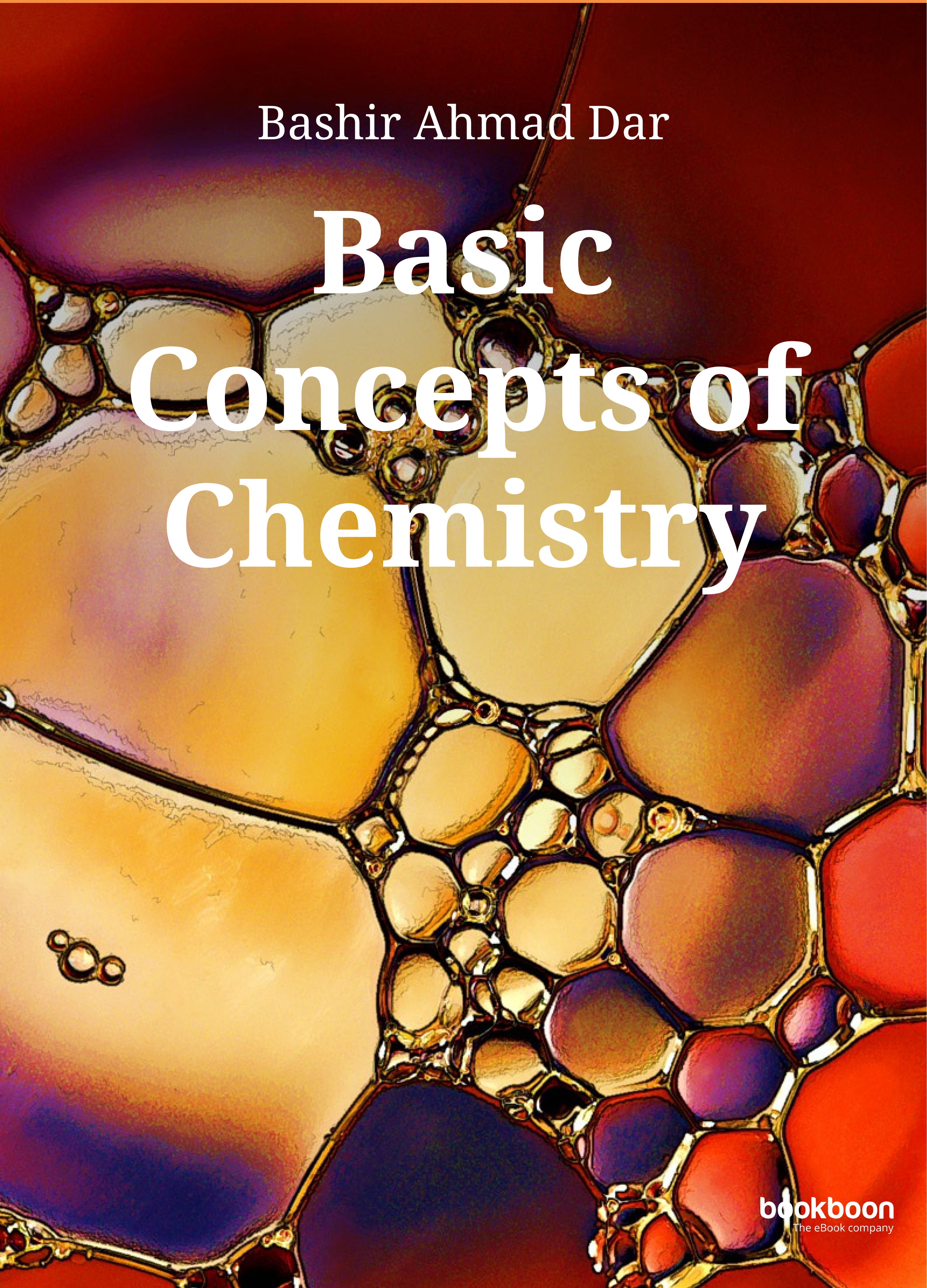

Bashir Ahmad Dar

Basic Concepts of Chemistry

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DR. BASHIR AHMAD DAR

BASIC CONCEPTS OF CHEMISTRY

Basic Concepts of Chemistry
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CONTENTS

1 THE SOLID STATE

Solid: Any substance which possesses rigidity, has definite shape & definite volume is called solid.

