n_2}{n_1 + n_2} = \frac{2}{8 + 2} = 0.2$

6. Two moles of ethanol and 8 moles of H_2O are mixed to get a binary solution. The vapour pressure of ethanol and H_2O at given temperature are 800 Pa and 500 Pa respectively. Calculate the partial vapour pressure of ethanol and H_2O and also vapour pressure of binary solution

$$X_{ethanol} = \frac{n_{ethanol}}{n_{ethanol} + n_{H_2O}} = \frac{2}{2 + 8} = 0.2$$

$$X_{water} = \frac{n_{water}}{n_{ethanol} + n_{H_2O}} = \frac{8}{2 + 8} = 0.8$$

$P^0_{ethanol}$ = 800 Pa P^0_{H2O} = 500 Pa

$P_{ethanol}$ = $P^0_{ethanol}$ $X_{ethanol}$ = 800 × 0.2 = 160 Pa

P_{water} = P^0_{water} X_{water} = 500 ×0.8 = 400 Pa

P_{total} = $P_{ethanol}$ + P_{water} = 160 + 400 = 560 Pa

7. Calculate the osmotic pressure of a solution containing 0.1 mole of non volatile solute per dm^3 at 273 K (R = 8.314 J mol^{-1} k^{-1})

$$\pi V = nRT$$

$$\pi = \frac{nRT}{V}$$

π → osmotic pressure n → number of moles of solute = 0.1

V → volume of solution = 1 $dm^3 = 10^{-3}$ m^3

T → absolute temperature = 273 K

R → solution constant = 8.314 J mol^{-1} K^{-1}

$$\pi = \frac{0.1 \times 8.314 \times 273}{10^{-3}}$$

π = 226.972 × 10^3Pa

= 226.972 k Pa

8. Calculate the osmotic pressure of solution containing 15 g of urea in 300 cm^3 of its solution at 300 K (R = 8.314 J mol^{-1} k^{-1})

$\pi V = nRT$

$$\pi = \frac{nRT}{V}$$

π → osmotic pressure n → number of moles of solute = 0.25

V → volume of solution = 300 cm^3 = 300 × 10^{-6} m^3

T → absolute temperature = 3 × 10^2 K

R → solution constant = 8.314 J mol^{-1} K^{-1}

$$\pi = \frac{0.25 \times 8.314 \times 300}{300 \times 10^{-6}} = 2078 \text{ k Pa}$$

9. Calculate the osmotic pressure of 5% of glucose at 18^0 C (5% means 5 g dissolved in 100 cc of water)

$\pi V = nRT$

$$\pi = \frac{nRT}{V}$$

π → osmotic pressure

n → number of moles of solute = 5 /182.3 = 0.0274

V → volume of solution = 100 cm^3 = 100 × ($10^{-2})^3$ = 100 × 10^{-6} m^3

T → absolute temperature = 18 + 273 = 291 K

R → solution constant = 8.314 J mol^{-1} K^{-1}

$$\pi = \frac{0.274 \times 8.314 \times 291}{100 \times 10^{-6}}$$

= 0.6629 ×10^6 = 662.9 ×10^{-3} ×10^6

= 662.9 ×10^3 Pa

= 662.9 k Pa

10. Calculate the osmotic pressure of 8% solution of sucrose at 298 K

$$\pi = \frac{RTW}{MV}$$

$$= \frac{8.314 \times 298 \times 8}{342 \times 100 \times 10^{-6}}$$

$$= \frac{19820.576}{34200 \times 10^{-6}}$$

= 0.5795 ×10^6 = 579.5 ×10^3 Pa = 579.5 kPa

11. Calculate the osmotic pressure of 5% solution of a compound at 300 K is 692.83 k Pa. Calculate the molecular mass of compound

$\pi V = nRT$

$$n = \frac{\pi V}{RT}$$

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

$$= \frac{5 \times 8.314 \times 300}{692.8 \times 10^3 \times 10^{-4}} = 180g$$

12. A solution of 100 gm of solute in a litre of water has a vapour pressure of 2.27 × 10^3 Nm^{-2} at 25^0 C. At the same temperature the vapour pressure of water is 2.34 × 10^3 Nm^{-2} . Calculate the molar mass of the solute

According to Raoult's law

$$\frac{P_0 - P_s}{P_0} = \frac{n_2}{n_1} = \frac{W_2 M_1}{M_2 W_1}$$

$$M_2 = \frac{W_2 M_1}{W_2}\left(\frac{P_0}{P_0 - P_s}\right)$$

M_2 = molar mass of solute M_1 = molar mass of solvent = 18

W_2 = mass of solute = 100 g W_1 = mass of solvent = 1 lit = 1000 g

P_0 = vapour pressure of pure solvent = 2.34 × 10^3 Pa

P_s = vapour pressure of solution = 2.27 ×10^3 Pa

$P_0 – P_s$ = 0.07 ×10^3 Nm^{-2}

$$M_2 = \frac{100 \times 18}{1000}\left(\frac{2.34 \times 10^3}{0.07 \times 10^3}\right)$$

$$= 60.17g$$

13. 12 g of urea is dissolved in 90 g of water.

(i) calculate the relative lowering in vapour pressure

(ii) Calculate the vapour pressure of solution if vapour pressure of pure water at that temperature is 3000 Pa

(i) $\frac{P_0 - P_s}{P_0} = \frac{n_2}{n_1}$

Relative lowering in vapour pressure = $\frac{n_2}{n_1}$

$$No. of\ moles = \frac{mass\ of\ substance}{molar\ mass}$$

(i) solute(n_2) = $\frac{12}{60} = 0.5$ mole (ii) solvent(n_1) = $\frac{90}{18} = 5$ mole

Relative lowering in vapour pressure = $\frac{n_2}{n_1}$ = $\frac{0.5}{5} = 0.1$

Relative lowering in vapour pressure = 0.2 / 5 = 0.2 /5 = 0.03846

(ii) we have

$$\frac{P_0 - P_s}{P_0} = 0.1$$

$$1 - \frac{P_s}{P_0} = 0.1$$

P_s = (1-0.1) P_0 = 0.9 ×3000= 2700 Pa

14. 1.065 g of substance dissolved in 30.14 g of ether raised its boiling point by 0.296^0 C. The molar elevation constant for ether 2.11. Calculate the molecule mass of the substance.

$$M_2 = \frac{1000 \times k_b \times W_2}{W_1 \times \Delta T_b}$$

$$= \frac{1000 \times 2.11 \times 1.065}{30.14 \times 0.296}$$

$$= 251.8g$$

15. Pure water boils at 100^0 C. A solution prepared by dissolving 1.2 g of solute in 9 g of water boil at 100.7^{0}C. Calculate molecular mass of solute (molal elevation constant of water = 0.52^0 /kg or 0.52^0 /1000 g)

$$M_2 = \frac{1000 \times k_b \times W_2}{W_1 \times \Delta T_b}$$

$$= \frac{1000 \times 0.52 \times 1.2}{9 \times 0.7}$$

$$= 99.04g$$

16. A solution containing 0.34 g of solute in 20 g of pure water freezes at 272.5 K. Calculate the molar mass of solute K_f = 1.86 /kg

$$M_2 = \frac{1000 \times K_f \times W_2}{W_1 \times \Delta T_f}$$

$$= \frac{1000 \times 1.86 \times 0.34}{20 \times 0.5} = 63.24g$$

17. A solution containing 5 g of solute in 100 g of pure water. The depression in freezing point is 1.55, k_f = 1.86 K^{-1} . Calculate the molecular mass of substance

$$M_2 = \frac{1000 \times K_f \times W_2}{W_1 \times \Delta T_f}$$

$$= \frac{1000 \times 1.86 \times 5}{100 \times 1.55} = 60g$$

2.SOLUTIONS

A solution is a homogenous mixture of two or more substances, the composition of which may vary within limits.

"A solution is a special kind of mixture in which substances are intermixed so intimately that they can not be observed as separate components".

The dispersed phase or the substance which is to be dissolved is called solute, while the dispersion medium in which the solute is dispersed to get a homogenous mixture is called the solvent. A solution is termed as binary, ternary and quartenary if it consists of two, three and four components respectively.

Types of solutions

Based on the physical state of the solvent, binary solutions are classified as

(1)Gaseous solutions (2)Liquid solutions (3) Solid solutions

Gaseous solutions: The solutions in which the solvent is gas and solute is either solid, liquid or a gas are called gaseous solutions.

Liquid solutions: The solutions in which the solvent is liquid and the solute is either a solid, liquid or a gas are called liquid so0lutions.

Solid solutions: The solutions in which the solvent is solid and the solute is either a solid, liquid or a gas, are called solid solutions.

Different types of solutions and some examples

Types of solutions	Solute	Solvent	Common example
Gaseous Solutions	Gas Liquid Solid	Gas Gas Gas	Mixture of oxygen and nitrogen gases Chloroform in nitrogen gas Camphor in nitrogen gas
Liquid Solutions	Gas Liquid Solid	Liquid Liquid Liquid	Oxygen dissolved in water Ethanol dissolved in water Glucose dissolved water
Solid Solutions	Gas Liquid Solid	Solid Solid Solid	Solution of hydrogen in palladium Amalgam of mercury with sodium Copper dissolved in gold

Note: In aqueous solution water is the solvent.

Methods of expressing concentration of solutions

The concentration of a solution is the amount of a solute present in a given quantity of solvent or solution.

(a) Molarity (M) (b) Molality (m) (c) Mole fraction (x)

Molarity (M): Molarity of a solution is defined as the number of moles of the solute dissolved in one litre of the solution.

$$\text{Molarity} = \frac{Number\ of\ moles\ of\ the\ solute}{Volume\ of\ the\ solution \in litre}$$

If W_B gram of the solute of molar mass M_B is dissolved in V dm^3 of the solution, then the molarity is given by,

$$\text{Molarity} = \frac{W_B \times 1000}{M_B \times V}$$ Units: mol/L or mol/dm^3

- Molarity is most common way of representing the concentration of solution.
- Molarity is depend on temperature as, $\text{Molarity} \propto \frac{1}{\text{Temperature}}$

Molarity of a solution decreases with the increase in temperature since the volume of the solutions increases with the increase in temperature.

Thus molarity is temperature dependent and cannot be used in experiments that involve temperature variations.

The exact amount of the solvent in a given volume of the solutions cannot be determined if the density of the solution is not known.

Molality (m): Molality of solution is defined as the number of moles of the solute dissolved in one kg of the solvent. Molality is denoted by 'm' and is calculated by the expression.

$$\text{Molality} = \frac{\text{Number of moles of the solute}}{\text{Mass of the solvent} \in kg}$$

If W_B gram of the solute of molar mass M_B is dissolved in W_A gram of the solvent, then molality is given by

$$\text{Molality} = \frac{W_B \times 1000}{W_A \times M_B}$$ Unit: mol/kg

Advantages of molality: Molality is temperature independent quantity. Therefore this unit can be conveniently used in experiments involving temperature variations

The exact mass of the solvent in given amount of the solution can be calculated easily.

Mole fraction(x): Mole fraction of a component in a solution is the ratio of number moles of that component to the total number of moles of all the components.

Let us consider a binary solution that contains n_A moles of solvent 'A' and n_B moles of the solute 'B'

Mole fraction of the solvent A is $x_A = \frac{n_A}{n_A + n_B}$

Mole fraction of the solute B is $x_B = \frac{n_B}{n_A + n_B}$

For a solution that contains a large number of components A, B,C,D,E.........I, mole fraction of component D is given by

$$x_D = \frac{n_D}{n_A + n_B + \ldots\ldots + n_I}$$

- Sum of mole fraction of all the components in a solution is always equal to one i.e., $x_A + x_B = 1$
- Mole fraction is defined to a component and not to the solution
- Mole fraction has no unit

This unit is highly useful in the

- Calculation of partial pressure of a component gas in a solution of gases.
- Calculation of relative partial pressures of the vapour which is in equilibrium with the solution.

Mass percentage (w/w): Mass percentage of a solution is defined as the number of parts by mass of the solute dissolved in100 parts by mass of the solution.

$$\text{Mass percentage} = \frac{Mass\ of\ the\ solute}{Mas\ of\ the\ solution} \times 100$$

Note: Units of the two masses should be same

Volume percentage (v/v): Volume percentage of a solution is defined as the number of parts by volume of the solute dissolved in 100 parts by volume of the solution.

$$\text{Volume percentage} = \frac{Volume\ of\ the\ solute}{Volume\ of\ the\ solution} \times 100$$

This unit is more useful when both the solute and solvents are liquids.

Mass by volume percentage (w/v): Mass by volume percentage of a solution is defined as the number of parts by mass of the solute dissolved in 100 parts by volume of the solution.

$$\text{Mass by volume percentage} = \frac{Mass\ of\ the\ solute}{Volume\ of\ the\ solution} \times 100$$

In this case, generally gram and cm^3 are used as the units. Otherwise system of units should be same.

Parts per million (ppm): Parts per million of a solute is defined as the member of parts of solute dissolved in one million parts of the solution.

$$\text{Parts per million} = \frac{Number\ of\ parts\ of\ the\ solute}{Number\ of\ parts\ of\ the\ solution} \times 10^6$$

Note: The units of the parts of the solute and the solution should be same.

Parts per million are also expressed in w/w, v/v and w/v.

This unit is suitable when solutes are present in trace quantities.

- Mass percentage, ppm, mole fraction, and molality are independent of temperature because mass is independent of temperature
- Molarity, volume percentage and mass by volume percentage depends on temperature because volume depends on temperature.

Solubility:

When a solute is mixed with a solvent, particles of the solute leave the solute phase and get mixed with the particles of the solvent phase. This process is known as dissolution. The solute is said to be dissolved in solvent.

Compounds like sugar, potassium nitrate, ammonium nitrate, etc., dissolve in water whereas they are insoluble in benzene or ether. Compounds like naphthalene, anthracene, diphenyl, etc., dissolve in solvents like benzene and ether but not in water. By these examples it may be broadly generalized that ‘Like dissolved like’. It means to say that polar solutes dissolve in polar solvents and non polar solutes dissolve in non polar solvents. Thus dissolution of a solute in a given solvent takes place when the nature of inter particle attractive forces in the solute and the solvent are same.

Solubility of a solid in a liquid:

Dissolution of a solute in a solvent is a reversible change. If dissolution is the forward change then crystallization is the backward change that takes place simultaneously.

When a large amount of solid solute is added to given amount of a solvent, initially dissolution of the solute takes place. But as the concentration of the solute particles in the solution phase increases, the back ward change, i.e., crystallization begins and its rate starts to increase.

At one stage the rates of dissolution and crystallization become equal resulting in a dynamic equilibrium between the solid solute and the solute particle in the solution phase. $\underset{(Solid)}{Solute}\ \underset{¿}{dissolution}$ solute particles in solution

Once the equilibrium is reached, the concentration of the solute particles in the solution remains constant. No more solute dissolves in the solvent. The solution thus formed is said to be saturated solution. A solution in which no more solute can be dissolved at the same temperature and pressure is called saturated solution. The amount of the solute present in a given quantity of the saturated solution at a given temperature and pressure is called solubility of the solute in the given solvent. A solution in which some more solute can be dissolved at the given temperature and pressure is called unsaturated solution.

Generally solubility is measured in mass percentage (w/w). Therefore, solubility of a solid solute in a given liquid solvent at a given temperature is the mass of the solute in gram dissolved in 100 grams of the saturated solution.

Effect of temperature on solubility of solid solute in a liquid solvent:

Since, solid solute and solvent particles in solution are in dynamic equilibrium, it follows Le-chatelier’s principle.

- According to this principle increase in temperature shifts the equilibrium towards endothermic change and decrease in temperature shifts the equilibrium towards the exothermic change.
- Therefore, if the dissolution of a solute in a given solvent is endothermic then its solubility increases with the increase in temperature.
- If the dissolution of a solute in a given solvent is exothermic, then the solubility of the solute decreases with increase in temperature.
- For exothermic dissolution, enthalpy solution, $\Delta_{sol}H<0$ and for endothermic dissolution, enthalpy of solution$\Delta_{sol}H>0$

Effect of pressure:

There is no significant effect of pressure on the solubility of a solid solute in a liquid solvent. This is because solids and liquids are highly incompressible and practically remain unaffected by changes in pressure.

Solubility of a gas in a liquid :

Gases dissolve in liquids to form liquid-gas solution. Example, carbon dioxide dissolves in water to form soda water. Water in wells, rivers, and sea contains dissolved air which is used by aquatic animals for their breathing.

Factors that influence solubility of gases in liquids:

The factors that influence the solubility of gases in liquids are

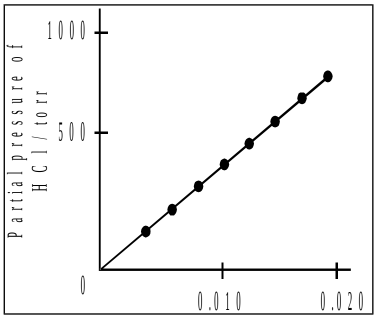
- The nature of the gas and solvent
- Nature of the solvent
- Temperature
- External pressure

The nature of gases and nature of solvents:

Non-polar gases are less soluble in polar solvents like water. For example, gases like, O_2, N_2, H_2 etc., which are non-polar are very less soluble in water which is a polar solvent at room temperature and pressure. But CO_2, HCl, NH_3 etc., being polar gases, are highly soluble in water under identical conditions.

Effect of temperature on the solubility of gases:

Generally solubility of all gases in liquids decreases with the increases in temperature. This is because of two reason ;



Generally dissolution of any gas in a liquid is exothermic. According to Le-Chatelier's principle, low temperature favours exothermic changes.

That is why gases dissolve more at low temperatures and less at high temperatures in liquids.

Increase in temperature increases the kinetic energy of dissolved gas molecules. As a result, the gas molecules escape more from the solution phase by overcoming the attractive forces.

Note: Solubility of oxygen is more in cold water than in warm water. That is why aquatic speices are more comfortable in cold waters than in warm waters.

Effect of pressure:

The solubility of a gas in a liquid increases with the increase in its partial pressure above the liquid.

Henry's law:

This law gives the quantitative relationship between the solubility of a gas in a liquid and the partial pressure of the gas above the liquid at a given temperature.

Henry's law states that "at constant temperature the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the solution".

If the solubility of a gas is in mole faction, the law can also be stated as " the partial pressure of the gas above the solution is directly proportional to the mole fraction of a gas in the solution".

i.e., $p \propto x$ where p is partial pressure of the gas and x is solubility in mole fraction

$$p = K_H x$$ Here, K_H is called Henry's law constant.

$$X = \frac{p}{K_H};$$

Characteristics of Henry's law constant:

Higher is the value of K_H lower is the solubility of gas.

Different gases have different K_H values. Therefore K_H value depends on nature of the gas.

For example, K_H value. of CO_2 and O_2 in water at 20^0 C are respectively 1.67k bar and 457k bar. That is why CO_2 is about 28 times more soluble in water than oxygen at given temperature.

K_H value increases by increasing the temperature. This indicates that solubility of gases in liquid decreases by increasing temperature. This is because the dissolution of gas in liquid is an exothermic process.

Units of Henry's law constant are same as pressure.

Applications of Henry's law:

(a) Carbonated beverages:To increase the solubility of carbon dioxide in soda water and soft drinks, bottles are sealed under high pressure of CO_2.

(b) Deep sea diving:Oxygen cylinders used by sea divers (Scuba divers) are filled with air which is diluted with helium to minimize the solubility of nitrogen in the blood by decreasing its partial pressure to avoid the risk of 'bends'.

(Otherwise more nitrogen will be dissolved due to high pressure deep under sea water. When a sea diver comes back to the surface, the solubility of nitrogen again decreases and the dissolved gas is released, leading to the formation of nitrogen bubbles in the blood. This results in the blockage of capillaries and leads to a medical condition known as 'bends' or decompression sickness which causes acute pain).

(c) High altitude sickness:At high altitudes, partial pressure of oxygen is less than that at a ground level. This leads to low concentrations of oxygen in the blood and tissues of mountain climbers. Low-blood oxygen causes climbers to become weak and unable to think clearly. These are symptoms of anoxia.

Equilibrium vapour pressure of a liquid:

Consider a liquid taken in a closed container. The liquid being volatile, molecules of the liquid escape from the liquid phase and occupy the space above the liquid forming vapour phase.

But after some time molecules of the vapour phase also starts condensing into liquid.

Thus at one stage there will be a dynamic equilibrium between the vapour phase and the liquid when the rate of vapourisation becomes equal to that of condensation.

The pressure exerted by the molecules of the vapour phase on the liquid phase at equilibrium is called equilibrium vapour pressure.

For simplicity it is also called vapour pressure. At constant temperature, different liquids have different vapour pressures since they depend on nature of the liquids.

Vapour pressure of a solution of liquid in liquid:

The vapour phase of a binary solution placed in a closed vessel consists of vapours of both the components. The French chemist F.M Raoult (1886) gave quantitative relationship between the partial pressures of the components in the vapour phase and their mole fractions in the solution phase. This relationship is known as Raoult's law.

Raoult's law for a solution of two liquid components:

Raoult's law states that for a solution of volatile liquids, the partial pressure of each component in the vapour phase is directly proportional to the mole fractions of the respective components in the solution phase at a given temperature.

Let us consider a solution containing two volatile components A and B (that have measurable vapour pressures) in a closed container. The equilibrium is established between vapour phase and the liquid phase at constant temperature.

Let P_{total} be the total vapour pressure of the vapour phase about the solution and p_A and p_B be the partial vapour pressure of the two components A and B.

These partial pressures are related to the mole fractions $x_A \wedge x_B$ of the two components A and B respectively. According to Raoult's law for component A,

$$p_A \propto x_A \quad \text{or} \quad p_A = p_A^0 x_A$$

Where p_A^0 is the vapour pressure of the pure component A at the same temperature.

Similarly, for component B $p_B \propto x_B$ or $p_B = P_B^0 X_B$

Where $p_B^0$is the vapour pressure of the pure component B at the same temperature.

According to Dalton's law of partial pressures, the total pressure is the sum of the partial pressures of all components at the same temperature.

$$p_{total} = p_A + p_B \quad \text{or} \quad p_{total} = p_A^0 x_A + p_B^0 x_B$$

$$p_{total} = p_A^0 (1 - x_B) + p_B^0 x_B \quad \text{or} \quad p_{total} = p_A^0 - p_A^0 x_B + p_B^0 x_B$$

$$p_{total} = p_A^0 + (p_B^0 - p_A^0) x_B$$

Total vapour pressure over the solution is directly proportional to the mole fraction of any one component ($x_A \vee x_B$¿.

Total vapour pressure of the vapour phase of the solutions varies linearly with the mole fraction of component B(orA).

Depending on the vapour pressures of the pure components A and B, total vapour pressure over the solution decreases or increases with the increase of the mole fraction of component A (or B).

The composition of vapour phase in equilibrium with the solution is determined by the partial pressures of the components. If $y_A \wedge y_B$are the mole fraction of the component A and B respectively in the vapour phase then, using Dalton's law of partial pressures:

$$p_A = y_A \, p_{total} \quad \text{or} \quad p_B = y_B \times p_{total}$$

In general $p_i = y_i \, p_{total}$

Raoult's law as a special case of Henry's law:

According Henry's law "the partial pressure of the gas (p) in vapour phase is proportional to the mole fraction of the gas (x) in the solution i.e., $p = K_H x$

According to Raoult's law "the partial pressure of each component of the solution is directly proportional to its mole faction present in the solution.

i.e., $p_i = p_i^0 x_i$

By comparing equations for Henry's law and Raoult's law, we can conclude that the partial pressure of volatile liquid or gas is directly proportional to its mole fraction in solution.

Only the difference is in their proportionality constants $K_H \wedge p_i^0$. Hence Raoult's law is a special case of Henry's law in which $K_H = p_i^0$.

Ideal and non- ideal solutions:

The binary solutions of the volatile liquids can be classified into two types. They are ideal and non-ideal solutions.

Ideal solutions:

A solution which obeys Raoult’s law at all concentration range of the components and temperature is called an ideal solution.

- In ideal solutions,solvent(A)–solute (B) interactions are equal to solute (B)–solute(B)and solvent(A)–solvent(A)interactions.A perfectly ideal solution is rare but some solutions are nearly ideal in behaviour.

A few examples are:

- Benzene and toluene
- Chlorobenzene and bromobenzene
- Carbon tetrachloride and silicon tetrachloride
- n-Hexane and n-heptane
- Ethylene bromide and ethylene chloride

Characteristics of Ideal solution

(i) It should obey Raoult’s law, i.e., $P_A = P^0_A X_A$ and $P_B = P^0_B X_B$.

(ii) $\Delta H_{\text{mixing}} = 0$

(iii) $\Delta V_{\text{mixing}} = 0$

Non-ideal solutions:

A solution which does not obey Raoult’s law at all concentration range of the components and temperature is called a non ideal solution.

The non ideal solutions are accompanied by change in enthalpy and volume during their formation i.e., $\Delta H_{mixing} \neq 0 \Delta V_{mixing} \neq 0$¿

In general, most of the solutions are non ideal and deviate from ideal behaviour.

It must be remembered that in non- ideal binary solution none of the components follows the Raoult’s law. The non-ideal solutions are further classified into two categories.

1. Non-ideal solution showing positive deviation
2. Non ideal solution showing negative deviation

The causes for these deviations lie in the nature of interactions at the molecular level.

Non-ideal solution showing positive deviation:

The solutions for which the total vapour pressure is higher than that expected from Raoult’s law are called solutions with positive deviations.

For solutions with positive deviations from Raoult’s law, partial vapour pressure of each component A and B is higher than that one that is calculated from Raoult’s law for the same composition.

In these solutions, the intermolecular attractive forces between the solute-solvent molecules are weaker than those between the solute-solute, solvent-solvent interactions.

This means that in such solutions, molecules of A (or B) will find it easier to escape than in pure state. This will increases the vapour pressure and result in positive deviation.

Due to decrease in magnitude of intermolecular attractive forces, the molecules are loosely held and thus increasing intermolecular distances. Therefore formation of a non ideal solution is associated with increase in volume and absorption of energy.

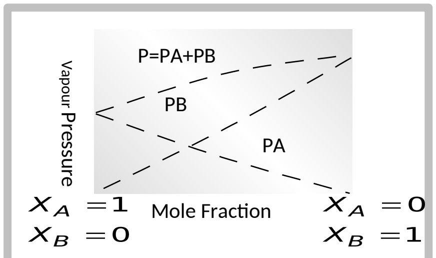
Characteristics:

$$p_A > p_A^0 x_A$$

$$p_B > p_B^0 x_B$$

$$\Delta H_{mixing} = +ve$$

$$\Delta V_{mixing} = +ve \; i.e., \left(V_{solution} > V_A + V_B\right).$$



Partial and total vapour pressure curves for solutions that show positive deviations from

Examples:

- Acetone + ethanol
- Water + ethanol
- Acetone + CS_2
- CCl_4 + toluene
- Water + methanol

Non-ideal solution showing negative deviation:

The solutions for which the total vapour pressure is lower than that of an ideal solution of same composition and temperature are called Solutions with negative deviations.

For solution with the negative deviation from Raoult's law, partial vapour pressure of each component A and B is lesser than the one that is calculated from Raoult's law for the same composition. So, the total vapour pressure of the solution is less than that of ideal solution of same composition

Boiling point of such a solution is relatively higher than the boiling points of A and B respectively.

In this case the intermolecular attractive forces between the solute-solvent molecules are stronger than those between the solute-solute and solvent-solvent molecules. This means that in such solutions, molecules of A (or B) will not find it easier to escape than in pure state. This will decrease the vapour pressure and result in negative deviation.

Characteristics:

$$p_A < p_A^0 x_A$$

$$p_B < p_B^0 x_B$$

$$\Delta H_{mixing} = -ve$$

$$\Delta V_{mixing} = -ve \; i.e., \left(V_{solution} < V_A + V_B\right).$$

Examples:

- Acetone +aniline
- H_2O + HNO_3
- Acetic acid + pyridine
- Acetone + chloroform
- Chloroform + diethylether
- Chloroform + benzene
- CH_3OH + CH_3COOH
- Water + HCl

Azeotropic Mixtures (or) constant Boiling Mixtures:

There are certain binary liquid mixture, which boil at constant temperature like a pure liquid such that both the components are distilled out simultaneously. The components of such mixtures cannot be separated during functional distillation. Such mixtures are named as Azotropic mixtures.

The mixture of liquids which boils at constant temperature and possess same composition for both liquid and vapour phases is named as azeotropic mixture.

Types of azeotropes:

Based on the relative values of boiling points of the components and the mixture, azeotrops are of 2 types:

1.Minimum boiling azeotropes: The azeotropic mixtures for which the boiling point is lower than the boiling points of both the component liquids are named as minimum boiling azeotropes.

Conditions for formation: Minimum boiling azeotropes are formed by non-ideal solutions with positive deviation.

The composition of mixtures at which the vapour pressure is highest represents the azeotropic composition.

Since the vapour pressure is highest, boiling point is minimum and hence is lower than both the components.

For example: a mixture of ethanol and water at a composition of 95.574% by mass of ethanol shows a constant boiling point of 351.1 K. This is lesser than both ethanol (b.p : 351.3 K) and water (b.p : 373 K).

2.Maximum boiling azeotropes:

The azeotropic mixtures for which the boiling point is higher than the boiling points of both the component liquids are named as maximum boiling azotropes.

Conditions for formation: Maximum boiling azeotropes are formed by non-ideal solutions with negative deviation.

The composition of mixtures at which the vapour pressure is lowest represents the azeotropic composition.

Since the vapour pressure is lowest, boiling point is maximum and hence is higher than both the components.

For example: a mixture of HNO_3 and water at a composition of 68% by mass of HNO_3 shows a constant boiling point of 393.5 K.

This is greater than both HNO_3 (b.p : 359 K) and water (b.p : 373 K).

Table 2 : Differences between ideal and non-ideal solutions of two liquids:

Ideal solutions	Non-ideal solutions
Obey Raoult's law at all range of concentration.	Do not obey Raoult's law at all range of concentration.
$\Delta H_{mixing}=0$(Neither heat is evolved nor absorbed during dissolution).	$\Delta H_{mixing}\neq 0.$ (Either heat is evolved or absorbed during dissolution).
$\Delta V_{mixing}=0$ (Volume of the solution is equal to the sum of volumes of the components).	$\Delta V_{mixing}\neq 0$ (Volume of the solution is not equal to the sum of volumes of the components).
$p_{total}=p_A^0 x_A+p_B^0 x_B$	$p_{total}\neq p_A^0 x_A+p_B^0 x_B$
The intermolecular attractive forces between A-A, B-B and A-B are same.	The intermolecular attractive forces between A-A, B-B and A-B are not

	same.

Differences between non ideal solution with positive and negative deviations:

Positive deviation from raoult's law	Negative deviation from Raoult's law
$\Delta H_{mixing} > 0$ (Heat is absorbed during dissolution.)	$\Delta H_{mixing} < 0$. Heat is evolved during dissolution
$\Delta V_{mixing} > 0$ (volume increases during dissolution.)	$\Delta H_{mixing} < 0$. Volume decreases during dissolution
$p_{total} > p_A^0 x_A + p_B^0 x_B$	$p_{total} > p_A^0 x_A + p_B^0 x_B$
Attractive force between A-B is weaker than A-A and B-B attractive forces.	Attractive force between A-B is stronger than A-A and B-B attractive forces.
Forms minimum boiling point azeotrope.	Forms maximum boiling point azeotrope.

Raoult's Law for solution of solid in Liquid:

The vapour pressure of a solution containing non volatile solute is directly proportional to the mole fraction of the solvent.

In case of a solution containing two components A (volatile solvent) and B(non volatile solute) the vapour pressure of solution is given as $P_A \alpha x_A$ Or $P_A = K x_A$

Where K is proportionality constant

Colligative properties and determination of molecular masses:

The properties of dilute solutions of non volatile solutes which depend only on the number of particle of the solute relative to the total number of particles in the solution and not on the nature of the solute are called colligative properties.

Thus, colligitive properties depend on the number of solute particles present, regardless of whether they are atoms, ions, or molecules.

The important colligative properties are:

1. Relative lowering of vapour-pressure of the solvent
2. Elevation of boiling-point of the solvent
3. Depression of freezing-point of the solvent
4. Osmotic pressure of the solution

1.Relative lowering of vapour pressure:

When a non volatile solute is dissolved in a volatile solvent, the vapour pressure of solvent decreases. So, the vapour pressure of solution is always lower than the vapour pressure of the pure solvent.

The difference in vapour pressures of pure solvent (p_A^0¿ and solution (p_A) is called lowering of vapour pressure (Δp¿ $\Delta p = p_A^0 - p_A$

The ratio of lowering of vapour pressure to the pure solvent is called relative lowering of vapour pressure.

Relative lowering of vapour pressure $= \dfrac{p_A^0 - p_A}{p_A^0}$

According to Raoult's law $p_A = p_A^0 x_A$

$$p_A = p_A^0 (1 - x_B) \qquad \text{or} \qquad p_A = p_A^0 - p_A^0 x_B$$

$$p_A^0 x_B = p_A^0 - p_A$$

$$\frac{p^0_{A-p_A}}{p_A^0} = x_B$$

So, “the relative lowering of vapour pressure of a solution containing non volatile solute is equal to mole fraction of solute”. This is called Raoult’s law of relative lowering of vapour pressure.

Thus relative lowering of vapour pressure depends only on the number of the solute particles and it is independent of their identity. Hence relative lowering of vapour pressure is a colligative property.

Mathematically, Raoult’s law of relative of vapour pressure is

$$\frac{p^0_{A-p_A}}{p_A^0} = x_B = \frac{n_B}{n_A + n_B}$$

Calculation of molar mass of solute using relative lowering of vapour pressure:

The mole fraction of solute $x_B = \frac{n_B}{n_A + n_B}$ From Roult’s Law, $\frac{p^0_{A-p_A}}{p_A^0} = \frac{n_B}{n_A + n_B}$

Here $n_A \wedge n_B$ are the number of moles of solvent and solute respectively present in the solution. For dilute solutions $n_B \ll n_A$, hence neglecting n_B in the denominator we have

$$\frac{p^0_{A-p_A}}{p_A^0} = \frac{n_B}{n_A} \quad \text{or} \quad \frac{p^0_{A-p_A}}{p_A^0} = \frac{w\,❑_B / M_B}{W_A / M_A}$$

$$\frac{p^0_{A-p_A}}{p_A^0} = \text{¿}\,\frac{w_B \times M_A}{w_A \times M_B} \quad \text{or} \quad M_B = \frac{w_B \times M_A \times p_A^0}{W_A \times \text{¿¿}}$$

Here W_A and w_B are the masses and $M_A \wedge M_B$are the molar masses of the solvent and solute respectively. Thus by determining the value of relative lowering of vapour pressure of a dilute solution of known concentration experimentally, the molar mass of the solute can be calculated

2.Elevation of boiling point:

Boiling point (T_b) of a liquid is the temperature at which its vapour pressure becomes equal to the external pressure. The vapour pressure of a non volatile solute is less than that of pure solvent. Therefore higher temperature is required to make the vapour pressure of the solution equal to the external pressure as shown in the graph. Hence, the boiling point of solution is more than that of pure solvent.

The difference in boiling points of the pure solvent and the solution is called the elevation in boiling point of solvent.

Let T_b^0be the boiling point of pure solvent and $T_b$be the boiling point of solution.

The increase in the boiling point $\Delta T_b = T_b - T_b^0$ where $\Delta T_b$is known as elevation in boiling point.

Experiments have shown that for dilute solutions, the elevation of boiling point (ΔT_b¿is directly proportional to the molal concentration of the solution. Thus

$$\Delta T_b \propto m \quad \text{or} \quad \Delta T_b = K_b m$$

Where m is the molality of the solution and K_b is the boiling point elevation constant or molal elevation constant or Ebullioscopic constant. Here molality is used because it is not affected by change in temperature.

When molality of solution, m=1, then $\Delta T_b = K_b$

Therefore, molal elevation constant of a solvent is defined as the elevation of boiling point caused by dissolving one mole of non volatile solute in one kg of solvent.

SI unit of the constant K_b is K Kg mol^{-1} and is specific for a given solvent.

Calculation of molar mass of the solute using elevation in boiling point:

Let W_B be the mass of the solute of molecular mass M_B dissolved in w_A gram of the solvent, then molality (m) of the solution is given by the equation:

$$m = \frac{w_B \times 1000}{M_B \times w_A}$$

Substituting the value of m in equation 1, we get, $\Delta T_b = K_b \times \frac{w_B \times 1000}{M_B \times w_A}$

The molar mass of the solute (M_B¿ is calculated using the equation,

$$M_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A}$$

Thus, in order to determine M_B, molar mass of the solute, known mass of solute in a known mass of the solvent is taken and ΔT_b is determined for a known solvent whose K_b value is known.

The value of K_b depends upon the nature of the solvent and it can be determined using the formula:

$$K_b = \frac{R \times M_A \times T^2_{b_{solvent}}}{1000 \times \Delta H_{vap}}$$

Where R = gas constant, M_A= molar mass of the solvent, $T_{b(solvent)}$= boiling pint of pure solvent, ΔH_{vap}=¿the enthalpy of vapourisation.

3.Depression in freezing point:

Freezing point (T_f¿ of a liquid is the temperature at which the vapour pressure of the liquid becomes equal to that of its solid. The vapour pressure of the solution is less than that of pure solvent. Therefore, the vapour pressure of the solution becomes equal to that of solid solvent at lower temperature than that of pure solvent. Hence, the freezing point of the solution is less than that of the solvent as shown in the graph.

Let T_f^0 be the freezing point of the pure solvent and T_f be the freezing point of the solution. The depression in freezing point, $\Delta T_f = T_f^0 - T_f$

So, depression of freezing point (ΔT_f¿ is the difference in the freezing point of the pure solvent and freezing point of solution.

Experiments have shown that for dilute solutions the depression of freezing point (ΔT_f¿ is directly proportional to the molal concentration of the solution. Thus

$$\Delta T_f \propto m \qquad \text{or} \qquad \Delta T_f = K_f m$$

Where m is the molality of the solution and K_f is the molal depression constant or freezing depression constant or cryoscopic constant.

When molality of solution, m = 1, then $\Delta T_f = K_f$

Therefore, molal depression constant of a solvent is defined as the depression in freezing point caused by dissolving one mole of non volatile solute in one kg of solvent.

SI unit of the constant K_b is Kkg mol^{-1} or Kmolal^{-1} and is specific for a given solvent.

Calculation of molar mass of a solute using depression in freezing point:

Let w_B be the mass of the solute of molecular mass M_B dissolved in w_A gram of the solvent, then molality (m) of the solution is given by the equation.

$$m = \frac{w_B \times 1000}{M_B \times w_A}$$

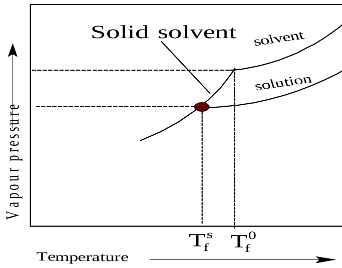
Substituting the value of m in equation 1, we get, $\Delta T_b = K_f \times \frac{w_B \times 1000}{M_B \times w_A}$

Therefore, the molar mass of the solute (M_B¿ can be determined according the equation, $M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A}$

Thus, in order to determine M_B, molar mass of the solute, known mass of the solute in a known mass of the solvent is taken and ΔT_f is determined experimentally for a solution whose K_f value is known.

The value of K_f depends upon the nature of the solvent and it can be determined using the formula: $K_f = \frac{R \times M_A \times T^2_{f(solvent)}}{1000 \times \Delta H_{fus}}$

Where R= gas constant, M= molar mass of the solvent, $T_{f(solvent)}$= freezing point of pure solvent, $\Delta H_{fus} =$¿ the enthalpy of fusion.



Osmosis:

A strong solution of sugar is taken in a thistle funnel, the mouth of which is covered with a piece of animal bladder or cellophane (semipermeable membrane). This is kept immersed in water taken in a beaker as shown in figure. It is observed that the level of the solution inside the stem of the thistle funnel starts raising. It must be due to the flow of solvent molecules (water) into the solution through the semi-permeable membrane. This phenomenon is known as osmosis.

The spontaneous movement of solvent molecules from the solution of lower concentration to the solution of higher concentration through semipermeable membrane is called osmosis.

Osmosis in natural processes:

- A raw mango placed in concentrated salt solution loses of water via osmosis and shrivel into pickle.
- Wilted flowers revive when placed in fresh water due to osmosis.
- A carrot that has become limp because of water loss, when placed in water, water will move into them through osmosis making it firm once again.
- When blood cells are placed in a solution containing more than 0.9% (mass/volume) of sodium chloride, blood cells shrink due to loss of water by osmosis.
- People taking a lot of salt or salty food experience water retention in tissue cells and intercellular spaces because of osmosis. The resulting puffiness or swelling is called edema.
- Water movement from soil into plant roots and subsequently into upper portion of the plant is partly due to osmosis.
- The preservation of meat by salting and of fruits by adding sugar against bacterial action through the process of osmosis, a bacterium on salted meat or candid fruit loss water, shrivels and dies.

  Note: 0.9% sodium chloride in water is called saline solution.

4.Osmotic pressure:

Osmotic pressure of a solution is defined as the pressure to be applied on the solution of higher concentration just to stop osmosis.

Osmotic pressure is a colligative property because it depends on the number of moles of solute in the solution and not on the nature of the solute.

For dilute solutions, it has been found experimentally that osmotic pressure is proportional to the molarity of the solution at a given temperature T.

$$\pi \propto C \qquad \text{or} \qquad \pi = kC$$

Where k is proportionally constant and is equal to RT where R is universal gas constant and T is the temperature in Kelvin. Therefore,

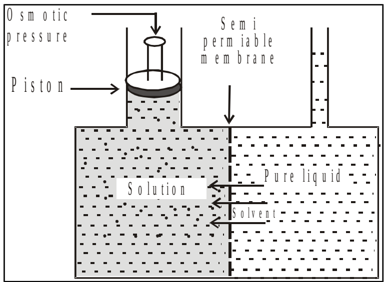
$\pi = CRT$ If n_B moles of solute is dissolved in V litres of the solution, C=$\frac{n_B}{V}$

$$\overset{\Rightarrow}{\square}\, \pi = \frac{n_B}{V} RT$$

If w_B grams of the solute of molar mass (M_B¿ is present in the solution, then $n_B = \frac{w_B}{M_B}$

$$\overset{\Rightarrow}{\square}\, \pi = \frac{w_B RT}{M_B V}$$

$$\overset{\Rightarrow}{\square}\, M_B = \frac{w_B RT}{\pi V}$$



Thus, by measuring the osmotic pressure of a solution of known concentration, molar mass of the solute can be calculated using the above equation.

Determination of molecular masses of solute by osmotic pressure measurements is highly useful in finding out the molecular masses of macromolecules like polymers, proteins, etc.

Isotonic, hypertonic and hypotonic solutions:

When such solutions are separated by semi-permeable membrane, no osmosis occurs. For example, the osmotic pressure of the fluid inside the blood cell is equivalent to that 0.9% (mass/volume) sodium chloride solution, called normal saline solution.

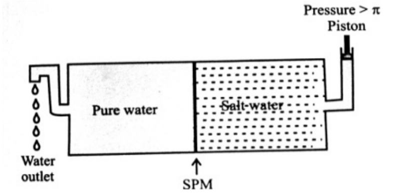
That is why normal saline solution is safe to inject intravenously because no osmosis takes place. On the other hand, if we place the cells in a solution containing more than 0.9%(mass/volume) sodium chloride, water will flow out of the cell and they would shrink . Such a solution is named as hypertonic

A solution having higher osmotic pressure with respect other is called hypertonic solution. If the sodium chloride concentration is less than 0.9%(mass/volume), then water will flow into the cells if placed in this solution and they would swell.

The solution having lower osmotic pressure with respect other is called hypotonic solution.

Reverse osmosis and water purification:

When a solvent and a solution are separated by a semiprmeable membrane, osmosis occurs. However, if an external pressure, which is just equivalent to osmotic pressure is applied on solution side, no osmosis occurs. If the external pressure is greater than the osmotic pressure, then water will be forced to pass from solution to solvent side.



The process of reversing the direction of osmosis by applying the pressure higher than the osmotic pressure to the solution of higher concentration is called reverse osmosis. During reverse osmosis, the pure solvent flows out the solution through the semi-permeable membrane. Reverse osmosis is used in desalination of sea water. When pressure, more than osmotic pressure (30 atm at $25°C$) is applied to the sea water, pure water is squeezed out of the sea water through the semi-permeable membrane as shown in figure.