Solids have Melting Point > Room Temperature

The characteristic properties of the solid state:

1. They have definite mass, volume and shape.
2. Intermolecular distances are short.
3. Intermolecular forces are strong.
4. Their constituent particles (atoms, molecules or ions) have fixed positions and can only oscillate about their mean positions.
5. They are incompressible and rigid.

Classification of Solids: On the basis of the nature of order present in the arrangement of their constituent particles, Solids are classified as **crystalline** and **amorphous**. The properties mentioned below

Crystalline solid/true solids/ non glassy solids	**Amorphous solids/ Non crystalline solids/pseudo solids Glassy solids**
1. Constituent particles are arranged in an ordered manner.	1. Constituent particles are arranged randomly.
2. Definite characteristic geometrical shape	2. They have Irregular shape
3. It has long range order which means that there is a regular pattern of arrangement of particles throughout the solid.	3. Amorphous solids have only short range order. There are only small regions in such solids which have an ordered arrangement, these crystalline parts of an otherwise amorphous solids are called crystallites
4. They have a definite heat of fusion	4. *They do not have definite heat of fusion.*
5. When cut with a sharp edged tool, they split into two pieces and the newly generated surfaces are plain and smooth	5. When cut with a sharp edged tool, they cut into two pieces with irregular surfaces
6. These are true solids	6. These are pseudo solids or super cooled liquids as they posses characteristics similar to liquids.
7. They have sharp melting point i.e they melt at a sharp and characteristic temperature	7. Their melting points are not sharp i.e. they gradually soften over a range of temperatures.
8. Crystalline solids are *anisotropic* in nature, that is, their physical properties like electrical resistance or refractive index show different values when measured along different directions in the same crystals.	8. Amorphous solids on the other hand are *isotropic* in nature, i.e their physical properties show same values when measured along different directions in the same crystals.
9. Examples : Sodium chloride , Quartz etc	9. Examples: Glass ,rubber, plastics etc

1.2 CLASSIFICATION OF CRYSTALLINE SOLIDS

Most of the solid substances are crystalline in nature. For example, all the metallic elements like iron, copper and silver; non – metallic elements like sulphur, phosphorus and iodine and compounds like sodium chloride, zinc sulphide and naphthalene form crystalline solids. Crystalline solids can be classified on the basis of nature of intermolecular forces operating in them into four categories viz., molecular, ionic, metallic and covalent solids. Let us now learn about these categories.

Different Types of Solids

Type of Solids	Constituents	Bonding	Example	Physical Nature	M.P.	B.P.	Electrical Conductivity
Ionic	Ions	Coulombic	NaCl, KCl, CaO, MgO	Hard but brittle	High (≃ 1000 K)	High (≃ 2000 K)	Conductor (in molten state and in aqueous solution)
Covalent	Atoms	Electron sharing	SiO_2 (Quartz) SiC C(diamond) C(graphite)	Hard Hard Hard Hard	V.High (≃ 4000K)	V.High (≃ 5000K)	Insulator
Molecular	Simple covalent molecules	Molecular interactions (intermolecular forces), Hydrogen bonding	I_2,S_8,P_4, CO_2,CCl_4 starch, sucrose, water, ice	Soft Soft	Low (≃300 K to 600K) Low (≃ 273 K to 400K)	Low(≃ 450 to 800K) Low (≃ 273K to 500 K)	Insulator
Metallic	Positive ions and electrons	Metallic	sodium, magnesium, metals and alloys	Ductile malleable	High (≃ 800K to 1000K)	High ((≃ 1500K to 2000K)	Conductor

Graphite is soft covalent solid and a good conductor of electricity. Its exceptional properties are due to its typical structure
When an amorphous solid is heated and then cooled slowly, it changes into the crystalline form, this process is known as annealing

Uses of Amorphous solids

1. Glass is used in the manufacture of window panes and laboratory apparatus.
2. Rubber is used in the manufacture of tyres, mats, shoes etc
3. Plastics are used in the preparation of toys, household items and electrical insulations.
4. Amorphous silicon is used for converting sunlight into electricity

1.3 STUDY OF CYRSTALS

Crystal: A crystal is a homogenous portion of a solid substance made by regular pattern of structural units bounded by plane surface making definite angles with each other.