A variety of membranes are used for reverse osmosis. Examples, Cellulose Tri-Acetate (CTA) membrane, Thin-Film-composite (TFC) membranes, etc.

Abnormal molar masses:

Molecular masses of solutes can be calculated by measuring any of the colligative properties of dilute solutions.

These methods are applicable only if

- The solution is dilute, so that Raoult's law is obeyed.
- The solute is non dissociable or non associable in the solution.

In case of solutes which either dissociate or associate in solutions, molecular masses of solutes determined by these methods will be abnormal.

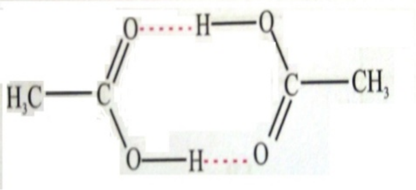
Association of solute molecules:

Certain solutions in solution are found to associate. This leads to decreases in the number of molecular particles in the solutions. Thus, it results in a decrease in the value of colligative properties.

$$\text{Molecular mass of solute} \propto \frac{1}{Colligative\ property}$$

Therefore, molecular masses determined, will be higher than the normal values for solutes which undergo association in solution.

Example: Acetic acid in benzene undergoes dimerization as indicated below.



Therefore, the molecular mass of acetic acid in benzene determined by collegative property method will be approximately double the actual value.

$$2CH_3COOH \rightleftharpoons (CH_3COOH)_2$$

Dissociation of solute molecules:

Certain solutes in solution are found to dissociate into ions. This leads to the increase in the number of particles in the solutions. Thus, it results in a increases in the value of collegative properties.

$$\text{Molecular mass of solute} \propto \frac{1}{Colligative\ property}$$

Therefore, molecular mass determined, will be lower than the normal values for solutes which undergoes dissociation in solution.

Example: The molecular mass of NaCl in water determined by colligative property method will be approximately reduced to half the actual value due to dissociation. NaCl $\rightarrow$ Na^+ + cl^-

Van't Hoff's factor (i):

In 1886, Van't Hoff introduced a factor 'i' called van't Hoff's factor, to express the extent of association or dissociation of solutes in solution. The van't Hoff's factor is a ratio of the normal molecular mass to the observed molecular mass of a solute.

$$i = \frac{Normal\ molecular\ mass}{Observed\ molecular\ mass} \quad \text{or} \quad i = \frac{Observed\ coligative\ property}{Calculated\ colligative\ property}$$

Consequently, introduction of the van't Hoff's factor modifies the equations for the colligative properties as:

Relative lowering of vapour pressure = $\frac{p_A^0 - p_A}{p_A^0} = i\,x_B$

Elevation of boiling point, $\Delta T_b = i\,K_b m$

Depression in freezing point, $\Delta T_f = i\,K_f m$

Osmotic pressure, $\pi = \frac{i\,nRT}{V}$ or $\pi = iCRT$

From the value of 'i', it is possible to calculate degree of dissociation or association of substances.

Degree of dissociation$= \frac{No.\,of\ moles\ of\ the\ substance\ dissociated}{Total\ no.\,of\ moles\ of\ the\ substance\ taken}$

Suppose a molecule of an electrolyte give 'n' ions after dissociation. If we start with 1 mole of the solute, and $'\alpha'$ is the degree of dissociation, then at equilibrium.

No. of moles of solute left undissociated =1-α

No. of moles of ions formed = nα

Total no. of moles of particles = 1-$\alpha + n\alpha = 1 + (n-1)\alpha$

Van't Hoff's factor, $i = \frac{Total\ no.\,of\ moles\ of\ particles\ after\ dissociation}{No.\,of\ moles\ of\ particles\ before\ dissociation} \text{¿} \frac{1+(n-1)\alpha}{1}$

Or Degree of dissolution, $\alpha = \frac{i-1}{n-1}$

Degree of Association:

It is defined as the fraction of total number of molecules which combine to form associated molecules.

Degree of association$= \frac{No.\,of\ moles\ of\ the\ substance\ associated}{Total\ no.\,of\ moles\ of\ the\ substance\ tasken}$

For example, suppose 'n' simple molecules of the solute associated to form the associated molecule A_n.

$nA \leftrightharpoons A_n$

If we start with 1 mole of simple molecule and α is the degree of association, then that at equilibrium

No. of moles of solute left unassociated $\text{¿} 1-\alpha$

Total no. of moles after association$\text{¿} 1-\alpha+\frac{\alpha}{n}$

Van't Hoff factor, $i = \frac{1-\alpha+\frac{\alpha}{n}}{1} \quad \text{¿} \frac{1+\alpha\left[\frac{1}{n}-1\right]}{1}$

(or) Degree of association, $\alpha = \frac{i-1}{\frac{1}{n}-1}$

One mark questions

1. What is binary solution?

   solution containing only two components is called binary solution. Example: salt solution (salt + water)
2. What is solid solution?

   A solution in which solid acts as a solvent is called solid solution.
3. What is liquid solution?

   A solution in which liquid acts as a solvent is called liquid solution.
4. What is gaseous solution?

   A solution in which gas acts as a solvent is called gaseous solution.
5. What is concentration?

   The amount of solute present in the given quantity of the solution is called concentration.
6. Name the units used to express concentrations.

   (i) Molarity (M) (ii) Molality (m) (iii) Mole fraction (x)
7. Among molarity and molality which is independent on temperature.

   Molality.
8. Define solubility.

   The maximum amount of a substance that can be dissolved in a specified amount of solvent at a specified temperature is called solubility.
9. What is the basic rule (principle) to decide the solubility of solute in solvent?

   "Like dissolves like"
10. What is dissolution?

    When a solute is added to the solvent, some solute dissolves and its concentration increases in solution. This process is called dissolution.
11. What is saturated solution?

    A solution in which no more solute can be dissolved at the same temperature and pressure is called a saturated solution.
12. What is unsaturated solution?

    A solution in which some more solute can be dissolved under the same temperature is called unsaturated solution.
13. What is the effect of pressure on solubility of solubility of solid in liquid?

    Pressure does not have any significant effect on solubility of solids in liquids.
14. What is the effect of temperature on the solubility of gas in liquid?

    Solubility of gas in liquid decreases when temperature is increased.
15. Solubility of gas in liquid decreases as temperature increases. Why?

    Because dissolution of gas in liquid is exothermic process.
16. Aquatic species are more comfortable in cold waters rather than in warm waters. Give reason.

    Solubility of O_2 in cold water is more than warm water.
17. What is the significance of Henry's law constant?

    The higher the value of K_H lower is the solubility.
18. At a given temperature and pressure nitrogen gas is more soluble in water than Helium gas. Which one of them has higher K_H value?

Helium.

19. What is vapour pressure?

The pressure exerted by the vapours above the liquid surface at constant temperature when they are in equilibrium with the liquid is called vapour pressure or saturated vapour pressure or equilibrium vapour pressure.

20. Write the mathematical form of Raoult's law for volatile solutes.

$P_{total} = p_A^o x_A + p_B^o x_B$

21. Name the types of azeotropes or azeotropic mixtures.

Azeotropic mixtures are of two types:

(i) Minimum boiling azeotropes (ii) Maximum boiling azeotropes.

22. What happens to the vapour pressure of the pure liquid when a non volatile solute is dissolved in it?

Vapour pressure decreases.

23. Write the mathematical form Raoult's law of relative lowering of vapour pressure.

$$\frac{p_A^o - P_A}{p_A^o} = \frac{n_B}{n_A + n_B}$$

24. What is boiling point?

The temperature at which the vapour pressure of the liquid becomes equal to the atmospheric pressure is called boiling point.

25. What happens to the boiling point of a liquid when a non volatile solute is dissolved in a pure solvent?

Boiling point increases.

26. Define Ebullioscopic constant or molal elevation constant.

It is the increase in the boiling point produced when one mole of non volatile solute is dissolved in 1 kg of a pure solvent.

27. What is the value of K_b for water?

0.52 K kg mol^{-1}.

28. What is the SI unit of K_b?

K kg mol^{-1}.

29. What is freezing point?

The temperature at which the vapour pressure of the liquid becomes equal to the vapour pressure of the solid is called freezing point.

30. What happens to the freezing point of a pure solvent when a non volatile solute is dissolved in it?

Freezing point decreases.

31. Give the relation between depression in freezing point and molality.

$\Delta T_f \propto m$ or $\Delta T_f = K_f \cdot m$

where K_f is called molal depression constant or cryoscopic constant.

32. Define cryoscopic constant or molal depression constant.

It is the decrease in the freezing point produced when one mole of non volatile solute is dissolved in one kg or 1000 g of a pure solvent.

33. What is the value of K_f for water?

K_f = 1.86 K kg mol^{-1} for water.

34. What is the SI unit of K_f?
K Kg mol^{-1}

35. What is osmosis?
The flow of solvent molecules from lower concentrated solution to higher concentrated solution through a semipermeable membrane is called osmosis.

36. What is semipermeable membrane?
A membrane which allows the movement of only solvent molecules through it but not the solute particles is called semipermeable membrane.

37. Give an example for natural semipermeable membrane.
Pig’s bladder, animal membranes, vegetable membranes, skin, parchment paper etc.,

38. Give an example for synthetic or artificial semipermeable membrane.
Cellophane, cupric ferrocyanide coated on porous pot, $Cu_2[Fe(CN)_6]$.

39. What is osmotic pressure?
The external pressure applied on the concentrated solution to stop osmosis is called osmotic pressure. It is denoted by π.

40. On what factor does the colligative property value depends.
It depends on the number of solute particles but not on their nature.

41. Give reason: Osmotic pressure or elevation in boiling point or depression in freezing point or relative lowering of vapour pressure is a colligative property.
Because it depends only on the number of solute particles present in the solution but not on their nature.

42. Give Reason: To clear the snow covered roads and hilly areas salt is sprinkled.
When salt is sprinkled on the snow covered roads and hilly areas, snow starts melting due to depression in freezing point as a result formation of water takes place which helps to clear roads.

43. The osmotic pressure of NaCl solution is more than glucose solution.
NaCl solution contains more particles(2)than the glucose solution(1).

44. Which of the following has high osmotic pressure?
(i) Pure water (ii) 1 M glucose (iii) 1 M NaCl (iv) 1M $CaCl_2$
1M $CaCl_2$ due to 3 particles ($1Ca^{2+}$ and $2Cl^-$) in the solution.

45. Which of the following has high osmotic pressure?
(i) 0.1 M NaCl (ii) 0.2 M $CaCl_2$ (iii) 0.5 M Urea (iv) 1 M glucose
0.2M $CaCl_2$

46. Among pure water and sea water which has high boiling point and lowest freezing point.
Sea water.

47. Give reason:The freezing point of sea water is less than 0°C (of 273 K).
Due to dissolved salts.

48. Among pure water and sea water which has highest vapour pressure.
Pure water

49. Which of the following has lowest vapour pressure?
(i) Pure water (ii) 1 M urea (iii) 1 M NaCl (iv) 1 M $BaCl_2$
1M $BaCl_2$

50. Name the semipermeable membrane used in reverse osmosis.
Cellulose acetate.

51. Name the disease caused to the people living at high altitudes.
Anoxia

52. Name the disease caused to the sea divers if they carry nitrogen oxygen mixture or air.
Bends

Two mark questions

53. What is abnormal molar mass?
The molar mass determined by colligative properties is found to be lower or higher than the expected or normal molecular mass. Such a molecular mass is called abnormal molecular mass.

54. Define molarity (M)
The number of moles of solute dissolved in 1 litre (1 dm^3) of 1000 cm^3 of a solution is called molarity.Molarity is denoted by 'M'
Molarity is calculated by the equation,

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of the solution in litres}} \quad \text{or} \quad \text{Molarity} = \frac{W_B \times 1000\ cm^3}{M_B \times V}$$

The unit of molarity is mole / litre or mol L^{-1}.
Molarity changes with temperature because of expansion or contraction of liquid with temperature.

55. Define molality (m).
The number of moles of solute dissolved in one kg or 1000 g of a solvent is called molality. Molality is denoted by 'm'. Molality is calculated by the equation.

$$\text{Molality} = \frac{\text{Number of moles of solute}}{\text{Mass of the solvent in kg}} = \frac{w_B \times 1000g}{M_B \times w_A}$$

Molality is independent of temperature because the mass of the solvent doesnot change with temperature. The unit of molality is mol / kg or mol kg^{-1}

56. Give two disadvantages of molarity.
(a) Molarity depends on temperature. So, this unit cannot be used in experiments that involve temperature variations.
(b) The exact amount of the solvent in a given volume of the solution cannot be determined if the density of the solution is not known.

57. Define mole fraction (x).
It is the ratio of number of moles of a particular component to the total number of moles of all the components in the solution. If n_2 moles of solute is present in 'n_1' moles of solvent, then

mole fraction of solute, $x_2 = \frac{n_2}{n_1 + n_2}$ mole fraction of solvent $x_1 = \frac{n_1}{n_1 + n_2}$

Sum of mole fractions of all components present in solution is equal to one
i.e., $x_1 + x_2 = 1$

58. Define volume percentage. For which type of solutions this unit is useful?

Volume percentage of a solution is defined as the number of parts by volume of the solute dissolved in 100 parts by volume of the solution.

$$\text{Volume percentage} = \frac{\text{Volume of the solute}}{\text{Volume of the solution}} \times 100$$

Note: Units of the two volumes unit be same.

This unit is more useful when both the solute and solvents are liquids.

59. Define mass percentage (w/w)

Mass percentage of a solution is defined as the number of parts by mass of the solute dissolved in 100 parts by mass of the solution.

$$\text{Mass percentage} = \frac{\text{Mass of the solute}}{\text{Mass of the solution}} \times 100$$

Note: Units of the two masses should be same

60. Define mass by volume percentage. Give the expression to calculate the volume percentage for the given mass and volume of solute and solvent.

Mass by volume percentage of a solution is defined as the number of parts by mass of the solute dissolved in 100 parts by volume of the solution.

$$\text{Mass by volume percentage} = \frac{\text{Mass of the solute}}{\text{Volume of the solution}} \times 100$$

Note: In this case, generally gram and cm^3 are used as the units. Otherwise system of units should be same.

61. Define parts per million.

Parts per million of a solute is defined as the member of parts of solute dissolved in one million parts of the solution.

$$\text{Parts per million} = \frac{\text{Number of parts of the solute}}{\text{Number of parts of the solution}} \times 10^6$$

Note: The units of the parts of the solute and the solution should be same.

Parts per million are also expressed in w/w, v/v and w/v.

This unit is suitable when solutes are present in trace quantities.

(1) Mass percent, ppm, mole fraction and molality are independent on temperature because mass is independent on temperature

(2) Molarity, volume percent and mass by volume percent depends on temperature because volume depends on temperature.

62. What is the effect of temperature on solubility of solid in liquid?

(i) Solubility of solid in liquid increases as temperature increases if the dissolution process is endothermic (ΔH = +ve).

(ii) Solubility of solid in liquid decreases as temperature increases if the dissolution process is exothermic (ΔH = - ve)

63. State Henry's law.

It states that, at constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas over the solution..

or

The partial presence of the gas in vapour phase (P) is directly proportional to the mole fraction of the gas in the solution.

i.e., $p = K_H x$

where K_H = Henry's law constant, x = mole fraction of the gas
p = Partial pressure of the gas in vapour phase.

64. What are isotonic solutions? Give an example.

Two solutions having the same osmotic pressure at a given temperature are called isotonic solutions.

Example: RBC (Red blood cells) is isotonic with 0.9% NaCl solution which is called normal saline. It is used in injections instead of distilled water.

65. What are hypertonic solutions?

The solutions whose osmotic pressure is higher than that of the given solution is called hypertonic solution.

Example: When RBC is placed in a sea water, water passes out of the cell due to osmosis and the cell shrinks.

66. What are hypotonic solutions?

The solutions whose osmotic pressure is lower than that of give solution are called hypotonic solutions.

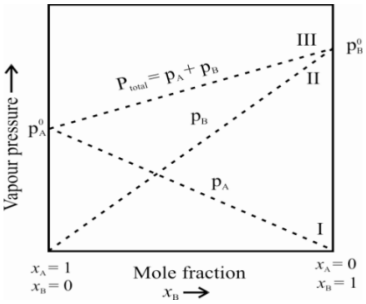
Example: When RBC is placed in hypotonic solution they swell and even burst due to the inflow of water.

67. What are ideal solutions? Give examples.

The solutions which obey Raoult's law at all concentrations are called ideal solutions.

68. Example: (i) Benzene and Toluene (ii) Ethyl bromide and ethyl iodide (iii) n-hexane and n-heptane

69. Draw the graph of vapour pressure against mole fraction for ideal solution.



70. What are non-ideal solutions give examples.

The solutions which do not obey Raoult's law at all concentrations are called non-ideal solutions.

Example: (i) HCl and water (ii) Ethyl alcohol and water.

71. Give any four conditions to form non-ideal solutions.

(i) They should not obey Raoult's law.

(ii) $\Delta V_{mix} \neq 0$

(iii) $\Delta H_{mix} \neq 0$

(iv) The forces of attraction between A and B molecules will be greater or lesser than that of A - A and B - B molecules.

72. Name the types of non-ideal solutions.

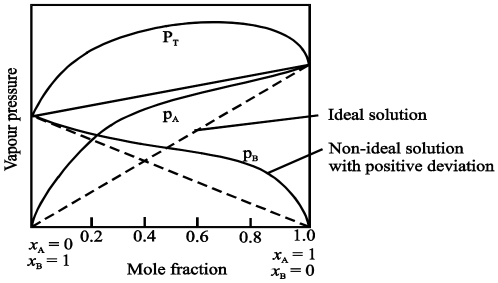
Non ideal solutions are of two types.

- Non ideal solution showing positive deviation from Raoult's law.
- Non ideal solution showing negative deviation from Raoult's law.

73. Which type of solutions show positive deviation?

If the vapour pressure of the solution is higher than that calculated from Raoult's law shows positive deviation. Example: (i) Ethyl alcohol and water, (ii) Chloroform and water, (iii) Methyl alcohol and water.

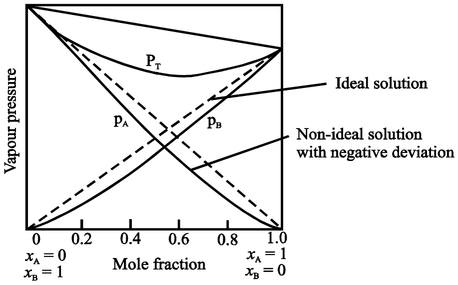
74. Draw the graph to show non ideal solutions with positive deviation from ideal behaviour.



75. Which type of solutions show negative deviation from Raoult's law?

If the vapour pressure of the solution is lower than that calculated by Raoult's law shows negative deviation from Raoult's law. Examples: HCl and water, HNO_3 and water, Chloroform and acetone

76. Draw the graph to show non ideal solutions with negative deviations.



77. What are azeotropes or azeotropic mixtures?

Binary liquid mixtures having the same composition in liquid and vapour phase and boil at a constant temperature are called azeotropic mixtures. Example: (i) 95.5% ethyl alcohol and 4.5% water (rectifiedspirit) (ii) 20.2% HCl and 79.8% water.

Note: In azeotropic mixtures the components cannot be separated by fractional distillation.

78. What are minimum boiling azeotropes? Give an example.

The solutions which show large positive deviation from Raoult's law are called minimum boiling azeotropes. They boil at lower temperature than the boiling point of the components.

Example: 95.5% Ethylalcohol and 4.5% water (rectified spirit). This mixture boils at 78.15°C (boiling point of water is 100°C and ethyl alcohol is 78.5°C.

79. What are maximum boiling azeotropes? Give an examples.

Solutions which shows the large negative deviations from Raoult's law are called maximum boiling azeotropes.

Example: (i) 20.2% HCl and 79.8% water. This mixture boils at 381.6 K which is higher than that of pure water (373 K) and HCl (188 K)

80. What are colligative properties?

The properties of dilute solutions depends only on the number of solute particles present in the dilute solution but not on their nature are called colligative properties.

81. Name the four colligative properties.

- Relative lowering of vapour pressure
- Elevation in boiling point or Ebuliscope or increase in boiling point.
- Depression in freezing point or Cryoscope or decrease in freezing point.
- Osmotic pressure.

82. Define lowering of vapour pressure.

When a non volatile solute is added in to the pure solvent, the vapour pressure of the solution decreases. It is the difference between the vapour pressure of the pure solvent and that of the solution.

Let p° be the vapour pressure of the pure solvent and p be the vapour pressure of the solution, then,

Lowering of vapour pressure $=p^\circ - p$

83. Define relative lowering of vapour pressure.

It is the ratio of lowering of vapour pressure to the vapour pressure of solvent.

$$\text{Relative lowering of vapour pressure} = \frac{p_A^0 - p_A}{p_A^0}$$

84. State Raoult's law of relative lowering of vapour pressure.

It states that in a solution containing non volatile solute the relative lowering of vapour pressure is equal to the mole fraction of the solute in dilute solutions.

$$\frac{p_A^0 - p_A}{p_A^0} = \frac{n_B}{n_A + n_B}$$

85. Define elevation in boiling point.

It is the difference between the boiling point of the solution and that of the pure solvent. i.e., $\Delta T_b = T_b - T_b^o$

where $\Delta T_b =$ elevation in boiling point, T_b = boiling point of the solution, $T_b^o =$ boiling point of the pure solvent.

86. Give the relation between elevation in boiling point and molality.

$\Delta T_b \propto m$ or $\Delta T_b = K_b \cdot m$

Where $\Delta T_b =$ elevation in boiling point, m = molality, K_b = molal elevation constant or ebullioscopic constant.

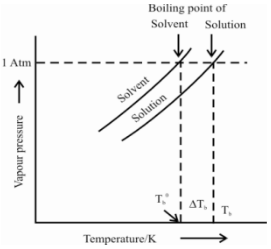
87. Give the relation to calculate molal elevation constant with respect to enthalpy of vapourisation.

$$K_b = \frac{R \times M_A \times T_{b\ (solvent)}^2}{1000 \times \Delta H_{vap}}$$

where R = gas constant, M_B = molar mass of the solvent,

$T_{b(solvent)}$ = boiling point of pure solvent, ΔH_{vap} = the enthalpy of vapourisation.

88. Draw the graph of vapour pressure with temperature to show elevation in boiling point of solvent and solution.



89. Define depression in freezing point.

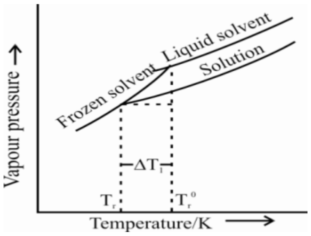
It is the difference between the freezing point of the pure solvent and that of the solution.

$\Delta T_f = T_f^o - T_f$ where ΔT_f depression in freezing point,

T_f^o = freezing point of the pure solvent.

T_f = freezing point of the solution.

90. Draw the graph of vapour pressure with temperature to show depression in freezing point of solvent and solution.



91. Derive the relation between depression in freezing point and the molecular mass of a solute.

We know that $\Delta T_f = K_f m$

where m is the molality of the solution and K_f is the molal depression constant or freezing point depression constant or cryoscopic constant.

But for the given mass of solute and solvent, molality is given by

$$m = \frac{w_B \times 1000}{M_B \times w_A} \qquad \therefore\ \Delta T_f = K_f\left(\frac{w_B \times 1000}{M_B \times w_A}\right) \qquad \because\ \Delta T_f = K_f\left(\frac{w_B \times 1000}{M_B \times w_A}\right)$$

or

$$M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A}$$

.

92. Give the relation to calculate molar depression constant with respect to enthalpy of fusion.

$$R = \frac{R \times M_A \times T^2_{f\,(\text{solvent})}}{1000 \times \Delta H_{fus}}$$

where R = universal gas constant

M_A= molecular mass of solvent

T_f = freezing point of solvent, ΔH_{fus} = Enthalpy of fusion.

93. What is reverse osmosis?

When a pressure larger than the osmotic pressure is applied on a concentrated solution, solvent flows from concentrated solution to dilute solution through a semi permeable membrane.

This phenomenon is called reverse osmosis. Reverse osmosis is used in the desalination of sea water to obtain fresh drinking water.

94. What is van't Hoff's factor?

It is the ratio of normal molar mass to the abnormal molar mass.

$i = \frac{\text{normal molar mass}}{\text{abnormal molar mass}}$ or $i = \frac{\text{observed colligative property}}{\text{calculated colligative property}}$

95. Give the significance of van't Hoff's factor.

- If i = 1, the solute doesn't undergo either dissociation or association.
- If i > 1, solute undergo dissociation.
- If i < 1 solute undergo association.

96. Write the colligative properties for solutes undergo dissociation or association.

- Elevation in boiling point, $\Delta T_b = i K_b m$
- Depression in freezing point, $\Delta T_f = i K_f m$
- Osmotic pressure $\pi = iCRT$
- Relative lowering of vapour pressure, $\frac{p^o - p}{p^o} = i x_2$

97. After removing the outer shell of two eggs in dilute HCl, one is placed in distilled water and the other is placed in a saturated solution of NaCl. What will you observe and why?

Egg in water swell and egg in NaCl solution shrinks because in water the solvent molecules enters into the egg cell (hypotonic). In NaCl solution egg shrinks because water flows out of the egg cell (hypertonic)

98. What do you expect to happen when RBC is placed in 1% NaCl solution and 0.5% NaCl solution.

In 1% NaCl solution RBC will shrink (hypertonic). In 0.5% NaCl solution RBC will swell and may even burst (hypotonic). The above phenomena is because RBC is isotonic 0.91% NaCl solution.

Three or four mark questions

99. Give any three applications of Henry's law.

(i) It is used in the preparation of carbonated beverages (To increase the solubility of CO_2 in soda water, soft drinks and in beer, the bottle is sealed under high pressure).

(ii) It is used by scuba or deep sea divers for respiration (To avoid bends and toxic effects of high concentration of nitrogen under deep sea).

(iii) It is used by mountain climbers for respiration. (At high altitudes the partial pressure of oxygen is less. The low concentration of oxygen in the blood and tissues causes climbers to become weak unable to think clearly which causes anoxia)

100. State Raoult's law of liquid solutions.

It states that in a solution of volatile liquids, the partial vapour pressure of each component is directly proportional to its mole fraction.

i.e., $p_A \propto x_1$ or $p_A = x_1 p_A^o$ Similarly $p_B = p_B^r x_B$

p_B = partial vapour pressure of solute in solution.

$p_B^o =$ vapour pressure of pure solute. x_B = mole fraction of solute.

∴ Vapour pressure of solution $=p=p_A+p_B \quad =p_A^o x_A+p_B^o x_B$

where $p_A^o=$ vapour pressure of the pure solvent,

x_A = mole fraction of the pure solvent, p_A = partial pressure of the pure solvent.

101. Give any four conditions to form ideal solutions.

(i) They should obey Raoult's law.

(ii) ΔV_{mix} = 0, i.e., threshold be no change in volume on mixing.

(iii) ΔH_{mix} = 0, i.e., there should be no change in enthalpy (heat) on mixing.

(iv) The forces of attraction between A and B (solvent and solute) molecules will be same as that of A - A (solvent – solvent) and B - B (Solute – solute) molecules.

102. Give differences between ideal and non-ideal solutions.

Sl.No.	Ideal solution	Non-ideal solution
1	They obey Raoult's law.	They do not obey Raoult's law.
2	$\Delta V_{mix}=0$	$\Delta V_{mix}\neq 0$
3	$\Delta H_{mix}=0$	$\Delta H_{mix}\neq 0$
4	The forces of attraction between A and B molecules will be same as that of A - A and B - B molecules.	The forces of attraction between A and B molecules will be greater or lesser than that of A - A and B - B molecules.

103. Give differences between solutions showing positive deviation and negative deviation from Raoult's law.

Sl. No.	Non ideal with positive deviation	Non ideal with negative deviation
1	$\Delta V_{mix}=+Ve$ (i.e., volume increases on mixing two components)	$\Delta V_{mix}=-ve$ (volume decreases on mixing two components)
2	$\Delta H_{mix}=+ve$ (heat is absorbed on mixing)	$\Delta H_{mix}=-ve$ (heat is liberated on mixing)
3	The vapour pressure is higher than that calculated from Raoult's law.	The vapour pressure is lower than that calculated from Raoult's law.
4	Forces of attraction between A and B molecules will be less than that of A - A and B - B molecules.	Forces of attraction between A and B molecules will be greater than that of A - A and B - B molecules.

104. Derive the relation to calculate is the molar mass or molecular mass or molecular weight using relative lowering of vapour pressure.

We know that from Raoult's law $\dfrac{p_A^o-p_A}{p_A^o}=\dfrac{n_B}{n_A+n_B}$

Here n_A and n_B are the number of moles of solvent and solute respectively present in the solution. For dilute solutions $n_B << n_A$, hence neglecting n_B in the denominator we have

$$\frac{p_A^o - p_A}{p_A^o} = \frac{n_B}{n_A} \qquad \frac{p_A^o - p_A}{p_A^o} = \frac{w_B/M_B}{w_A/M_A}$$

$$\frac{p_A^o - p_A}{p_A^o} = \frac{w_B \times M_A}{w_A \times M_B} \qquad M_B = \frac{w_B \times M_A \times p_A^o}{w_A \times (p_A^o - p_A)}$$

105. How is the molecular mass of a solute calculated by ebullioscopic method (elevation in boiling point).

We know that $\Delta T_b = K_b m$ ...(1)

Let w_B be the mass of the solute of molecular mass M_B dissolved in w_A gram of the solvent, then molality (m) of the solution is given by the equation:

$$m = \frac{w_B \times 1000}{M_B \times w_A}$$

Substituting the value of m in equation 1, we get, $\Delta T_b = K_b \times \frac{w_B \times 1000}{M_B \times w_A}$

The molar mass of the solute (M_B) is calculated using the equation,

$$M_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A}$$

Thus, in order to determine M_B, molar mass of the solute, known mass of solute in a known mass of the solvent is taken and ΔT_b is determined experimentally for a known solvent whose K_b value is known.

Derive the expression to calculate the molar mass of solute by osmotic pressure experiment. $\pi \propto C$

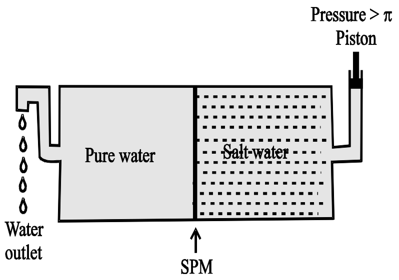
$\pi = CRT$ or $\pi = n_B CRT$ but $C = \frac{1}{V}$ and $n_B = \frac{w_B}{M_B}$

$\therefore \pi = \frac{w_B}{M_B} \times \frac{1}{V} RT$ $\therefore M_B = \frac{w_B RT}{\pi V}$

where R = solution constant whose value is same as that of gas constant. The above equation is used to calculate the molecular mass of a solute.

106. Explain the desalination of sea water (purification of water) by reverse osmosis.

The process of reversing the direction of osmosis by applying the pressure higher than the osmotic pressure to the solution of higher concentration is called reverse osmosis.



During reverse osmosis, the pure solvent flows out of the solution through the semi permeable membrane. Reverse osmosis is used in desalination of sea water.

When pressure, more than osmotic pressure (30 atm at $25^{o}C$) is applied to the sea water, pure water is squeezed out of the sea water through the semipermeable membrane as shown in figure.

Worked out numerical problems

1. Calculate the molarity of a solution containing 5g of NaOH in 450 mL solution.

Molar mass of NaOH = $M_B = 23 + 16 + 1 = 40\ g\ mol^{-1}$

Molarity = $\frac{w_B \times 1000}{M_B \times V} = \frac{5 \times 1000}{40 \times 450} = 0 \cdot 278\ M$.

2. Calculate the amount of benzoic acid [C_6H_5COOH] required for preparing 250 mL of 0.15 M solution in methanol

Molarity $= \frac{w_B \times 1000}{M_B \times V}$ $M_B = 6 \times 12 + 6 \times 1 + 2 \times 16 = 122\ g\ mol^{-1}$

$0 \cdot 15 = \frac{w_B \times 1000}{122 \times 250}$ $w_B = \frac{0 \cdot 15 \times 122 \times 250}{1000} = 4 \cdot 575\ g$.

3. Calculate molality of 2.5 g of ethanoic acid (CH_3COOH) in 75 g of benzene.

Molality $= \frac{w_B \times 1000}{M_B \times w_A}$ $w_B = 2 \cdot 5\ g,\ w_A = 75\ g$ $M_B = 2 \times 12 + 4 \times 1 + 2 \times 16 = 60\ g\ mol^{-1}$

Molality $= \frac{2 \cdot 5 \times 1000}{60 \times 75} = 0 \cdot 5556\ m$.

4. Calculate the mass of urea (NH_2CONH_2) required in making 2.5 kg of 0.25 molal aqueous solution

w_B = ?, $M_B = 2 \times 14 + 4 \times 1 + 12 + 16 = 60\ g\ mol^{-1}$, mass of solution = 25 kg = 2500 g

$m = 0 \cdot 25$ molal Mass of solute = moles of solute × molecular mass

$= 0 \cdot 25 \times 60 = 15\ g$

Mass of solvent, w_A = 2500 – 15 = 2485 g.

Molality $= \frac{w_B \times 1000}{M_B \times w_A}$ $0 \cdot 25 = \frac{w_B \times 1000}{60 \times 2485}$ $w_B = \frac{0 \cdot 25 \times 60 \times 2485}{1000}$ = 37.275 g

5. If the density of some lake water is 1.25 g mL^{-1} and contains 92 g of Na^+ ions per kg of water. Calculate the molality of Na^+ ion in the lake

$w_A = 1$ kg water $= 1000\ g,\ M_B =$ Atomic mass of Na $= 23\ g\ mol^{-1},\ w_B = 92\ g$

Molality $= \frac{w_B \times 1000}{M_B \times w_A}$ $= \frac{92 \times 1000}{23 \times 1000}$ = 4 m

6. Calculate the mole fraction of ethylene glycol ($C_2H_6O_2$) in a solution containing 20% of $C_2H_6O_2$ by mass.

20% ethylene glycol means 20 g ethylene glycol present in 100g solution

$\therefore\ w_B = 20\text{ g}\quad w_A = 100 - 20 = 80\text{ g}$

$M_{C_2H_6O_2} = 62\text{ g mol}^{-1}$, $M_{H_2O} = 18\text{ g mol}^{-1}$

Number of moles of $C_2H_6O_2 = n_B = \dfrac{w_B}{M_B} = \dfrac{20}{62} = 0.322\text{ mol}$

Number of moles of $H_2O = n_A = \dfrac{w_A}{M_A} = \dfrac{80}{18} = 4.444\text{ mol}$

Mole fraction of ethylene glycol $= x_B = \dfrac{n_B}{n_A + n_B} = \dfrac{0.322}{4.444 + 0.322} = 0.0675$.

7. Calculate the mole fraction of benzene in solution containing 30% by mass of it in carbon tetrachloride.

Molar mass of $C_6H_6 = 6\times12 + 6\times1 = 78\text{ g mol}^{-1}$

Molar mass of $CCl_4 = 1\times12 + 4\times35.5 = 154\text{ g mol}^{-1}$

30% benzene by mass means 30 g benzene in 100 g solution

∴ Mass of benzene = 30 g Mass of CCl_4 = 100 – 30 = 70 g

$n_{C_6H_6} = \dfrac{30}{78} = 0.385\text{ mol}\qquad n_{CCl_4} = \dfrac{70}{154} = 0.454\text{ mol}$

$x_{C_6H_6} = \dfrac{n_{C_6H_6}}{n_{C_6H_6} + n_{CCl_4}} = \dfrac{0.385}{0.385 + 0.454} = 0.459$.

8. Calculate (a) molality (b) molarity and (c) mole fraction of KI if the density of 20% (mass / mass) aqueous KI is 1.202 g mL^{-1}.

20% (w/w) aqueous KI solution means 20 g KI is present in 100 g of the solution.

Mass of KI = w_B = 20 g, Mass of water = w_A = 100 g – 20 g = 80 g

Volume of solution $= \dfrac{\text{mass of solution}}{\text{density of solution}}$

∴ Volume of solution $= V = \dfrac{100\text{ g}}{1.202} = 83.1947\text{ mL}$

Molar mass of KI = M_B = 16 g mol^{-1}, Molar mass of H_2O = M_A = 18 g mol^{-1}

Number of moles of KI $= n_B = \dfrac{20}{166} = 0.12048\text{ mol}$

Number of moles of water $= n_A = \dfrac{80}{18} = 4.444\text{ mol}$

(a)Calculation of molality of KI Molality $= \dfrac{w_B \times 1000}{M_B \times w_A} = \dfrac{20\times1000}{166\times80} = 1.506\text{ m}$

(b)Calculation of molarity of KI Molarity $= \dfrac{w_B \times 1000}{M_B \times V} = \dfrac{20\times1000}{166\times83.1947} = 1.448\text{ M}$

(c)Calculation of mole fraction of KI $x_{KI} = \dfrac{n_B}{n_A + n_B} = \dfrac{0.12048}{4.444 + 0.12048} = 0.02639$.

9. If nitrogen gas is bubbled through water at 293 K, how many millimoles of N_2 gas would dissolve in 1 litre of water? Assume that N_2 exerts a partial pressure of 0.987 bar. Given that Henry's law constant for N_2 at 293 K is 76.48 K bar.

According to Henry's law

$$p = K_H x$$

$$x_{N_2} = \frac{p}{K_H} = \frac{0\cdot987\ \text{bar}}{76\cdot48 \times 10^3\,\text{bar}} = 1\cdot29 \times 10^{-5}$$

$$x_{N_2} = \frac{n_{N_2}}{n_{H_2O} + n_{N_2}}$$

$$n_{H_2O} = \frac{\text{Mass of 1L water}}{\text{Molecular mass}} = \frac{1000\ \text{g}}{18} = 55\cdot55\ \text{moles}$$

$$1\cdot29 \times 10^{-5} = \frac{n_{N_2}}{55\cdot55 + n_{N_2}}$$

n_{N_2} in denominator is neglected as $n_{N_2} << 55\cdot55$

$$\therefore 1\cdot29 \times 10^{-5} = \frac{n_{N_2}}{55\cdot5}$$

$n_{N_2} = 55\cdot55 \times 1\cdot29 \times 10^{-5} = 71\cdot66 \times 10^{-5}$ moles

$$\therefore n_{N_2} = 0\cdot716\ \text{m mol}$$

10. H_2S, a toxic gas with rotten egg smell, is used for the qualitative analysis. If the solubility of H_2S in water at STP is 0.195 m, calculate Henry's law constant.

Solubility of H_2S = 0.195 m = 0.195 mole in 1000g water

∴ Mass of water = 1000 g

Number of moles of water $= n_{H_2O} = \frac{1000}{18} = 55\cdot55$ moles

Mole fraction of $H_2S = x_{H_2S} = \frac{n_{H_2S}}{n_{H_2O} + n_{H_2S}} = \frac{0\cdot195}{55\cdot55 + 0\cdot195} = 0\cdot003498$

Pressure at STP = 0.987 bar

According to Henry's law $p = K_H x$

$$K_H = \frac{p}{x_{H_2S}} = \frac{0\cdot987}{0\cdot003498} = 282\cdot16\ \text{bar}$$

11. Henry's law constant for the molality of methane in benzene at 298 K is 4.27 × 10^5 mm Hg. Calculate the solubility of methane in benzene at 298 K under 760 mm Hg.

According to Henry's law

$$p_{CH_4} = K_H x_{CH_4}$$

$$x_{CH_4} = \frac{p_{CH_4}}{K_H} = \frac{760\ \text{mm Hg}}{4\cdot27 \times 10^5\,\text{mm Hg}} = 1\cdot78 \times 10^{-3}$$

Note: Mole fraction represents the solubility of methane in benzene.

12. Heptane and octane form an ideal solution. At 373 K, the vapour pressures of the two liquid components are 105.2 kpa and 46.8 kpa respectively. What will be the vapour pressure of a mixture of 26g heptane and 35g of octane?

According to Raout's law

$p_{octane} = x_{octane} \times p^0_{octane}$ $\qquad$ $p_{heptane} = x_{heptane} \times p^0_{heptane}$

Molar mass of octane (C_8H_{18}) = 8 × 12 + 18 × 1 = 114 g mol^{-1}

Molar mass of heptane (C_7H_{16}) = 7 × 12 + 1 × 16 = 100 g mol^{-1}

Number moles of octane $= \frac{w}{M} = \frac{35}{114} = 0.31 \text{ mol}$

Number of moles of heptane $= \frac{w}{M} = \frac{26}{100} = 0.26 \text{ mol}$

Mole fraction of octane $= x_{octane} = \frac{n_{octane}}{n_{octane} + n_{heptane}} = \frac{0.31}{0.31 + 0.26} = 0.544$

$x_{heptane} = 1 - x_{octane} = 1 - 0.544 = 0.456$

$p_{octane} = 0.544 \times 46.8$ kpa = 25.46 kpa

$p_{heptane} = 0.456 \times 105.2$ kpa = 47.97 k pa

Total vapour pressure $P_{total} = p_{octane} + p_{heptane}$ = 25.46 + 47.97 = 73.43 k pa

13. The vapour pressure of pure liquids A and B are 450 and 700 mm Hg respectively, at 350 K. Find out the composition of the liquid mixture if total vapour pressure is 600 mm Hg. Also find the composition of the vapour phase.

It is given that: $p_A^o = 450$ mm of Hg $p_B^o = 700 \text{ mm of Hg}$ $P_{total} = 600$ mm of Hg

From Raoult's law, $p_A = p_A^o x_A$ and $p_B = p_B^o x_B$ $P_{total} = p_A + p_B$

$x_B = 1 - x_A$

$P_{total} = p_A^o x_A + p_B^o (1 - x_A)$ $P_{total} = p_A^o x_A + p_B^o - p_B^o x_A$ $P_{total} = (p_A^o - p_B^o) x_A + p_B^o$

100 = (450 – 700)x_A + 700

–100 = –250x_A $x_A = 0.4$

Therefore, $x_B = 1 - x_A$ = 1 – 0.4 = 0.6

Now, $p_A = p_A^o x_A$ = 450 × 0.4 = 180 mm of Hg

$p_B = p_B^o x_B$ = 700 × 0.6 = 420 mm of Hg

Now, in the vapour phase:

$\text{Mole fraction of A} = \frac{p_A}{p_A + p_B} = \frac{180}{180 + 420} = 0.3$

Mole fraction of B = 1– 0.3 = 0.7

14. The vapour pressure of water is 12.3 kpa at 300K. Calculate vapour pressure of 1 molal solution of non volatile solute in it.

According to the Raoult's law

$$\frac{p_A^0 - p_A}{p_A^0} = \frac{n_B}{n_B + n_A} \qquad \begin{pmatrix} A = H_2O \\ B = \text{solute} \end{pmatrix}$$

1 molal means 1 mole of non volatile solute present in 1000g H_2O

Molar mass of H_2O = 18 g mol^{-1}

Number of moles in $1000\text{g }\ H_2O = \frac{1000}{18} = 55.56 \text{ moles.}$

Number of moles of solute = 1 mol.

$$\therefore \frac{12.3 - p_A}{12.3} = \frac{1}{1 + 55.56}$$

12.3 – p_A = 0.0177 × 12.3

p_A = 12.3 – 0.2177 = 12.08 k pa

15. Vapour pressure of water at 293 K is 17.535 mm Hg. Calculate the vapour pressure of water at 293 K when 25 g of glucose is dissolved in 450 g water

Molar mass of glucose ($C_6H_{12}O_6$) = 6 × 12 + 12 × 1 + 6 × 16 = 180 g mol^{-1}

Number of moles of glucose $= \frac{25\text{ g}}{180\text{ g mol}^{-1}} = 0.139\text{ mol}$

Number of moles of water $= \frac{450\text{g}}{18\text{ g mol}^{-1}} = 25\text{ mol}$

According to Raoult's law, $\frac{p_A^0 - p_A}{p_A^0} = \frac{n_B}{n_B + n_A}$

$p_A^0 = \text{Vapour pressure of water}$ and p_A= Vapour pressure of solution

$\frac{17.535 - p_A}{17.535} = \frac{0.139}{0.139 + 25}$ $\qquad 17.535 - p_A = \frac{0.139 \times 17.535}{25.139}$

17.535 – p_A = 0.097 $\qquad$ p_A = 17.535 – 0.097 = 17.44 mm Hg

16. Calculate the mass of a non–volatile solute (molar mass 40 g mol^{-1}) which should be dissolved in 114 g octane to reduce its vapour pressure to 80%.

Molecular mass of octane (C_8H_{18}) = M_A = 8 × 12 + 18 × 1 = 114 g mol^{-1}

Vapour pressure of octane after dissolving solute $= \frac{80 p_A^o}{100} = 0.8 p_A^o$

$\frac{p_A^o - p_A}{p_A^o} = \frac{n_B}{n_A + n_B}$ $\qquad n_B = \frac{w_B}{40}$ mol, $\quad n_A = \frac{114}{114} = 1$ mol

$\therefore \frac{p_A^o - 0\cdot8p_A^o}{p_A^o} = \frac{\frac{w_B}{40}}{\left(\frac{w_B}{40} + 1\right)}$; $\qquad \frac{p_A^0 - 0\cdot8p_A^0}{p_A^0} = \frac{w_B}{w_B + 40}$

$0\cdot2 = \frac{w_B}{w_B + 40}$ $\qquad \therefore\ w_B = 10\text{g}$

17. The boiling point of a solution of 0.1050 g of a substance in 15.84 g of ether was found to be 0.1^{o}C higher than that of ether. What is the molecular weight of the substance? (K_b = 2.02 K kg mol^{-1})

$$M_B = \frac{K_b \times w_B \times 1000}{\Delta T_b \times w_A} \qquad = \frac{2\cdot02 \times 0\cdot1050 \times 1000}{0\cdot1 \times 15\cdot84} = 133\cdot9\text{ g mol}^{-1}$$

18. The molecular weight of an organic compound is 58 g mol^{-1}. Calculate the boiling point of a solution containing 24 g of the solute and 600 g of water. The boiling point of water = $100^{o}C$. K_b for water = 0.52 K kg mol^{-1}.

$$\Delta T_b = \frac{K_b \times w_B \times 1000}{M_B \times w_A}$$

$$T_b - T_b^o = \frac{0 \cdot 52 \times 24 \times 1000}{58 \times 600} \qquad T_b = 0 \cdot 358 + T_b^o = 0 \cdot 358 + 100 = 100 \cdot 358^{\circ}C$$

19. Acetone boils at $56.38^{o}C$ and a solution of 1.41 grams of an organic compound in 20 g of acetone boils at $56.88^{o}C$. If K_b for acetone is 1.67 K kg mol^{-1}. Calculate the mass of one mole of the organic solid.

$$M_B = \frac{w_B \times K_b \times 1000}{\Delta T_b \times w_A} \qquad \Delta T_b = T_b - T_b^o = 56 \cdot 88 - 56 \cdot 38 = 0 \cdot 5^{\circ}C$$

$$M_B = \frac{1 \cdot 41 \times 1 \cdot 67 \times 1000}{0 \cdot 5 \times 20} = 235 \cdot 47 \text{ g mol}^{-1}$$

20. In a cold climate, water gets frozen causing damage to the radiator of a car. Ethylene glycol is used as an antifreezing agent. Calculate the amount of ethylene glycol to be added to 4 kg of water to prevent it from freezing at – 6^{o}Cp

(K_f for water = 1.85 K kg mol^{-1} molar mass of ethylene glycol = 62 g mol^{-1}).

$$\Delta T_f = \frac{K_f \times w_B \times 1000}{M_B \times w_A} \qquad 6 = \frac{1 \cdot 85 \times w_B \times 1000}{62 \times 4 \times 10^3} \qquad w_B = 804 \cdot 32 \text{ g}$$

21. Addition of 0.643 g of a compound to 50 mL of a liquid (density = 0.879 g/mL) lowers the freezing point from $5.51^{o}C$ to $5.03^{o}C$. Calculate the molar mass of the compound. (K_f for benzene = 5.12 K kg mol^{-1}).

$$M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A} \qquad w_A = 50 \times 0 \cdot 879 = 43 \cdot 95 g \quad (\because \text{ mass} = v \times d)$$

$$\Delta T_f = T_f^o - T_f = 5 \cdot 51 - 5 \cdot 03 = 0 \cdot 48^{\circ}C \qquad \therefore M_B = \frac{5 \cdot 12 \times 0 \cdot 643 \times 1000}{0 \cdot 48 \times 43 \cdot 95} = 156 \cdot 056 \text{ g mol}^{-1}$$

22. 45 g of ethylene glycol ($C_2H_6O_2$) is mixed with 600 g of water. Calculate (a) the freezing point depression and (b) the freezing point of the solution. (K_f = 1.86 K kg mol^{-1})

Freezing point depression (ΔT_f) is given by $\Delta T_f = \frac{K_f \times w_B \times 1000}{M_B \times w_A}$

Molecular mass of ethylene glycol ($C_2H_6O_2$) = $2 \times 12 + 6 \times 1 + 2 \times 16$ = 62 g mol^{-1}.

$$\Delta T_f = \frac{1 \cdot 86 \times 45 \times 1000}{62 \times 600}$$

$$\Delta T_f = 2 \cdot 25 K \qquad \Delta T_f = T_f^0 - T_f$$

T_f^0 = freezing point of water = 273.15 K $\qquad$ T_f = freezing point of solution

$T_f = T_f^0 - \Delta T_f \qquad = 273\cdot15 - 2\cdot25 = 270\cdot9\ \text{K}$.

23. 1.4 g acetone dissolved in 100 g benzene gave a solution which freezes at 277.12 K. Pure benzene freezes at 278.4 K. 2.8 g of a solute dissolved in 100 g benzene gave a solution which froze at 277.76 K. Calculate the molecular weight of solute.

$$K_f = \frac{\Delta T_f \times w_A \times M_B}{w_B \times 1000} \qquad \Delta T_f = T_f^o - T_f = 278\cdot4 - 277\cdot12 = 1\cdot28\ \text{K}$$

$$= \frac{1\cdot28 \times 100 \times 58}{1\cdot4 \times 1000} = 5\cdot3\ \text{K kg mol}^{-1} \qquad M_B = \frac{K_f \times w_B \times 1000}{\Delta T_f \times w_A} = \frac{5\cdot3 \times 2\cdot8 \times 1000}{0\cdot64 \times 100} = 231\cdot87\ \text{g mol}^{-1}$$

24. The osmotic pressure of blood is 7.65 atm at 37$^{\text{o}}$C. How much glucose should be used per litre for an intravenous injection that is to have the same osmotic pressure as blood? (Molar mass of glucoses = 180 g mol^{-1})

$$M_B = \frac{w_B RT}{\pi V} \qquad w_B = \frac{M_B \pi V}{RT} \qquad = \frac{180\ \text{g mol}^{-1} \times 7\cdot65\ \text{atm} \times 1\text{L}}{0\cdot0821\ \text{L atm mol}^{-1}\text{K}^{-1} \times 310\ \text{K}} = 54\cdot14\ \text{g}$$

25. What is the osmotic pressure of 0.05% urea solution in water at 20$^{\text{o}}$C? R = 0.0821 lit atm mol^{-1} K^{-1} molar mass of urea = 60 g mol^{-1}.

0.05% urea means 0.05 g urea present in 100 mL water.

$$\pi = \frac{w_B RT}{M_B V} \qquad = \frac{0\cdot05 \times 0\cdot0821 \times 293}{60 \times 0\cdot1\ \text{L}} \qquad (\because\ 100\ \text{nL} = 0\cdot1\ \text{L}) \qquad = 0\cdot2\ \text{atm}$$

26. 200 cm^3 of an aqueous solution of a protein contains 1.26 g of the protein. The osmotic pressure of such a solution at 300 K is found to be 2.57 × 10^{-3} bar. Calculate the molar mass of the protein. (R = 0.083L bar mol^{-1} K^{-1})

$$M_B = \frac{w_B RT}{\pi V} \qquad V = 200\ \text{cm}^3 = 0\cdot2\ \text{L}$$

$$= \frac{1\cdot26 \times 0\cdot083 \times 300}{2\cdot57 \times 10^{-3} \times 0\cdot2} = 61039\ \text{g mol}^{-1}.$$

27. Calculate the osmotic pressure in pascals exerted by a solution prepared by dissolving 1.0 g of polymer of molar mass 185000 in 450 mL of water at 37$^{\text{o}}$C (R = 0.0821 L atm K^{-1} mol^{-1}).

$$\pi = \frac{w_B RT}{M_B V} \qquad V = 450\ \text{mL} = 0\cdot45\text{L}$$

$$= \frac{1 \times 0\cdot0821 \times 310}{185000 \times 0\cdot45} = 0\cdot00030572\ \text{atm} \qquad = 0\cdot00030572 \times 101325 = 30.9768\ \text{Pa}.$$

4. CHEMICAL KINETICS

The branch of Chemistry that deals with the rate of chemical reaction, factors affecting the rate and the mechanism of a reaction is called **Chemical Kinetics**.

Rate of a chemical reaction

The rate of a chemical reaction is the change in concentration of any one of the reactant or product in unit time. Or, it is the rate of decrease in concentration of any one of the reactant or the rate of increase in concentration of any one of the product.

For a chemical reaction, if Δx is the change in concentration of a reactant or a product in a time Δt, the rate of reaction (r) = Δx/Δt.

For a hypothetical reaction $R \longrightarrow P$, the rate of reaction can be expressed by decrease in concentration of reactants or by increase in concentration of products.

i.e., Rate of reaction = Rate of disappearance of R

$$r = \frac{\text{Decrease in concentration of R}}{\text{Time taken}} \qquad \text{Or} \qquad r = \frac{-\Delta[R]}{\Delta t}$$

[Since, Δ[R] is a negative quantity (as concentration of reactants is decreasing), it is multiplied with –1 to make the rate of the reaction a positive quantity].

Or, Rate of reaction = Rate of appearance (formation) of P = Increase in concentration of P Time taken $\Delta t = t_2 - t_1$

$\Delta[R] = [R]_2 - [R]_1$

$\Delta[P] = [P]_2 - [P]_1$ i.e., $r = \frac{-\Delta[P]}{\Delta t}$

The above rate expressions are also called Average rate.

The rate of reaction is not constant throughout the reaction but decreases with time due to decrease in the concentration of reacatant and hence average rate of reaction is determined.

$$\textbf{Average rate} = \frac{\textbf{Change in concentration of reactants or products}}{\textbf{Time in which change takes place}}$$

For example, in the synthesis of ammonia $N_2 + 3H_2 \longrightarrow 2NH_3$

$$rates\ of\ reaction = -\frac{\Delta[N_2]}{\Delta t} = -\frac{1}{3}\cdot\frac{\Delta[H_2]}{\Delta t} = +\frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$$

It can be concluded from these expressions that the rate of disappearance of H_2 is $\frac{3}{2}$ of the rate of appearance of NH_3.

Units of Rate of reaction: concentration is in mol L^{-1} and time is in seconds then the units will be mol $L^{-1}s^{-1}$. However, in gaseous reactions, when the concentration of gases is expressed in terms of their partial pressures, then the units of the rate equation will be atm s^{-1}.

If concentration is expressed in moles/L and time is in second, the unit of rate of reaction is mol/L/s. In general the dimension of rate of reaction is Concentration/Time.

For gaseous reactions, the concentration is replaced by partial pressure and so the unit of rate of reaction is atm/s.

Instantaneous Rate of a reaction

The rate of a reaction at a particular instant of time is called Instantaneous Rate of a reaction. Or, it is the rate of a reaction when the time interval approaches zero.

i.e. instantaneous rate = average rate as Δt approaches zero.

$$= {}_{\Delta t\to 0}\left[\frac{\Delta[x]}{\Delta t}\right] = \frac{d[x]}{dt}$$

1. **For the reaction R $\longrightarrow$ P, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.**

   Average rate of reaction $= -\frac{\Delta[R]}{\Delta t} = -\frac{[R]_2 - [R]_1}{t_2 - t_1} = -\frac{0\cdot 02 - 0\cdot 03}{25}\text{M min}^{-1}$

   $= -\frac{-0\cdot 01}{25}\text{M min}^{-1}$ $= 4\times 10^{-4}\text{ M min}^{-1}$

   $= \frac{4\times 10^{-4}}{60}\text{M}\,s^{-1}$ $= 6.667 \times 10^{-6}\text{ Ms}^{-1}$

2. **In a reaction 2A $\longrightarrow$ products,the concentration of A decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes.Calculate the rate during this interval?**

   Average rate $= -\frac{1}{2}\frac{\Delta[A]}{\Delta t} = -\frac{1}{2}\left[\frac{[A]_2 - [A]_1}{t_2 - t_1}\right] = -\frac{1}{2}\left[\frac{0\cdot 4 - 0\cdot 5}{10}\right]$

   $= -\frac{1}{2}\times\frac{-0\cdot 1}{10} = 0\cdot 005\text{ mol L}^{-1}\text{ min}^{-1} = 5\times 10^{-3}\text{ M min}^{-1}$

3. **The decomposition of N_2O_5 in CCl_4 at 318K has been studied by monitoring the concentration of N_2O_5 in the solution. Initially the concentration of N_2O_5 is 2.33 mol L^{-1} and after 184 minutes, it is reduced to 2.08 mol L^{-1}. The reaction takes place according to the equation**

   $$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

4. **Calculate the average rate of this reaction in terms of hours, minutes and seconds. What is the rate of production of NO_2 during this period?**

   Average Rate $= -\frac{1}{2}\left\{-\frac{\Delta[N_2O_5]}{\Delta t}\right\} = -\frac{1}{2}\left[\frac{(2\cdot 08 - 2\cdot 33)\text{mol L}^{-1}}{184\text{ min}}\right]$

   $= 6\cdot 79\times 10^{-4}\text{mol L}^{-1}/\text{min} = (6\cdot 79\times 10^{-4}\text{mol L}^{-1}\text{min}^{-1})\times(60\text{ min}/1\text{h})$

   $= 4\cdot 07\times 10^{-2}\text{mol L}^{-1}/\text{h}$ $= 6\cdot 79\times 10^{-4}\text{mol L}^{-1}\times 1\text{ min}/60\text{s}$

$$=1\cdot 13\times 10^{-5}\,\text{mol L}^{-1}\text{s}^{-1}$$

$$\text{Rate} = \frac{1}{4}\left\{\frac{\Delta[\text{NO}_2]}{\Delta t}\right\} \qquad \therefore \frac{\Delta[\text{NO}_2]}{\Delta t} = 6\cdot 79\times 10^{-4}\times 4\,\text{mol L}^{-1}\text{min}^{-1} = 2\cdot 72\times 10^{-3}\,\text{mol L}^{-1}\text{min}^{-1}.$$

5. Hydrogen gas has a nonpolluting combustion product (water vapour). It is used as a fuel abord the space shuttle and in earthbound cars with prototype engines:

$$2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(g)}$$

(a) Express the rate in terms of changes in $[H_2]$, $[O_2]$, and $[H_2O]$ with time.

(b) When $[O_2]$ is decreasing at 0.23 mol L^{-1} s^{-1}, at what rate is $[H_2O]$ increasing?

(a) $$\text{Rate} = -\frac{1}{2}\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

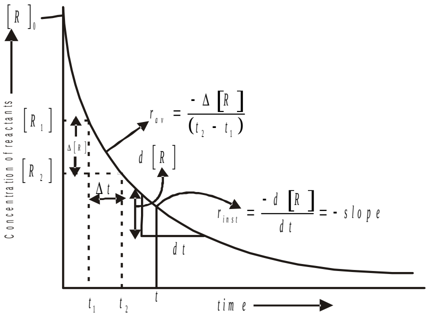
(b) $$\frac{1}{2}\frac{\Delta[\text{H}_2\text{O}]}{\Delta t} = -\frac{\Delta[\text{O}_2]}{\Delta t}$$

$$\frac{\Delta[\text{H}_2\text{O}]}{\Delta t} = 2\times\left(-\frac{\Delta[\text{O}_2]}{\Delta t}\right) = 2[-(-0\cdot 23\,\text{mol L}^{-1}s^{-1})] = 0\cdot 46\,\text{mol L}^{-1}s^{-1}$$

Determination of Instantaneous Rate of a reaction

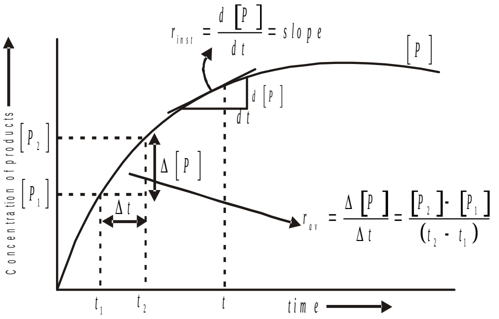
Instantaneous Rate of a reaction can be determined graphically. First conduct the chemical reaction and find out the concentration of reactants or product at a regular interval of time.

Then plot a graph between concentration along y-axis and time along x-axis.



In order to determine the Instantaneous Rate at a particular time, mark the point on the graph at that time and draw a tangent at the point. The slope of this tangent gives the instantaneous rate at that time.

Average rate depends upon the change in concentration of reactants or products and the time taken for that change to occur.



Factors affecting rate of a reaction

The important factors which affect the rate of a chemical reaction are:

1. Nature of the reactants
2. Concentration of the reactants
3. Temperature
4. Pressure (for gaseous reaction only)
5. Effect of catalyst
6. Influence of radiation

Dependence of Rate of reaction on concentration

The representation of rate of reaction in terms of concentration of the reactants is known as **rate law**. It is also called as rate equation or rate expression.

It is found experimentally that Rate of reaction is directly proportional to the concentration of reactants.

Thus for a general reaction, aA + bB $\longrightarrow$ cC + dD,

Rate α $[A]^x[B]^y$ Or, $r = k [A]^x[B]^y$ (where x and y may or may not be equal to a and b)

This expression is known as **rate law or rate equation**. Thus rate law is a "mathematical equation relating the rate of a chemical reaction and concentration of reactants, in which each concentration term is raised to a power which may or may not be equal to the stoichiometric coefficients in the balanced chemical equation."

In the above equation 'k' is a constant called rate constant or velocity constant or specific reaction rate of the reaction.

It is defined as the rate of the reaction when the concentration of each of the reactants is unity.

Units of rate constant

For a general reaction aA + bB $\longrightarrow$ cC + dD

Rate = $k [A]^x [B]^y$ Where x + y = n = order of the reaction

Order of reaction

Order is the sum of the powers of the concentration terms of the reactants in the rate law.

- It is an experimental quantity.
- It can have the values 0,1,2,3,…… or a fraction.
- It is applicable to both elementary and complex reactions.
- The stoichiometric coefficients present in the balanced chemical equation have nothing to do with the order of the reaction.

For a general reaction, aA + bB $\longrightarrow$ cC + dD

$r = k[A]^x[B]^y$, Order of the reaction = x + y

If the order of a reaction is zero, it is called zero order reaction, if it is one, it is called first order reaction, if it is two, it is called second order reaction and so on.

- $NH_4NO_2 \longrightarrow N_2 + 2H_2O$ rate=k$[NH_4NO_2]$ *first order reaction*
- $PCl_5 \longrightarrow PCl_3 + Cl_2$ rate=k$[PCl_5]$ *first order reaction*
- $2HI \longrightarrow H_2 + I_2$ rate=k$[H_2][I_2]$ *second order reaction*
- $NO + O_3 \longrightarrow NO_2 + O_2$ rate=k$[NO][O_3]$ *second order reaction*
- $CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COONa + C_2H_5OH$
  rate=k$[CH_3COOC_2H_5][NaOH]$ *second order reaction*

Molecularity of a reaction

It is **the total number of reacting species collides simultaneously in a chemical reaction**.

It is a theoretical quantity. It cannot be zero or fractional. It can have values 1,2,3 etc. it is applicable only to elementary reactions.

If the molecularity of a reaction is 1, it is called unimolecular reaction.

e.g. Decomposition of ammonium nitrite $NH_4NO_2 \longrightarrow N_2 + 2H_2O$

If the molecularity of a reaction is 2, it is called bimolecular reaction.

e.g. Decomposition of Hydrogen Iodide $2HI \longrightarrow H_2 + I_2$

Differences between Order and Molecularity of a reaction

Molecularity	Order
1. It is the total number of molecules as present in balanced chemical reaction leading to formation of products.	It is the total number of molecule whose concentration changes.
2. Molecularity of reaction can never be in fractions.	Order of reaction can be in fractions.
3. Molecularity of reaction cannot be zero.	Order of reaction can be zero.

Elementary and complex reactions

A reaction that takes place in a single step is called elementary reaction. While a reaction that occurs in more than one step is called a complex reaction.

In a complex reaction one of the steps is slower than the other steps and this step is called the Rate determining step.

The overall rate of the reaction is controlled by this slowest step.

The sequence of steps by which a chemical reaction occurs is called the mechanism of the reaction.

Consider the decomposition of hydrogen peroxide which is catalysed by iodide ion in alkaline medium.

First order reactions: some more details of the first order reactions are as follows;

Rate equation for a first order reaction: a first order reaction is an exponential process and the concentration of the reactant decreases exponentially with time. Let us consider the following reaction which is of first order.

Consider a first order reaction of the type $R \longrightarrow P$
A first order reaction is one in which the rate is directly proportional to first power of the reactant concentration.
Therefore, according to rate law,

$$\text{Rate} = k[R]^1$$

Where k is rate constant or velocity constant

But rate is defined by, $\text{Rate} = -\frac{d[R]}{dt}$ $\quad \therefore -\frac{d[R]}{dt} = k[R]$

Rearranging the equation, we get $\frac{d[R]}{[R]} = -k\,dt$

Integrate both sides of the equation $\int \frac{1}{[R]} d[R] = -k \int dt$

$$\ln[R] = -kt + I \qquad \left(\because \int \frac{1}{x} dx = \ln x\right) \qquad \text{...(1)}$$

Where I is called integration constant

When $t = 0,\ [R] = [R]_0$

$\ln[R]_0 = -k \times 0 + I$

$I = \ln[R]_0$ ...(2)

Where $[R]_0$ is the initial concentration of reactant R.

Substituting the value of I in equation (1) we get,

$$\ln[R] = -kt + \ln[R]_0 \qquad \text{...(3)}$$

$$kt = \ln[R]_0 - \ln[R]$$

$$kt = \ln\frac{[R]_0}{[R]} \quad \text{or} \quad t = \frac{1}{k}\ln\frac{[R]_0}{[R]} \qquad \text{...(4)}$$

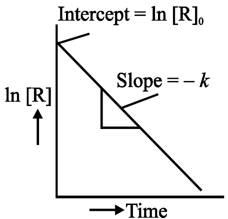
$$\mathbf{k = \frac{2 \cdot 303}{t}\log_{10}\frac{[R]_0}{[R]}} \qquad \text{...(5)}$$

Graphical representation of a first order reaction:

Note: To create another form of rate law, rearrange equation (3) to get,

$$\ln[R] - \ln[R]_0 = -kt$$

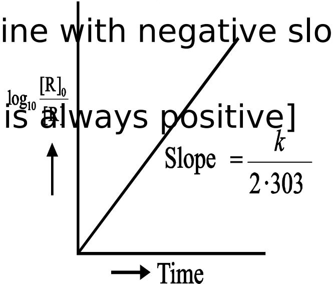
$$\ln\frac{[R]}{[R]_0} = -kt \qquad \therefore \qquad [R] = [R]_0 e^{-kt}$$



Equation (3) $\ln[R] = -kt + \ln[R]_0$ is in the form of $y = mx + c$

This suggests that a plot of ln [R] *versus* 't' gives straight line with negative slope (–*k*) and y intercept = ln$[R]_0$.

[Note that the slope is negative but that the rate constant is always positive]
The first order equation (5) can also be written as



$$\log_{10}\frac{[R]_0}{[R]}=\frac{k}{2{\cdot}303}\times t$$

The plot of $\log_{10}\frac{[R]_0}{[R]}$ *versus* time gives the following graph with a slope of $\frac{k}{2{\cdot}303}$.

1. **For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.**

For a first order reaction, the time required for 99% completion is

$$t_{99\%}=\frac{2{\cdot}303}{k}\log\frac{100}{100-99}\quad=\frac{2{\cdot}303}{k}\log 100=2\times\frac{2{\cdot}303}{k}$$

For a first order reaction, the time required for 90% completion is

$$t_{99\%}=\frac{2{\cdot}303}{k}\log\frac{100}{100-90}\quad=\frac{2{\cdot}303}{k}\log 10=\frac{2{\cdot}303}{k}$$

$$\frac{t_{99\%}}{t_{90\%}}=\frac{2\times\frac{2{\cdot}303}{k}}{\frac{2{\cdot}303}{k}}\qquad\frac{t_{99\%}}{t_{90\%}}=2$$

Therefore, $t99\% = 2t90\%$

Hence, the time required for 99% completion of a first order reaction is twice the time required for the completion of 90% of the reaction.

Half life of a first order reaction:

first order reaction, half life period is independent of initial concentration of the reactants. We know that

$$k=\frac{2{\cdot}303}{t}\log_{10}\frac{[R]_0}{[R]}\qquad\text{...(1)}$$

Where k = rate constant, t = time [R]₀ = initial concentration,

[R] = concentration at any time. When $t=t_{1/2},\ \text{then}\ [R]=\frac{[R]_0}{2}$

$$k=\frac{2{\cdot}303}{t_{1/2}}\log_{10}\frac{\cancel{[R]}_0}{\frac{\cancel{[R]}_0}{2}}$$

Substitute these values in equation (1), we get

$$k=\frac{2{\cdot}303}{t_{1/2}}\log_{10}2\qquad k=\frac{2{\cdot}303}{t_{1/2}}\times 0{\cdot}3010$$

$$k=\frac{0{\cdot}693}{t_{1/2}}\qquad\boxed{\therefore\ t_{1/2}=\frac{0{\cdot}693}{k}}$$

The above relation shows, the half life period of a first order reaction is independent of initial concentration

Characteristics of a first order reaction:

- the rate of reaction is directly proportional to the concentration of the reactant i.e.
  rate α [A]
- The rate constant has the units of time-1
- A first order reaction obeys equations. (i), (ii) and (iii) given above.
- A plot of log [A] against t is a straight line with slope equal to –k/2.303.
- The half life of first order reaction is independent of the initial concentration.

- The time taken for the completion of any fraction of a first order reaction is independent of initial Concentration.

Integrated rate equation for zero order reaction or expression for rate constant or velocity constant of a zero order reaction.

Consider a zero order reaction $R \longrightarrow P$

Zero order reaction is one in which rate is proportional to zeroth power of reactant concentration. According to rate law for zero order reaction,

$$\text{Rate} = k[R]^0 \quad \text{or} \quad \text{Rate} = k \times 1$$

where k is rate constant or velocity constant.

But rate is defined by, $\text{Rate} = -\frac{d[R]}{dt}$ $\quad \therefore \quad -\frac{d[R]}{dt} = k$

Rearranging the equation, we get $d[R] = -k\,dt$

On integration $\int d[R] = -k \int dt$

$$[R] = -k\,t + I \qquad \ldots(1)$$

where I is called integration constant.

To get, I, when t = 0, $[R] = [R]_0$, the initial concentration of the reactant.

$$[R]_0 = -k \times 0 + I$$

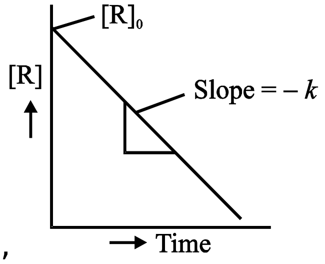
$$I = [R]_0 \qquad \ldots(2)$$

Substitute I value in equation (1), we get

$$[R] = -kt + [R]_0$$

$$[R]_0 - [R] = kt$$

$$\boxed{k = \frac{[R]_0 - [R]}{t}}$$



On rearranging, $[R] = -kt + [R]_0$

This equation is in $y = mx + c$ form and suggests that,

A plot of [R] *versus* ‘t’ gives a straight line with a slope = – k and y - intercept = $[R]_0$.

Determination of order of a reaction: following methods are used to determine the order of a reaction.

i) Graphical method: this method is used when the reaction involves only one reactant. The method is based on the fact that for a reaction of order n, Rate α $[A]^n$

For a first order reaction, n =1, Hence, rate α [A].Thus a plot of rate of reactions Vs conc. Will be a Straight line.

For a second order reaction, n=2. Hence rate α $[A]^2$.Thus a plot of rate of reaction Vs conc. will be a Straight line.

ii) Initial rate method: in this method, the rate law of the reaction is determined by determining the orders of reaction with respect to all the reactants one by one. This is done by changing the initial concentration of only one reactant keeping the concentrations of all other reactants constant and measuring the rate of the reaction. The procedure is repeated with respect to each reactant and the order determined. The overall order of the reaction can be obtained by summing up the individual orders of reaction with respect to the reactants involved.

iii) Integrated rate law method: in this method, the data obtained from an experiment is fed into the rate equation of a particular order and the values of k are calculated for different sets of observations.

If the values of k are found to be constant for all the sets, the reactions is supposed to obey that particular rate law and follows the order suggested by that integrated rate law. In case, the values of k are not constant, the data is used in the rate equation of other order. The rate equation for first and second order reactions are as follows.

For first order reactions: k = $\frac{2.303}{t}\log_{10}\frac{a}{a-x}$

For second order reactions: k = $\frac{1}{t} X \frac{x}{(a-x)}$

iv) Half life method: the half life (t1/2) of a reaction is related to the initial concentration of the reactant as $t_{1/2} \alpha \frac{1}{[A]^{n-1}{}_0}$

Where [A]^0 is the initial concentration of the reactant and n is the order of reaction.

Suppose t$_{1/2}$ is the half life of a reaction when the initial conc. Is [A]^0 and **t$_{1/2}$** is the half life of the same reaction when the initial conc. Is [A]^0 .

Then we have $\frac{t_{1/2}}{t_{1/2}} = (\frac{[A]_0}{[A]_0})^{n-1}$

Thus, the order n of the reaction can be determined.

Effect of temperature on reaction rate: the rate of a chemical reaction is significantly affected by a change in temperature. For most of the chemical reactions, the rate increases with increase in temperature. The rate usually becomes doubled for each 10º rise in temperature.

a) Temperature coefficient: it is defined as the ratio of the rate constant of a reaction at two different temperatures separated by 10 C. the two temperatures generally taken are 35 C and 25 C. thus, Temperature coefficient = $\frac{k_{35C}}{k_{25C}}$

For most of the homogeneous reactions, the value of temperature coefficient lies between 2 and 3.

Molecularity of a reaction: the number of reacting species which must collide simultaneously in Order to bring about a chemical reaction is called the molecularity of that reaction.

The molecularity of a reaction is a whole number and may have values 1, 2, 3 etc.

The reactions with molecularity 1 are called unimolecular reactions.

Similarly, we have bimolecular and trimolecular reactions when the values of molecularity are 2 and 3 respectively.

Molecularity of elementary reactions: The simple chemical reactions which occur only in one step are called elementary reactions. The molecularity of an elementary reaction is equal to the number of reacting species as represented by the balanced chemical equation of the reaction, for example.

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2 (molecularity = 1, unimolecular reaction)$$

$$2HI \rightarrow H_2 + I_2 (molecularity = 2, bimolecular reaction)$$

$$2NO + O_2 \rightarrow 2NO_2 (molecularity = 3, trimolecular reaction)$$

Molecularity of complex reactions: the reactions which occur in two or more steps are called complex reactions.

Complex reactions proceed through a series of steps, each involving one, two, or at the most three molecules. Each step is an elementary reaction and has its own rate.

The overall rate of a complex reaction is governed by the rate of the slowest elementary step called the rate determining step.

The number of reacting species taking part in the slowest elementary step of a complex reaction is called the molecularity of the complex reaction.

For example, the reaction $2NO + 2H_2 \longrightarrow N_2 + H_2O$ is a complex reaction and takes place in the following two steps.

Step1. $2NO + H_2 \rightarrow N_2 + H_2O_2 (slow)$

Step2. $H_2O_2 + H_2 \rightarrow 2H_2O \ (fast)$

Obviously, step 1 is the rate determining step and therefore the molecularity of the overall complex reaction is 3.

Most of the chemical reactions involve the simultaneous collisions of one, two or at the most three molecules.

Therefore, the molecularity of most of the reactions is either 1 or 2. Even the reactions with molecularity 3 are only a few in number.

The reactions with higher molecularity are rare.

$$KClO_3 + 6FeSO_4 + 3H_2SO_4 \longrightarrow KCl + 3Fe_2(SO_4)_3 + 3H_2O$$

This reaction which apparently seems to be of tenth order but it is actually a second order reaction. This shows that the reaction takes place in several steps. Which step controls the rate of the overall reaction. or slow reaction that is called as rate determining step.

Consider the decomposition of hydrogen peroxide which is catalysed by iodide ion in an alkaline medium. $2H_2O_2 \xrightarrow[Alkaline\,medium]{I^-} 2H_2O + O_2$

The rate equation for this reaction is found to be Rate = $\frac{-d\left[H_2O_2\right]}{dt}=k\left[H_2O_2\right]\left[I^-\right]$

This reaction is first order with respect to both H_2O_2 and I^-.

Evidences suggest that this reaction takes place in two steps.

Pseudo-unimolecular reactions: for elementary reactions, the molecularity and order are usually the same.

However, there are several first order reactions in which molecularity differs from the order.

The first order reactions having molecularity greater than one are called pseudo-unimolecular reactions.

A pseudo-unimolecular reaction is obtained when one of the reactants is present in large excess.

The reactant present in large excess does not contributes to the rate of reactions.

Its concentration remains almost constant during the course of reaction and therefore the rate of the reaction does not depend upon its concentration. Some examples of pseudo-unimolecular reactions are as follows.

$CH_3COOC_2H_5+H_2O \longrightarrow CH_3COOH+C_2H_5OH$ rate=$k[CH_3COOC_2H_5]$

$C_{12}H_{22}O_{11}+H_2O \longrightarrow C_6H_{12}O_6+C_6H_{12}O_6$ rate=$k[C_{12}H_{22}O_{11}]$

5.SURFACE CHEMISTRY

It is the branch of chemistry that deals with the study of nature of surfaces and the different processes taking place at the surface.

The important surface phenomena are adsorption, corrosion, electrode process, heterogeneous catalysis, dissolution etc.

ADSORPTION It is the process of concentration or accumulation of a substance on the surface of another substance.

The substance which is adsorbed is called adsorbate and the substance whose surface on which adsorption takes place is called adsorbent.

The commonly used adsorbents are charcoal, silica gel, alumina gel, clay, colloids, metals in finely divided state etc.

Adsorption is a surface phenomenon. Some examples of adsorption are:

1. Powdered charcoal adsorbs gases like H_2, O_2, CO, Cl_2, NH_3, SO_2 etc.
2. Silica gel adsorbs moisture.
3. Animal charcoal adsorbs colouring material from sugar solutions.

Desorption: The process of removal of an adsorbed substance from the surface of adsorbent is called desorption. i.e. it is the reverse of adsorption.

Distinction between adsorption and absorption

In adsorption, the substance is concentrated only at the surface while in absorption, the substance is uniformly distributed throughout the bulk of the solid. So adsorption is a surface phenomenon while absorption is a bulk phenomenon.

Sorption: If adsorption and absorption occur simultaneously, the process is called sorption.

Absorption	Adsorption
1.It is the phenomenon in which the particles of gas or liquid get uniformly distributed throughout the body of the solid. 2.The concentration is the same throughout the material. Therefore, it is a bulk phenomenon. 3.Absorption occurs at uniform rate.	1.it is the phenomenon of higher concentration of particles of gas or liquid on the surface than in the bulk of the solid. 2.The concentration on the surface of the adsorbent is different from that in the bulk. 3.Adsorption is rapid in the beginning and its rate slowly decreases.

Mechanism of Adsorption The surface particles of the adsorbent are not in the same environment as the particles inside the bulk (inner part).

Inside the adsorbent, all the forces are mutually balanced. But at the surface, there is always some unbalanced or residual forces.

These forces of the adsorbent are responsible for adsorption.

Heat of adsorption (Enthalpy of Adsorption) Adsorption is an exothermic process. i.e. some heat is always evolved during adsorption.

The amount of heat evolved when 1 mole of an adsorbate is adsorbed on the surface of an adsorbent is called heat of adsorption.

Thermodynamic aspects of adsorption Adsorption is an exothermic process. When a gas is adsorbed, the degree of freedom (randomness) of its molecules decreases and hence the entropy decreases.i.e.,ΔS becomes negative.

Adsorption is thus accompanied by decrease in enthalpy as well as decrease in entropy of the system. For a process to be spontaneous, ΔG must be negative.

On the basis of equation, $\Delta G = \Delta H - T\Delta S$, ΔG can be negative if $\Delta H > T\Delta S$.

As the adsorption proceeds, ΔH becomes less and less negative ultimately ΔH becomes equal to $T\Delta S$ and ΔG becomes zero. At this state equilibrium is attained.

Types of adsorption Depending on the force of attraction between adsorbent and adsorbate, adsorption is of two types–physical adsorption or physisorption and chemical adsorption or chemisorption.

1.physical adsorption or physisorption: If the force of attraction between adsorbent and adsorbate is weak van der Waals force, it is called physical adsorption or physisorption.

For physisorption, the heat of adsorption is low and it is not specific since the van der Waals forces are universal. That is any substance can form van der Waals force with any surface.

2.chemical adsorption or chemisorptions: If the force of attraction between adsorbent and adsorbate is chemical bond. It is also called activated adsorption since it involves some activation energy.

For chemisorption, the enthalpy of adsorption is high and it takes place at high temperature.

It is highly specific in nature and it will occur only if there is some possibility of chemical bonding between adsorbent and adsorbate.

A physisorption at low temperature may pass into chemisorption at high temperature. For e.g. Hydrogen gas is first adsorbed on nickel by van der Waals force. But at high temperature, the molecules of H_2 dissociate to form H atoms and they are adsorbed on the surface of Ni by chemical bond.

Both physisorption and chemisorption increases with increase in surface area of the adsorbent. Surface area can be increased by powdering the adsorbent.

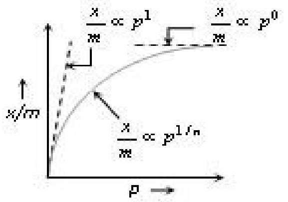
Distinction between physisorption and chemisorptions

	physisorption	**Chemisorption**
1.	In this type of adsorption, the adsorbate is attached to the surface of the adsorbent with weak van der Waal’s forces of attraction.	In this type of adsorption, strong chemical bonds are formed between the adsorbate and the surface of the adsorbent.
2.	No new compound is formed in the process.	New compounds are formed at the surface of the adsorbent.
3.	It is generally found to be reversible in nature.	It is usually irreversible in nature.
4.	Enthalpy of adsorption is low as weak van der Waal’s forces of attraction are involved. The values lie in the range of 20-40 kJ mol^{-1}.	Enthalpy of adsorption is high as chemical bonds are formed. The values lie in the range of 40-400 kJ mol^{-1}.
5.	It is favoured by low temperature conditions.	It is favoured by high temperature conditions.
6.	It is an example of multi-layer adsorption	It is an example of mono-layer adsorption.

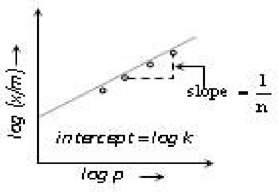
Adsorption Isotherms The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a graph called adsorption isotherm.

Freundlich adsorption isotherm:

Freundlich gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure, at a particular temperature.



Freundlich adsorption isotherm: plot of x/m against



Plot of log x/m against log p for the adsorption of a gas on a solid

The relationship can be expressed by the following equation:

$$x/m = k.P^{1/n} \quad \text{(where } n > 1)$$

where x is the mass of the gas adsorbed, m is the mass of the adsorbent, k and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature.

The above relationship can be represented in the form of a graph as follows:

From the graph it is clear that x/m (extend of adsorption) increases with pressure upto a certain pressure called saturation pressure (Ps) and after that it becomes constant. If we take logarithm of the above equation, we get log x/m = logk + 1/n logP

This equation is of the form y = mx+c, equation for a straight line.

So if we plot log x/m against log P, we get a straight line, which verifies Freundlich isotherm.

The value of 1/n in Freundlich isotherm ranges from 0 to 1

When 1/n = 0, x/m = a constant.

When 1/n = 1, x/m = k.p, the adsorption varies linearly with pressure.

Freundlich adsorption isotherm failed to explain adsorption at very high pressures.

Adsorption from solution

Certain solid adsorbents can adsorb solute particles from solution. This is known as adsorption from solution. E.g.:

1. When a solution of acetic acid in water is shaken with charcoal, a part of the acid is adsorbed by the charcoal and the concentration of the acid decreases in the solution.
2. Animal charcoal adsorbs colouring materials from sugar solution. So it is used for the purification of sugar.

The important characteristics of adsorption from solution are:

(i) The extent of adsorption decreases with an increase in temperature.

(ii) The extent of adsorption increases with an increase of surface area of the adsorbent.

(iii) The extent of adsorption depends on the concentration of the solute and the nature of the adsorbent and the adsorbate.

Freundlich adsorption isotherm is applicable to adsorption from solution also. Here instead of pressure, concentration of the solution is used.

i.e., $x/m = kC^{1/n}$ (where C is the equilibrium concentration).

On taking logarithm of the above equation, we have log x/m = logk + 1/n logC.On plotting log x/m against log C, a straight line is obtained which verifies Freundlich isotherm.

Applications of adsorption

The important applications of adsorption are:

1. **Production of high vacuum:** For the complete evacuation of a vessel, activated charcoal is used.

2. **Gas masks:** The poisonous gases in coal mines can be removed by using gas masks containing activated charcoal.
3. **Control of humidity:** Silica and aluminium gels are used as adsorbents for removing moisture and controlling humidity.
4. Animal charcoal is used for the purification of cane sugar solution.
5. Adsorption finds application in heterogeneous catalysis.
6. A mixture of noble gases can be separated by adsorption on coconut charcoal at different temperatures.
7. In curing diseases: A number of drugs are used to kill germs by getting adsorbed on them.
8. In froth floatation process for the purification of sulphide ores in metallurgy.
9. Adsorption indicators like eosin, fluorescein etc. are used in volumetric analysis.
10. Chromatographic analysis for the separation of a mixture is based on adsorption.

CATALYSIS

A catalyst is a substance that changes the rate of a chemical reaction without undergoing any permanent chemical change by itself.

The process of changing the rate of a chemical reaction by a catalyst is known as Catalysis. Eg: MnO_2 (Manganese dioxide) acts as a catalyst in the decomposition of $KClO_3$

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3\ O_2$$

Promoters and poisons: Promoters are substances that enhance the activity of a catalyst while poisons decrease the activity of a catalyst.

For example, in Haber's process for the manufacture of ammonia, molybdenum (Mo) acts as a promoter for the catalyst iron. $N_2 + 3H_2 \xrightarrow{Fe/Mo} 2NH_3$

Types of Catalysis

Positive and Negative Catalyst

A catalyst that increases the rate of a chemical reaction is called Positive catalyst and that decreases the rate of a chemical reaction is called negative catalyst (inhibitors).

E.g. In the Haber's process for the manufacture of ammonia, Fe acts as a positive catalyst

$$N_2 + 3H_2 \xrightarrow{Fe/Mo} 2NH_3$$

For decreasing the rate of dissociation of H_2O_2, Phosphoric acid is used as a negative catalyst.

Shape-Selective Catalysis by Zeolites

The catalytic reaction that depends upon the pore structure of the catalyst and the size of the reactant and product molecules is called shape-selective catalysis.

Zeolites are good shape-selective catalysts because of their honey comb-like structures. They are microporous aluminosilicates with three dimensional networks of silicates in which some silicon atoms are replaced by aluminium atoms. They contain Al–O–Si framework.

The reactions taking place in zeolites depend upon the size and shape of reactant and product molecules as well as upon the pores and cavities of the zeolites. They are found in nature as well as prepared artificially.

Zeolites are used as catalysts in petrochemical industries for cracking of hydrocarbons and isomerisation.

An important zeolite catalyst used in the petroleum industry is ZSM-5.

It converts alcohols directly into gasoline (petrol) by dehydrating them to give a mixture of hydrocarbons.

THE COLLOIDAL STATE

Colloid is an intermediate state between true solution and suspension. In a true solution, the size of the particles is < 1nm.

The particles do not settle down under the influence of gravity or by any method and they cannot be filtered by a filter paper. A true solution is homogeneous and transparent.