Face: The plane surface of the crystal is called face.

Edge: An edge is formed by the intersection of two adjacent faces.

Interfacial angles: The angle between the two intersecting faces perpendicular to each other is called interfacial angles.

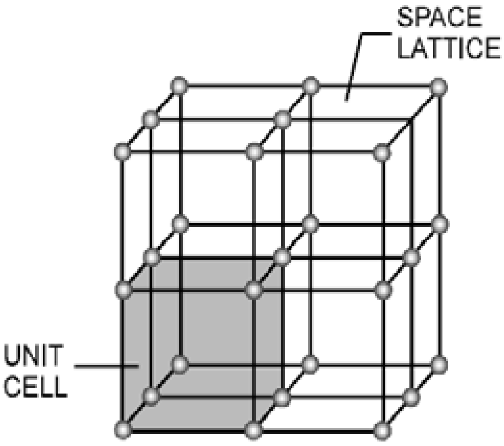
1.4 CRYSTAL LATTICE OR SPACE LATTICE

The arrangement of points showing how molecules, atoms or ions are arranged at different sites in three-dimensional space is known as **space lattice** or **crystal lattice**. The positions occupied by molecules, atoms or ions in the crystal lattice are called lattice points or lattice sites

There are only 14 possible three dimensional lattices. These are called Bravais Lattices.

The following are the characteristics of a crystal lattice

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.

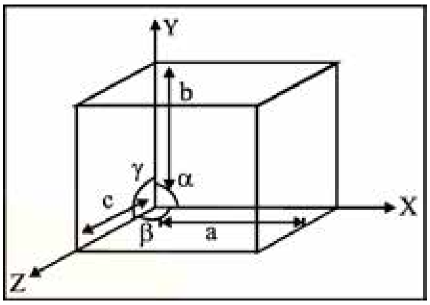


1.5 UNIT CELL

The unit cell is the smallest portion of a crystal lattice which, when repeated in different directions, generates the entire lattice.

A unit cell is characterized by:

1. Its dimensions along the three edges, a, b and c. These edges may or may not be mutually perpendicular.
2. Angles between the edges, α (between b and c) β (between a and c) and γ (between a and b). Thus, a unit cell is characterized by six parameters, a, b, c, α, β and γ.