In a suspension the size of the particles is > 1000nm. The particles settle down under the influence of gravity.

They can be filtered by an ordinary filter paper. It is heterogeneous and opaque.

In colloids, the particle size is in between **1 nm and 1000nm**. The particles do not settle down under the influence of gravity. They cannot be filtered by ordinary filter paper, but can be filtered by ultra filters.

They are heterogeneous and translucent.

Colloids are heterogeneous systems containing two phases–dispersed phase and dispersion medium.

The substance which is dispersed (distributed) is called dispersed phase and the medium in which the particles are dispersed is called dispersion medium.

e.g.: In starch solution, starch is the dispersed phase and water is the dispersion medium.

Classification colloids

1. Based on the physical state of dispersed phase and the dispersion medium

Depending upon physical state of the dispersed phase and the dispersion medium, there are eight types of colloidal systems. A gas mixed with another gas forms a homogeneous mixture and hence is not a colloidal system. The different types colloidal dispersion are:

Sr. no	Dispersed phase	Dispersion medium	Type of colloid	Example
1.	Solid	Solid	Solid Sol	Gemstone
2.	Solid	Liquid	Sol	Paint
3.	Solid	Gas	Aerosol	Smoke
4.	Liquid	Solid	Gel	Cheese
5.	Liquid	Liquid	Emulsion	Milk
6.	Liquid	Gas	Aerosol	Fog
7.	Gas	Solid	Solid foam	Pumice stone
8.	Gas	Liquid	Foam	Froth

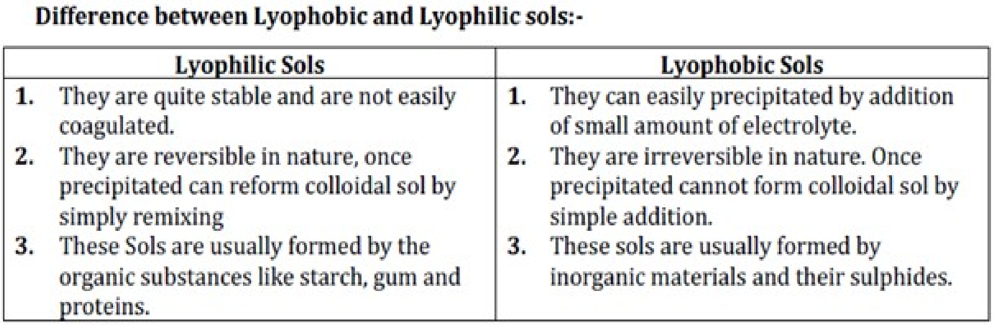
2. Based on the dispersion medium, colloids are classified as follows:

Dispersion medium	Name of sol
Water	Aquasol or hydrosol
Alcohol	Alcosol
Benzene	Benzosol
Gases	Aerosol

3. Based on the attraction between the dispersed phase and the dispersion medium, colloids are of two types: **lyophilic** (solvent loving) and **lyophobic** (solvent hating). If the force of attraction between dispersed phase and dispersion medium is strong, it is called lyophilic sol e.g. gum, gelatin, starch, rubber etc in suitable dispersion medium.

If the force of attraction between dispersed phase and dispersion medium is weak, it is called lyophobic sol.

e.g. Arsenic sulphide (As_2S_3) sol, sulpher sol and metal sols like gold sol, silver sol etc.



Difference between Lyophobic and Lyophilic sols:-

Lyophilic Sols	Lyophobic Sols
1. They are quite stable and are not easily coagulated.	**1.** They can easily precipitated by addition of small amount of electrolyte.
2. They are reversible in nature, once precipitated can reform colloidal sol by simply remixing	**2.** They are irreversible in nature. Once precipitated cannot form colloidal sol by simple addition.
3. These Sols are usually formed by the organic substances like starch, gum and proteins.	**3.** These sols are usually formed by inorganic materials and their sulphides.

Based on the nature of particles: Based on this, colloids are of three types – Multimolecular colloids,Macro molecular colloids and Associated colloids.

1.Multimolecular colloids: They contain an aggregate of atoms or molecules having dimension < 1nm.

These particles are bind together by weak van der Waal's force of attraction and form particles of colloidal dimension.

e.g. Arsenic sulphide (As_2S_3) sol, sulpher sol and metal sols like gold sol, silver sol etc.

2.Macromolecular colloids: Macromolecules (Polymers) in suitable solvents form solutions in which the size of the particle is in the colloidal range. Such systems are called macromolecular colloids. These colloids are quite stable and resemble true solutions in many properties.

Example: solutions of starch, cellulose, proteins, enzymes, polythene, nylon, polystyrene, synthetic rubber, etc. in suitable dispersion medium.

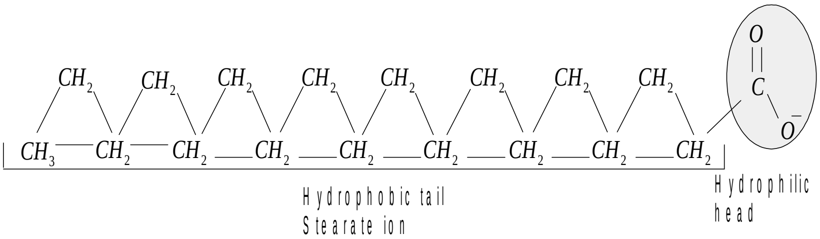
3.Associated colloids: These are substances which behave as normal strong electrolytes at low concentrations, but as colloids at higher concentrations. The colloidal behavior is because of the formation of aggregates. They are also called **micelles**.

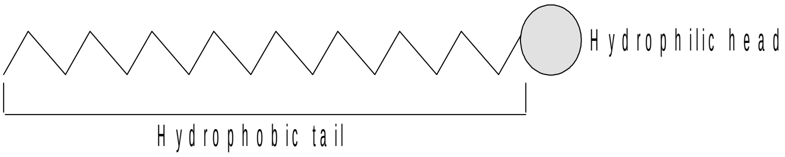
The formation of micelles takes place only above a particular temperature called **Kraft temperature** (**Tk**) and above a particular concentration called **critical micelle concentration** (**CMC**).

Surface active agents such as soaps and synthetic detergents are examples for micelles. These colloids have both lyophobic and lyophilic parts.

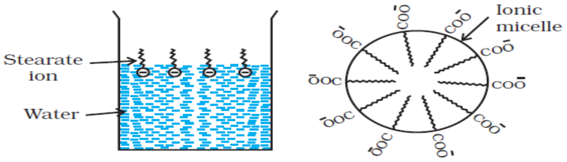
Mechanism of micelle formation An example for micelle is soap solution. Soap is sodium or potassium salt of a higher fatty acid and may be represented as RCOO–Na+. When dissolved in water, it dissociates into RCOO– and Na+ ions.

The RCOO– ions consist of two parts — a long hydrocarbon chain R (also called non-polar 'tail') which is hydrophobic (water repelling), and a polar group COO– (also called polar-ionic 'head'), which is hydrophilic (water loving).





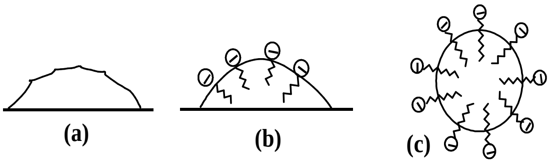
The RCOO– ions are present on the surface with their COO– groups in water and the hydrocarbon chains (R) at the surface. But at critical micelle concentration, the anions are pulled into the bulk of the solution and aggregate to form a spherical shape. Thus a micelle is formed.



Cleansing action of soaps The cleansing action of soap is due to micelle formation. The soap molecules form micelle around the oil droplet in such a way that hydrophobic part is in the oil droplet and hydrophilic part projects out.

Since the polar groups (hydrophilic end) can interact with water, the oil droplets are pulled in water and removed from the dirty surface.

Thus soap helps in emulsification and washing away of oils and fats.



(a) Grease on cloth (b) Stearate ions arranging around the grease droplet and (c) Grease droplet surrounded by stearate micelle

Preparation of colloids

Some of the methods used for the preparation of colloids are:

a) Chemical methods:

Colloidal solutions can be prepared by chemical reactions like oxidation, reduction, double decomposition, hydrolysis etc.

1. **Oxidation**: Sulphur sol can be prepared by passing H_2S gas through an aqueous solution of sulphur dioxide.

$$SO_2 + 2H_2S \xrightarrow{Oxidation} 3S(sol) + 2H_2O$$

2. **Reduction**: Sols of metals like silver, gold and platinum are obtained by the reduction of their salts with reducing
agents like formaldehyde, stannous chloride etc.

$$2AuCl_3 + 3HCHO + 3H_2O \xrightarrow{Reduction} 2Au(sol) + 3HCOOH + 6HCl$$

3. **Hydrolysis**: Ferric hydroxide sol is obtained when concentrated solution of ferric chloride is added drop-wise to hot water.

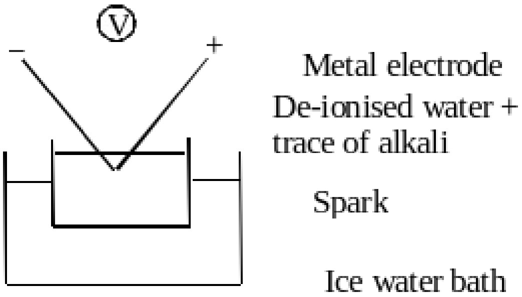
$$FeCl_3 + 3H_2O \xrightarrow{Hydrolysis} Fe(OH)_3\ (sol) + 3HCl$$

4. **Double decomposition**: A colloidal solution of arsenic sulphide is formed by passing H_2S through a dilute solution of arsenious oxide in water.

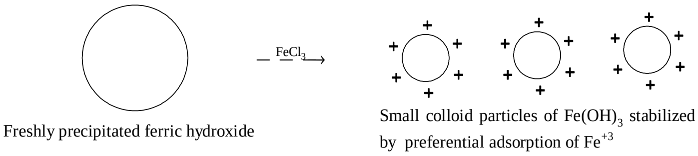
$$As_2O_3 + 3H_2S \xrightarrow{Double\ decomposition} As_2S_{3(sol)} + 3H_2O$$

b) Electrical disintegration (Bredig's arc method): This method is used for the preparation of metal sols like Ag, Au, Pt etc. The metal whose sol is to be prepared is taken in the form of two rods and it is kept in suitable dispersion medium containing small amount of electrolyte.

The whole arrangement is kept in an ice bath. When high voltage is passed through the metal, the intense heat produced vapourises the metal, which then condensed to form particles of colloidal dimension.



c) Peptization: The process of conversion of a freshly prepared precipitate into a colloidal sol by shaking it with suitable dispersion medium in the presence of small amount of electrolyte is called peptization. The electrolyte added is called peptizing agent.



During peptization, the precipitate adsorbs one of the ions of the electrolyte on its surface and forms a positive or negative charge on it. Thus the particles of the precipitate break up into smaller particles of the colloidal size.

Purification of colloids The colloidal solution prepared contains excess amount of electrolyte and some other soluble impurities.

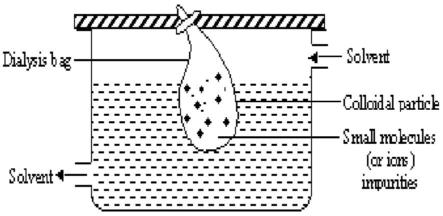
Even though small amount of electrolyte is required for the stability of colloid, large amount may cause precipitation.

The process of reducing the concentration of electrolyte and other impurities is known as purification of colloids.

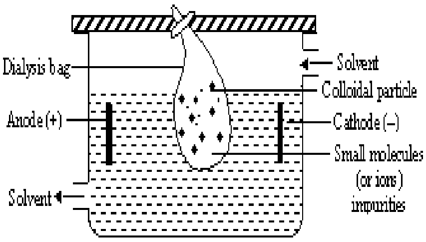
Some methods used for purification are:

1. Dialysis: It is the process of removing dissolved substances from a colloidal solution by means of diffusion through a semi-permeable membrane. Here the sol particles are taken in a parchment or cellophane bag and it is suspended in a running stream of water.

The impurities are diffused through the membrane and the sol particles are left behind. These particles are then suspended in suitable dispersion medium so as to get a colloidal dispersion.



The speed of dialysis can be increased by using hot water instead of cold water. Then the process is known as hot water dialysis.



The speed of dialysis can also be increased by dipping two electrodes and passing electricity. Then the process is known as **electrodialysis.**

2. Ultrafiltration:

It is the process of separating the colloidal particles from the impurities by using a special type of filter paper called ultrafilters or ultra filter paper.

It is prepared by dipping ordinary filter paper in collodion solution (a 4% solution of nitrocellulose in a mixture of alcohol and ether).

When colloidal particles are filtered using ultrafilters, the sol particles are retained on the filter paper while the impurities and the electrolyte are passed through it.

When these sol particles are suspended in suitable dispersion medium, we get a colloidal solution.

Properties of colloids

1. Colligative properties: In colloids, the number of particles are very small compared to that of true solution.

So the values of colligative properties such as relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure are small compared to that of true solution.

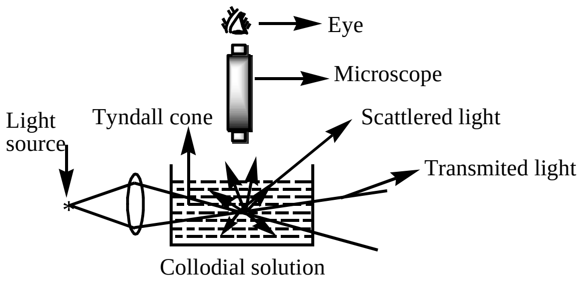
2. Tyndall effect: When a light beam is passed through a colloidal solution, we can see the path of the light beam. This phenomenon is known as Tyndall effect.

It is due to the scattering of light beam by the colloidal particles. The visible path is called tyndall cone.

Tyndall effect is observed only when the following conditions are satisfied:

(i) The diameter of the dispersed particles is much larger than the wavelength of the light used.

(ii) The refractive indices of the dispersed phase and the dispersion medium differ greatly in magnitude.



True solutions do not show tyndall effect since the size of particles are very small so that they cannot scatter the light beam. Thus tyndall effect is used to distinguish a colloidal solution from a true solution.

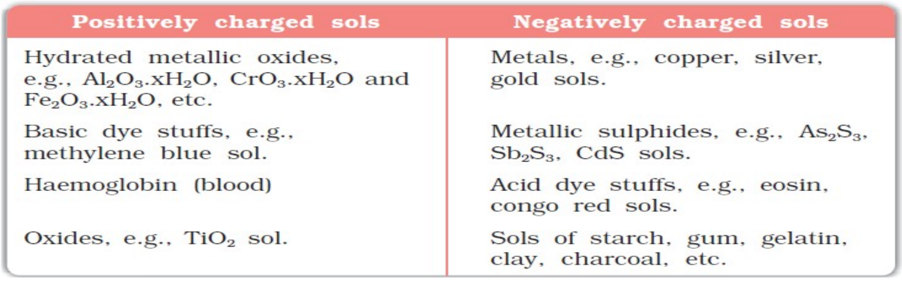
Ultramicroscope used to see the colloidal particles works on the principle of tyndall effect.

3. Brownian movement In colloids, the particles of dispersion medium are in a state of continuous zig-zag motion. This motion was first observed by Robert Brown and it is known as Brownian movement. It is independent of the nature of the colloidal particles but depends on the size of the particles and viscosity of the solution. Smaller the size and lesser the viscosity of the medium, faster is the motion.

Brownian movement is due to the unbalanced bombardment of particles of the dispersed phase by the particles of dispersion medium. It is responsible for the stability of colloids.

4. **Charge on colloidal particles:**

Colloidal particles always carry an electric charge. For a given colloidal solution, the nature of the charge is the same on all the particles.



Positively charged sols	Negatively charged sols
Hydrated metallic oxides, e.g., $Al_2O_3.xH_2O$, $CrO_3.xH_2O$ and $Fe_2O_3.xH_2O$, etc.	Metals, e.g., copper, silver, gold sols.
Basic dye stuffs, e.g., methylene blue sol.	Metallic sulphides, e.g., As_2S_3, Sb_2S_3, CdS sols.
Haemoglobin (blood)	Acid dye stuffs, e.g., eosin, congo red sols.
Oxides, e.g., TiO_2 sol.	Sols of starch, gum, gelatin, clay, charcoal, etc.

The charge on the sol particles is mainly due to preferential adsorption of ions from solution.

When 2 or more ions are present in the dispersion medium, preferential adsorption of the ion common to the colloidal particle takes place.

e.g. when $AgNO_3$ is added to KI, AgI is precipitated, which adsorbs iodide ions from the dispersion medium and thus get a negative charge.

$AgNO_3 + KI \longrightarrow AgI + KNO_3$

But when KI is added to $AgNO_3$, the precipitated AgI adsorbs Ag+ ions from the solution and thus get a positive charge.

AgI/I^- Negatively charged

AgI/Ag^+ Positively charged

If is added to excess of hot water, a positively charged sol of ferric hydroxide is formed due to adsorption of Fe^{3+} ions.

$Fe(OH)_3/Fe^{3+}$ Positively charged

How ever, when ferric chlorde is added to NaOH a negatively charged sol is obtained with adsorption of ions.

Due to the positive or negative charge in the sol particles, they attract the counter ions (opposite ions) from the medium. Thus a double layer of opposite charges is formed. This is known as **Helmholtz electrical double layer**.

The layer in which the ions are directly adsorbed to the sol particles is termed as fixed layer. The second layer is mobile and is termed as diffused layer.

Due to the opposite charges on the fixed and diffused layers, there arises a potential difference between these layers.

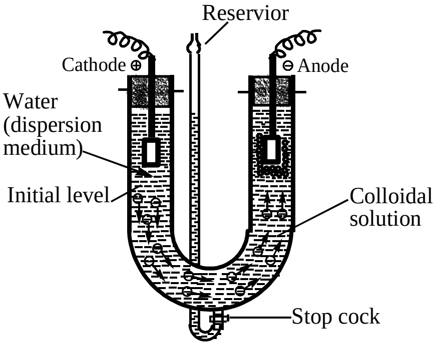
This potential difference between the fixed layer and the diffused layer of opposite charges is called the **electrokinetic potential or zeta potential**.

The presence of similar charges on colloidal particles leads to repulsion between the particles and prevent them from coagulation when they come closer.

So the charge on the sol particles is mainly responsible for the stability ofcolloidal solution.

5.Electrophoresis: Since colloidal particles carry charge, they move under the influence of an electric field. This movement of colloidal particles is called electrophoresis.

The positively charged sol particles move towards cathode (cataphoresis) and the negatively charged particles move towards the anode (anaphoresis).



If the movement of the sol particles is prevented by some suitable method, the particles of dispersion medium itself move under the presence of electric field. This migration is termed as **electro-osmosis**.

6. Coagulation (precipitation or flocculation)

The process of settling of colloidal particles is called coagulation or precipitation of the sol. This can be done by different ways:

i) By electrophoresis
ii) By mixing two oppositely charged sols
iii) By continuous dialysis
iv) By boiling
v) By the addition of electrolyte

When an electrolyte is added to the sol, the ions carrying opposite charge to that of the sol neutralize the charge and causes precipitation.

The ion of the electrolyte which causes the precipitation is called the coagulating ion or the flocculating ion.

Hardy-Schulze rule A negatively charged ion causes the precipitation of positively charged sol and vice versa.enerally, **the greater the valency of the coagulating ion, the greater will be the coagulating power. This is known as Hardy – Schulze rule**.

Thus for the coagulation of a negative sol like As_2S_3, the flocculating power of the +ve ions is of the order: $\mathbf{Al^{3+} > Ba^{2+} > Na^{+}}$

Similarly for a +ve sol like ferric hydroxide, the flocculating power of the counter ion is of the order: $\mathbf{[Fe(CN)_6]^{4-} > PO_4^{3-} > SO_4^{2-} > Cl^{-}}$

Coagulating value: The minimum concentration of an electrolyte in millimoles per litre required for the coagulation of a sol within 2 hours is called coagulating value.

The smaller the coagulating value, the higher will be the coagulation power.

Protection of colloids

Lyophilic sols are self stabilized, while lyophobic sols require some stabilizing agents. For this purpose, some lyophilic sols are added to lyophobic sols.

These lyophilic sols are called protective colloids.

When a lyophilic sol is added to a lyophobic sol, the lyophilic particles form a layer around lyophobic particles and thus protect them from electrolytes.

EMULSIONS

These are colloidal solutions in which a liquid is dispersed in another liquid. Generally one of the two liquids is water.

There are two types of emulsions:

1. Oil in water (O/W) type and 2. Water in oil (W/O) type

In oil in water type emulsion, oil is the dispersed phase and water is the dispersion medium.

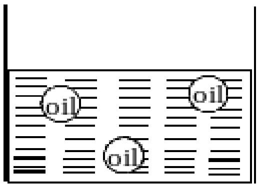
E.g. milk. In milk, the liquid fat is dispensed in water In water in oil type emulsion, water is the dispersed phase and oil is the dispersion medium.

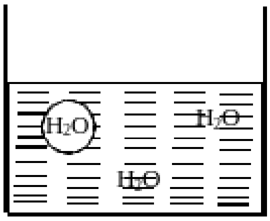
E.g. butter and cream an emulsion obtained by mixing oil with water or water with oil is not stable.

In order to prepare a stable emulsion, a third substance called emulsifying agent is added.

The emulsifying agent forms an inter facial film between dispersed phase and the dispersion medium.

The common emulsifying agents for O/W emulsions are proteins, gums, natural and synthetic soaps, etc., and for W/O, heavy metal salts of fatty acids, long chain alcohols, lampblack, etc.





The two types of emulsions can be distinguished by dilution with dispersion medium.

The droplets in emulsions carry negative charge and they can be precipitated by electrolytes. They also show Brownian movement and Tyndall effect.

Uses of emulsions:

(i) Cleansing action of soaps is based on the formation of emulsions.

(ii) Digestion of fats in intestines takes place by the process of emulsification.

(iii) Antiseptics and disinfectants when added to water form emulsions.

(iv) The process of emulsification is used to make medicines

Applications of Colloids

1. Formation of Delta: Deltas are formed at the river mouth. This is because river water is a negatively charged colloid of sand particles.

When this water enters into sea, the positive ions present in sea water coagulate the colloidal solution of sand and so the particles settle down. This will result in the formation of delta.

2. Electrical precipitation of smoke (Cottrell precipitation): Smoke is a colloidal solution of carbon, arsenic compounds, dust particles etc. in air.

The smoke before coming out of the chimney is passed through a chamber (Cottrell precipitator)containing plates having a charge opposite to that of smoke particles.

Thus neutralization of charges occurs and the particles settle down and pure air flows out of the chimney.

3. Purification of drinking water: The water obtained from natural sources often contains suspended impurities. In order to coagulate these impurities, alum is added to water.

The positive ions present in alum neutralize the suspended impurities and hence get purified.

4. Medicines: Most of the medicines are colloidal in nature. This is because they have large surface area and are therefore easily assimilated.

For example, argyrol is a silver sol used as an eye lotion. Colloidal antimony is used in curing kalaazar. Colloidal gold is used for intramuscular injection.

5. Tanning: Animal hides are colloidal in nature. When a hide, which has positively charged particles, is soaked in tannin (which contains negatively charged colloidal particles) mutual coagulation takes place. This results in the hardening of leather. This process is termed as tanning.

6. Photographic plates and films: Photographic plates or films are prepared by coating an emulsion of the light sensitive silver bromide in gelatin over glass plates or celluloid films.

7. Rubber industry: Rubber latex is a colloidal solution of rubber particles which are negatively charged. Rubber is obtained by coagulation of the latex.

8. Food articles: Milk, butter, halwa, ice creams, fruit juices, etc., are all colloids in nature.

9. Blood: Blood is a colloidal solution of an albuminoid substance. When alum and ferric chloride ($FeCl_3$) solution are added to blood, then coagulation of particles take place which results in clotting of blood.

10. Industrial products: Paints, inks, synthetic plastics, rubber, graphite lubricants, cement, etc., are all colloidal in nature.

6.General Principles and Processes of Isolation of Elements

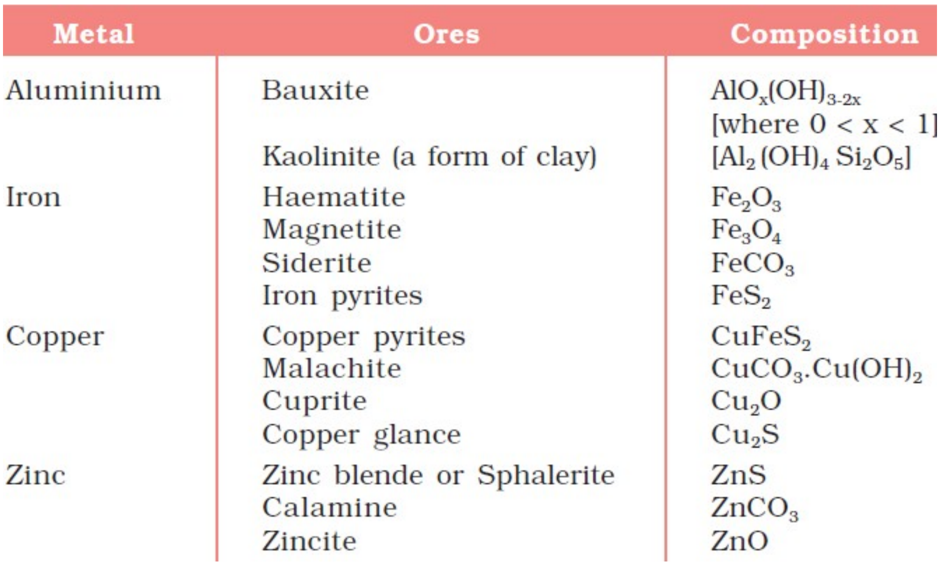
Minerals: Which are naturally occurring chemical substances in the earth’s crust which includes Metal and impurities.

Ores: The Minerals in which metal is extracted profitably called ores.

Ex: Copper glance (Cu_2S), Haematite (Fe_2O_3)

Gangue: Undesired materials which present along with the metal in the earth crust known as gangue.

Metallurgy: The entire scientific and technological process used for isolation of the metal from its ores is known as metallurgy



Metal	Ores	Composition
Aluminium	Bauxite	$AlO_x(OH)_{3-2x}$ [where $0 < x < 1$]
	Kaolinite (a form of clay)	$[Al_2(OH)_4 Si_2O_5]$
Iron	Haematite	Fe_2O_3
	Magnetite	Fe_3O_4
	Siderite	$FeCO_3$
	Iron pyrites	FeS_2
Copper	Copper pyrites	$CuFeS_2$
	Malachite	$CuCO_3.Cu(OH)_2$
	Cuprite	Cu_2O
	Copper glance	Cu_2S
Zinc	Zinc blende or Sphalerite	ZnS
	Calamine	$ZnCO_3$
	Zincite	ZnO

The extraction and isolation of metals from ores involve the following major steps:

A) Concentration of the ore (or) Purification of the Ore

B) Isolation of the metal from its concentrated ore

C) Purification of the metal (Or) Refining of the Metal.

A) Concentration of the ore (or) Purification of the Ore:

i) Hand picking: In this process the earthy impurities (heavy impurities) which are present in the ore like rocky materials, pellets are picked with hand.

ii) Hydraulic washing:

In this process the lighter impurities are removed.

The ore is fed in to the tank from the top, and the water is allowed with high pressure from the bottom of the tank.

During this process the lighter impurities which are adhere to the ore float over the water which can be removed .

The ore particles will settle down at the bottom of the tank.

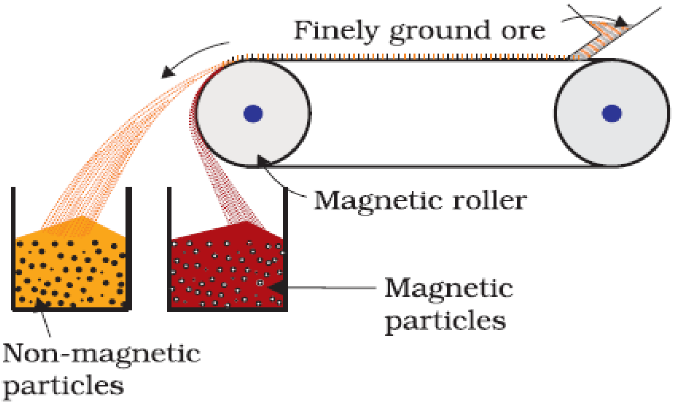
iii) Electromagnetic Separation:

This process is used for the Iron ore only.

The ore is passed through a belt which is connected by two rotating wheels, one among is made up of magnetic material.

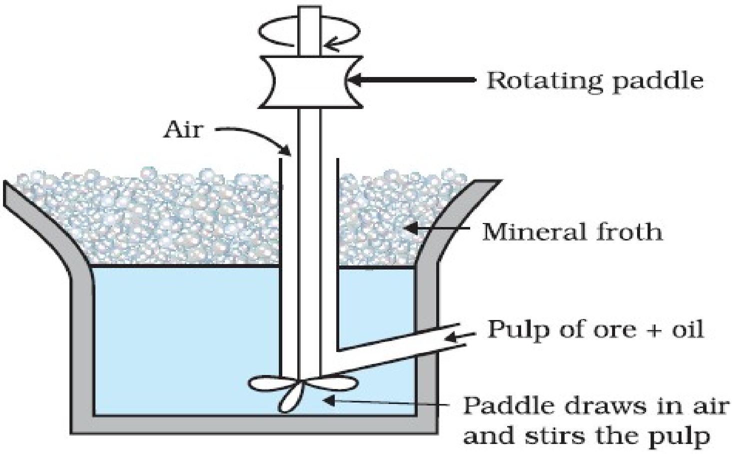
Once the ore is passed through the belt, the ore particles are attracted by the magnetic wheel, and fall near to it.

The impurities which are nonmagnetic are not attracted by the magnetic wheel, and fall away from the magnetic wheel as shown in the figure.



iv) Froth Floatation Process:

Principle: The mineral particles become wet by oils while the gangue particles by water.



Method: In this process, a suspension of the powdered ore is made with water. To it, collectors and froth stabilisers are added.

A rotating paddle agitates the mixture and draws air in it. As a result, froth is formed which carries the mineral particles.

The froth is light and is skimmed off. It is then dried for recovery of the ore particles

Collectors : The chemical substances which enhance non-wettability of the mineral particles. Ex : pine oils, fatty acids, xanthates

Froth stabilizers: The chemical substances stabilise the froth. Ex: cresols, aniline.

Depressants: It is possible to separate two sulphide ores by adjusting proportion of oil to water.

For example, in case of an ore containing ZnS and PbS, the depressant used is NaCN. It electively prevents ZnS from coming to the froth but allows PbS to come with the froth.

V) Leaching: It is often used if the ore is soluble in some suitable solvent. It is chemical method used for purification of ore.

The following examples illustrate the procedure:

(a) Leaching of Alumina from Bauxite:

→ The ore consists of two chemical impurities a) Iron oxide (Fe_2O_3) b) Silica (SiO_2). These impurities are removed in the following process.

The ore is treated with Sodium hydroxide solution (NaOH), in which Iron oxide (Fe_2O_3) impurity does not react with it and can be removed by filtration.

$$Al_2O_3 + 2NaOH + 3H_2O \longrightarrow Na[Al(OH)_4]$$

The aluminate in solution is neutralised by passing CO_2 gas and hydrated Al_2O_3 is precipitated.

$$2Na[Al(OH)_4] + CO_2 \longrightarrow Al_2O_3.xH_2O + NaHCO_3$$

$Al(OH)_3$ is ignited to get pure Bauxite called Alumina.

$$Al_2O_3.xH_2O \xrightarrow{heat} Al_2O_3\,(s) + 3\,H_2O$$

(b) Leaching of Silver Ore :

→ In the metallurgy of silver and that of gold, the respective metal is leached with a dilute solution of NaCN or KCN in the presence of air (for O_2) from which the metal is obtained later by replacement.

$$4Au + 8NaCN + 2H_2O + O_2 \longrightarrow 4Na[Au(CN)_2 + 4NaOH$$

$$2Na[Ag(CN)_2] + Zn \longrightarrow Na_2[Zn(CN_4] + 2Ag$$

B) Isolation of the metal from its concentrated ore:

i) Conversion of Ore in to Metal oxide:

Roasting: The process in which the ores are heated in presence of excess of oxygen. This process is mainly used for Sulphide ores.

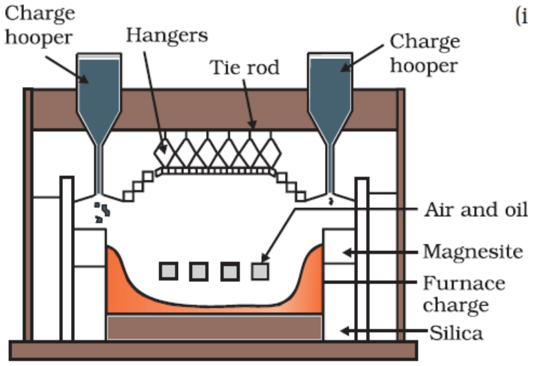
$$ZnS + O_2 \longrightarrow ZnO + SO_2$$

Calcination: It involves heating when the volatile matter escapes leaving behind the metal oxide.This process is mainly used for Carbonate and hydroxide ores.

$$Fe_2O_3.xH_2O \longrightarrow Fe_2O_3 + xH_2O$$

$$ZnCO_3 \longrightarrow ZnO + CO_2$$

$$CaCO_3.MgCO_3 \longrightarrow CaO + MgO + 2CO_2$$



ii) Conversion of Metal oxide in to Metal through Thermodynamical principles:

Reduction of the metal oxide usually involves heating it with some other substance acting as a reducing agent (C or CO or even another metal). The reducing agent (e.g., carbon) combines with the oxygen of the metal oxide.

$$MxOy + yC \longrightarrow xM + yCO$$

Some metal oxides get reduced easily while others are very difficult to be reduced. In any case, heating is required. To understand the variation in the temperature requirement for thermal reductions (pyrometallurgy) and to predict which element will suit as the reducing agent for a given metal oxide (MxOy), Gibbs energy interpretations are made.

The change in Gibbs energy, ΔG for any process at any specified temperature, is described by the equation:

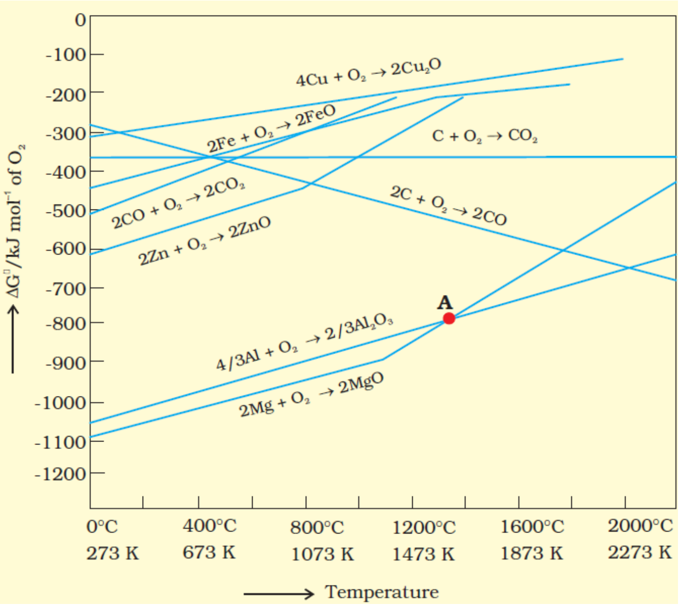
$$\Delta G = \Delta H - T\Delta S$$

where, ΔH is the enthalpy change and ΔS is the entropy change for the process.

1. If the value of ΔG is negative then only then the reaction will proceed. If ΔS is positive, on increasing the temperature (T), the value of $T\Delta S$ would increase ($\Delta H < T\Delta S$) and then ΔG will become –ve.

2. If reactants and products of two reactions are put together in a system and the net ΔG of the two possible reactions is –ve, the overall reaction will occur. So the process of interpretation involves coupling of the two reactions, getting the sum of their ΔG and looking for its magnitude and sign. Such coupling is easily understood through Gibbs energy (ΔG) vs T plots for formation of the oxides in Ellingham Diagram.

Ellingham Diagram provides a suitable reducing agent in the reduction of oxides. Such diagrams help us in predicting the feasibility of thermal reduction of an ore.



Ellingham Diagram

The following examples explains better understanding of Ellingham Diagram in reduction of metal oxide to metal using suitable reducing agent at different temperatures.

Extraction of some metals from their metal oxides:

1) Iron from Iron oxide:

a) Removal of chemical impurity:

Silica (SiO_2) is a chemical impurity which is acidic in nature present along with the ore.

A basic flux like calcium oxide (CaO) is added to remove Silica.

CaO is obtained from the Lime stone ($CaCO_3$) which decomposes to CaO and CO_2 in the furnace due to intense heat.

$$CaCO_3 \longrightarrow CaO + CO_2.$$

The impurity SiO_2, combines with CaO to form calcium silicate ($CaSiO_3$) called Slag.

$$CaO + SiO_2 \longrightarrow CaSiO_3.$$

b) Extraction of Iron:

The pure Haematite ore, Ferric oxide (Fe_2O_3) is reduced to iron in presence of a reducing agent Coke (carbon).

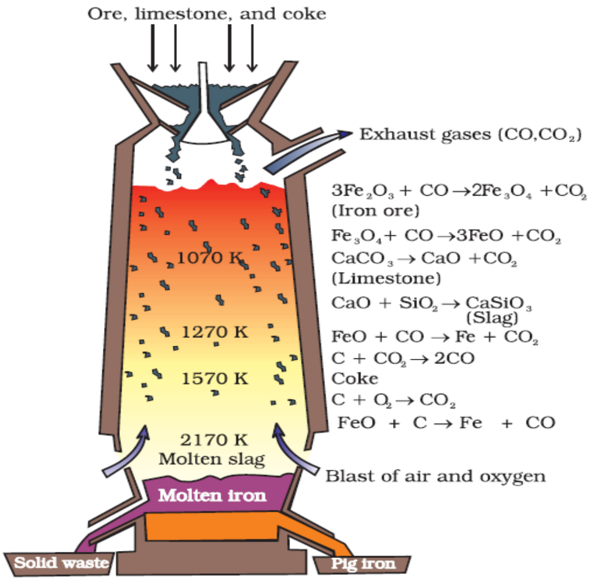
Coke (C) combines with CO_2 to form carbon monoxide which is a very good reducing agent which reduces Fe_2O_3 in to Iron (Fe).

$$C\ (Coke) + CO_2 \longrightarrow 2CO$$

$$Fe_2O_3 + 3\ CO \longrightarrow 2Fe\ (molten) + 3\ CO_2$$

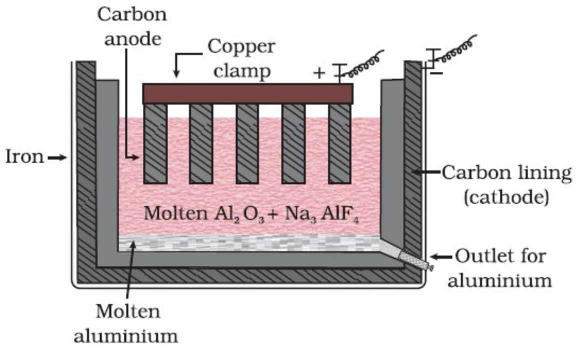
The slag calcium silicate ($CaSiO_3$), is lighter than molten Iron which floats over the molten iron and also which also prevents the molten Iron to oxidize in presence of oxygen in the furnace.

The slag and the molten Iron are collected separately as shown in the figure.



2) Aluminium from Alumina (Aluminium oxide):

Electrolytic Reduction : Hall's Process :



The Pure Alumina having high melting point i.e 2348K., it is highly expensive to carry the electrolytic reduction process at this temperature. To reduce the melting point and by increase the electrical conductivity of Alumina a substance called Cryolite (Na_3AlF_6) is added.

The electrolytic reduction process carried as shown as

$$\text{Cathode reaction : } Al^{+3} + 3e^{-} \longrightarrow Al$$

$$\text{Anode Reaction : } 2O^{-2} - 4e^{-} \longrightarrow O_2$$

The oxygen gas liberated at anode reacts with graphite anode and form CO_2 gas, so anode is to be replaced from time to time.

$$C_{(graphite)} + O_2 \longrightarrow CO_2 .$$

The pure aluminium (Al) is collected from the cathode from time to time.

3) Copper from Copper Oxide :

a) Removal of chemical impurity:

The ore contains FeO is a basic impurity which is removed by adding an acidic flux silica. Iron oxide 'slags of' as iron silicate and copper is produced in the form of copper matte. This contains **Cu_2S and FeS.**

$$\underset{(Slag)}{FeO + SiO_2 \dashrightarrow FeSiO_3}$$

Copper matte is then charged into silica lined convertor. hot air blast is blown to convert the remaining FeS_2, FeO and Cu_2S/Cu_2O to the metallic copper. Following reactions take place:

$$2FeS + 3O_2 \dashrightarrow 2FeO + 2SO_2$$

$$FeO + SiO_2 \dashrightarrow FeSiO_3$$

b) Extraction of Copper:Auto reduction/ Self Reduction:

Method 1: Process takes place in a reverbatory furnace:

Hot air is blown to convert the Cu_2S to Cu_2O. The Cu_2O formed converted in to metallic copper in the presence of remaining Cu_2S which acts as a reducing agent.

$$2Cu_2S + 3O_2 \dashrightarrow 2Cu_2O + 2SO_2$$

$$2Cu_2O + Cu_2S \dashrightarrow 6Cu + SO_2$$

The solidified copper obtained has blistered appearance due to the evolution of SO_2 and so it is called blister copper.

Method 2: Process takes place with the help of a reducing agent C/CO :

In the Ellingams diagram the Cu_2O line is almost at the top.

So it is quite easy to reduce oxide ores of copper directly to the metal by heating with coke (both the lines of C, CO and C, CO_2 are at much lower positions in the graph particularly after 500 – 600K).

The sulphide ores are roasted/smelted to give oxides

$$2Cu_2S + 3O_2 \dashrightarrow 2Cu_2O + 2SO_2$$

The oxide can then be easily reduced to metallic copper using coke:

$$Cu_2O + C \rightarrow 2\ Cu + CO$$

4) Extraction of zinc from zinc oxide:

The reduction of zinc oxide is done using coke. The temperature in this case is higher than that in case of copper. For the purpose of heating, the oxide is made into brickettes with coke and clay.

$$ZnO + C\ (coke) \dashrightarrow Zn + CO \text{ at } 673K$$

The metal is distilled off and collected by rapid chilling.

C) Purification of the metal (Or) Refining of the Metal:

A metal extracted by any method is usually contaminated with some impurity. For obtaining metals of high purity, several techniques are used depending upon the differences in properties of the metal and the impurity. Some of them are listed below.

(a) Distillation:

This is very useful for low boiling metals like zinc and mercury. The impure metal is evaporated to obtain the pure metal as distillate.

(b) Liquation:

In this method a low melting metal like tin can be made to flow on a sloping surface. In this way it is separated from higher melting impurities.

(c) Electrolytic refining:

In this method,

- The impure metal is made to act as anode.
- A strip of the same metal in pure form is used as cathode.
- They are put in a suitable electrolytic bath containing soluble salt of the same metaL
- The more basic metal remains in the solution and the less basic ones go to the anode mud.
- The reactions are:

$$\text{Anode:} \quad M \longrightarrow M^{n+} + ne^-$$

$$\text{Cathode:} \quad M^{n+} + ne^- \longrightarrow M$$

Example: Copper is refined using an electrolytic method. Anodes are of impure copper and pure copper strips are taken as cathode. The electrolyte is acidified solution of copper sulphate and the net result of electrolysis is the transfer of copper in pure form from the anode to the cathode:

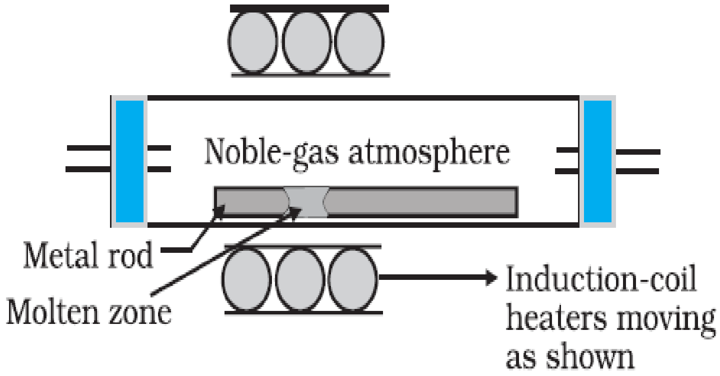
$$\text{Anode: } Cu \longrightarrow Cu^{2+} + 2e^-$$

$$\text{Cathode: } Cu^{2+} + 2e^- \longrightarrow Cu$$

Impurities from the blister copper deposit as anode mud which contains antimony, selenium, tellurium, silver, gold and platinum.

(d) Zone refining :

Principle: The impurities are more soluble in the melt than in the solid state of the metal.



Method: Circular mobile heater is fixed at one end of a rod of the impure metal. The molten zone moves along with the heater which is moved forward. As the heater moves forward, the pure metal crystallises out of the melt and the impurities pass on into the adjacent molten zone.

The process is repeated several times and the heater is moved in the same direction. At one end, impurities get concentrated.

This end is cut off.

This method is very useful for producing semiconductor and other metals of very high purity, e.g., germanium, silicon, boron, gallium and indium.

(e) Vapour phase refining :

In this method, the metal is converted into its volatile compound. It is then decomposed to give pure metal. So, the two requirements are:

(i) The metal should form a volatile compound with an available reagent,

(ii) The volatile compound should be easily decomposable, so that the recovery is easy.

Examples :.

1) Mond Process for Refining Nickel:

In this process, nickel is heated in a stream of carbon monoxide forming a volatile complex, nickel tetracarbonyl.

$$Ni + 4CO \xrightarrow{330-350\,K} Ni(CO)_4$$

The carbonyl is subjected to higher temperature so that it is decomposed giving the pure metal

$$Ni(CO)_4 \xrightarrow{450-470\,K} Ni + 4CO$$

2) Van Arkel Method for Refining Zirconium or Titanium:

This method is very useful for removing all the oxygen and nitrogen present in the form of impurity in certain metals like Zr and Ti.

The crude metal is heated in an evacuated vessel with iodine. The metal iodide being more covalent, volatilizes.

$$Zr + 2I_2 \longrightarrow ZrI_4$$

The metal iodide is decomposed on a tungsten filament, electrically heated to about 1800K. The pure metal is thus deposited on the filament.

$$ZrI_4 \longrightarrow Zr + 2I_2$$

(f) Chromatographic methods:

Principle: This method is based on the principle that different components of a mixture are differently adsorbed on an adsorbent.

Method: The mixture is put in a liquid medium which is moved through the adsorbent.

Different components are adsorbed at different levels on the column. Later the adsorbed components are removed by using suitable solvents.

Column chromatography: In one such method the column of Al_2O_3 is prepared in a glass tube and the moving medium containing a solution of the components is in liquid form.

This is very useful for purification of the elements which are available in minute quantities and the impurities are not very different in chemical properties from the element to be purified.

7. THE P-BLOCK ELEMENTS

The elements in which the last electron enters in the valence p-sub shell are called the
p-block elements.

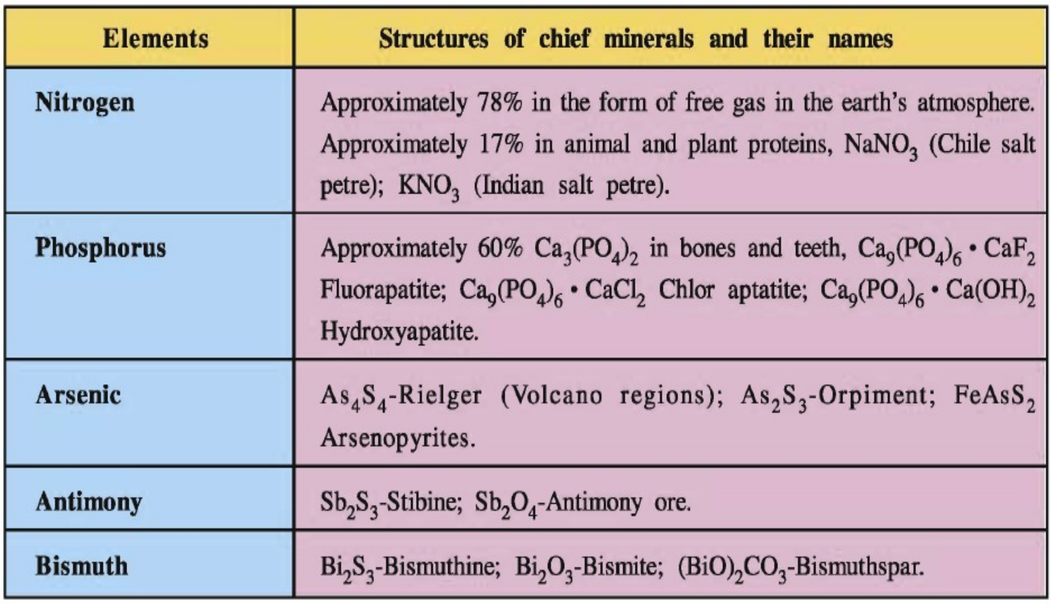
They include elements of the groups 13 to 18. Their general outer electronic configuration is ns^2np^{1-6} (except He which has $1s^2$ configuration).They includes metals, non-metals and metalloids.

Group 15 Elements

Group15 includes nitrogen(N),phosphorus (P),arsenic(As),antimony(Sb)and bismuth (Bi).

Elements	**Electronic configuration ($ns^2\ np^3$)**
$_{7}N$	$[He]\,2s^2 2p^3$
$_{15}P$	$[Ne]\,3s^2 3p^3$
$_{33}As$	$[Ar]\,3d^{10} 4s^2 4p^3$
$_{51}Sb$	$[Kr]\,4d^{10} 5s^2 5p^3$
$_{83}Bi$	$[Xe]\,4f^{14} 5d^{10} 6s^2 6p^3$

Occurrence



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, $Ca_9(PO_4)_6 \cdot CaF_2$ Fluorapatite; $Ca_9(PO_4)_6 \cdot CaCl_2$ Chlor aptatite; $Ca_9(PO_4)_6 \cdot Ca(OH)_2$ Hydroxyapatite.
Arsenic	As_4S_4-Rielger (Volcano regions); As_2S_3-Orpiment; $FeAsS_2$ Arsenopyrites.
Antimony	Sb_2S_3-Stibine; Sb_2O_4-Antimony ore.
Bismuth	Bi_2S_3-Bismuthine; Bi_2O_3-Bismite; $(BiO)_2CO_3$-Bismuthspar.

- As we go down the group, the metallic character increases. Nitrogen and phosphorus are non-metals, arsenic and antimony metalloids and bismuth is a typical metal.
- The valence shell electronic configuration of these elements is ns^2np^3.
- The s orbital in these elements is completely filled and p orbitals are half-filled, making their electronic configuration extra stable.
- Covalent and ionic radii increase down the group.
- There is a considerable increase in covalent radius from N to P. However, from As to Bi only a small increase in covalent radius is observed.
- This is due to the presence of completely filled d or f orbitals in heavier members. Ionisation enthalpy decreases down the group due to gradual increase in atomic size.
- Because of the extra stable half-filled p orbitals and smaller size, the ionisation enthalpy of the group 15 elements is much greater than that of group 14 elements.

Oxidation states and trends in chemical reactivity

- The common oxidation states of these elements are –3, +3 and +5. The tendencies to exhibit –3 oxidation state decreases down the group due to increase in size and metallic character.

- The last member of the group, bismuth does not form any compound in –3 oxidation state. The stability of +5 oxidation state decreases and that of +3 state increases (due to inert pair effect) down the group.
- Nitrogen exhibits +1,+2, and +4 oxidation states also when it reacts with oxygen. Phosphorus also shows +1 and +4oxidation states in some oxoacids.
- Nitrogen is restricted to a maximum covalency of 4 since only fourorbitals (one s and three p) are available for bonding.

Anomalous properties of nitrogen

Nitrogen differs from the rest of the members of this group due to its smaller size, high electro negativity, high ionisation enthalpy and non-availability of d orbitals.
Some of the anomalous properties shown by nitrogen are:

1. Nitrogen has the ability to form **p**p-**p**p **multiple** bonds with itself and with other elements like C and O. Other elements of this group do not form pp-pp bonds.
2. Nitrogen exists as a diatomic molecule with an N≡ N triple bond. So its bond enthalpy is very high. While other elements of this group are poly atomic with single bonds.
3. The N–N single bond is weak. So the catenation tendency is weaker in nitrogen.
4. Due to the absence of d orbitals in its valence shell, the maximum covalency of nitrogen is four.
5. N cannot form **d**p–**p**p **bond or d**p–**d**p **bond.** While Phosphorus and arsenic can form **d**p–**d**p **bond** with transition metals and with C and O.

Hydrides of Group 15 Elements

- All the elements of Group 15 form hydrides of the type EH_3 (where E= N, P, As, Sb or Bi).
- E.g. NH_3 – ammonia, PH_3-Phosphine, AsH_3-Arsine, SbH_3-Stebine and
- BiH_3-Bismuthine.The hydrides show regular gradation in their properties.
- In hydrides, as the size of the central atom (E) increases, the bond length (E-H) increases and hence the bond dissociation enthalpy of E – H decreases from NH_3 to BiH_3. So the thermal stability decreases from NH_3 to BiH_3 and the reducing character increases.
- All the hydrides contain a lone pair of electrons on the central atom. So they act as Lewis bases (i.e. lone pair electron donors).
- The basicity decreases in the order $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.
- This is because as the atomic size increases, the electron density on the central atom decreases.
- The melting point of these hydrides increases from top to bottom. This is due to increase in the atomic size of the central atom which increases the van der Waal's force of attraction. NH_3 has the highest melting and boiling points due to inter molecular hydrogen bonding.

Q1.Though nitrogen exhibits +5 oxidation state, it does not form pentahalides. Give reason.

Nitrogen with n = 2, has s and p orbitals only. It does not have d orbitals to expand its covalence beyond four. So it cannot form pentahalides.

Q2. PH3 has lower boiling point than NH_3. Why?

Unlike NH_3, PH_3 molecules are not associated through inter molecular hydrogen bonding in liquid state.
That is why the boiling point of PH_3 is lower than NH_3.

Dinitrogen (N_2)

Preparation: Dinitrogen is produced commercially by the liquefaction and fractional distillation of air.
In the laboratory, dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.

$$NH_4Cl(aq) + NaNO_2(aq) \longrightarrow N_2(g) + 2H_2O(l) + NaCl\ (aq)$$

It can also be obtained by the thermal decomposition of ammonium dichromate.

$$(NH4)_2Cr_2O_7 \xrightarrow{heat} N_2 + 4H_2O + Cr_2O_3$$

Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide. $Ba(N_3)_2 \xrightarrow{heat} Ba + 3N_2$

Properties

Dinitrogen is inert at room temperature because of the high bond enthalpy of N≡N bond. At higher temperatures, it directly combines with some metals to form ionic nitrides and with non-metals to form covalent nitrides.

$$6Li + N_2 \xrightarrow{heat} 2Li_3N$$

$$3Mg + N_2 \xrightarrow{heat} Mg_3N_2$$

It combines with hydrogen at about 773 K in the presence of a catalyst (spongy iron) to form ammonia (Haber's Process).

$$N_2 + 3H_2 \xrightarrow{Fe,\ 773K} 2NH_3$$

Dinitrogen combines with dioxygen at very high temperature (at about 2000 K) to form nitric oxide. $N_2 + O_2 \longrightarrow 2\,NO$

Uses: 1. The main use of dinitrogen is in the manufacture of ammonia and other industrial chemicals containing nitrogen (e.g., calcium cyanamide).

2. It also used to create an inert atmosphere in metallurgy.

3. Liquid dinitrogen is used as a refrigerant to preserve biological materials, food items and in cryosurgery.

Ammonia

Preparation: In laboratory, ammonia is obtained by treating ammonium salts with caustic soda (NaOH) or slaked lime.

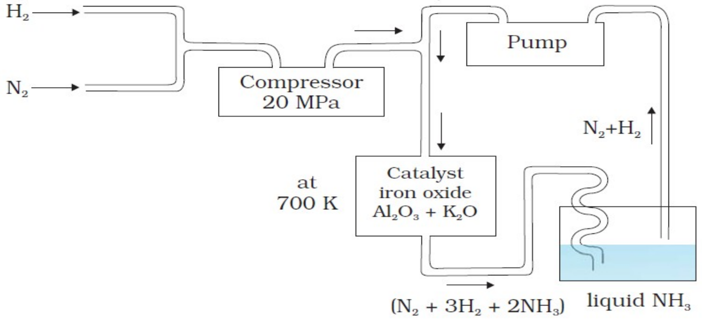
$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3 + 2H_2O + Na_2SO_4$$

$$2NH_4Cl + Ca(OH)_2 \longrightarrow 2NH_3 + 2H_2O + CaCl_2$$

On a large scale, ammonia is manufactured by Haber's process.

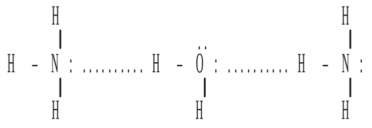
$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

In accordance with Le Chatelier's principle, high pressure of about 200 atm, a temperature of about 700K and the catalyst such as iron oxide with small amount of K_2O and Al_2O_3 are employed to increase the rate of this reaction.



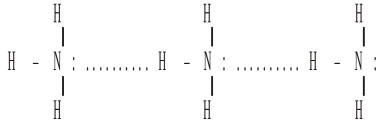
Properties

Ammonia is a colourless gas with pungent smell. It is highly soluble in water because of its ability to form inter molecular hydrogen bond with water.



hydrogen bonding between NH_3 and H_2O molecules

Liquid ammonia has high melting and boiling points because of inter molecular hydrogen bonding.



intermolecular hydrogen bonding in ammonia

The ammonia molecule has a trigonal pyramidal geometry. It has three bond pairs and one lone pair of electrons.

Its aqueous solution is weakly basic due to the formation of OH^- ions.

$$NH_3(g) + H_2O(l) \longrightarrow NH_4^+(aq) + OH^-(aq)$$

As a weak base, it precipitates the hydroxides of many metals from their salt solutions. For example,

$$2FeCl_3(aq) + 3NH_4OH(aq) \longrightarrow Fe_2O_3.xH_2O(s) + 3NH_4Cl(aq)$$

$$ZnSO_4(aq) + 2NH_4OH(aq) \longrightarrow Zn(OH)_2(s) + (NH_4)_2SO_4(aq)$$

The presence of a lone pair of electrons on the nitrogen atom of the ammonia molecule makes it a Lewis base. It donates the electron pair and forms complex compounds with Cu2+, Ag+ etc. So it is used for the detection of these metal ions.

$$\underset{\text{(blue)}}{Cu^{2+}(aq)} + 4NH_3(aq) \longrightarrow \underset{\text{(deep blue)}}{[Cu(NH_3)_4]^{2+}(aq)}$$

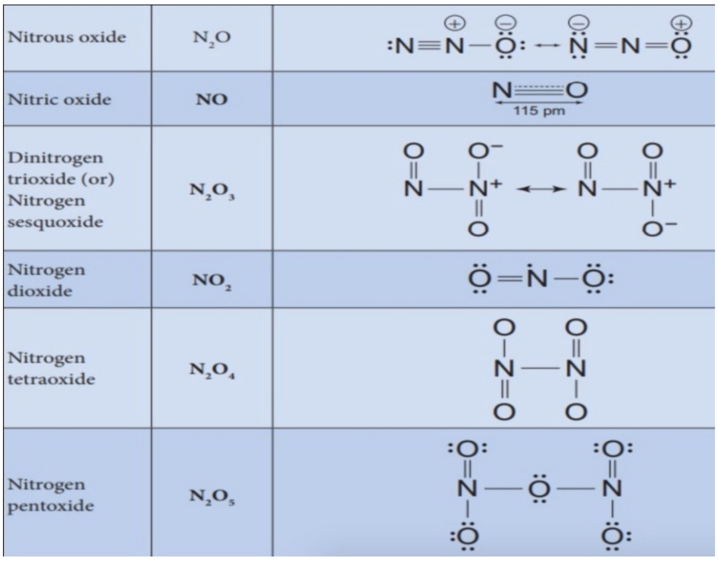
$$\underset{\text{(colourless)}}{Ag^+(aq)} + Cl^-(aq) \longrightarrow \underset{\text{(white ppt)}}{AgCl(S)}$$

$$\underset{\text{(white ppt)}}{AgCl} + 2NH_3(aq) \longrightarrow \underset{\text{(colourless)}}{[Ag(NH_3)_2]Cl(aq)}$$

Uses: Ammonia is used i) to produce various nitrogenous fertilizers (ammonium nitrate, urea, ammonium phosphate and ammonium sulphate) ii) in the manufacture of nitric acid iii) liquid ammonia is used as a refrigerant.

Oxides of Nitrogen

Nitrogen forms a number of oxides in different oxidation states. They are:



Nitrous oxide	N_2O
Nitric oxide	NO
Dinitrogen trioxide (or) Nitrogen sesquoxide	N_2O_3
Nitrogen dioxide	NO_2
Nitrogen tetraoxide	N_2O_4
Nitrogen pentoxide	N_2O_5

Nitric Acid (HNO_3)

Preparation: In the laboratory, nitric acid is prepared by heating KNO_3 or $NaNO_3$ and concentrated H_2SO_4 in a glass retort.

$$NaNO_3 + H_2SO_4 \longrightarrow NaHSO_4 + HNO_3$$

On a large scale it is prepared by **Ostwald's process**. It involves three steps:

1. The catalytic oxidation of NH_3 by atmospheric oxygen in presence of platinum/ rhodium gauge (wire) catalyst.

$$4NH_3(g) + 5O_2(g) \xrightarrow{Pt/Rh\ gauge\ catalyst,\ 500K\ \&\ 9\ bar} 4NO(g) + 6H_2O(g)$$

2. The nitric oxide is converted to NO_2

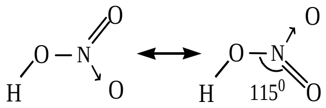
$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

3. Absorption of nitrogen dioxide in water to get nitric acid.

$$3NO_2(g) + H_2O(l) \longrightarrow 2NO_3(aq) + NO(g)$$

The aqueous HNO_3 can be concentrated by distillation up to 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H_2SO_4. 98% HNO_3 is known as fuming nitric acid.

Properties: It is a colourless liquid. In the gaseous state,HNO_3 exists as a planar molecule with the structure as shown below:



In aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions. $HNO_3(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + NO_3^-(aq)$

Concentrated nitric acid is a strong oxidising agent and attacks most metals except noble metals such as gold and platinum. The products of oxidation depend upon the concentration of the acid, temperature and the nature of the material undergoing oxidation.

$$3Cu + 8HNO_3(dilute) \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$$

$$Cu + 4HNO_3(conc.) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$$

Zinc reacts with dilute nitric acid to give N_2O and with concentrated acid to give NO_2.

$$4Zn + 10HNO_3(dilute) \longrightarrow 4\,Zn(NO_3)_2 + 5H_2O + N_2O$$

$$Zn + 4HNO_3(conc.) \longrightarrow Zn(NO_3)_2 + 2H_2O + 2NO_2$$

Some metals (e.g., Cr, Al) do not dissolve in concentrated nitric acid because of the formation of a passive film of oxide on the surface.

Concentrated nitric acid also oxidises non–metals and their compounds.

Iodine is oxidised to iodic acid,carbon to carbon dioxide,sulphur to H_2SO_4, and phosphorus to phosphoric acid.

$$I_2 + 10HNO_3 \longrightarrow 2HIO_3 + 10NO_2 + 4H_2O$$

$$C + 4HNO_3 \longrightarrow CO_2 + 2H_2O + 4NO_2$$

$$S_8 + 48HNO_3(conc.) \longrightarrow 8H_2SO_4 + 48NO_2 + 16H_2O$$

$$P_4 + 20HNO_3(conc.) \longrightarrow 4H_3PO_4 + 20NO_2 + 4H_2O$$

Brown Ring Test: It is a test used for the detection of nitrates. The test is carried out by adding dilute ferrous sulphate solution to an aqueous solution containing nitrate ion, and then carefully adding concentrated sulphuric acid along the sides of the test tube. A brown ring at the interface between the solution and sulphuric acid layers indicate the presence of nitrate ion in solution.

$$NO_3^- + 3Fe^{2+} + 4H^+ \longrightarrow NO + 3Fe^{3+} + 2H_2O$$

$$[Fe(H_2O)_6]^{2+} + NO \longrightarrow \underset{\text{(brown ring)}}{[Fe(H_2O)_5(NO)]^{2+}} + H_2O$$

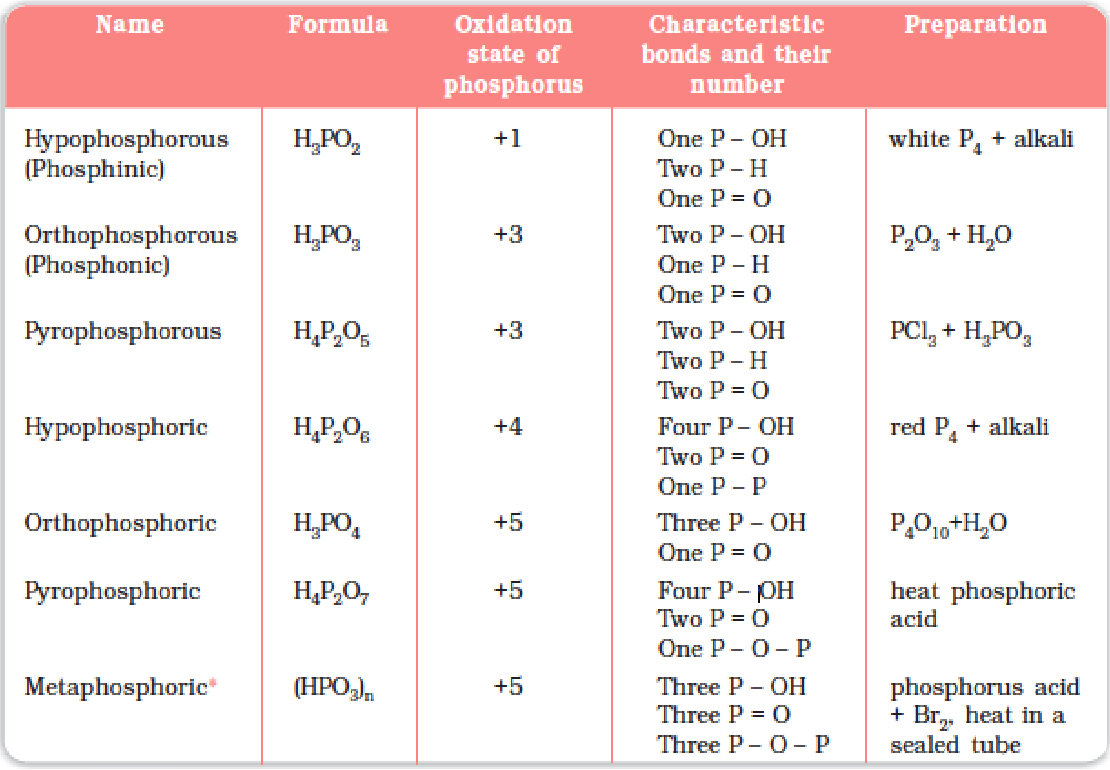
Uses: It is used

i) in the manufacture of ammonium nitrate for fertilizers and other nitrates for use in explosives and pyrotechnics.

ii) for the preparation of nitro-glycerine, trinitrotoluene and other organic nitro compounds.

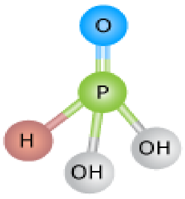
iii) in the pickling of stainless steel, etching of metals and as an oxidiser in rocket fuels.

Oxoacids of Phosphorus: Phosphorus forms a number of oxoacids.

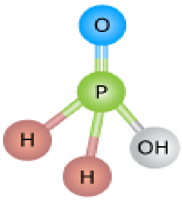


Name	Formula	Oxidation state of phosphorus	Characteristic bonds and their number	Preparation
Hypophosphorous (Phosphinic)	H_3PO_2	+1	One P – OH Two P – H One P = O	white P_4 + alkali
Orthophosphorous (Phosphonic)	H_3PO_3	+3	Two P – OH One P – H One P = O	$P_2O_3 + H_2O$
Pyrophosphorous	$H_4P_2O_5$	+3	Two P – OH Two P – H Two P = O	$PCl_3 + H_3PO_3$
Hypophosphoric	$H_4P_2O_6$	+4	Four P – OH Two P = O One P – P	red P_4 + alkali
Orthophosphoric	H_3PO_4	+5	Three P – OH One P = O	$P_4O_{10}+H_2O$
Pyrophosphoric	$H_4P_2O_7$	+5	Four P – OH Two P = O One P – O – P	heat phosphoric acid
Metaphosphoric*	$(HPO_3)_n$	+5	Three P – OH Three P = O Three P – O – P	phosphorus acid + Br_2, heat in a sealed tube

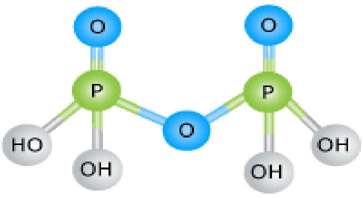
* *Exists in polymeric forms only. Characteristic bonds of $(HPO_3)_3$ have been given in the Table.*



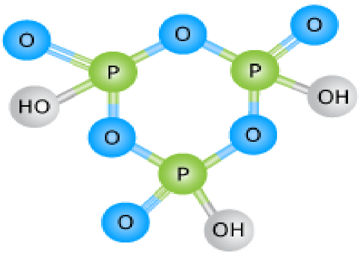
H_3PO_4
Orthophosphoric acid



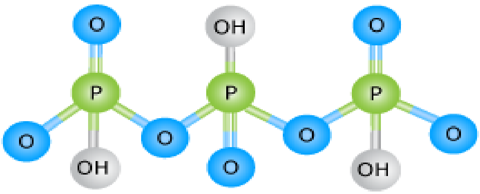
H_3PO_2
Hypophosphorous acid



$H_4P_2O_7$
Pyrophosphoric acid



Orthophosphoric acid, $(HPO_3)_3$



Polymetaphosphoric acid, $(HPO_3)_n$

Group 16 Elements

The members of this group are oxygen (O), sulphur (S), selenium (Se), tellurium (Te) and polonium (Po).

Elements	Electronic configuration ($ns^2\ np^4$)
$_8O$	$[He]\,2s^2 2p^4$
$_{16}S$	$[Ne]\,3s^2 3p^4$
$_{34}Se$	$[Ar]\,3d^{10} 4s^2 4p^4$
$_{52}Te$	$[Kr]\,4d^{10} 5s^2 5p^4$
$_{84}Po$	$[Xe]\,4f^{14} 5d^{10} 6s^2 6p^4$

They are also called chalcogens (means ore producing).

Oxygen and sulphur are non-metals, selenium and tellurium are metalloids, while polonium is a radioactive metal.

Ionisation enthalpy of these elements decreases down the group. It is due to increase in size. However, the elements of this group have lower ionisation enthalpy values compared to those of Group15 elements.

This is due to the fact that Group 15 elements have extra stable half- filled p orbitals electronicconfigurations.

Oxygen atom has less negative electron gain enthalpy than sulphur because of the compact nature of its shells due to which the electronic repulsion is greater.

Oxidation states:

- The elements of Group 16 exhibit a number of oxidation states(-2,+2,+4 & +6).
- The stability of -2 oxidation state decreases down the group.
- Since electronegativity of oxygen is very high, it shows only –2 oxidation state
- (except in the case of OF_2 where its oxidation state is + 2).
- Other elements of the group exhibit + 2, + 4 & + 6 oxidation states.
- But + 4 and + 6 are more common.
- Sulphur, selenium and tellurium usually show + 4 oxidation state in their
- compounds with oxygen and + 6 with fluorine.
- Down the group, the stability of + 6 oxidation state decreases and
- that of + 4 oxidation state increases (due to inert pair effect).

Hydrides of 16th group elements

All the elements of Group 16 form hydrides of the type H_2E (E = S, Se, Te, Po).

Their acidic character increases from H_2O to H_2Te.

This is due to the decrease in bond (H–E) dissociation enthalpy down the group.

So the thermal stability also decreases down the group.

All the hydrides except water possess reducing property and this character increases from H_2S to H_2Te.

Dioxygen (O_2)

Preparation: (i) By heating chlorates, nitrates and permanganates.

$$2KClO_3 \xrightarrow{MnO_2/\Delta} 2KCl + 3O_2$$

(ii) By the thermal decomposition of the oxides of metals low in the electrochemical series and higher oxides of some metals.

$$2Ag_2O(s) \longrightarrow 4Ag(s) + O_2(g);\ 2Pb_3O_4(s) \rightarrow 6PbO(s) + O_2(g)$$

$$2HgO(s) \longrightarrow 2Hg(l) + O2(g)\ ;\ 2PbO2(s) \rightarrow 2PbO(s) + O_2(g)$$

(iii) By the decomposition of Hydrogen peroxide (H2O2) in presence of manganese dioxide. $2H_2O_2(aq) \longrightarrow 2H_2O(1) + O2(g)$

(iv) On large scale it can be prepared from water or air. Electrolysis of water leads to the release of hydrogen at the cathode and oxygen n at the anode. It is also obtained by the fractional distillation of air.

Properties:

Dioxygen directly reacts with metals and non-metals (except with some metals like Au, Pt etc and with some noble gases).

e.g. $2Ca + O_2 \longrightarrow 2CaO$ $P_4 + O_2 \longrightarrow P_4O_{10}$

$4Al + 3O_2 \longrightarrow 2Al_2O_3$ $C + O_2 \longrightarrow CO_2$

Uses: 1) oxygen is used in oxyacetylene welding, in the manufacture of many metals, particularly steel.

2) Oxygen cylinders are widely used in hospitals, high altitude flying and in mountaineering.

3) Liquid O_2 is used in rocket fuels.

Oxides

Oxides are binary compounds of oxygen with other elements. There are two types of oxides – simple oxides (e.g., MgO, Al_2O_3) and mixed oxides (Pb_3O_4, Fe_3O_4)

Simple oxides can be further classified on the basis of their acidic, basic or amphoteric character.

An oxide that combines with water to give an acid is called acidic oxide.

(e.g., SO_2, Cl_2O_7, CO_2, N_2O_5).

Generally, non-metal oxides are acidic but oxides of some metals in higher oxidation states also have acidic character (e.g., Mn_2O_7, CrO_3, V_2O_5 etc.).

The oxide which gives an alkali on dissolved in water is known as basic oxide. (e.g. Na_2O, CaO, BaO).

Generally, metallic oxides are basic in nature.

Some metallic oxides exhibit a dual behaviour. They show the characteristics of both acidic and basic oxides. Such oxides are known as amphoteric oxides.

They react with acids as well as alkalies. E.g.: Al_2O_3, Ga_2O_3 etc.

There are some oxides which are neither acidic nor basic. Such oxides are known as neutral oxides. Examples of neutral oxides are CO, NO and N_2O.

Ozone (O_3)

Ozone is an allotropic form of oxygen.

Preparation: When a slow dry stream of oxygen is passed through a silent electric discharge, oxygen is converted to ozone. The product is known as ozonised oxygen.

$$3\ O_2(g) \longrightarrow 2\ O_3(g);\ \Delta H = +142\ kJ/mol.$$

Since the formation of ozone from oxygen is an endothermic process, a silent electric discharge should be used, unless the ozone formed undergoes decomposition.

Properties: Pure ozone is a pale blue gas, dark blue liquid and violet-black solid. Ozone has a characteristic smell.

Ozone is thermodynamically unstable with respect to oxygen since its decomposition into oxygen results in the liberation of heat (ΔH is negative) and an increase in entropy (ΔS is positive).

So the Gibbs energy change (ΔG) for this process is always negative ($\Delta G = \Delta H - T\Delta S$).

Due to the ease with which it liberates nascent oxygen ($O_3 \longrightarrow O_2 + O$), it acts as a powerful oxidising agent. For e.g., it oxidises lead sulphide to lead sulphate

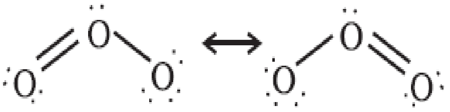
$$PbS(s) + 4O_3(g) \longrightarrow PbSO4(s) + 4O_2(g)$$

Oxides of nitrogen (particularly nitric oxide) combine very rapidly with ozone and deplete it.

Thus nitrogen oxides emitted from the exhaust systems of supersonic jet aeroplanes, slowly depleting the concentration of the ozone layer in the upper atmosphere.

$$NO(g) + O_3(g) \longrightarrow NO_2(g) + O_2(g)$$

Structure: O_3 has an angular structure. It is a resonance hybrid of the following two forms:



Uses: It is used as a germicide, disinfectant and for sterilising water. It is also used for bleaching oils, ivory, flour, starch, etc. It acts as an oxidising agent in the manufacture of potassium permanganate.

Allotropes of Sulphur

Sulphur forms a large number of allotropes. Among these **yellow rhombic** (α-sulphur) and **monoclinic** (β -sulphur) forms are the most important. The stable form at room temperature is rhombic sulphur, which transforms to monoclinic sulphur when heated above 369 K.

1. Rhombic sulphur (α-sulphur)

It is prepared by evaporating the solution of roll sulphur in CS_2. It is insoluble in water but readily soluble in CS_2.

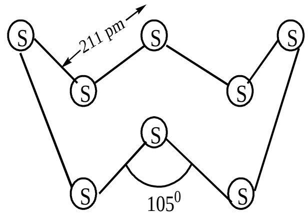
2. Monoclinic sulphur (β-sulphur)

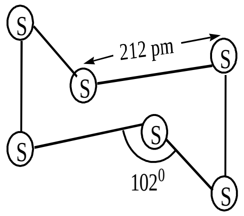
It is prepared by melting rhombic sulphur in a dish and cooling, till a crust is formed. Two holes are made in the crust and the remaining liquid is poured out.

On removing the crust, colourless needle shaped crystals of β-sulphur are formed. It is stable above 369 K and transforms into α-sulphur below it. At 369K both the forms are stable. This temperature is called **transition temperature**.

$$\alpha\text{ - Sulphur} \overset{368.5K}{\longleftrightarrow} \beta\text{ - Sulphur}$$

Both rhombic and monoclinic sulphur have S_8 molecules.
The S_8 ring in both the forms is puckered and has a crown shape.





Sulphur Dioxide (SO_2)

Preparation: 1. Sulphur dioxide is formed when sulphur is burnt in air or oxygen:

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

2. In the laboratory it is obtained by treating a sulphite with dilute sulphuric acid.

$$SO_3^{2-}(aq) + 2H^+(aq) \longrightarrow H_2O(l) + SO_2(g)$$

3. Industrially, it is produced by roasting of sulphide ores.

$$4\,FeS_2(s) + 11O_2(g) \longrightarrow 2\,Fe_2O_3(s) + 8SO_2(g)$$

Properties: Sulphur dioxide is a colourless gas with pungent smell and is highly soluble in water.

With water, it forms a solution of sulphurous acid which is a dibasic acid and form two types of salts with alkalies – normal salt (sulphite) and acid salt (bisulphate or hydrogen sulphite).

$$SO_2(g) + H_2O(l) \longrightarrow H_2SO_3(aq)$$

With sodium hydroxide solution, it forms sodium sulphite, which then reacts with more sulphur dioxide to form sodium hydrogen sulphite.

$$2NaOH + SO_2 \longrightarrow Na_2SO_3 + H_2O$$

$$Na_2SO_3 + H_2O + SO_2 \longrightarrow 2NaHSO_3$$

SO_2 is oxidised to sulphur trioxide by oxygen in the presence of vanadium pentoxide (V_2O_5) catalyst.

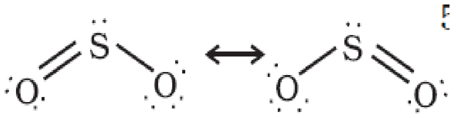
$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

Moist sulphur dioxide behaves as a reducing agent. It converts iron(III) ions to iron(II) ions and decolourises acidified potassium permanganate(VII) solution (This used as a test for SO_2).

$$2Fe^{3+} + SO_2 + 2H_2O \longrightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

$$5\,SO_2 + 2MnO_4^- + 2H_2O \longrightarrow 5\,SO_4^{2-} + 4H^+ + 2Mn^{2+}$$

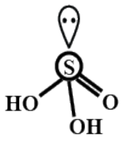
Structure: SO_2 has an angular shape. It is a resonance hybrid of the following two canonical forms:



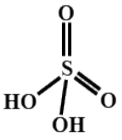
Uses: Sulphur dioxide is used (i) in refining petroleum and sugar (ii) in bleaching wool and silk and (iii) as an anti-chlor, disinfectant and preservative (iv) for the production of Sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite (v) Liquid SO_2 is used as a solvent to dissolve a number of organic and inorganic chemicals.

Oxoacids of Sulphur

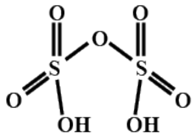
Sulphur forms a number of oxoacids such as Sulphurous acid (H_2SO_3),Thiosulphuric acid ($H_2S_2O_3$),Dithionous acid ($H_2S_2O_4$),Peroxomonosulphuric acid (Caros acid, H_2SO_5), Sulphuric acid (H_2SO_4),Pyrosulphuric acid (oleum, $H_2S_2O_7$),Peroxodisulphuric acid ($H_2S_2O_8$). Structures of some important oxoacids are:



sulphurous acid
(H_2SO_3)

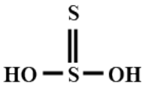


sulphuric acid
(H_2SO_4)

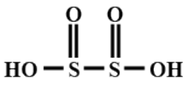


oleum pyrosulphuric acid
($H_2S_7O_7$)

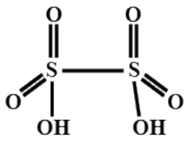
All the acids are dibasic as it has two replaceable H which are attached through O to the central sulphur atom



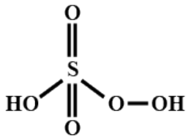
thiosulphorous acid
($H_2S_2O_2$)



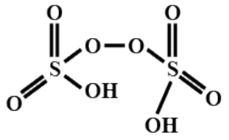
dithionous acid
($H_2S_2O_4$)



dithionic acid
($H_2S_2O_6$)



peroxomonsulphuric acid
or Caro's acid
(H_2SO_5)



peroxodisulphuric acid
($H_2S_2O_8$)

Among these H_2SO_4 is the most important.

Sulphuric Acid (H_2SO_4)

Properties

Sulphuric acid is a colourless, dense, oily liquid. It dissolves in water with the evolution of a large quantity of heat. Hence, for diluting the acid, the concentrated acid must be added slowly into water with constant stirring.

Chemical properties: The chemical reactions of sulphuric acid are due to the following reasons:

(a) its low volatility
(b) strong acidic character
(c) strong affinity for water and
(d) its ability to act as an oxidising agent.

In aqueous solution, sulphuric acid ionises in two steps.

$$H_2SO_4(aq) + H_2O(l) \longrightarrow H_3O^{+(}aq) + HSO_4^-$$

$$H_5O_4^-(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + SO_4^{2-}$$

So it is dibasic and forms two series of salts: normal sulphates and acid sulphates.

Because of its low volatility sulphuric acid can be used for the manufacture of more volatile acids from their corresponding salts.

$2\ MX + H_2SO_4 \longrightarrow 2HX + M_2SO_4$ (where X = F, Cl, NO3 etc. and M is a metal)

Concentrated sulphuric acid is a strong dehydrating agent and drying agent. Many wet gases can be dried by passing them through sulphuric acid. Sulphuric acid removes water from organic compounds.

e.g.: $C_{12}H_{22}O_{11} + H_2SO_4 \longrightarrow 12C + 11H_2O$

Hot concentrated sulphuric acid is a moderately strong oxidising agent. It oxidises both metals and non-metals and the acid itself reduces to SO_2.

$$Cu + 2\ H_2SO_4(conc.) \longrightarrow CuSO_4 + SO_2 + 2H\ _2O$$

$$3S + 2H\ _2SO_4(conc.) \longrightarrow 3SO_2 + 2H_2O$$

$$C + 2H_2SO_4(conc.) \longrightarrow CO_2 + 2\ SO_2 + 2H_2O$$

Uses: The important uses of Sulphuric acid are:

1) In the manufacture of fertilizers
2) in petroleum refining
3) in the manufacture of pigments, paints and dyestuff intermediates
4) in detergent industry
5) in metallurgical applications
6) as electrolyte in storage batteries
7) in the manufacture of nitrocellulose products and

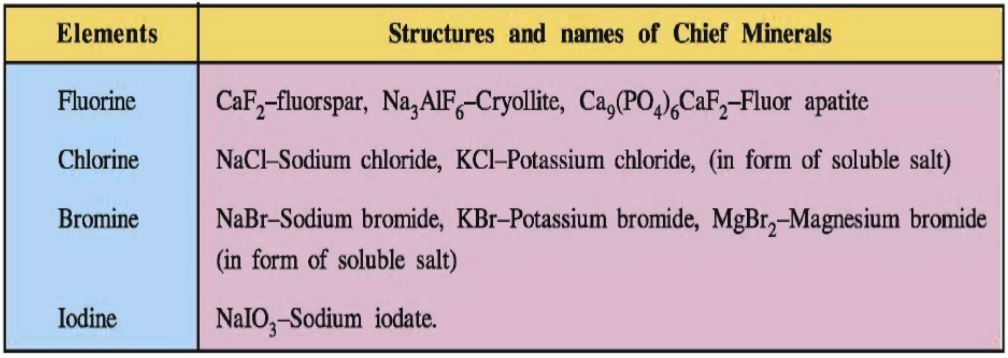
8) as a laboratory reagent.

Group 17 Elements

Fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At) are the members of Group 17.

Elements	**Electronic configuration ($ns^2\ np^5$)**
$_{9}F$	$[He]\,2s^2 2p^5$
$_{17}Cl$	$[Ne]\,3s^2 3p^5$
$_{35}Br$	$[Ar]\,3d^{10} 4s^2 4p^5$
$_{53}I$	$[Kr]\,4d^{10} 5s^2 5p^5$
$_{85}At$	$[Xe]\,4f^{14} 5d^{10} 6s^2 6p^5$

Occurrence



Elements	Structures and names of Chief Minerals
Fluorine	CaF_2–fluorspar, Na_3AlF_6–Cryollite, $Ca_9(PO_4)_6CaF_2$–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.

They are collectively known as the halogens (means salt producers). They are highly reactive non-metallic elements. All these elements have seven electrons in their outermost shell (ns^2np^5) and so they do not readily lose their electron.

So they have very high ionisation enthalpy.

Halogens have maximum negative electron gain enthalpy in the corresponding periods. This is due to the fact that the atoms of these elements have only one electron less than stable noble gas configurations. Electron gain enthalpy of these elements decreases down the group. However, the negative electron gain enthalpy of fluorine is less than that of chlorine. It is because, in fluorine the incoming electron goes to the 2p subshell, but in Cl it enters in to the 3p subshell.

Due to the compactness of 2p subshell compared to 3p subshell, the electron – electron repulsion is greater in fluorine than in chlorine. So F does not easily gains electron.

Halogens have very high electronegativity.

The electronegativity decreases down the group.

Fluorine is the most electronegative element in the periodic table.

All halogens have characteristic colour.

For example, F_2 has yellow, Cl_2-greenish yellow, Br_2-red and I_2, violet colour.

This is due to absorption of radiations in visible region which results in the excitation of outer electrons to higher energy level.

The bond dissociation enthalpy of F_2 is low. This is due to the relatively large electron-electron repulsion among the lone pairs in F2 molecule.

All the halogens are highly reactive. They react with metals and non-metals to form halides.

The reactivity of the halogens decreases down the group.

Halogens are strong oxidising agents since they readily accept electron.

F_2 is the strongest oxidising halogen and it oxidises other halide ions in solution or in the solid phase.

Oxidation states

All the halogens exhibit –1 oxidation state. Chlorine, bromine and iodine also show +1, +3, +5 and +7 oxidation states in their oxides, oxy acids and in inter halogen compounds.

Due to the absence of vacant d orbitals and the maximum electronegativity, fluorine exhibits only –1 oxidation state.

Anomalous behavior of fluorine

Due to the small size, highest electronegativity, low F-F bond dissociation enthalpy, and non availability of d orbitals in valence shell, fluorine shows properties different from other halogens.