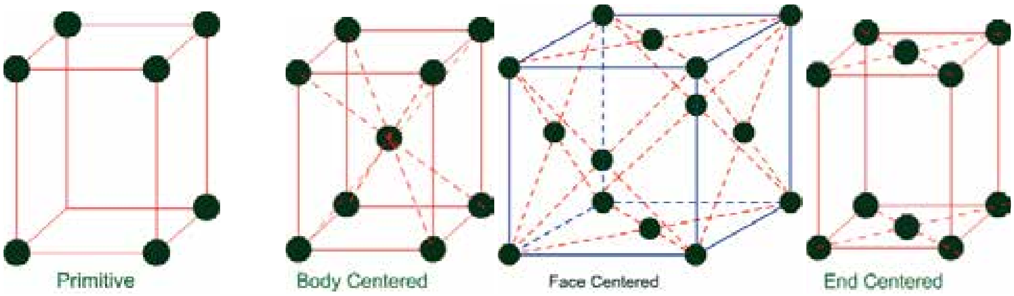


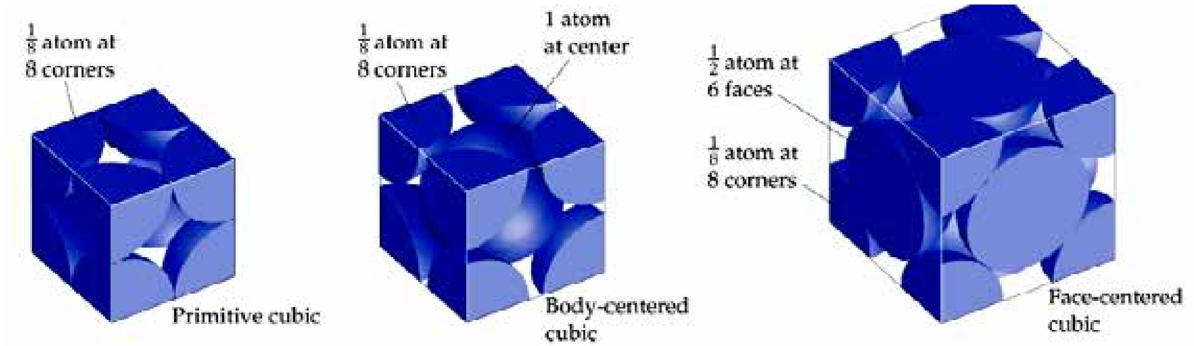
Types of Unit Cells: Unit cells can be broadly divided into two categories, i) Primitive and ii) Centered unit cells.

a. **Primitive Unit Cells**: When constituent particles are present only on the corner positions of a unit cell, it is called as primitive unit cell.
b. **Centered Unit Cells:** When a unit cell contains one or more constituent particles present at positions other than corners in addition to those at corners, it is called a centered unit cell.

Centered unit cells are of three types

1. **Body-Centered Unit Cells**: A unit cell contains one constituent particle (atom, molecule or ion) at its body-centre and eight particles are at its corners.
2. **Face-Centered Unit Cells**: A unit cell contains one constituent particle present at the centre of each face, along with eight particles at its corners.
3. **End-Centered Unit Cells:** A unit cell, one constituent particle is present at the centre of any two opposite faces along with eight particles at its corners.

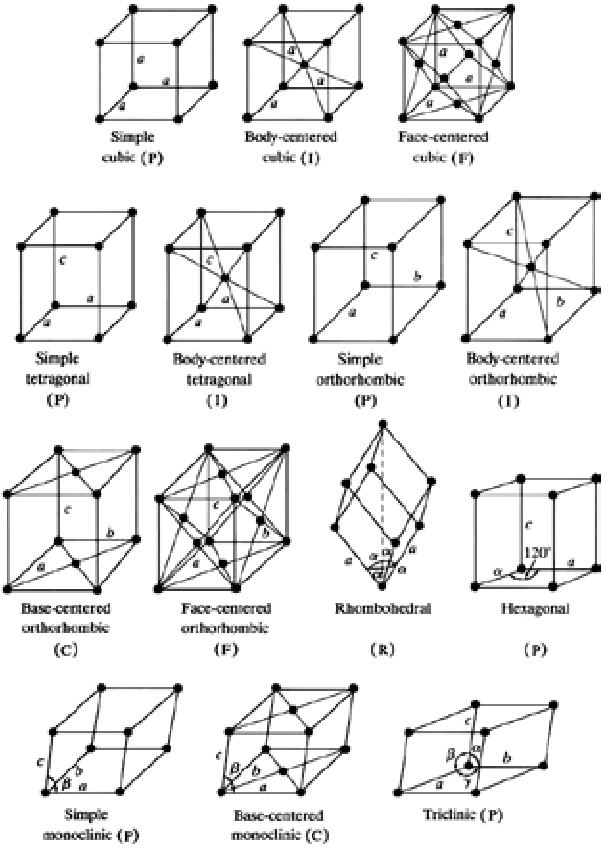

Primitive
Body Centered
Face Centered
End Centered


$\frac{1}{8}$ atom at 8 corners
Primitive cubic
$\frac{1}{8}$ atom at 8 corners
1 atom at center
Body-centered cubic
$\frac{1}{2}$ atom at 6 faces
$\frac{1}{8}$ atom at 8 corners
Face-centered cubic