Some of the anomalous properties of fluorine are:

1. Ionisation enthalpy, electronegativity, enthalpy of bond dissociation and electrode potentials are higher for fluorine than expected.
2. Ionic and covalent radii, m.p. and b.p. and electron gain enthalpy are quite lower than expected.
3. Most of the reactions of fluorine are exothermic (due to the small and strong bond formed by it with other elements).
4. F forms only one oxoacid while other halogens form a number of oxoacids.
5. Hydrogen fluoride is a liquid due to strong hydrogen bonding. While the hydrogen halides of other elements are gases.

Hydrides of halogens

Halogens react with hydrogen to give hydrogen halides which dissolve in water to form hydrohalic acids. The acidic strength of these acids varies in the order: $HF < HCl < HBr < HI$. The stability of these halides decreases down the group due to decrease in bond dissociation enthalpy from HF to HI.

Chlorine (Cl_2)

Preparation: It can be prepared by any one of the following methods:

(i) By heating manganese dioxide with concentrated hydrochloric acid.

$$MnO_2 + 4HCl \longrightarrow MnCl_2 + Cl_2 + 2H_2O$$

Conc. HCl can be replaced by a mixture of common salt and concentrated H_2SO_4

$$4NaCl + MnO_2 + 4H_2SO_4 \longrightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$$

(ii) By the action of HCl on potassium permanganate.

$$2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$$

Manufacture of chlorine

(i) **Deacon's process**: By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of $CuCl_2$ (catalyst) at 723 K.

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

(ii) **Electrolytic process**: Chlorine is obtained by the electrolysis of brine solution (concentrated NaCl
solution). During electrolysis chlorine is liberated at the anode.

Properties: It is a greenish yellow gas with pungent and suffocating odour.

It is soluble in water.

It reacts with a number of metals and non-metals to form chlorides.

$$2Al + 3Cl_2 \longrightarrow 2AlCl_3 \qquad P_4 + 6Cl_2 \longrightarrow 4PCl_3$$

$$2Na + Cl_2 \longrightarrow 2NaCl \qquad S_8 + 4Cl_2 \longrightarrow 4S_2Cl_2$$

$$2Fe + 3Cl_2 \longrightarrow 2FeCl_3\ ;$$

With excess ammonia, chlorine gives nitrogen and ammonium chloride whereas with excess chlorine, nitrogen trichloride (explosive) is formed.

$$\underset{\text{(excess)}}{8NH_3} + 3Cl_2 \longrightarrow 6NH_4Cl + N_2 \qquad NH_3 + \underset{\text{(excess)}}{3Cl_2} \longrightarrow NCl_3 + 3HCl$$

With cold and dilute alkalies chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkalies it gives chloride and chlorate.

$$\underset{\text{(cold and dilute)}}{2NaOH} + Cl_2 \longrightarrow NaCl + NaOCl + H_2O$$

$$\underset{\text{(hot and conc.)}}{6\,NaOH} + 3Cl_2 \longrightarrow 5NaCl + NaClO_3 + 3H_2O$$

With dry slaked lime it gives bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \longrightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$$

Chlorine reacts with hydrocarbons and gives substitution products with saturated hydrocarbons and addition products with unsaturated hydrocarbons.

$$\underset{\text{Methane}}{CH_4 + Cl_2} \xrightarrow{UV} \underset{\text{Methyl chloride}}{CH_3Cl + HCl}$$

$$\underset{\text{Ethene}}{C_2H_4 + Cl_2} \longrightarrow \underset{\text{1,2-Dichloroethane}}{C_2H_4Cl_2}$$

Chlorine water on standing loses its yellow colour due to the formation of HCl and HOCl.

Hypochlorous acid (HOCl) so formed is unstable and dissociates to give nascent oxygen which is responsible for oxidising and bleaching properties of chlorine.

(i) It oxidises ferrous to ferric, sulphite to sulphate, sulphur dioxide to sulphuric acid and iodine to iodic acid.

$$2FeSO_4 + H_2SO_4 + Cl_2 \longrightarrow Fe_2(SO_4)_3 + 2HCl$$

$$Na_2SO_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl$$

$$SO_2 + 2H_2O + Cl_2 \longrightarrow H_2SO_4 + 2HCl$$

$$I_2 + 6H_2O + 5Cl_2 \longrightarrow 2HIO_3 + 10HCl$$

(ii) It is a powerful bleaching agent; bleaching action is due to oxidation.

$$Cl_2 + H_2O \longrightarrow 2HCl + [O]$$

Coloured substance + [O] $\longrightarrow$ Colourless substance

It bleaches vegetable or organic matter in the presence of moisture. Its bleaching action is permanent.

Uses: It is used

- for bleaching wood pulp, bleaching cotton and textiles,
- in the extraction of gold and platinum
- in the manufacture of dyes, drugs and organic compounds such as CCl_4,$CHCl_3$, DDT, refrigerants, etc.
- in sterilising drinking water
- preparation of poisonous gases such as phosgene ($COCl_2$),tear gas (CCl_3NO_2), mustard gas ($ClCH_2CH_2SCH_2CH_2Cl$).

Hydrogen Chloride (HCl)

Preparation: It is prepared in the laboratory, by heating sodium chloride with concentrated sulphuric acid.

$$NaCl + H_2SO_4 \xrightarrow{420K} NaHSO_4 + HCl$$

$$NaHSO_4 + NaCl \xrightarrow{823K} Na_2SO_4 + HCl$$

Properties: It is a colourless and pungent smelling gas. It is extremely soluble in water and ionises as: $HCl + H_2O \longrightarrow H_3O^+ + Cl^-$

Its aqueous solution is called hydrochloric acid, which is a strong acid in water. It reacts with NH_3 and gives white fumes of NH_4Cl.

$$NH_3 + HCl \longrightarrow NH_4Cl$$

When three parts of concentrated HCl and one part of concentrated HNO_3 are mixed, aqua regia is formed which is used for dissolving noble metals, e.g., gold, platinum.

$$Au + 4\,H^+ + NO_3^- + 4Cl^- \longrightarrow AuCl_4^- + NO + 2H_2O$$

$$3Pt + 16H^+ + 4NO_3^- + 18Cl^- \longrightarrow 3PtCl_6^{2-} + 4NO + 8H_2O$$

Hydrochloric acid decomposes salts of weaker acids like carbonates, hydrogen carbonates, sulphites, etc.

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$

$$NaHCO_3 + HCl \longrightarrow NaCl + H2O + CO_2$$

$$Na_2SO_3 + 2HCl \longrightarrow 2NaCl + H_2O + SO_2$$

Uses: It is used

(i) in the manufacture of chlorine, NH_4Cl and glucose (from corn starch),

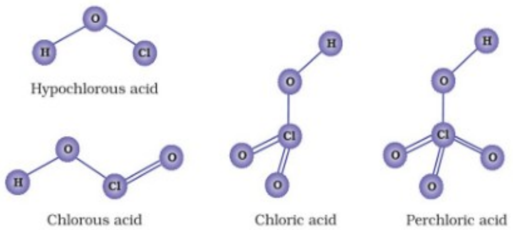
(ii) for extracting glue from bones and purifying bone black,
(iii) in medicine and as a laboratory reagent.

Oxoacids of Halogens

Due to high electronegativity and small size, fluorine forms only one oxoacid, HOF known as fluoric (I) acid or hypofluorous acid. The other halogens form several oxoacids like Hypohalous acid (HOX), halous acid (HOXO) , halic acid($HOXO_2$) and perhalic acid ($HOXO_3$). They are stable only in aqueous solutions or in the form of their salts.

Chlorine forms 4 types of oxoacids – hypochlorous acid (HOCl), Chlorous acid (HOClO or $HClO_2$), Choric acid ($HOClO_2$ or $HClO_3$) and perchloric acid ($HOClO_3$ or $HClO_4$).

The structures of oxoacids of chlorine



The structures of them are:

Interhalogen Compounds

When two different halogens react with each other, interhalogen compounds are formed. They can be assigned general compositions as AX, AX_3, AX_5 and AX_7, where both A and X are halogens. A is larger and more electropositive than X. As the size of the central atom (A) increases, the stability of the compound also increases.

Preparation

The interhalogen compounds can be prepared by the direct combination or by the action of halogen on lower interhalogen compounds.

$Cl_2 + F_2 \xrightarrow{437K} 2ClF$
(equal volume)

$I_2 + 3Cl_2 \longrightarrow 2ICl_3$
(excess)

$Cl_2 + 3F_2 \xrightarrow{573K} 2ClF_3$
(excess)

$Br_2 + 3F_2 \longrightarrow 2BrF_3$
(diluted with water)

$I_2 + Cl_2 \longrightarrow 2ICl$
(equimolar)

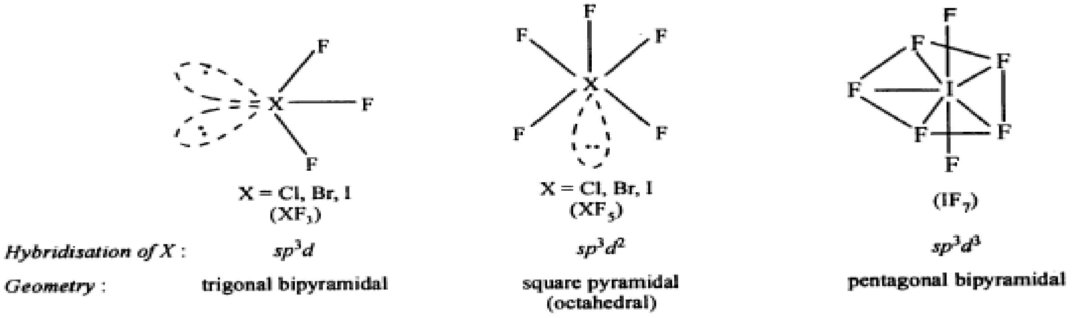
$Br_2 + 5F_2 \longrightarrow 2BrF_5$
(excess)

Properties:

These are all covalent molecules and are diamagnetic in nature. They are volatile solids or liquids except ClF which is a gas at 298 K. Their physical properties are intermediate between those of constituent halogens.

The interhalogen compounds are more reactive than halogens (except fluorine). This is because A–X bond in interhalogens is weaker than X–X bond in halogens except F–F bond. The types of inter halogen compounds and their structures are as follows:

AX	AX_3	AX_5	AX_7
ClF BrF, BrCl, ICl IBr, IF	ClF_3, BrF_3 IF_3, ICl_3	$BrF_5 IF_5$	IF_7



Uses: These compounds can be used as non aqueous solvents. Interhalogen compounds are very useful fluorinating agents.

Group 18 Elements

Group 18 consists of six elements- helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn). All these are gases and chemically unreactive. So they are called inert gases or noble gases.

$$^{226}_{88}\mathrm{Ra} \rightarrow {}^{222}_{86}\mathrm{Rn} + {}^{4}_{2}\mathrm{He}$$

Elements	Discovery	Electronic configuration ($ns^2\ np^6$)
$_2He$	Lockyer and Janssen (1868)	$1s^2$
$_{10}Ne$	Ramsay	$1s^2, 2s^2 2p^6$
$_{18}Ar$	Rayleigh and Ramsay (1894)	$1s^2, 2s^2 2p^6, 3s^2 3p^6$
$_{36}Kr$	Ramsay and Travers (1898)	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10},\quad 4s^2 4p^6$
$_{54}Xe$	Ramsay and Travers (1898)	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10},\quad 4s^2 4p^6 4d^{10} 4f^{14},$ $5s^2 5p^6$
$_{86}Rn$	Dorn (1900)	$1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10},\quad 4s^2 4p^6 4d^{10} 4f^{14},$ $5s^2 5p^6 5d^{10}, 6s^2 6p^6$

All noble gases have general electronic configuration ns^2np^6 (except helium which has $1s^2$).

Due to stable electronic configuration these gases have very high ionisation enthalpy and electron gain enthalpy.

Even though these elements are chemically inert,Kr and Xe form some compounds with oxygen and fluorine under special conditions.

(a) Xenon-fluorine compounds

Xenon forms three binary fluorides, XeF_2, XeF_4 and XeF_6 by the direct reaction of elements under suitable conditions.

$$Xe\,(g) + F_2\,(g) \xrightarrow{673K,\ 1bar} XeF_2(s)$$
(xenon in excess)

$$Xe\,(g) + 2F_2\,(g) \xrightarrow{873K,\ 7\ bar} XeF_4(s)$$
(1:5 ratio)

$$Xe\,(g) + 3F_2\,(g) \xrightarrow{573K,\ 60\text{-}70bar} XeF_6(s)$$
(1:20 ratio)

XeF_6 can also be prepared by the interaction of XeF_4 and O_2F_2 at 143K.

$$XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$$

XeF_2, XeF_4 and XeF_6 are colourless crystalline solids. They are powerful fluorinating agents. They are readily hydrolysed even by traces of water.

For example, XeF_2 is hydrolysed to give Xe, HF and O_2.

$$2XeF_2\,(s) + 2H_2O(l) \longrightarrow 2Xe\,(g) + 4\,HF(aq) + O_2(g)$$

Structures

XeF_2 and XeF_4 have linear and square planar structures respectively. XeF_6 has seven electron pairs (6 bonding pairs and one lone pair) and thus, have a distorted octahedral structure

(b) Xenon-oxygen compounds

1. **XeO_3**: It is obtained by the hydrolysis of XeF4 and XeF6 with water.

$$6XeF_4 + 12\,H_2O \longrightarrow 4Xe + 2XeO_3 + 24\,HF + 3\,O_2$$

$$XeF_6 + 3\,H_2O \longrightarrow XeO_3 + 6\,HF$$

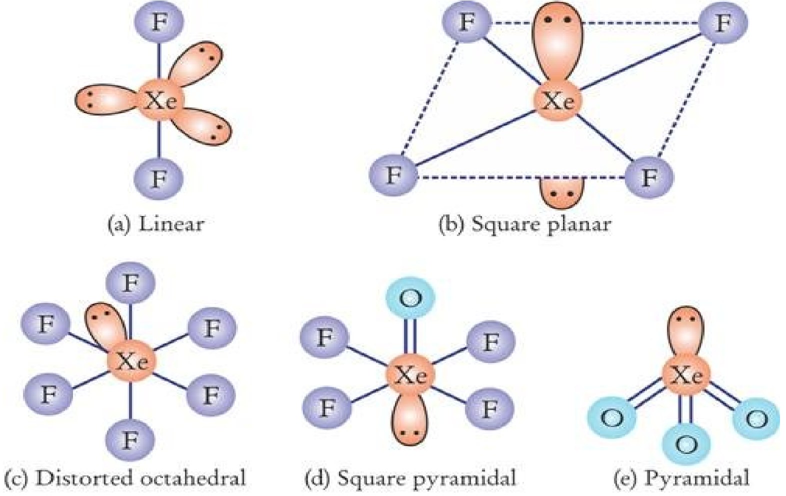
2. **$XeOF_4$ & XeO_2F_2**:

Partial hydrolysis of XeF_6 gives oxyfluorides, $XeOF_4$ and XeO_2F_2.

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

$$XeF_6 + 2\,H_2O \longrightarrow XeO_2F_2 + 4HF$$

XeO_3 is a colourless explosive solid and has a pyramidal molecular structure. $XeOF_4$ is a colourless volatile liquid and has a square pyramidal molecular structure.



(a) Linear (b) Square planar

(c) Distorted octahedral (d) Square pyramidal (e) Pyramidal

Structures of (a) XeF_2 (b) XeF_4 (c) XeF_6 (d) $XeOF_4$ and (e) XeO_3

Uses of noble gases:

Helium is used in filling balloons for meteorological observations. It is also used in gas-cooled nuclear reactors. Liquid helium is used as cryogenic agent for carrying out various experiments at low temperatures.

It is used as a diluent for oxygen in modern diving apparatus because of its very low solubility in blood.

Neon is used in discharge tubes and fluorescent bulbs for advertisement display purposes.

Neon bulbs are used in botanical gardens and in green houses.

Argon is used to provide an inert atmosphere in high temperature metallurgical processes and for filling electric bulbs. It is also used in the laboratory for handling substances that are air-sensitive.

Xenon and Krypton are used in light bulbs designed for special purposes.

8. The d and f Block Elements

Elements from 3rd group to 12th group in the Modern Periodic table are called d-block elements.

In these elements their last electron enters in the penultimate d- sub shell. They are placed in between s-block and p-block elements.

They show a regular transition from the highly electropositive metals of sblock elements to the less electropositive p-block elements. So they are called transition elements.

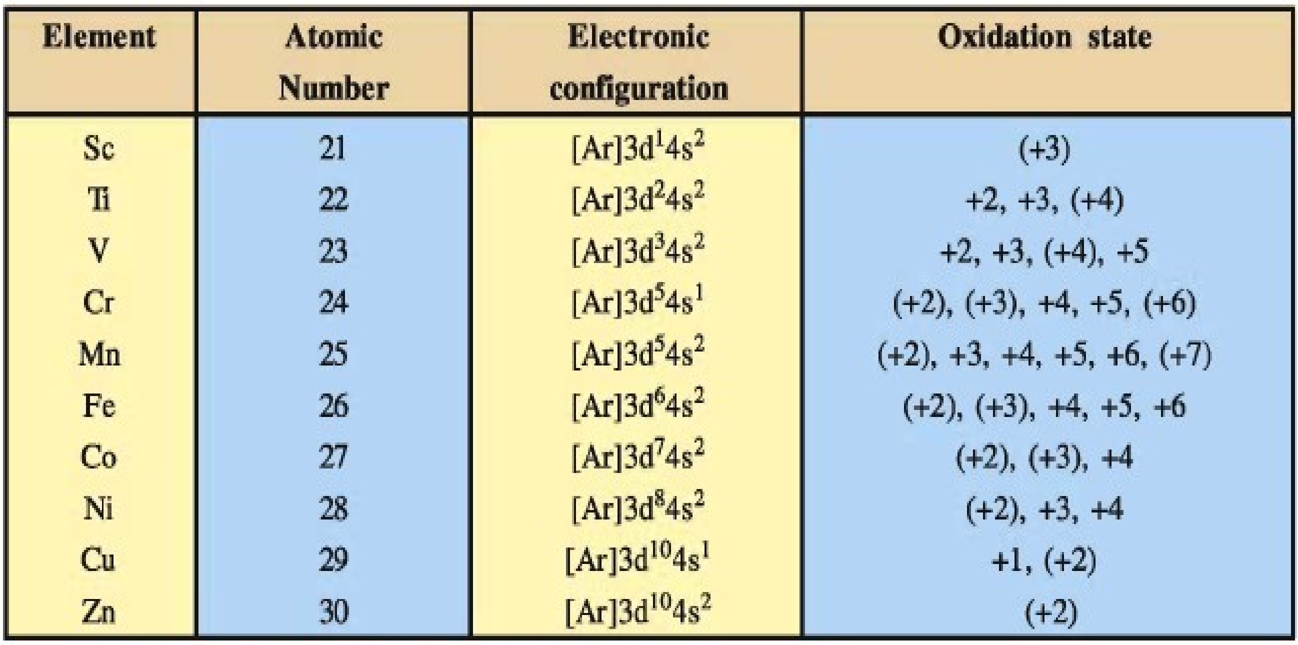
Transition elements can be defined as elements which contain partially filled d orbitals in their atomic state or in any of their oxidation state. This definition does not include Zn, Cd and Hg. So they are not regarded as transition elements. Or, they are called pseudo transition elements. There are four series of transition elements.

1) 3d series [from Sc (z = 21) to Zn (z = 30)]
2) 4d series [from Y (z = 39) to Cd (z = 48)]
3) 5d series [from La (z =57), Hf (z = 72) to Hg (z=80)]
4) 6d series [from Ac (z=89), Rf (z=104) to Cp (z=112)]

Electronic Configuration

General outer electronic configuration of d-block elements is (n-1) d^{1-10} ns^{1-2}. There is only a small difference in energy between (n-1)d orbital and ns orbital. So in some cases ns electrons are also transferred to (n-1)d level.

The electronic configuration of first transition series in ground state and their oxidation states



Element	Atomic Number	Electronic configuration	Oxidation state
Sc	21	$[Ar]3d^14s^2$	(+3)
Ti	22	$[Ar]3d^24s^2$	+2, +3, (+4)
V	23	$[Ar]3d^34s^2$	+2, +3, (+4), +5
Cr	24	$[Ar]3d^54s^1$	(+2), (+3), +4, +5, (+6)
Mn	25	$[Ar]3d^54s^2$	(+2), +3, +4, +5, +6, (+7)
Fe	26	$[Ar]3d^64s^2$	(+2), (+3), +4, +5, +6
Co	27	$[Ar]3d^74s^2$	(+2), (+3), +4
Ni	28	$[Ar]3d^84s^2$	(+2), +3, +4
Cu	29	$[Ar]3d^{10}4s^1$	+1, (+2)
Zn	30	$[Ar]3d^{10}4s^2$	(+2)

Note: Stable oxidation state is shown in parenthesis.

The electronic configurations of Cr and Cu in the 3d series show some exceptions.

$_{24}$Cr – [Ar] 3d5 4s1
$_{29}$Cu – [Ar] 3d10 4s1

This is due to the extra stability of half-filled and completely-filled electronic configurations. (d^5 or d^{10}).

The electronic configurations of Zn, Cd and Hg are represented by the general formula (n-1)d^{10} ns^2. The orbitals in these elements are completely filled in the ground state as well as in their common oxidation states. So they are not regarded as transition elements.

General characteristics of transition elements

1. Atomic and ionic radii

In a given transition series, the atomic and ionic radii first decreases, then become constant and increases towards the end of the series. This is because in transition elements the new electron enters in a d orbital.

Initially since there is a few numbers of d electrons, the shielding effect is very poor. As the atomic number increases, the nuclear charge also increases, so the atomic radius decreases.

Towards the middle of the series, the increase in nuclear charge is balanced by the shielding effect and so the atomic radius becomes constant.

Towards the end of the series, as the e^- - e^- repulsion increases the atomic radius also increases.

The atomic and ionic radii of 2nd and 3rd row transition metals are quite similar. This is due to the Lanthanide contraction.

In between the 2nd and 3rd row transition elements, 4f electrons are present. The 4f electrons have very poor shielding effect and as a result the atomic and ionic radii of Lanthanides decrease from left to right (Lanthanide contraction).

2. Melting and boiling points

In a given transition series the melting and boiling points 1st increases up to the middle and then decreases.

This can be explained in terms of metallic bond strength which depends on the number of unpaired electrons. As the number of unpaired electron increases, the metallic bond strength increases. Hence the melting point also increases.

In a given transition series, the number of unpaired electrons increases up to the middle and then decreases.

Another factor which affects the m.p is heat of atomization. Mn and Tc have low melting point even though they have d5 configuration. This is because of their low heat of atomization.

The m.ps of second and third row transition series is higher than that of the first row due to their higher enthalpies of atomization.

3. Ionisation enthalpy

The ionisation enthalpy of transition elements generally increases from left to right. This is due to increase in nuclear charge. But the increase is not regular. This can be explained as follows.

After the removal of one electron, the relative energies of 4s and 3d orbitals get changed. Hence the remaining electron in the 4S level is transferred to 3d level. So the unipositive ions have d^n configuration with no 4s electrons.

During this re-organisation of electrons, some energy is released and it is known as exchange energy. So the net energy required to remove the 1st electrons is equal to the sum of ionisation enthalpy and exchange energy.

The first ionisation enthalpies of Cr and Cu are low. This is because the removal of one electron does not change their d configuration. Similarly first ionisation enthalpy of Zn is high becauseafter the removal of one electron there is no change in the d configuration

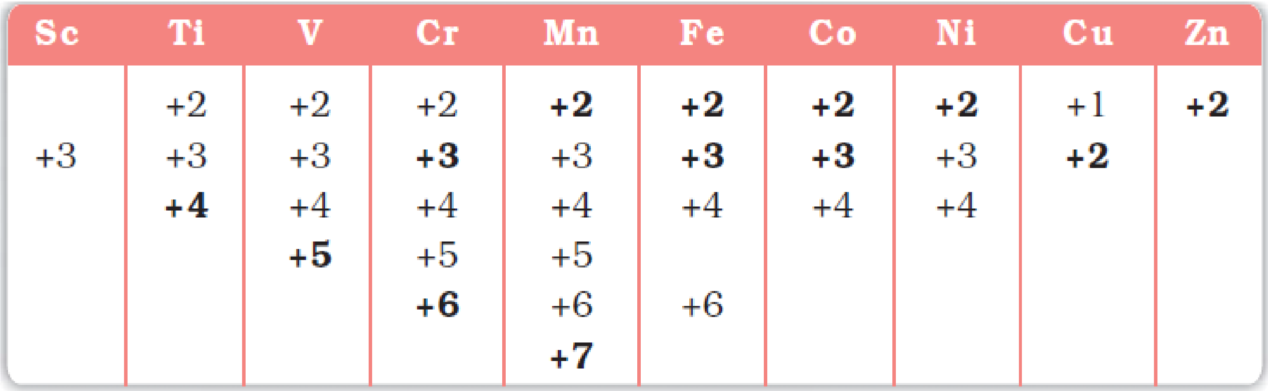
$$\underset{3d^{10}4s^{2}}{Zn} \rightarrow \underset{3d^{10}4s^{1}}{Zn^{+}} + e^{-}$$

The 2nd I.E of Cr and Cu are very high. This is because the removal of one more e- from these metals disrupted their stable configuration (d^5 or d^{10})
The 2nd I.Es of Mn and Zn are low, this is because after the removal of one more electron, they attain the stable half filled or completely filled electronic configuration.

4. Oxidation State

Transition metals show variable oxidation states. This is because in these elements d and s electrons have comparable energies.
So in chemical reaction along with s-electrons, d-electrons also participate. In a given transition series, the maximum oxidation state increases up to the middle and then decreases.
This is due to the half-filled or noble gas configuration. The common oxidation state of 1st row transition elements is +2.
The maximum oxidation state increases from top to bottom in a group. In lower oxidation state, the transition element mainly forms ionic compounds.
Sc generally shows +3 oxidation state because after the removal of 3 electrons, it gets a stable noble gas configuration. The oxidation state of Zn is +2 because of the completely filled configuration of Zn^{2+}.

Oxidation States of the first row Transition Metals
(the most common ones are in bold types)



Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	**+2**	**+2**	**+2**	**+2**	+1	**+2**
+3	+3	+3	**+3**	+3	**+3**	**+3**	+3	**+2**	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

5. Electrode Potential

The electrode potential values of first row transition series generally increases from left to right with some exceptions. The $E^0(Cu^{2+}/Cu)$ is positive (+0.34V), while the E^0 values of all the other first row transition elements are –ve.
This is because the high energy to transform Cu(s) to Cu^{2+}(aq) is not balanced by its hydration enthalpy. So Cu does not easily reacts with acid and liberate H_2.Only oxidizing acids [HNO_3 and hot Conc. H_2SO_4] react with Cu and the acid get reduced.
Along the series the E^0 values become less –ve due to the increase in the sum of 1st and 2nd ionisation enthalpies.
The E^0 values of Mn^{2+} and Zn^{2+} are more –ve, this is because of the half filled configuration of Mn^{2+} (d^5) and completely filled configuration of Zn^{2+} (d^{10}). $E^0(M^{3+}/M^{2+})$ value of Sc is very low and that for Zn is very high. This is because of their stable electronic configuration.
E^0 (Mn^{3+}/Mn^{2+}) is high because of the stable half filled configuration of Mn^{2+}. Similarly E^0 (Fe2+/Fe3+) is low, this is because after the removal of one electron from Fe^{2+}, it gets a stable electronic configuration.

$$Fe^{2+} \rightarrow Fe^{3+} + e^-$$

Q. Explain why Cu+ is not stable in aqueous solution?

This is due to the much more –ve hydration enthalpy of Cu^{2+} (aq) than Cu^{+}. In the case of Cu^{2+}, the hydration enthalpy is more compensated by ionisation enthalpy than in Cu^{+}.

6. Magnetic Properties

Transition metals show mainly two types of magnetic properties- paramagnetism and diamagnetism.

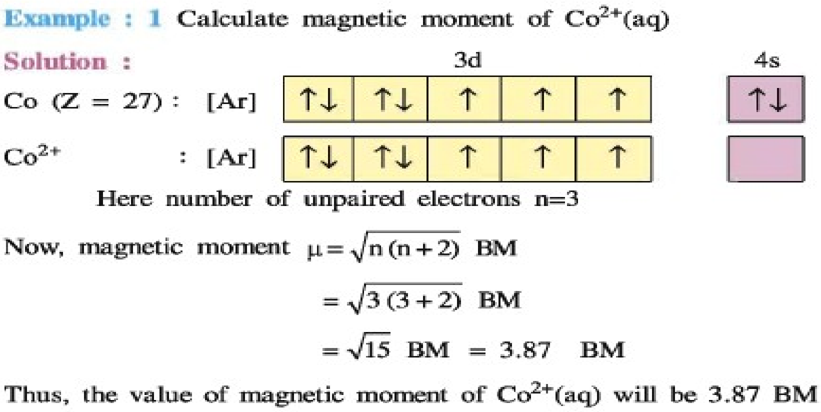
Some transition metals also show ferromagnetism which is an extreme case of paramagnetism.

Paramagnetism arises from the presence of unpaired electrons. Each unpaired e- is associated with a spin magnetic moment and an orbital magnetic moment.

For the compounds of 1st row transition elements, the contribution of orbital magnetic moment is effectively cancelled and so only spin magnetic moment is considered.

It is determined by the no. of unpaired e-s and is calculated by the spin only formula:

$\mu = \sqrt{n(n+2)}$ BM where n is the no. of unpaired electrons and μs is the spin only magnetic moment in the unit of Bohr Magneton (B.M).



Example : 1 Calculate magnetic moment of Co^{2+}(aq)

Solution :

		3d					4s
Co (Z = 27) :	[Ar]	↑↓	↑↓	↑	↑	↑	↑↓
Co^{2+} :	[Ar]	↑↓	↑↓	↑	↑	↑	

Here number of unpaired electrons n=3

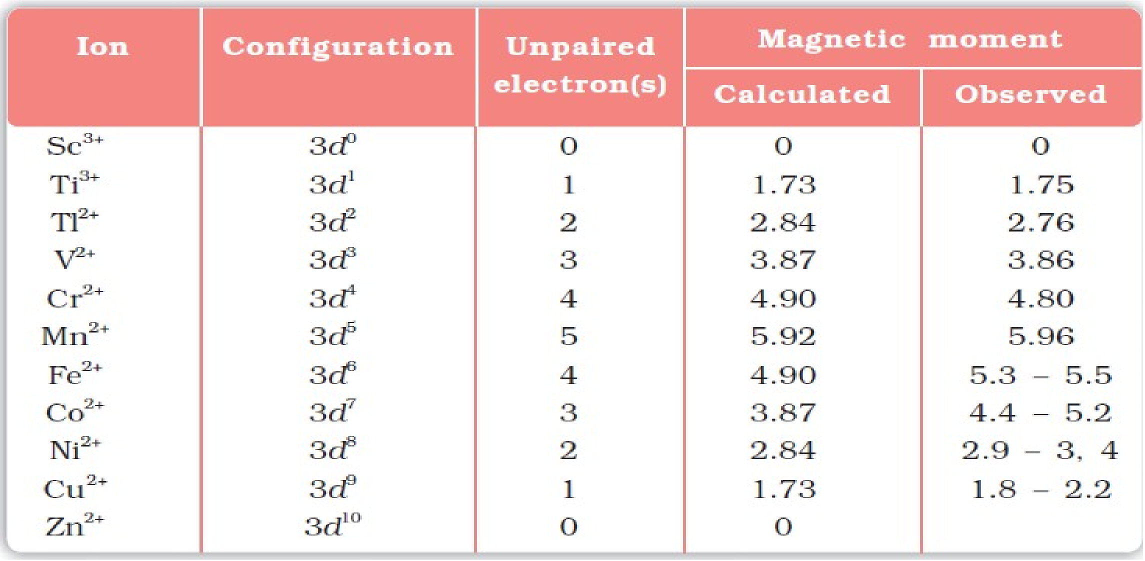
Now, magnetic moment $\mu = \sqrt{n(n+2)}$ BM

$= \sqrt{3(3+2)}$ BM

$= \sqrt{15}$ BM = 3.87 BM

Thus, the value of magnetic moment of Co^{2+}(aq) will be 3.87 BM

The magnetic moment increases with increase in no. of unpaired e^{-}s. Thus the observed magnetic moment gives an idea about the no. of unpaired e-s present in the atom or ion.



Ion	Configuration	Unpaired electron(s)	Magnetic moment	
			Calculated	Observed
Sc^{3+}	$3d^0$	0	0	0
Ti^{3+}	$3d^1$	1	1.73	1.75
Tl^{2+}	$3d^2$	2	2.84	2.76
V^{2+}	$3d^3$	3	3.87	3.86
Cr^{2+}	$3d^4$	4	4.90	4.80
Mn^{2+}	$3d^5$	5	5.92	5.96
Fe^{2+}	$3d^6$	4	4.90	5.3 – 5.5
Co^{2+}	$3d^7$	3	3.87	4.4 – 5.2
Ni^{2+}	$3d^8$	2	2.84	2.9 – 3, 4
Cu^{2+}	$3d^9$	1	1.73	1.8 – 2.2
Zn^{2+}	$3d^{10}$	0	0	

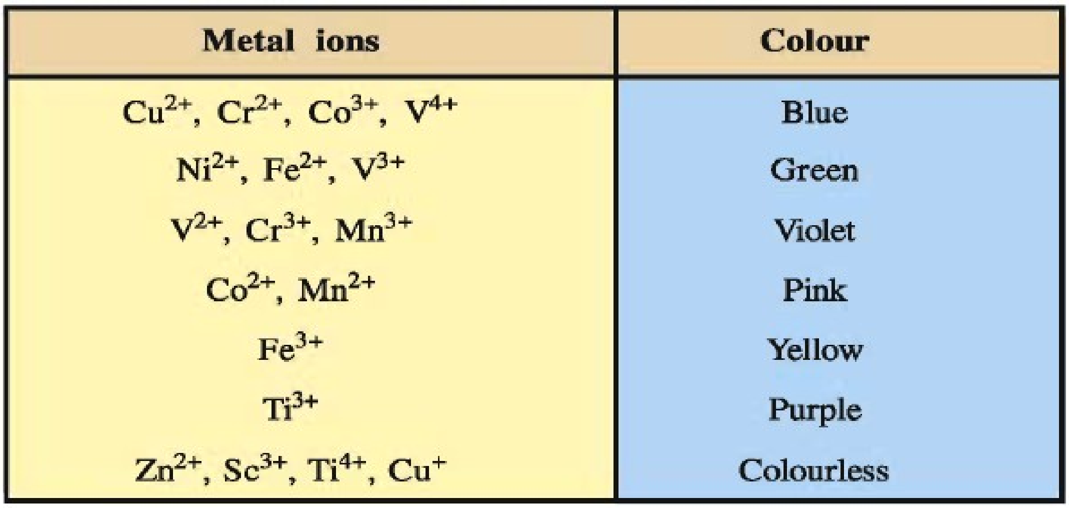
7. Formation of coloured ions or compounds

Most of the Transition metals ions or compounds are coloured. This is because of the presence of partially filled d orbitals. When an electron from a lower energy d orbital is exited to higher d level, it absorbs energy and this is equal to the energy of certain colours in visible region.

So the colour observed is the complementary colour of the light absorbed.

In aqueous solution most of the Transition metal ions are coloured since water molecules act as the ligands.

Among Ti^{2+} and Ti^{4+}, Ti^{2+} is coloured while Ti4+ is colourless. This is because Ti^{4+} has no partially filled d orbitals. Ti^{2+} - [Ar] $3d^2$ Ti^{4+} - [Ar] $3d^0$ Similarly among Cu^+ and Cu^{2+}, Cu^{2+} is coloured while Cu+ is colourless. This is due to the lack (absence) of partially filled d orbitals in Cu^+.



Metal ions	Colour
Cu^{2+}, Cr^{2+}, Co^{3+}, V^{4+}	Blue
Ni^{2+}, Fe^{2+}, V^{3+}	Green
V^{2+}, Cr^{3+}, Mn^{3+}	Violet
Co^{2+}, Mn^{2+}	Pink
Fe^{3+}	Yellow
Ti^{3+}	Purple
Zn^{2+}, Sc^{3+}, Ti^{4+}, Cu^+	Colourless

8. Formation of Complexes

Transition metals form a large no. of complexes. This is due to:

1. Comparatively smaller size
2. High ionic charge
3. Presence of partially filled d orbitals
4. Ability to show variable oxidation state

Eg: $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$, $[Ni(CO)_4]$ etc.

9. Catalytic Property

Transition metals act as catalysts in a large no. of chemical reactions. This is due to their large surface area and their ability to show variable oxidation state.

10. Interstitial Compound Formation

These are formed when smaller atoms like H, N, C, B etc. are trapped inside the crystal lattice of the metal. They are usually non-stoichiometric and neither typically ionic nor covalent. E.g.: Fe_3H, Mn_4N, TiC, $VH_{0.56}$, $TiH_{1.7}$ etc.

Some the properties of these compounds are:

1) They have high melting point.
2) They are very hard.
3) They retain metallic conductivity.
4) They are chemically inert.

11. Alloy Formation

Alloys are homogeneous solid solutions of elements in which at least one element is a metal. They are formed by atoms with metallic radii within about 15% of each other.

Because of similar radii and other characteristics of Transition metals, they readily form alloys.

The alloys formed are hard and have high m.p. e.g.: Bronze (Cu, Zn), Stainless steel (Fe, C, Ni, Mn and Cr).

THE INNER TRANSITION ELEMENTS (f-BLOCK)

The elements in which the last electron enters in the anti-penultimate f-subshell are called f-block elements. They include lanthanides of the 6th period and actinides of the 7th period.

They are also called inner transition elements. Since lanthanum ($_{57}La$) closely resembles lanthanides, it is also included along with them. Similarly, actinium ($_{89}Ac$) is included along with actinoids because of its close resemblance with them.

The Lanthanoids or lanthanides

The 14 elements after lanthanum of the 6th period are called lanthanides or lanthanoids or lanthanones or rare earths.

They include elements from $_{58}Ce$ to $_{71}Lu$. They are generally represented as Ln.

Atomic and ionic radii - Lanthanide Contraction

In lanthanides, the atomic and ionic radii decrease regularly from lanthanum to lutetium. This regular decrease in the atomic and ionic radii along lanthanide series (though very slightly) is called lanthanide contraction.

Reason: In lanthanides, as the atomic number increases, the nuclear charge increases one by one and the electrons are added to the anti-penultimate f subshell. Due to its diffused shape, f orbitals have poor shielding effect. So the nucleus can attract the outer most electrons strongly and as a result the radii decreases.

Consequences:

1) Due to Lanthanide Contraction the 2nd and 3rd row transition series elements have similar radii. E.g. Zr –160pm and Hf -159pm

2) Lanthanides have similar physical properties and they occur together in nature. So their isolation is difficult.

3) The basic character of their hydroxides decreases from lanthanum to lutetium. i.e, $La(OH)_3$ is more basic than $Lu(OH)_3$.

Uses of Lanthanides

The main use of the lanthanoids is for the production of alloy steels. An important alloy is mischmetall which consists of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al. A great deal of mischmetall is used in Magnesium based alloy to produce bullets, shell and lighter flint.

Mixed oxides of lanthanoids are employed as catalysts in petroleum cracking. Some Ln oxides are used as phosphors in television screens and similar fluorescing surfaces.

The Actinoids or Actinones

The 14 elements after actinium in the 7th period of modern periodic table are called actinides or actinoids or actinones. They include elements from $_{90}Th$ to $_{103}Lr$. Most of them are artificially prepared and are short lived. They are radioactive. The elements after Uranium are artificially prepared and so they are called **trans-uranium elements or trans-uranic elements**.

9.CO-ORDINATION COMPOUNDS

Double salt and Complex salt

A salt that keeps its identity only in solid state is called a double salt. In solution they dissociate into component ions.

E.g.: Mohr's salt [$FeSO_4.(NH_4)_2SO_4.6H_2O$], Carnalite [$KCl.MgCl_2.6H_2O$], Potash alum [$K2SO_4.Al_2(SO_4)_3.24H_2O$].

The salt that keeps its identity both in solid and solution states is called a complex salt.

E.g.: $K_4[Fe(CN)_6]$, $[Cu(NH_3)_4]SO_4$, $K_2[PtCl_4]$, $[Ni(CO)_4]$ etc.

Some definitions

1.Co-ordination entity: The central metal atom or ion and ligands form a co-ordination entity. For example,

$[CoCl_3(NH_3)_3]$ is a co-ordination entity in which the cobalt ion is surrounded by three ammonia molecules and three chloride ions. Other examples are $[Ni(CO)_4]$, $[PtCl_2(NH_3)_2]$, $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_6]^{3+}$.

2.Central atom/ion: In a co-ordination entity, the atom/ion to which a fixed number of ions/neutral molecules are attached is called the central atom or ion.

For example, the central atom/ion in the co-ordination entities: $[NiCl_2(H_2O)_4]$, $[CoCl(NH_3)_5]^{2+}$ and $[Fe(CN)_6]^{3-}$ are Ni^{2+}, Co^{3+} and Fe^{3+} respectively.

These central atoms/ions are also referred to as Lewis acids, since they accept electron pairs from ligands.

3.Ligands: The ions or neutral molecules bound to the central atom/ion in the coordination entity are called ligands.

For a species to act as ligand, it can donate atleast one pair of electron to the central atom. The atom of the ligand which is directly bonded to the central atom or ion is called co-ordinating atom or donor atom.

Examples for ligands are Cl^-, Br-, F^-, I^-, OH^-, CN^-, NC^-, CNO^-, NCO^-, SO_4^{2-}, NO_3^-, CNS^-, H_2O, NH_3, CO etc.

Types of ligands Based on the number of donor atoms of the ligand that binds to a metal ion or atom, the ligands are classified as follows:

a) **Monodentate or unidentate ligand**: A ligand that binds to the central atom/ ion through a single donor atom, is said to be unidentate ligand. E.g.: Cl^-, Br^-, I^-, OH^-, H_2O, NH_3, CN^-, NC^-, SCN^- etc.

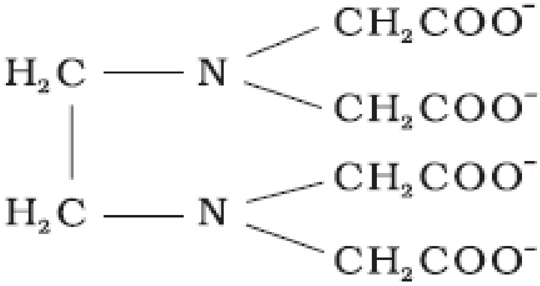
b) **Bidentate (Didentate) ligands**: A ligand that binds to the central atom through two donor atoms is called a bidentate ligand. E.g.: Ethane-1,2-diamine or ethylenediamine ($H_2NCH_2CH_2NH_2$) notated as 'en' and oxalate ion ($C_2O_4^{2-}$).

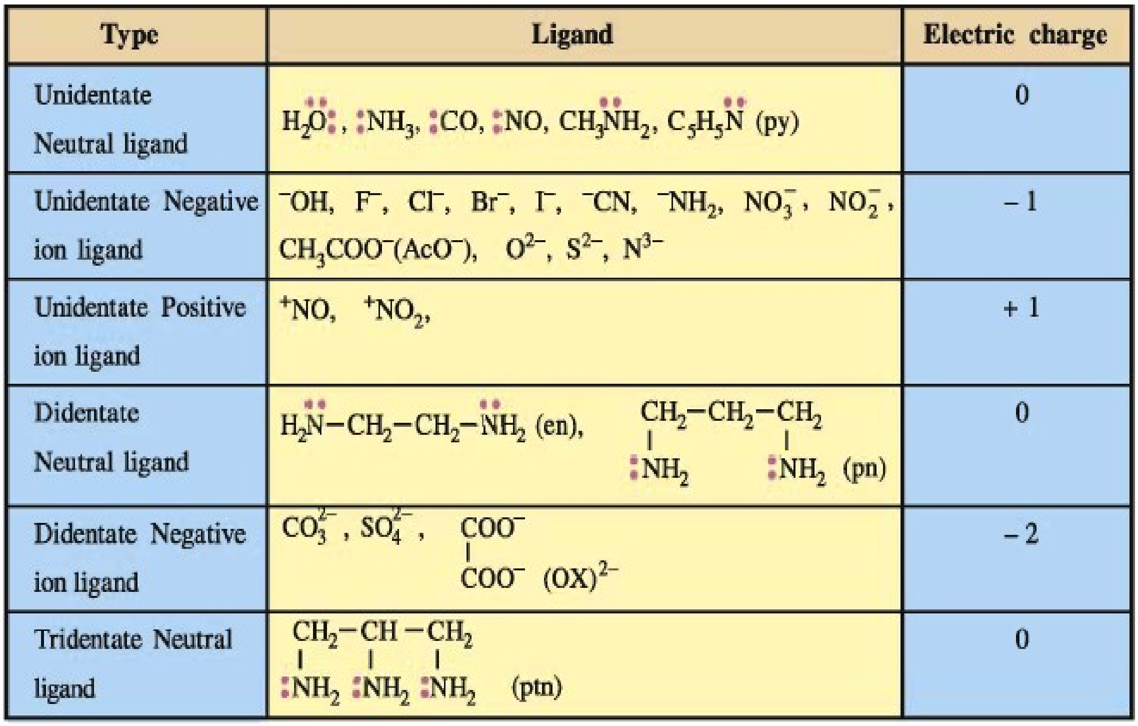
c) **Polydentate ligand**: A ligand that binds to the central atom through more than two donor atoms is called polydentate ligand.

E.g.: Triethylamine ammonia [$N(CH_2\text{-}CH_2\text{-}NH_2)_3$],

Ethylenediamine tetraacetate ion ($EDTA^{4-}$) etc.

Ethylenediamine tetraacetate ion ($EDTA^{4-}$) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.





Type	Ligand	Electric charge
Unidentate Neutral ligand	$H_2\ddot{O}:$, $:NH_3$, $:CO$, $:NO$, $CH_3\ddot{N}H_2$, $C_5H_5\ddot{N}$ (py)	0
Unidentate Negative ion ligand	^-OH, F^-, Cl^-, Br^-, I^-, ^-CN, $^-NH_2$, NO_3^-, NO_2^-, $CH_3COO^-(AcO^-)$, O^{2-}, S^{2-}, N^{3-}	– 1
Unidentate Positive ion ligand	^+NO, $^+NO_2$,	+ 1
Didentate Neutral ligand	$H_2\ddot{N}-CH_2-CH_2-\ddot{N}H_2$ (en), $\underset{:NH_2}{\underset{\vert}{CH_2}}-CH_2-\underset{:NH_2}{\underset{\vert}{CH_2}}$ (pn)	0
Didentate Negative ion ligand	CO_3^{2-}, SO_4^{2-}, $\begin{array}{l}COO^-\\ \vert\\ COO^-\end{array}$ $(OX)^{2-}$	– 2
Tridentate Neutral ligand	$\underset{:NH_2}{\underset{\vert}{CH_2}}-\underset{:NH_2}{\underset{\vert}{CH}}-\underset{:NH_2}{\underset{\vert}{CH_2}}$ (ptn)	0

Ligands are also classified as:

i) Ambidentate ligands: They are unidentate ligands which contain more than one donor atoms. They can coordinate through two different atoms. Examples of such ligands are the NO_2^-, CN^-, SCN^-, CNO^- etc. NO_2^- ion can coordinate either through nitrogen or through oxygen atom to the central metal atom/ion.

If the donor atom is N, it is written as NO_2^- and is called nitrito (N) and if it is O, it is written as ONO^- and is called nitrito(O).

Similarly, SCN– ion can coordinate either through sulphur atom ($\leftarrow SCN^-$ thiocyanato) or through nitrogen atom ($\leftarrow NCS^-$ isothiocyanato).

ii) Chelating Ligands: Di- or polydentate ligands can bind to the central atom through two or more donor atoms and form ring complexes. Such complexes are called chelates and such types of ligands are said to be chelating ligands.

Complexes containing chelating ligands are more stable than those containing unidentate ligands. For e.g. the complex $[Co(en)_3]^{3+}$ is a chelate and ethane-1,2-diamine (en) is a chelating ligand.

4.Denticity: The number of donor atoms of a particular ligand that are directly bonded to the central atom is called denticity.

For unidentate ligands, the denticity is 1, for didentate ligands it is 2 and so on

5.Co-ordination number: The co-ordination number (C.N) of a metal ion in a complex can be defined as the total number of ligand donor atoms to which the metal is directly bonded.

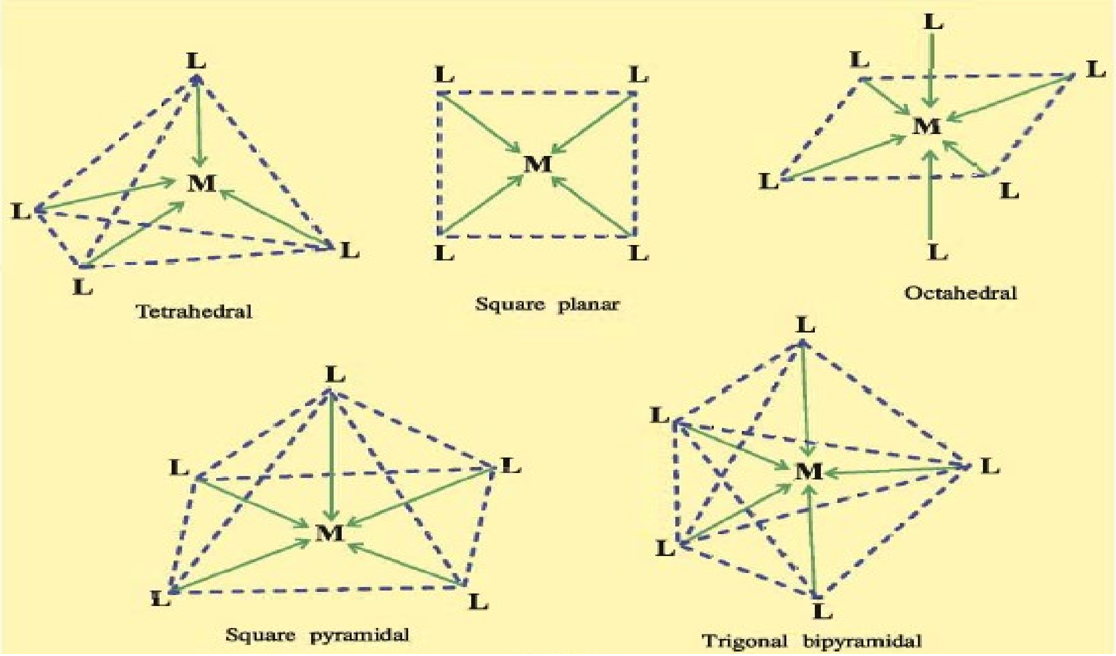
For example, in the complex ion $[PtCl_6]^{2-}$ the coordination number of Pt is 6 and in $[Ni(NH_3)_4]^{2+}$, the co-ordination number of Ni is 4. Similarly, in the complex ions, $[Fe(C_2O_4)_3]^{3-}$ and $[Co(en)_3]^{3+}$, the co-ordination number of both Fe and Co, is 6 because $C_2O_4^{2-}$ and en (ethane-1,2-diamine) are bidentate ligands.

The co-ordination number of the central atom/ion is determined only by the number of sigma bonds formed by the ligand with the central atom/ion. Generally, the co-ordination number of most of the
complexes is 2, 4 or 6.

6.Co-ordination sphere: The central atom/ion and the ligands attached to it are enclosed in square bracket and is collectively termed as the co-ordination sphere. The ionisable groups are written outside the bracket and are called simple ions or

counter ions. For example, in the complex $K_4[Fe(CN)_6]$, the coordination sphere is $[Fe(CN)_6]^{4-}$ and the
counter ion is K+.

7.Co-ordination polyhedron: The spatial arrangement of the ligands around the central atom/ion defines a coordination polyhedron about the central atom. The most common co-ordination polyhedra are octahedral, square planar and tetrahedral. For example, $[Co(NH_3)_6]^{3+}$ is octahedral, $[Ni(CO)_4]$ is tetrahedral and $[PtCl_4]^{2-}$ is square planar.



8.Oxidation number of central atom: The oxidation number of the central atom in a complex is defined as the residual charge on it, if all the ligands are removed along with their electron pairs that are shared with the central atom. The oxidation number is represented by a Roman numeral in simple brackets. For example, oxidation number of copper in $[Cu(CN)_4]^{3-}$ is +1 and it is written as Cu(I).

9.Homoleptic and Heteroleptic complexes: Complexes which contain only one type of ligand are called homoleptic complexes.
E.g.: $[Co(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{4-}$ etc.
Complexes which contain more than one type of ligands are called heteroleptic complexes.
e.g., $[Co(NH_3)_4Cl_2]^{+}$, $[Cu(NH_3)2Cl_2]$ etc.

IUPAC Nomenclature of Co-ordination Compounds

The following rules are used while naming co-ordination compounds:

(i) The cation is named first in both positively and negatively charged co-ordination entities.

(ii) The ligands are named in alphabetical order before the name of the central atom/ion.

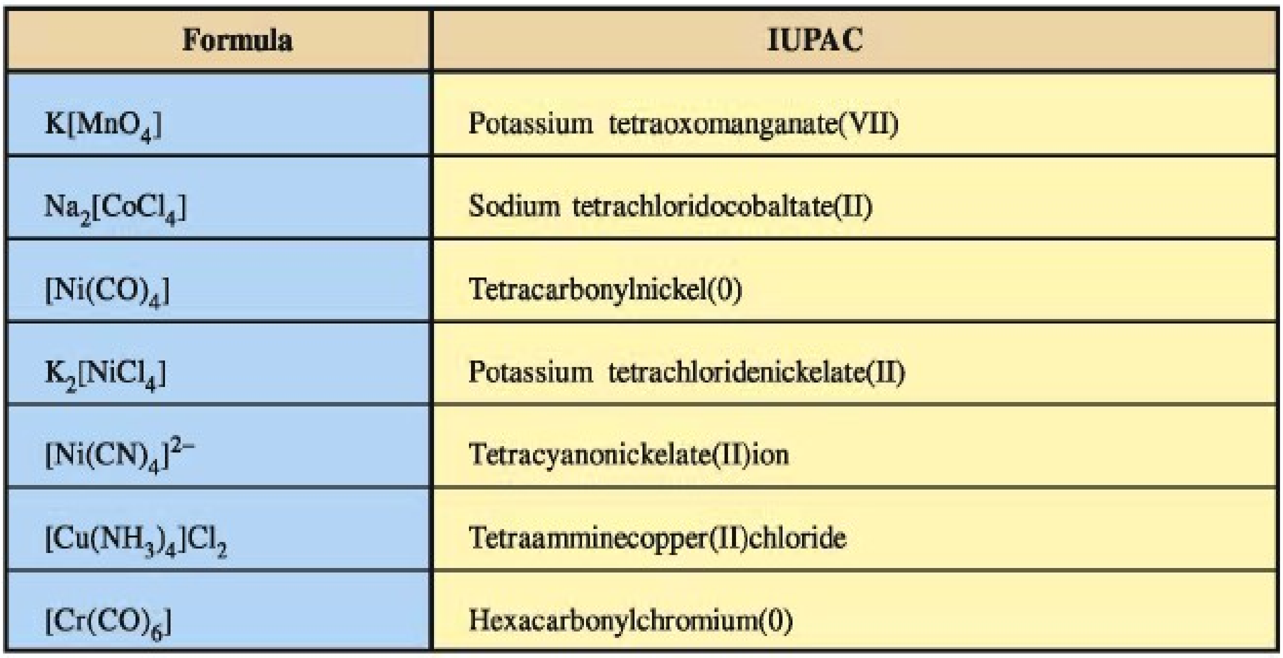
(iii) Names of the anionic ligands end in –o, those of neutral and cationic ligands are the same except 'aqua' for H_2O,'ammine' for NH_3, 'carbonyl' for CO and 'nitrosyl' for NO.

(iv) Prefixes mono, di, tri, etc., are used to indicate the number of individual ligands in the co-ordination entity. When the names of the ligands include a numerical prefix, then the terms bis (for 2 such ligands), tris (for 3), tetrakis (for 4) are used. Here the name of the ligand is placed in simple bracket.

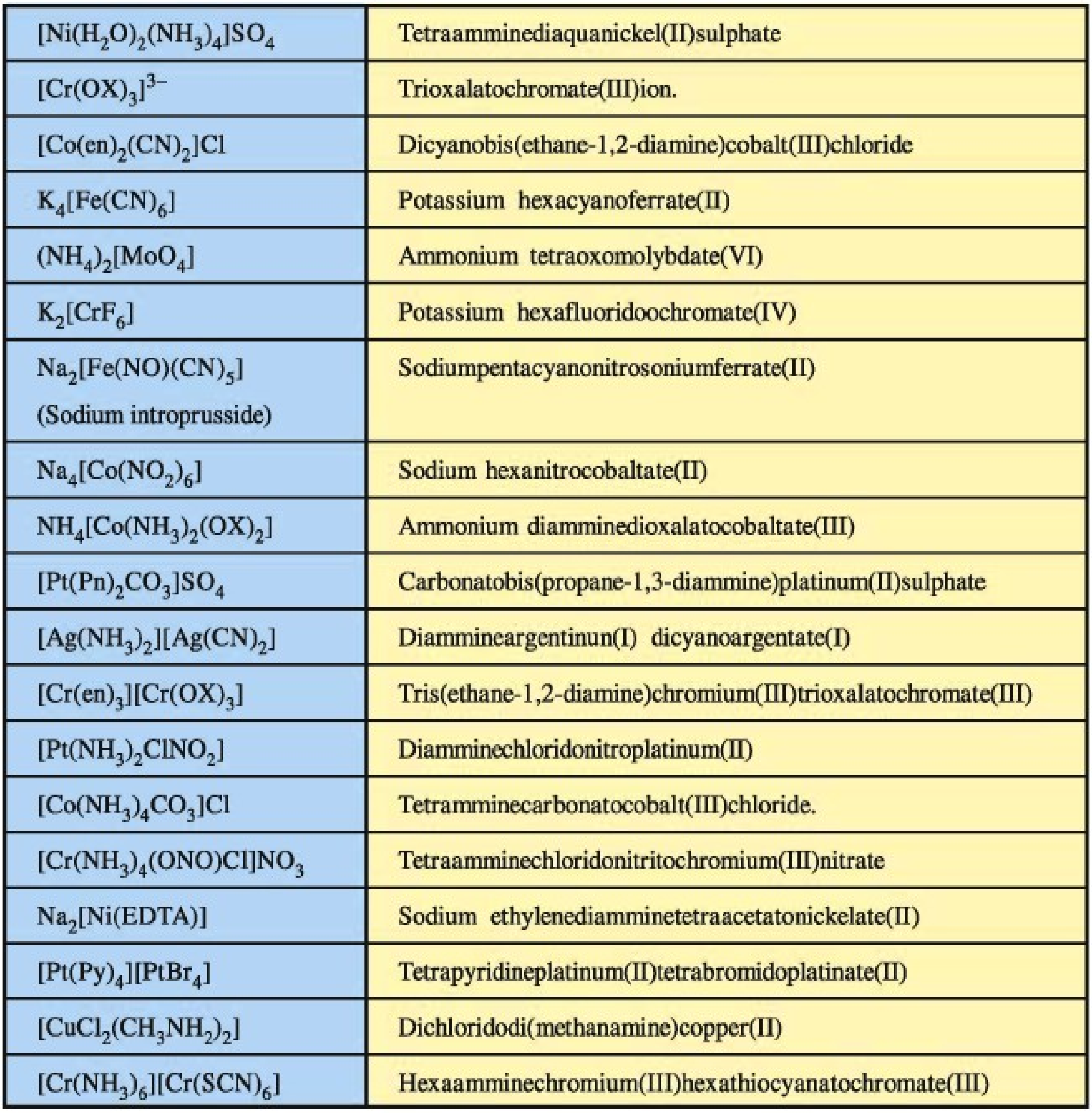
(v) Oxidation state of the metal is indicated by Roman numeral in simple bracket.

(vi) If the complex ion is a cation, the central atom is named same as the element. If the complex ion is an anion, the name of the metal ends with the suffix –ate. For example ferrate for iron, cobaltate for cobalt, zincate for Zn etc.

(vii) The neutral complex molecule is named similar to that of the cationic complex.



Formula	IUPAC
$K[MnO_4]$	Potassium tetraoxomanganate(VII)
$Na_2[CoCl_4]$	Sodium tetrachloridocobaltate(II)
$[Ni(CO)_4]$	Tetracarbonylnickel(0)
$K_2[NiCl_4]$	Potassium tetrachloridenickelate(II)
$[Ni(CN)_4]^{2-}$	Tetracyanonickelate(II)ion
$[Cu(NH_3)_4]Cl_2$	Tetraamminecopper(II)chloride
$[Cr(CO)_6]$	Hexacarbonylchromium(0)



$[Ni(H_2O)_2(NH_3)_4]SO_4$	Tetraamminediaquanickel(II)sulphate
$[Cr(OX)_3]^{3-}$	Trioxalatochromate(III)ion.
$[Co(en)_2(CN)_2]Cl$	Dicyanobis(ethane-1,2-diamine)cobalt(III)chloride
$K_4[Fe(CN)_6]$	Potassium hexacyanoferrate(II)
$(NH_4)_2[MoO_4]$	Ammonium tetraoxomolybdate(VI)
$K_2[CrF_6]$	Potassium hexafluoridoochromate(IV)
$Na_2[Fe(NO)(CN)_5]$ (Sodium introprusside)	Sodiumpentacyanonitrosoniumferrate(II)
$Na_4[Co(NO_2)_6]$	Sodium hexanitrocobaltate(II)
$NH_4[Co(NH_3)_2(OX)_2]$	Ammonium diamminedioxalatocobaltate(III)
$[Pt(Pn)_2CO_3]SO_4$	Carbonatobis(propane-1,3-diammine)platinum(II)sulphate
$[Ag(NH_3)_2][Ag(CN)_2]$	Diammineargentinun(I) dicyanoargentate(I)
$[Cr(en)_3][Cr(OX)_3]$	Tris(ethane-1,2-diamine)chromium(III)trioxalatochromate(III)
$[Pt(NH_3)_2ClNO_2]$	Diamminechloridonitroplatinum(II)
$[Co(NH_3)_4CO_3]Cl$	Tetramminecarbonatocobalt(III)chloride.
$[Cr(NH_3)_4(ONO)Cl]NO_3$	Tetraamminechloridonitritochromium(III)nitrate
$Na_2[Ni(EDTA)]$	Sodium ethylenediamminetetraacetatonickelate(II)
$[Pt(Py)_4][PtBr_4]$	Tetrapyridineplatinum(II)tetrabromidoplatinate(II)
$[CuCl_2(CH_3NH_2)_2]$	Dichloridodi(methanamine)copper(II)
$[Cr(NH_3)_6][Cr(SCN)_6]$	Hexaamminechromium(III)hexathiocyanatochromate(III)

Theories of Co-ordination Compounds

1. Werner's Co-ordination Theory

It was Alfred Werner who first proposed a theory for co-ordination compounds. He studied the amino complexes of Co, Pt etc. and proposed the following postulates:

1) Every metal has two types of valencies – primary (1^0) valency and secondary (2^0) valency. Primary valency is ionisable, while secondary valency is non-ionisable.

2) Primary valency is denoted by doted lines, while secondary valency is denoted by thick lines.

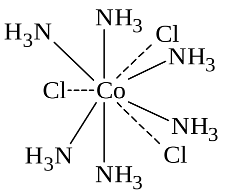
3) Primary valency gives the oxidation state of the metal, while secondary valency gives the co-ordination number of the metal.

4) Primary valency is always satisfied by –ve ions, while secondary valency may be satisfied by –ve ions or neutral molecules.

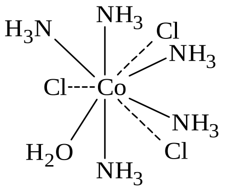
5) Every metal has a fixed number of secondary valencies. In order to satisfy this requirement, some –ve ions may perform dual character – i.e., they act as primary and secondary valencies simultaneously.

6) The primary valencies are non-directional, while the secondary valencies are directional. i.e. they are directed to some fixed positions in space.

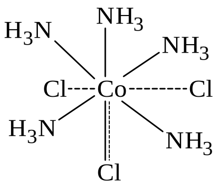
7) Since secondary valencies are directional, co-ordination compounds have a definite geometry and they show isomerism.



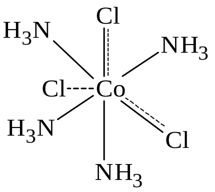
$CoCl_3.6NH_3$ or
$[(Co^{III}(NH_3)_6]^{3+}(Cl^-)_3$



$CoCl_3.5NH_3H_2O$ or
$[(Co^{III}(NH_3)_5(H_2O)]^{3+}(Cl^-)_3$



$CoCl_3.5NH_3$ or
$[(Co^{III}(NH_3)_5Cl]^{2+}(Cl^-)_2$



$CoCl_3.4NH_3H_2O$ or
$[(Co^{III}(NH_3)_4Cl_2]^+Cl^-$

Demerits: Werner could not explain why only certain elements form co-ordination compounds. Also he could not explain the directional nature of bonds in co-ordination compounds and their magnetic and optical properties.

In order to explain the above properties, many theories such as Valence Bond Theory (VBT), Crystal Field Theory (CFT), Ligand Field Theory (LFT) and Molecular Orbital Theory (MOT) are proposed.

2. The Valence Bond Theory (VBT)

This theory was put forward by Linus Pauling. The important postulates of this theory are:

1) In co-ordination compounds, the central metal atom/ion provides some vacant orbitals in order to accommodate the electrons donated by the ligands. The number of vacant orbitals formed is equal to the co-ordination number of the metal atom.

2) The vacant orbitals of the metal undergo hybridisation to form a set of new orbitals called hybrid orbitals. The type of hybridisation gives the shape of the compound.

3) Tetrahedral, square planar and octahedral complexes are formed as a result of sp^3, dsp2 and d^2sp^3 (sp^3d^2) hybridisation respectively.

4) Each ligand should contain at least one pair of electron.

5) The vacant hybrid orbitals of the metal overlap with the filled orbitals of the ligands to form ligand – metal coordinate bond.

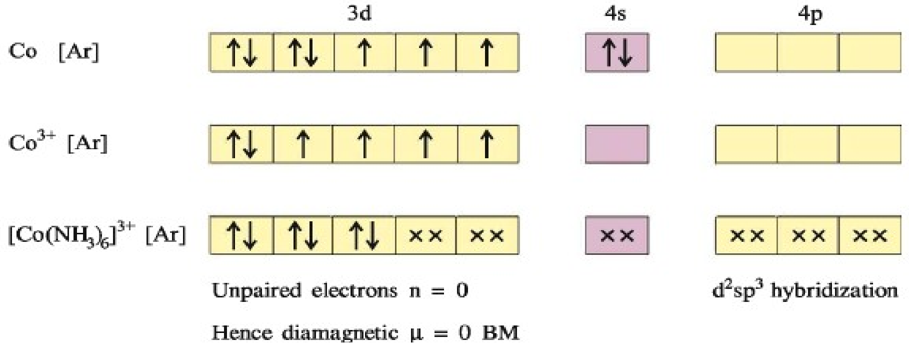
6) If a complex contains unpaired electron, it is paramagnetic and if it contains only paired electron, it is diamagnetic.

Coordination number	Type of hybridisation	Distribution of hybrid orbitals in space
4	sp^3	Tetrahedral
4	dsp^2	Square planar
5	sp^3d	Trigonal bipyramidal
6	sp^3d^2	Octahedral
6	d^2sp^3	Octahedral

Applications of VBT

It is usually possible to predict the geometry of a complex from the knowledge of its magnetic behaviour on the basis of the valence bond theory.

E.g.: 1) **$[Co(NH_3)_6]^{3-}$** Here the central atom **Co** is in +3 oxidation state.



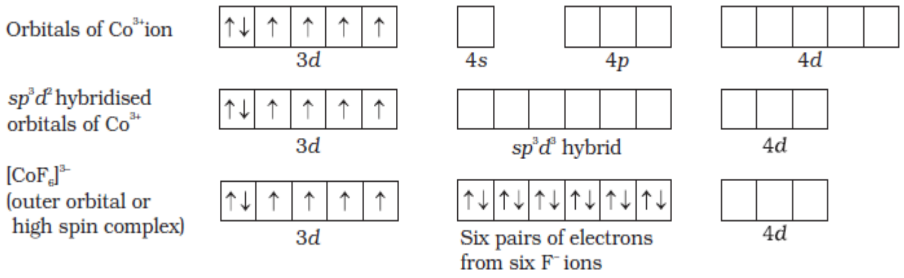
In this complex, the co-ordination number of Fe is 6 and hence the no. of vacant orbitals required = 6. In presence of the ligand NH_3, the electrons in 3d level get paired.

Now the two 3d orbitals, one 4s orbital and three 4p orbitals undergo d^2sp^3 hybridization to form 6 new orbitals.

Six pairs of electrons, one from each NH_3 , occupy these six hybrid orbitals. Thus, the complex has octahedral geometry and is paramagnetic because of the presence of one unpaired electron.

In the formation of this complex, since the inner d orbitals (3d) are used for hybridization, the complex is called an **inner orbital** or **low spin** or **spin paired complex**

E.g.: 2) **$[CoF_6]^{3-}$** Here the central atom **Co** is in +3 oxidation state.

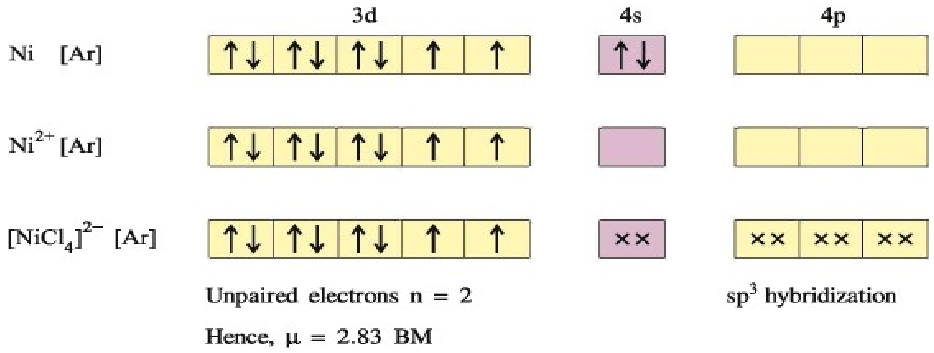


In this complex the co-ordination number of **Co** is 6 and hence the no. of vacant orbitals required = 6. In presence of the ligand F-, the electrons in 3d level do not get paired.

Now the one 4s orbital, three 4p orbitals and two 4d orbitals undergo sp^3d^2 hybridization to form 6 new orbitals. These hybrid orbitals overlap with the filled orbitals of the ligand to form ligand– metal co-ordinate bond.

Since the hybridization is sp^3d^2, the shape of the molecule is octahedral and due to the presence of 5 unpaired electrons, it is highly paramagnetic. In the formation of this complex, since the outer orbitals (4d) are used for hybridisation (sp^3d^2), it is called **outer orbital** or **high spin** or **spin free complex**.

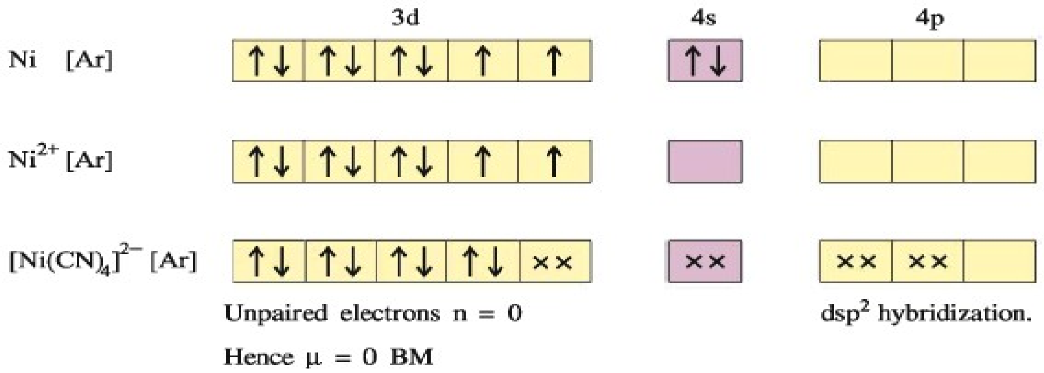
E.g.: 3) **$[NiCl_4]^{2-}$** Here the central atom **Ni** is in +2 oxidation state.



In this complex the co-ordination number of Ni is 4 and hence the no. of vacant orbitals required = 4. In presence of the ligand Cl-, the electrons in 3d level do not get paired.

Now the one 4s orbitals and three 4p orbitals undergo sp3 hybridization to form 4 new orbitals. These four hybrid orbitals are occupied by the four electron pairs from each Cl- ligands. Thus, the complex has tetrahedral geometry and is paramagnetic because of the presence of unpaired electron.

E.g.: 4) **$[Ni(CN)_4]^{2-}$** Here the central atom **Ni** is in +2 oxidation state.



In this complex the co-ordination number of Ni is 4 and hence the no. of vacant orbitals required = 4. Even though it contains 4 orbitals, in presence of the ligand CN-, the electrons in 3d level get paired.

Now the one 3d orbital, one 4s orbital and two 4p orbitals undergo dsp^2 hybridization to form 4 new orbitals. Four pairs of electrons, one from each CN- ions, occupy these four hybrid orbitals. Thus, the complex has square planar geometry and is diamagnetic, because of the absence of unpaired electron.

Magnetic Properties of Co-ordination Compounds

By knowing the magnetic moment, we can predict the geometry of complexes. For e.g. $[Mn(CN)_6]^{3-}$ has magnetic moment of two unpaired electrons while $[MnCl_6]^{3-}$ has a paramagnetic moment of four unpaired electrons. $[Fe(CN)_6]^{3-}$ has magnetic moment of a single unpaired electron while $[FeF_6]^{3-}$ has a paramagnetic moment of five unpaired electrons.

$[CoF_6]^{3-}$ is paramagnetic with four unpaired electrons while $[Co(C_2O_4)_3]^{3-}$ is diamagnetic.

This can be explained by valence bond theory in terms of formation of inner orbital and outer orbital co-ordination entities. $[Mn(CN)_6]^{3-}$, $[Fe(CN)_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$ are inner orbital complexes involving d^2sp^3 hybridisation, the former two complexes are paramagnetic and the latter diamagnetic. On the other hand, $[MnCl_6]^{3-}$, $[FeF_6]^{3-}$ and $[CoF_6]^{3-}$ are outer orbital complexes involving sp^3d^2 hybridisation and are paramagnetic corresponding to four, five and four unpaired electrons.

Limitations of Valence Bond Theory

Even though the VB theory explains the formation, structures and magnetic behaviour of co-ordination compounds, it has the following limitations:

(i) It involves a number of assumptions.

(ii) It does not give quantitative interpretation of magnetic data.

(iii) It does not explain the colour exhibited by co-ordination compounds.

(iv) It does not give a quantitative interpretation of the thermodynamic or kinetic stabilities of co-ordination compounds.

(v) It does not make exact predictions regarding the tetrahedral and square planar structures of 4-co-ordinated complexes.

(vi) It does not distinguish between weak and strong ligands.

3.Crystal Field Theory

The crystal field theory (CFT) is an electrostatic model which considers the metal-ligand bond as purely ionic.

Here the ligands are treated as point charges in case of anions or as dipoles in case of neutral molecules. The five d orbitals in an isolated gaseous metal atom/ion have same energy, i.e., they are degenerate. This degeneracy is maintained if a spherically symmetrical field of negative charges surrounds the metal atom/ion. But when this negative field is due to ligands in a complex, the degeneracy of the d orbitals is lost. It results in splitting of the d orbitals. This splitting of d-orbitals is termed as Crystal field splitting and it depends on the nature of the field.

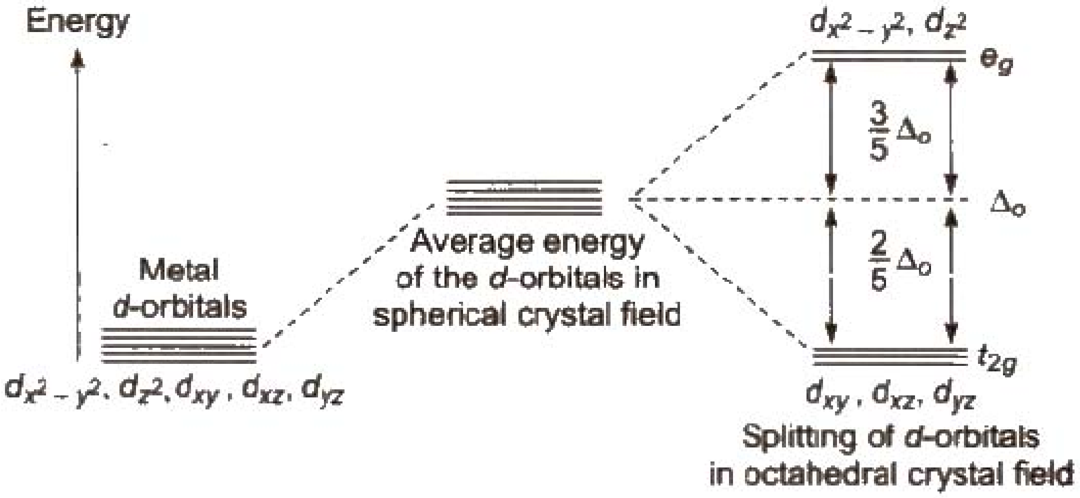
(a) Crystal field splitting in octahedral co-ordination entities (octahedral field)

In an octahedral co-ordination entity there are six ligands surrounding the metal atom/ion and they are along the axis of the octahedron.

So the repulsion between the electrons in metal d orbitals and the electrons (or negative charges) of the ligands is greater for the d_{x2-y2} and d_{z2} orbitals, which are pointing towards the axes, than the d_{xy}, d_{yz} and d_{xz}

orbitals, which are directed between the axes. So the energy of the d_{x2-y2} and d_{z2} orbitals (called eg orbitals) will be raised and that of the dxy, dyz and dxz orbitals (called t_2g orbitals) will be lowered. Thus, the degeneracy of the d orbitals has been removed.

This splitting of the degenerate levels due to the presence of ligands in a definite geometry is termed as **crystal field splitting** and the energy separation is denoted by Δo (the subscript o is for octahedral). Thus, the energy of the two eg orbitals will increase by (3/5) Δo and that of the three t_2g orbitals will decrease by (2/5) Δo.



Strong field ligands produce large splitting whereas weak field ligands produce small splitting of d orbitals.

Filling of electrons

For d^1, d^2 and d^3 coordination entities, the d electrons occupy the t_2g orbitals singly in accordance with the Hund's rule. For d^4 ions, two possible patterns of electron distribution arise:

(i) the fourth electron could either enter the t_2g level and pair with an existing electron, or (ii) it could enter into the eg level.

Here the electron distribution depends on the relative magnitude of the crystal field splitting (Δo) and the pairing energy (P).

If $\Delta o < P$, the fourth electron enters one of the eg orbitals giving the configuration $t_2g^3eg^1$. Ligands for which $\Delta o < P$ are known as weak field ligands and form high spin complexes.

If $\Delta o > P$, the fourth electron occupy a t_2g orbital with configuration $t_2g^4eg^0$. Ligands for which $\Delta o < P$ are known as strong field ligands and form low spin complexes.

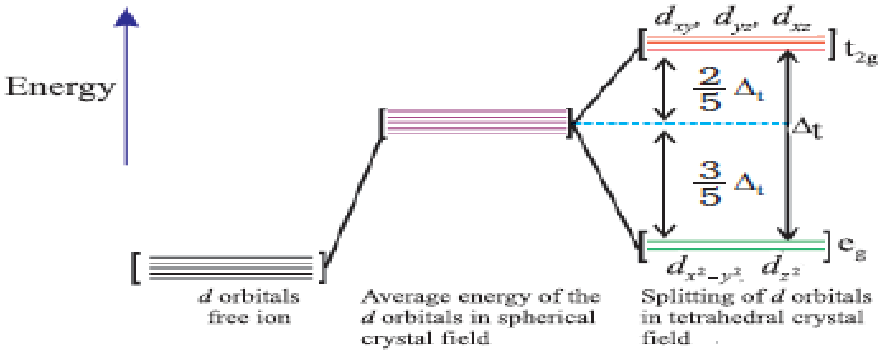
b) Crystal field splitting in Tetrahedral coordination entities (tetrahedral field)

A tetrahedron can be considered as a cube in which only alternate corners are occupied by ligands and the metal ion is at the centre of the cube.

The $d_{x^2-y^2}$ and d_{z^2} orbitals (called e orbitals) point towards the centre of each faces of the cube and the dxy, dyz and dxz orbitals (called t_2 orbitals) point towards the edge centre of the cube.

Since the ligands are approaching through the corners, there is no direct interaction between the ligands and the d-orbitals. However, the 't2' orbitals lie closer to the ligands than the 'e' orbitals.

As a result the energy of the 't_2' orbitals increases and that of 'e' orbitals decreases. So the d orbitals split into two – triply degenerate **'t_2' orbitals** with higher energy and doubly degenerate **'e' orbitals** with lower energy.



The splitting in tetrahedral field is less than that in octahedral field.

It is found that $\Delta t = 4/9\ \Delta o$.

This is because in tetrahedral field, there are only four ligands (but in octahedral field, the number of ligands is six) and there is no direct interaction between the ligands and the d-orbitals.

Spectrochemical series

It is a series in which the ligands are arranged in the increasing order of their field strength. The series is: $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- <$ $edta^{4-} < NH_3 <$ en $< CN^- < CO$.

It is an experimentally determined series based on the absorption of light by complexes with different ligands.

Colour in Coordination Compounds

Most of the complexes of transition metals are coloured. This can be explained in terms of the crystal field theory.

In presence of the ligands, the crystal field splitting occurs. So the electrons from lower d level (t_2g level) can excite to higher d level (eg level). For this some energy is required, which is absorbed from the white light.

The colour of the complex is complementary to that which is absorbed. Thus **according to crystal field theory the colour of the coordination compounds is due to**
d-d transition of the electron.

For example, the complex $[Ti(H_2O)_6]^{3+}$ is violet in colour. This is an octahedral complex where the single electron (Ti^{3+} is a $3d^1$ system) in the metal d orbital is in the t2g level in the ground state of the complex. The next higher state available for the electron is the empty eg level. If light corresponding to the energy of yellow-green region is absorbed by the complex, it would excite the electron from t2g level to the eg level. Consequently, the complex appears violet in colour.

In the absence of ligand, crystal field splitting does not occur and hence the substance is colourless. For example, when $[Ti(H_2O)_6]^{3+}$ is heated it becomes colourless. Similarly, anhydrous $CuSO_4$ is white, but $CuSO_4.5H_2O$ is blue in colour.

The colour of a complex depends on the strength of ligand and the nature of the field.

Limitations of Crystal Field Theory

1. From the assumptions, that the ligands are point charges, it follows that anionic ligands should exert the greatest splitting effect. But the anionic ligands actually are found at the low end of the spectrochemical series.
2. It does not take into account the covalent character of bonding between the ligand and the central atom.

Stability of Coordination Compounds

The stability of a complex in solution refers to the degree of association between the metal ion and ligands in the state of equilibrium. The magnitude of the (stability or formation) equilibrium constant for the association, quantitatively expresses the stability.

For a reaction of the type:

$$M + 4L \rightleftarrows ML_4 \qquad \beta = [ML_4]/[M][L]^4$$

As the value of the stability constant increases, the stability of the complex also increases. The above reaction can be considered to take place in 4 steps:

$$M + L \quad ML \qquad K_1 = [ML]/[M][L]$$

$$ML + L \rightleftarrows ML_2 \qquad K_2 = [ML_2]/[ML][L]$$

$$ML_2 + L \rightleftarrows ML_3 \qquad K_3 = [ML_3]/[ML_2][L]$$

$$ML_3 + L \rightleftarrows ML_4 \qquad K_4 = [ML_4]/[ML_3][L]$$

Where K_1, K_2,K_3 and K_4 are referred to as **stepwise stability constants.**

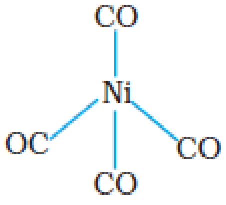
The **overall stability constant**, $\beta = K_1 \times K_2 \times K_3 \times K_4$

The stability of a complex depends on the following factors:

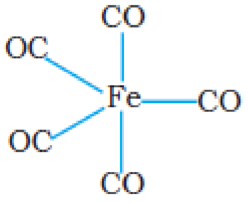
1. **The nature of the metal ion**: Greater the charge to radius of the metal ion, greater will be the stability of the complex.
2. **Nature of the ligand**: The greater the basic strength of the ligand, the greater will be the stability of the complex.
3. **Presence of chelating ligands**: increases the stability of the complex.

Bonding in Metal Carbonyls

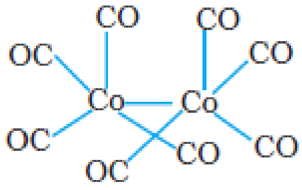
Transition metals form a large number of homoleptic carbonyls. Eg. $[Ni(CO)_4]$, $[Fe(CO)_5]$, $[Cr(CO)_6]$, $[Co_2(CO)_8]$, $[Mn_2(CO)_{10}]$ etc. These carbonyls have simple, well defined structures



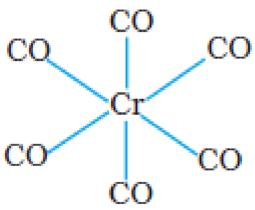
$Ni(CO)_4$
Tetrahedral



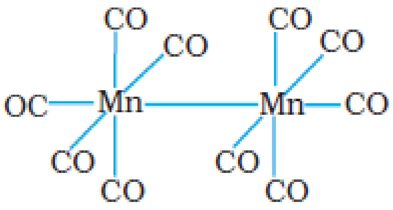
$Fe(CO)_5$
Trigonal bipyramidal



$[Co_2(CO)_8]$

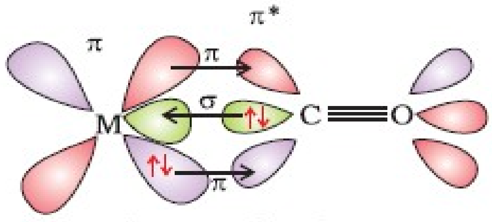


$Cr(CO)_6$ Octahedral



$[Mn_2(CO)_{10}]$

The metal-carbon bond in metal carbonyls possess both s and p character. The M–C s bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal. The M–C p bond is formed by the donation of a pair of electrons from a filled d orbital of metal into the vacant anti-bonding p* orbital of carbon monoxide. Thus the metal to ligand bonding creates a synergic effect which strengthens the bond between CO and the metal.



Synergic bonding

Application of Co-ordination Complexes

1. In Qualitative & Quantitative Analysis: Co-ordination compounds find use in many qualitative and quantitative chemical analyses. For e.g. Ni^{2+} is detected and estimated by the formation of a complex with Dimethyl Glyoxime (DMG). The brown ring test for the detection of nitrate ion is due to the formation of the brown complex $[Fe(H_2O)_5NO]^{2+}$. The Ca^{2+} and Mg^{2+} ions are estimated by the formation of stable complexes with EDTA.

2. In water treatment: The Hardness of water is estimated by simple titration with Na2EDTA (sodium salt of EDTA). The Ca^{2+} and Mg^{2+} ions form stable complexes with EDTA. The hardness of water can be removed by the formation of a complex with calgon (Sodium polymetaphosphate)

3. In Metallurgy: Metals like silver and gold are extracted by the formation of complexes with CN^- ligands. Gold forms the complex $[Au(CN)_2]^-$ and silver forms $[Ag(CN)_2]^-$ which are separated with Zn.

Similarly, coordination compounds also find application in the refining of some metals. For example, impure nickel is converted to $[Ni(CO)_4]$, which is decomposed to yield pure nickel

4. Biological Applications: Coordination compounds are of great importance in biological systems. Chlorophyll is a coordination compound of **magnesium**, Haemoglobin, is a co-ordination compound of **iron** and Vitamin B_{12} (cyanocobalamine) is a co-ordination compound of **cobalt**.

5.In Catalysis: Co-ordination compounds are used as catalysts for many industrial processes. For e.g. Tris(triphenylphosphine)rhodiumchloride, $[(Ph_3P)_3RhCl]$ (Wilkinson catalyst), is used for the hydrogenation of alkenes.