Seven types of crystal systems and their possible variations

Crystal Systems	Edge lengths	Axial angles	Possible variations	Examples
Cubic	a = b = c	$\alpha = \beta = \gamma = 90^0$	Primitive, body centred, face centred	blende (ZnS), Cu NaCl, Zinc
Tetragonal	a =b ≠ c	$\alpha = \beta = \gamma = 90^0$	Primitive, body-centred	White tin, TiO_2, SnO_2, $CaSO_4$
Orthorhombic	a ≠ b ≠ c	$\alpha = \beta = \gamma = 90^0$	Primitive, body-centred, face-centred, end-centred	Rhombic sulphur, KNO_3, $BaSO_4$
Monoclinic	a ≠ b ≠ c	$\alpha = \gamma = 90^0$, $\beta \neq 90^\circ$	Primitive, endcentred	Monoclinic sulphur, $Na_2SO_4.10H_2O$
Triclinic	a ≠ b ≠ c	$\alpha \neq \beta \neq \gamma \neq 90^0$	Primitive	$K_2Cr_2O_7$, H_3BO_3, $CuSO_4.5H_2O$
Rhombohedral or trigonal	a = b = c	$\alpha = \beta = \gamma \neq 90^0$	Primitive	Calcite($CaCO_3$), HgS (Cinnabar)
Hexagonal	a = b ≠ c	$\alpha = \beta = 90^\circ$, $\gamma = 120^0$	Primitive	Graphite, ZnO, CdS

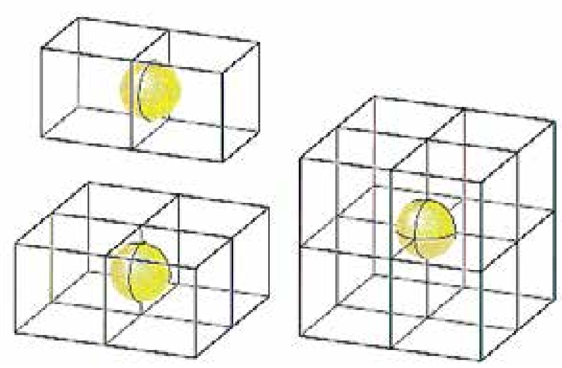
Bravais Lattices: There are about 230 crystal forms, which have been grouped into 14 types of space lattices called Bravais Lattices, on the basis of their symmetry and seven different crystal systems on the basis of interfacial angles and axes.


Simple cubic (P)
Body-centered cubic (I)
Face-centered cubic (F)
Simple tetragonal (P)
Body-centered tetragonal (I)
Simple orthorhombic (P)
Body-centered orthorhombic (I)
Base-centered orthorhombic (C)
Face-centered orthorhombic (F)
Rhombohedral (R)
Hexagonal (P)
Simple monoclinic (P)
Base-centered monoclinic (C)
Triclinic (P)

Calculation of no. of particles per unit cell (called Rank or Z)

The no. of atoms present in a unit cell can be calculated keeping in view the following points

1. An atom at corner is shared by eight unit cells, therefore contribution of an atom at the corner =1/8
2. An atom at face is shared by two unit cells, therefore contribution of an atom at the face =1/2
3. An atom at edge is shared by four unit cells, therefore contribution of an atom at the edge =1/4
4. An atom within the body centre is shared by no other unit cell, therefore contribution of an atom within the body = 1



Type of Unit cell	Particle present at	Contribution	No. of atoms	Total No. of atoms
Simple unit cell	8 Corners	1/8	8× 1/8 =1	1
Face centered	8 Corners 6 Faces	1/8 1/2	8× 1/8 =1 6× 1/2 =3	4
Body centered	8 Corners 1 body centr	1/8 1	8× 1/8 =1 1× 1 =1	2
Edge centered	8Corners 12 Edges	1/8 1/4	8× 1/8 =1 12× 1/4=3	4
End centered	8 Corners 2 Faces	1/8 1/2	8× 1/8 =1 2× 1/2 =1	2

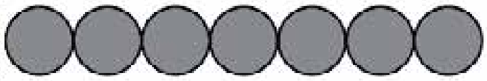
Close packing of constituent particles in a crystal

To understand the packing of constituent particles in a crystal it is assumed that the constituent particles are hard spheres of identical size. Close packing in solids can take place in following manner.

Close packing

The packing of spheres in such a way that they occupy maximum available space and left minimum empty space is called close packing.