6.In electroplating: Articles can be electroplated with silver and gold by using the solutions of the complexes, $[Ag(CN)_2]^-$ and $[Au(CN)_2]^-$ respectively as electrolytes.

7. In Photography: In black and white photography, the developed film is fixed by washing with hypo solution which dissolves the undecomposed AgBr to form a complex ion, $[Ag(S_2O_3)_2]^{3-}$.

8. In medicine: Cis-platin is used for the treatment of cancer. Excess of copper and iron in animal or plant body are removed by the chelating ligands D–penicillamine and desferrioxime B through the formation of co-ordination compounds. EDTA is used in the treatment of lead poisoning.

10.HALOALKANES AND HALOARENES

These are compounds containing halogen atoms attached to an alkyl or aryl group. The general representation of **haloalkanes** is **R-X** and that of **haloarenes** is **Ar-X** [where X = F, Cl, Br, I].

Classification

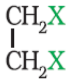
I) On the basis of number of halogen atoms:

Based on this, haloalkanes and haloarenes are classified as mono, di or polyhalogen compounds.

Monohalogen compounds contain only one halogen atom, dihalocompounds contain 2 halogen atoms and polyhalogen compounds contain more than 2 halogen atoms.

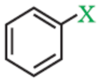
C_2H_5X

Monohaloalkane

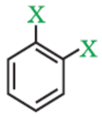


Dihaloalkane

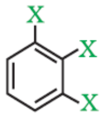
Trihaloalkane



Monohaloarene



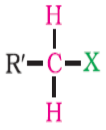
Dihaloarene



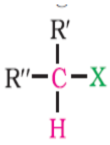
Trihaloarene

II) Compounds containing sp^3 C-X bond: They include

a) Alkyl halides or haloalkanes (R-X): Here the halogen atom is directly bonded to an sp3 hybridized C atom of an alkyl group. They are further classified as primary, secondary or tertiary according to the nature of carbon to which halogen atom is attached.



Primary (1°)

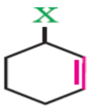


Secondary (2°)

Tertiary (3°)

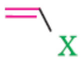
b)Allylic halides: Here the halogen atom is bonded to an sp3 hybridized carbon atom next to a C = C bond. E.g.: $CH_2=CH-CH_2X$

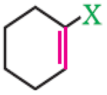
c)Benzylic halides: These are compounds in which the halogen atom is bonded to an sp3 hybridized carbon atom next to an aromatic ring. E.g.: $C_6H_5-CH_2-X$



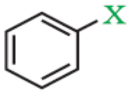
III) Compounds having sp^2 C-X bond: They include

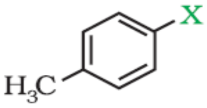
a)Vinylic halides: Here the halogen atom is directly bonded to an sp2 hybridized carbon atom of a C=C bond. E.g.:





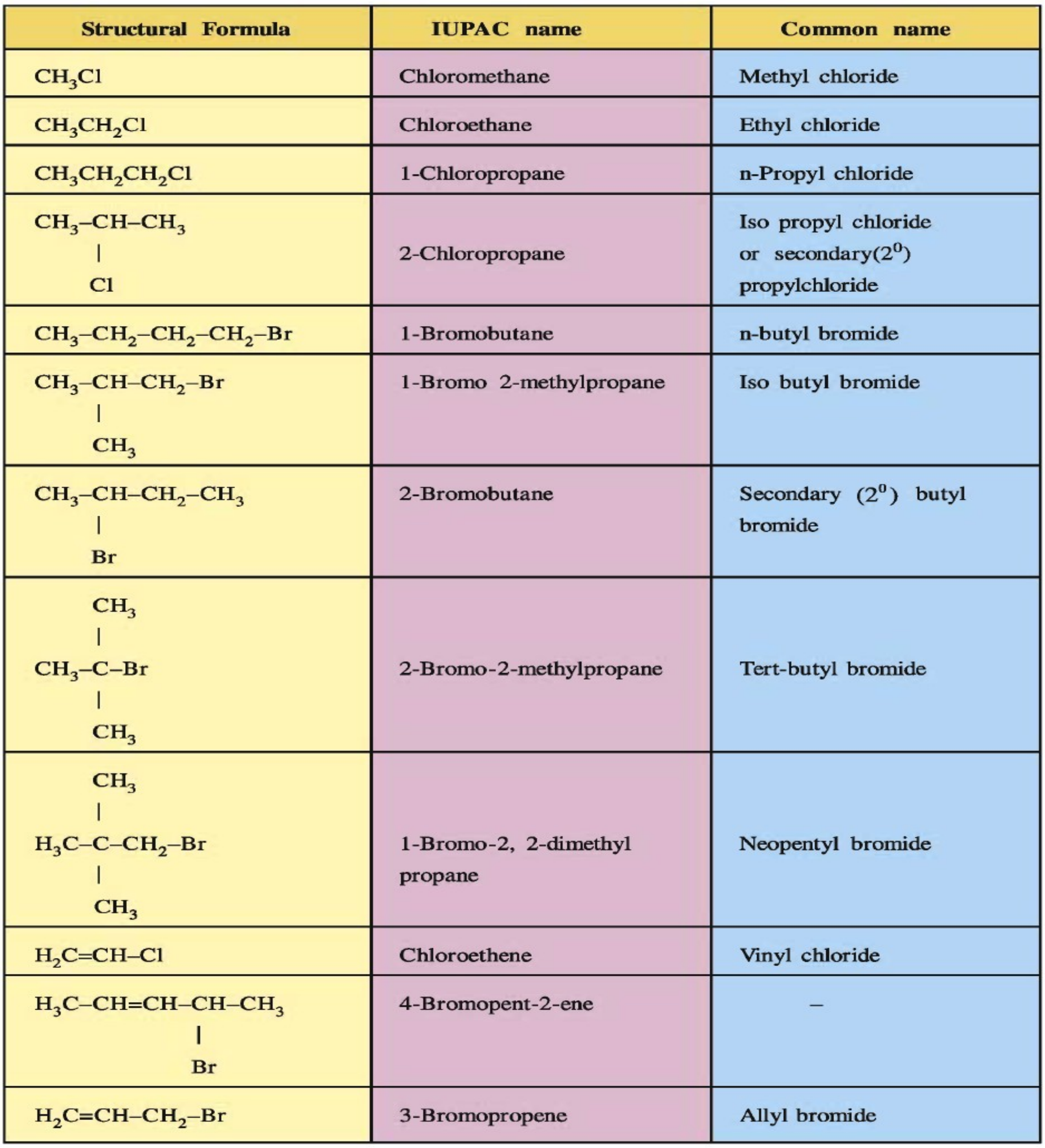
b) Aryl halides: Here the halogen atom is directly bonded to an sp2 hybridized carbon atom of an aromatic ring. E.g. : C6H5-X



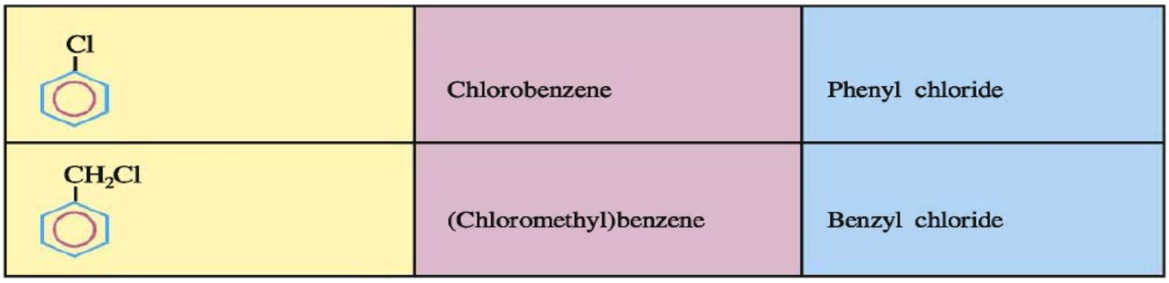


Nomenclature

Common name of alkyl halides is obtained by adding –yl halide to the word root (i.e. word root + yl halide) and the IUPAC name is obtained by adding the prefix ‘halo’ to the name of the parent alkane (i.e. halo + alkane). Some examples are:



Structural Formula	IUPAC name	Common name
CH_3Cl	Chloromethane	Methyl chloride
CH_3CH_2Cl	Chloroethane	Ethyl chloride
$CH_3CH_2CH_2Cl$	1-Chloropropane	n-Propyl chloride
$CH_3-\underset{Cl}{\underset{\mid}{CH}}-CH_3$	2-Chloropropane	Iso propyl chloride or secondary(2^0) propylchloride
$CH_3-CH_2-CH_2-CH_2-Br$	1-Bromobutane	n-butyl bromide
$CH_3-\underset{CH_3}{\underset{\mid}{CH}}-CH_2-Br$	1-Bromo 2-methylpropane	Iso butyl bromide
$CH_3-\underset{Br}{\underset{\mid}{CH}}-CH_2-CH_3$	2-Bromobutane	Secondary (2^0) butyl bromide
$CH_3-\overset{CH_3}{\overset{\mid}{\underset{CH_3}{\underset{\mid}{C}}}}-Br$	2-Bromo-2-methylpropane	Tert-butyl bromide
$H_3C-\overset{CH_3}{\overset{\mid}{\underset{CH_3}{\underset{\mid}{C}}}}-CH_2-Br$	1-Bromo-2, 2-dimethyl propane	Neopentyl bromide
$H_2C=CH-Cl$	Chloroethene	Vinyl chloride
$H_3C-CH=CH-\underset{Br}{\underset{\mid}{CH}}-CH_3$	4-Bromopent-2-ene	–
$H_2C=CH-CH_2-Br$	3-Bromopropene	Allyl bromide



Cl	Chlorobenzene	Phenyl chloride
CH_2Cl	(Chloromethyl)benzene	Benzyl chloride

Methods of preparation

I) From alcohols:

a) By the action of concentrated halogen acids on alcohols in presence of anhydrous $ZnCl_2$ as catalyst.

$$R\text{-}OH + HX \xrightarrow{an.\ ZnCl_2} R\text{-}X + H_2O$$

Reactions of primary and secondary alcohols with HI require the presence of an. ZnCl2, while tertiary alcohols do not require the catalyst.

b) Alkyl chlorides are obtained by the action of PCl_3,PCl_5 or $SOCl_2$ with alcohols.

$$3R\text{-}OH + PCl_3 \longrightarrow 3\ R\text{-}Cl + H_3PO_3.$$

$$R\text{-}OH + PCl_5 \longrightarrow R\text{-}Cl + POCl_3 + HCl$$

$$R\text{-}OH + SOCl_2 \longrightarrow R\text{-}Cl + SO_2 + HCl$$

Among these methods, the reaction with thionyl chloride ($SOCl_2$) is preferred, since the byproducts are gases and are easily escaped from the reaction medium.

For the preparation of alkyl bromides and iodides, alcohols are treated with bromine or iodine in presence of red phosphorus, since PBr_3 and PI_3 are unstable.

R-OH $\xrightarrow{X_2/Red\ P}$ R-X (where X_2 = Br_2 or I_2)

II)From Hydrocarbons

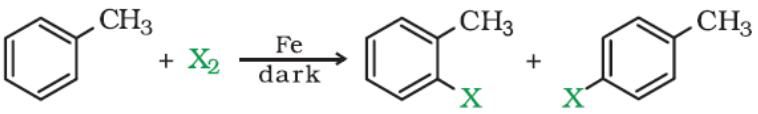
a)Free radical halogenation:

Alkanes react with chlorine or bromine in presence of sunlight; we get a mixture of mono, di and polyhaloalkanes.

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{Cl_2/\text{UV light}} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CHClCH_3$$

b)Electrophilic substitution:

Benzene or its derivatives when heated with Cl_2 or Br_2 in presence of iron or Lewis acids like anhydrous $FeCl_3$ (ferric chloride) or $AlCl_3$, we get aryl chlorides or bromides.



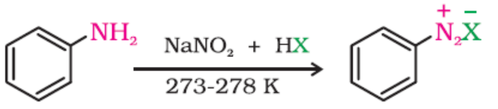
o-Halotoluene p-Halotoluene

The ortho and meta isomers can be easily separated due to their large difference in melting point.

For the preparation of aryl iodides, arenes are treated with I_2 in presence of an oxidising agent like HNO_3 or HIO_4 (periodic acid) to oxidise the HI formed during the reaction.

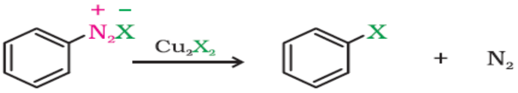
c)Sandmeyer's reaction:

Aromatic primary amines when treated with mineral acids like HCl and sodium nitrite ($NaNO_2$) at cold condition (0 – 5^{0}C), an aromatic diazonium salt is formed. This reaction is called Diazotisation.



Benzene diazonium halide

When a diazonium salt is treated with HX in presence of cuprous halide (Cu_2X_2), we get a halobenzene. This reaction is called Sandmeyer's reaction.

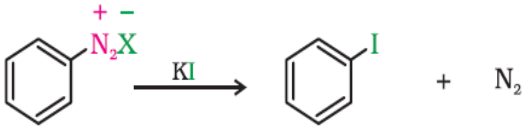


Aryl halide

X = Cl, Br

Note: If the cuprous halide is replaced by copper powder, the reaction is called Gattermann's reaction.

For the preparation of iodobenzene, the diazonium salt is treated with potassium iodide.



d) From alkene:

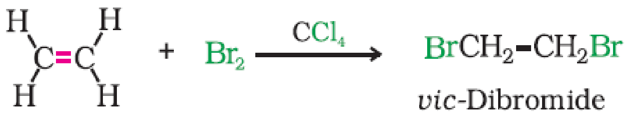
i) **Addition of hydrogen halide (HX)**: Alkenes add HX (HCl, HBr or HI) to form alkyl halides. In the case of unsymmetrical alkenes, the addition takes place according to Markownikoff's rule. [The rule states that "when an unsymmetrical reagent is added to an unsymmetrical alkene, the negative part of the addendum (adding molecule) gets attached to the carbon containing lesser number of hydrogen atoms"].

$$CH_3CH=CH_2 + H{-}I \longrightarrow \underset{\text{minor}}{CH_3CH_2CH_2I} + \underset{\text{major}}{CH_3CHICH_3}$$

ii)**Addition of halogen**: Alkenes add halogen to form vicinal dihalides (2 halogen atoms on adjacent C atoms).

For e.g. addition of bromine in CCl_4 to an alkene results in the formation of vicinal dibromides and also in the discharge of the reddish brown colour of Br_2 in CCl_4.

So this is used as a test for unsaturation.



III)Halogen Exchange Reactions

a) Finkelstein reaction: Alkyl chlorides or bromides when treated with NaI in dry acetone, alkyl iodides are formed. This reaction is known as Finkelstein reaction.

$$R{-}X + NaI \longrightarrow R{-}I + NaX$$

$X=Cl, Br$

b) Swarts reaction: This method is used for the preparation of alkyl fluorides. Here alkyl chloride or bromide is treated with a metallic fluoride like AgF, Hg_2F_2, CoF_2 or SbF_3, to get alkyl fluoride.

$$H_3C{-}Br + AgF \longrightarrow H_3C{-}F + AgBr$$

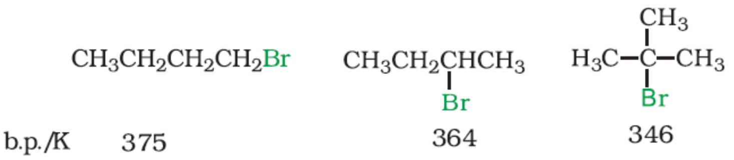
Physical Properties

Melting and boiling points:

In haloalkanes, the C-X bond is polar due to the greater electronegativity of halogen atom. Due to greater polarity and higher molar mass, the inter molecular forces of attraction (dipole-dipole and van der Waals forces) are strong and so they have higher melting and boiling points than hydrocarbons of comparable molar mass.

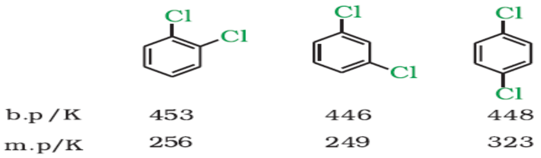
For the same alkyl group, the boiling points of alkyl halides decrease in the order: RI> RBr> RCl> RF. This is because with the increase in size and mass of halogen atom, the magnitude of van der Waal forces increases.

The boiling points of isomeric haloalkanes decrease with increase in branching. This is because as branching increases, the surface area of the molecule decreases. So the van der forces decreases and hence the b.p.



Among isomeric dihalobenzenes, the para-isomers are high melting as compared to their ortho and metaisomers.

It is due to symmetry of para-isomers that fits in crystal lattice better as compared to ortho- and metaisomers.



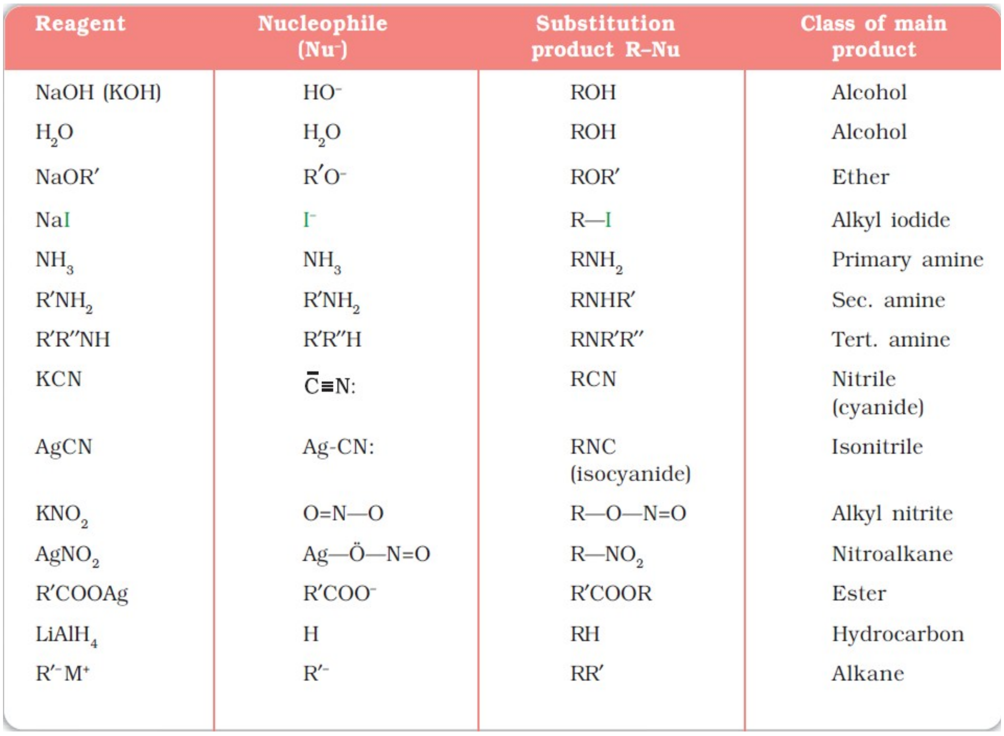
Solubility

The haloalkanes are only very slightly soluble in water. This is because they cannot form hydrogen bonds with water (except alkyl fluorides).

CHEMICAL REACTIONS OF HALOALKANES

i) Nucleophilic Substitution Reactions:

These are reactions in which a weak nucleophile is replaced by a strong nucleophile [Nucleophiles are electron rich species attacks at electron deficient centre]. In general these reactions can be represented by:



Reagent	Nucleophile (Nu^-)	Substitution product R–Nu	Class of main product
NaOH (KOH)	HO^-	ROH	Alcohol
H_2O	H_2O	ROH	Alcohol
NaOR′	$R'O^-$	ROR′	Ether
NaI	I^-	R—I	Alkyl iodide
NH_3	NH_3	RNH_2	Primary amine
$R'NH_2$	$R'NH_2$	RNHR′	Sec. amine
R′R″NH	R′R″H	RNR′R″	Tert. amine
KCN	$\bar{C}\equiv N:$	RCN	Nitrile (cyanide)
AgCN	Ag-CN:	RNC (isocyanide)	Isonitrile
KNO_2	O=N—O	R—O—N=O	Alkyl nitrite
$AgNO_2$	Ag—Ö—N=O	$R—NO_2$	Nitroalkane
R′COOAg	$R'COO^-$	R′COOR	Ester
$LiAlH_4$	H	RH	Hydrocarbon
R'^-M^+	R'^-	RR′	Alkane

CN^- is an **ambident nucleophile**. i.e. here both C and N contain lone pair of electrons and can bind to the carbon atom of the alkyl group either through C or through N. Another e.g. is NO_2^- Reaction with KCN gives alkyl cyanides.

This is because KCN is mainly ionic and gives CN^- ions in solution. So both C and N are free to donate electron pairs. But C – C bond is stronger than C – N bond. So cyanides are formed as the major product.

But AgCN is mainly covalent and only N is free to donate an electron pair. So isocyanides are the main product.

Mechanism of Nucleophilic Substitution Reactions

There are two types of mechanisms: Substitution Nucleophilic bimolecular (SN^2) and Substitution Nucleophilic unimolecular (SN^1)

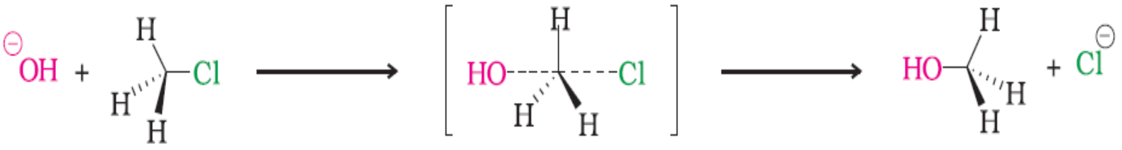
1. **Substitution Nucleophilic Bimolecular (SN^2) Mechanism**

Here the incoming nucleophile interacts with alkyl halide causing the carbon-halogen bond to break while forming a new carbon-OH bond. These two processes take place simultaneously in a single step and no intermediate is formed. As the reaction proceeds, the bond between the nucleophile and the carbon atom starts forming and the

bond between carbon atom and leaving group (the halogen atom) weakens. In the case of optically active alkyl halides, during this process, the configuration of carbon atom inverts and hence this process is called as **inversion of configuration**. In the transition state, the carbon atom is simultaneously bonded to five atoms and therefore is unstable.

An example is the reaction between CH_3Cl and hydroxide ion to yield methanol and chloride ion. This reaction follows a second order kinetics, i.e., the rate depends upon the concentration of both the reactants.

Mechanism of this reaction is:



Since this mechanism requires the approach of the nucleophile to the carbon bearing the leaving group, the presence of bulky substituents on or near the carbon atom decreases the rate of this reaction.

Thus the order of reactivity of alkyl halides towards SN^2 reaction is:

Primary halide > Secondary halide > Tertiary halide.

2. **Substitution nucleophilic unimolecular (SN^1)**:

SN^1 reactions are generally carried out in polar protic solvents (like water, alcohol, acetic acid, etc.). Here the reaction occurs in two steps. In the first step, the C—X bond undergoes slow cleavage to produce a carbocation and a halide ion. In the second step, the carbocation is attacked by the nucleophile to form the product. Here first step is the slowest and reversible. So it is the rate determining step. Since this step contains only one reactant, it follows first order kinetics.

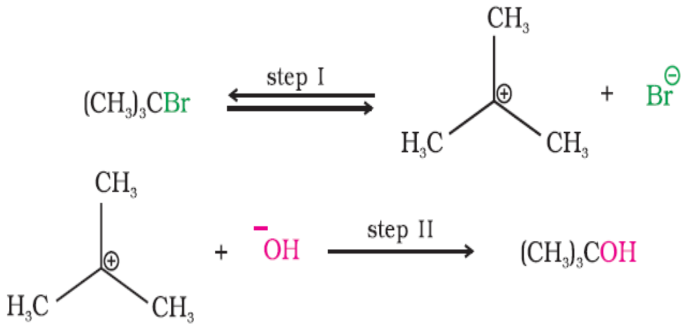
E.g.: The reaction between tert-butyl bromide and hydroxide ion to give tert-butyl alcohol.

$$(CH_3)_3CBr + {}^{-}OH \longrightarrow (CH_3)_3COH + Br^{-}$$

2-Bromo-2-methylpropane 2-Methylpropan-2-ol

This reaction occurs in two steps. In step I, the polarised C—Br bond undergoes slow cleavage to produce a carbocation and a bromide ion.

The carbocation thus formed is then attacked by nucleophile in step II to form the product.



Thus in SN^1 reaction, there is an intermediate called carbocation. The greater the stability of the carbocation, the greater will be the rate of the reaction.

In case of alkyl halides, 3^0 alkyl halides undergo SN^1 reaction very fast because of the high stability of 3^0 carbocations. So the order of reactivity of alkyl halides towards SN^1 reaction is: $3^0 > 2^0 > 1^0$.

Allylic and benzylic halides show high reactivity towards the SN^1 reaction. This is because of the higher stability of the carbocation formed. The allyl and benzyl halides are stabilized through resonance as follows:

Allyl carbocation

For both the mechanisms, the reactivity of halides follows the order: R–I> R–Br>R–Cl>>R–F.

Stereochemical Aspects of nucleophilic substitution Reactions Plane Polarised light

It is a light beam in which the particles vibrate in only one direction. It is produced by passing ordinary light beam through a Nicol prism. When such a light beam is passed through solutions of certain compounds, they rotate the plane of polarisation.

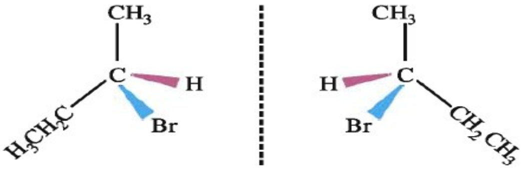
Such compounds are called **optically active compounds**.

The angle by which the plane polarised light is rotated is called optical rotation, which is measured by an instrument called polarimeter. If a compound rotates the plane polarised light towards right (i.e. clock-wise direction), it is called dextro rotatory or d-form or + form and if it rotates the plane polarised light towards left (i.e. anticlock-wise direction), it is called laevo rotatory or l-form or – form. The d and l form of a compound are called **optical isomers** and the phenomenon is called **optical isomerism**.

Molecular asymmetry and Optical isomerism

Optical isomerism is due to molecular asymmetry. If all the 4 valencies of a carbon atom are satisfied by 4 different groups, it is called **asymmetric carbon or chiral carbon or stereo centre**. The resulting molecule is called asymmetric molecule. Such molecules are non-super imposable to their mirror images and are called **chiral molecules** and this property is known as **chirality**. The molecules which are super imposable to their mirror images are called achiral molecules. e.g. 2-Bromobutane

Enantiomers: The stereo isomers related to each other as non-super imposable mirror images are called **enantiomers**. They have identical physical properties. They differ only in the direction of rotation of the plane polarised light. If one of the enantiomers is dextro rotatory, the other will be laevo rotatory.



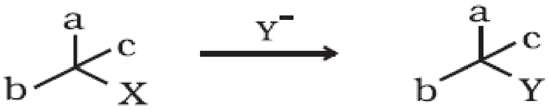
2-bromobutane

Racemic mixture

A mixture containing d and l form of a compound in equal proportion has zero optical rotation and such a mixture is called **racemic mixture or racemic modification**. It is denoted by dl or (+). Here the rotation due to one isomer is cancelled by the rotation due to the other isomer. The process of conversion of an enantiomer in to a racemic mixture is called racemisation.

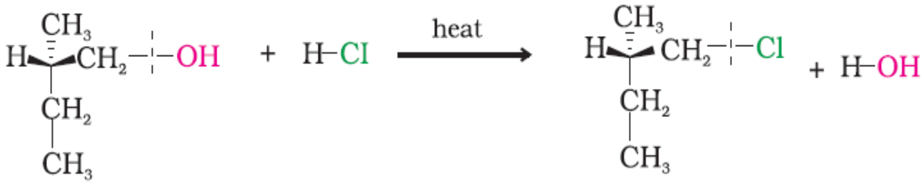
Retention and Inversion of configuration

If during a chemical reaction, there is no change in the spatial arrangement of bonds to an asymmetric centre, we can say that the reaction proceeds through retention of configuration. (Or, preservation of the integrity of configuration of a compound is termed as retention).



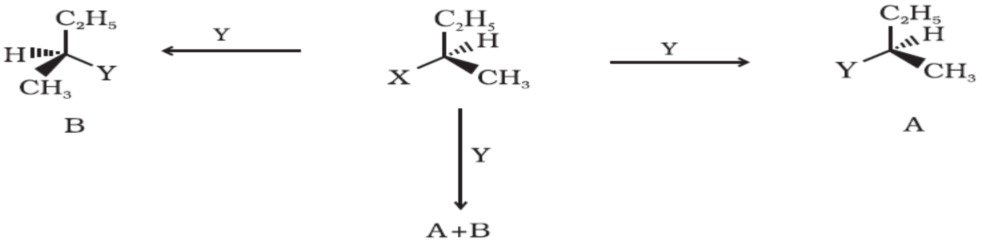
In general, if during a chemical reaction, no bond to the stereo centre is broken, the product will have the same configuration as that of the reactant. Such reactions always proceed through retention of configuration.

E.g. Reaction of 2-Methyl-1-butanol with HCl.



(−)-2-Methylbutan-1-ol (+)-1-Chloro-2-methylbutane

If during a chemical reaction, the incoming group is attached to a position opposite to that of the leaving group, the configuration of the resulting product is inverted and we can say that the reaction proceeds through inversion of configuration.

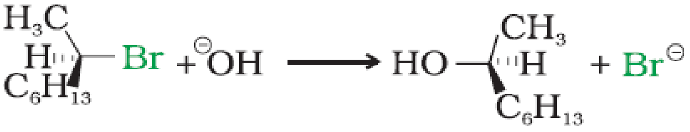


If (A) is the only compound obtained, the process is called retention of configuration.

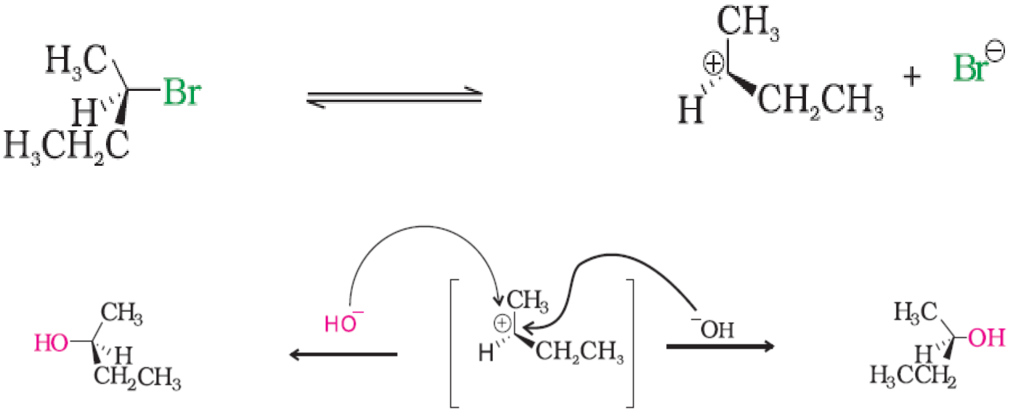
If (B) is the only compound obtained, the process is called inversion of configuration.

Nucleophilic Substitution and Optical Activity

In the case of optically active alkyl halides, the product formed as a result of SN^2 mechanism has the inverted configuration. This is because here the nucleophile attacks on the side opposite to that of the halogen atom.



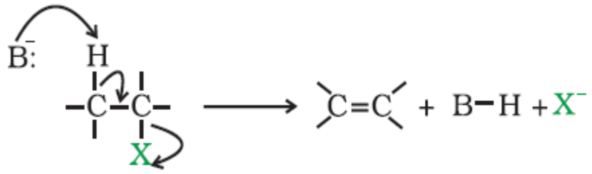
In the case of optically active alkyl halides SN^1 reactions follow through racemisation. Here the intermediate carbocation formed is SP^2 hybridised and hence it is planar. So the attack of nucleophile can take place from either side resulting in a mixture of products with opposite configuration. e.g. Hydrolysis of optically active 2- bromobutane results in the formation of (±)-butan-2-ol. , a racemic mixture.



(+)-Butan-2-ol (−)Butan-2-ol

ii) Elimination Reactions

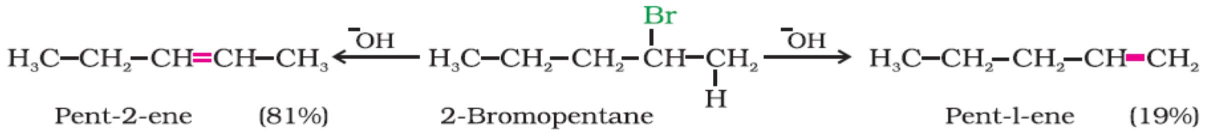
Alkyl halides having β-hydrogen atom when treated with alcoholic solution of KOH, they undergo elimination of one hydrogen halide molecule (dehydrohalogenation) to form alkenes. Since β-hydrogen atom is eliminated, the reaction is also called β-elimination.



B=Base ; X=Leaving group

If there is possibility of formation of more than one alkene during dehydrohalogenation reaction, the major product is selected by Zaitsev (Saytzeff) rule. The rule states that "in dehydrohalogenation reactions, if there is possibility of formation of more than one alkene the preferred product is that alkene which contains greater number of alkyl groups attached to the doubly bonded carbon atoms."

So if 2-bromobutane is treated with alcoholic KOH, 2-butene is formed as the major product.



$$H_3C-CH_2-CH{=}CH-CH_3 \xleftarrow{^{-}OH} H_3C-CH_2-CH_2-\overset{Br}{C}H-\underset{H}{C}H_2 \xrightarrow{^{-}OH} H_3C-CH_2-CH_2-CH{=}CH_2$$

Pent-2-ene (81%) 2-Bromopentane Pent-1-ene (19%)

iii) Reaction with metals

a) Alkyl halides react with Mg metal in ether medium to form alkyl magnesium halide (an organometallic compound) commonly called Grignard reagent.

$$\underset{\text{Halo alkane}}{R-X} + Mg \xrightarrow{\text{Dry ether}} \underset{\substack{\text{Alkyl magnesium halide}\\ \text{(Grignard reagent)}}}{R-Mg-X}$$

$$CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} \underset{\text{Grignard reagent}}{CH_3CH_2MgBr}$$

Grignard reagent is an example for organometallic compound. These are compounds in which carbon atom of an organic compound is directly bonded to metal atom. Other examples are tetraethyl lead, trimethyl aluminium etc.

In the Grignard reagent, the carbon-magnesium bond is covalent but highly polar and the magnesium halogen bond is ionic.

Grignard reagents are highly reactive and react with any source of proton (water, alcohols, amines etc) to give hydrocarbons (alkanes). It is therefore necessary to avoid even traces of moisture from a Grignard reagent.

$$RMgX + H_2O \longrightarrow RH + Mg(OH)X$$

b)Wurtz reaction: Alkyl halides react with sodium in dry ether to give alkanes with double the number of carbon atoms. This reaction is known as Wurtz reaction.

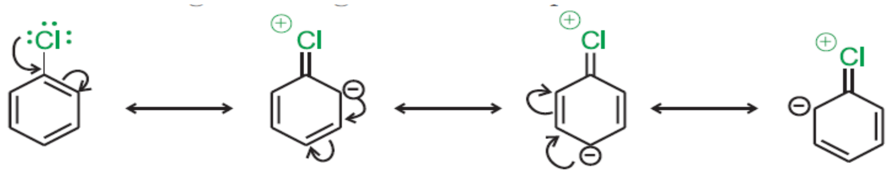
$$2RX + Na \longrightarrow RR + NaX$$

Reactions of Haloarenes

1.Nucleophilic Substitution Reaction:

Aryl halides are less reactive towards Nucleophilic substitution reactions due to the following reasons:

i)**Resonance effect**: In haloarenes, the electron pairs on halogen atom are in conjugation with π-electrons of the ring and the following resonating structures are possible.



So the C—X bond acquires a partial double bond character. Since it is difficult to break a C=C bond, the replacement of halogen atom by other atoms is not easy. So haloarenes are less reactive towards nucleophilic substitution reactions.

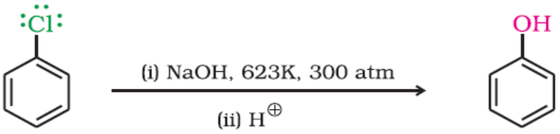
ii) **Difference in hybridisation of carbon atom in C—X bond**: In haloalkane, the halogen atom is attached to an sp^3 hybridised carbon while in haloarene, it is attached to an sp^2 hybridised carbon. Due to the greater scharacter of sp^2 hybridised carbon, it is more electronegative and can hold the electron pair of C—X bond more tightly than sp^3-hybridised carbon in haloalkane. So the C – X bond in haloarene is shorter than that in haloalkane. Since it is difficult to break a shorter bond than a longer bond, haloarenes are less reactive than haloalkanes towards Nucleophilic substitution reaction.

iii)**Instability of phenyl cation**: In haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilized by resonance and therefore, SN^1 mechanism does not occur.

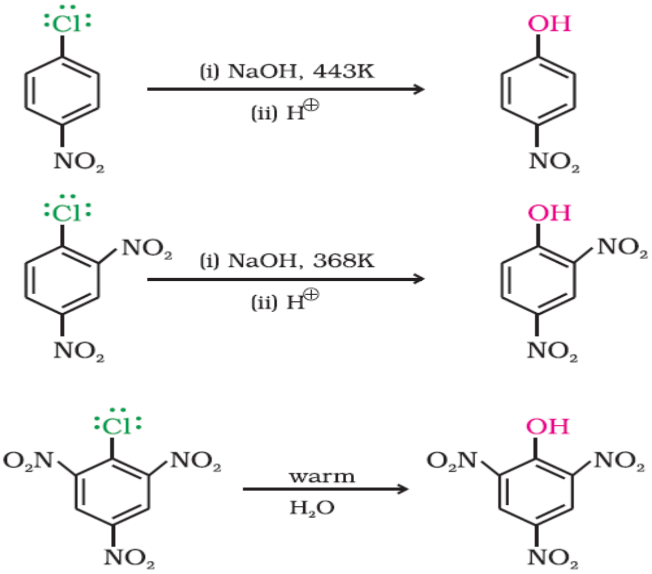
iv)**Repulsion between nucleophile and electron rich benzene ring**: Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.

Replacement by hydroxyl group (Conversion to phenol)

Chlorobenzene when heated with aqueous sodium hydroxide solution at a temperature of 623K and a pressure of 300 atmospheres followed by acidification, we get phenol.

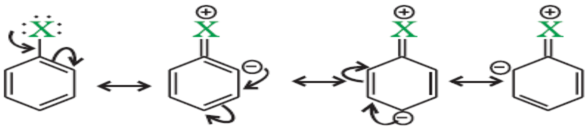


The presence of an electron withdrawing group ($-NO_2$) at ortho- and para-positions increases the reactivity of haloarenes.



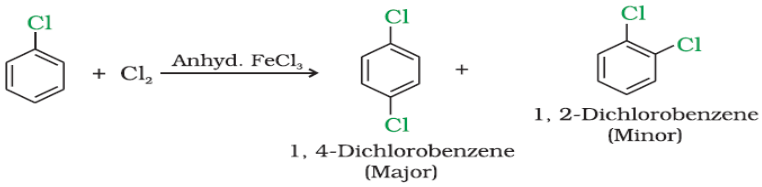
The effect is more when $-NO_2$ group is present at ortho and para- positions. However, no effect on reactivity is observed by the presence of electron withdrawing group at meta-position.

2.Electrophilic substitution reactions: Haloalkanes are resonance stabilized as follows:

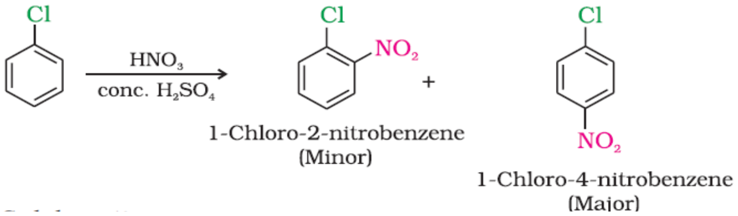


In the resonating structures, the electron density is greater on ortho-para positions. So the electrophile enters at these positions and hence halo group is an ortho-para directing group. Also because of its –I effect, the halogen atom has a tendency to withdraw electrons from the benzene ring. So it is a deactivating group. Hence the electrophilic substitution reactions in haloarenes occur slowly and require more vigorous conditions.

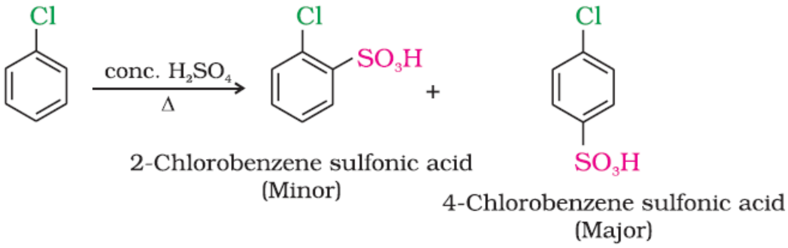
i)**Halogenation**: Haloalkanes react with halogen (Chlorine or bromine) in presence of anhydrous ferric chloride to form o-dichlorobenzene and p-dichlorobenzene.



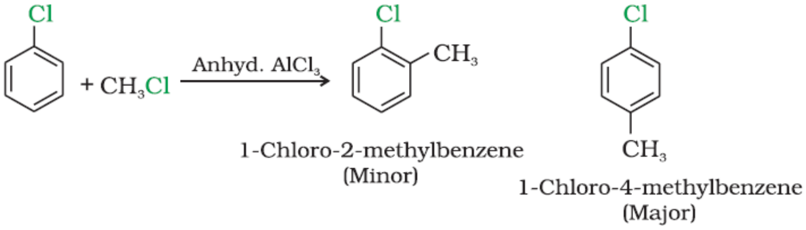
ii)**Nitration**: On nitration using Conc. HNO_3 and Conc. H_2SO_4, chlorobenzene gives p-nitrochlorobenzene as the major product.



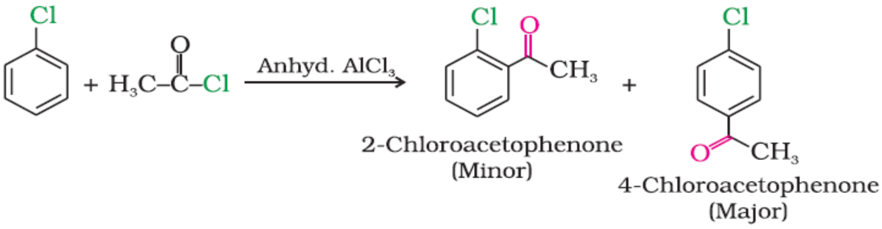
iii) **Sulphonation**: On sulphonation using Conc. H_2SO_4,chlorobenzene gives p-chlorobenzenesulphonic acid as the major product



iv)**Friedel – Crafts Alkylation**: Chlorobenzene when treated with methyl chloride (CH_3-Cl) in presence of anhydrous $AlCl_3$, we get p-chlorotoluene as the major product.

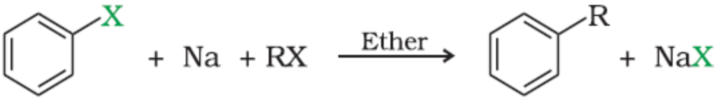


v)**Friedel – Crafts Acylation**: Chlorobenzene when treated with acetyl chloride (CH_3-CO-Cl) in presence of anhydrous $AlCl_3$, we get p-chloroacetophenone as the major product.

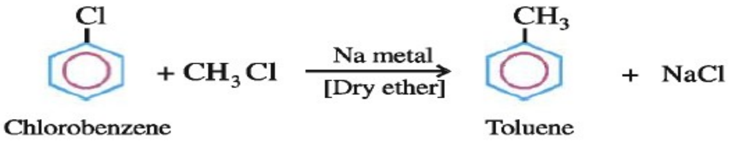


3.Reaction with metals:

a) Wurtz-Fittig reaction: When a mixture of alkyl halide and aryl halide is treated with sodium in dry ether, an alkyl arene is formed and this reaction is called Wurtz-Fittig reaction.



For e.g. when Chlorobenzene is treated with methyl chloride in presence of metallic sodium in ether medium, we get toluene.



b)Fittig reaction: Aryl halides when treated with sodium in dry ether, we get diaryls (diphenyls). This reaction is called Fittig reaction.