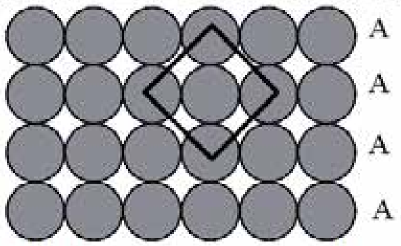
a. **Close packing in one dimension:** In one dimension the spheres can be arranged in a row touching each other called packing in one dimension, each sphere touches two of its neighbors so its coordination no. is 2.



Linear packing in one dimension

b. **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.

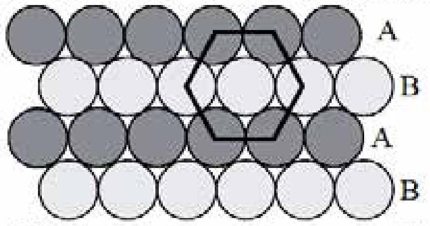
1. ***Square close packing***: Here the spheres of second row are placed exactly above those of the first row. In this arrangement, each sphere is in contact with four adjacent spheres. So the co-ordination number of each sphere is 4. When we join the centers of these spheres, we get a square. So this close packing is called square close packing in two dimensions.



AAAA type, square close packing

2. ***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 centers 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.



ABAB type, hexagonal close packing

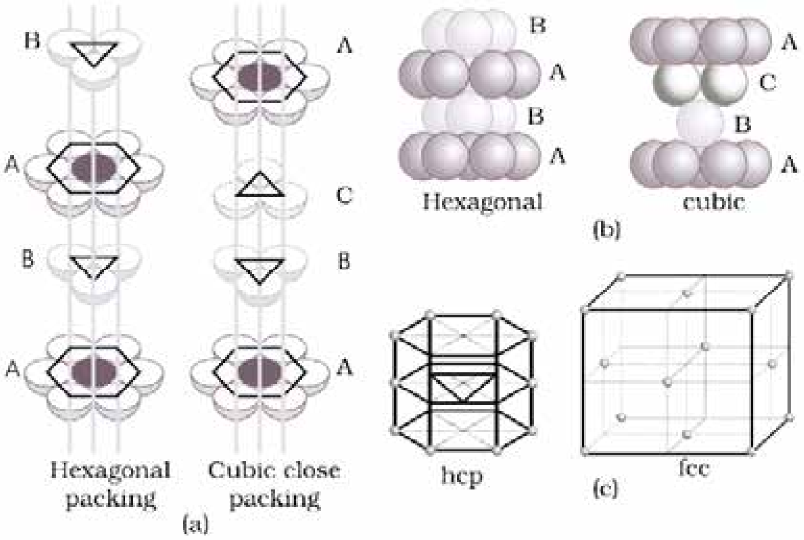
c. **Close packing in three Dimensions:** Here the particles are arranged in layers. This can be possible in two ways.

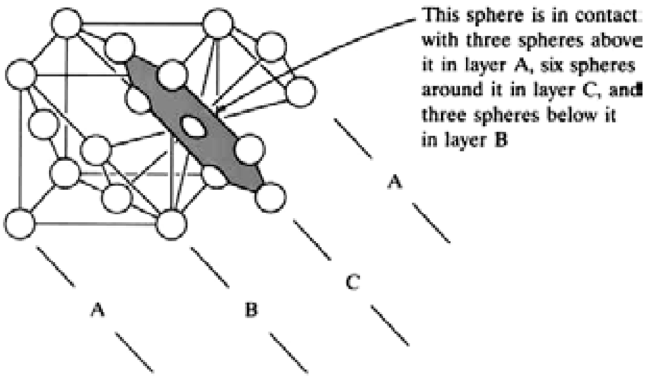
1. **Three dimensional close packing from two dimensional square close-packed layers:**
   Here the spheres of the second layer are placed exactly above those of the first layer. In this arrangement spheres of both the layers are perfectly aligned horizontally as well as vertically. The spheres of the 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.

2. **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.


B
A
B
A
A
C
B
A
Hexagonal packing
Cubic close packing
(a)
B
A
B
A
Hexagonal
A
C
B
A
cubic
(b)
hcp
fcc
(c)



Coordination number is defined as the number of particles immediately adjacent to each particle in the crystal lattice.

[In simple cubic lattice, CN is 6, in body centered lattice, CN is 8 and in face centered cubic lattice, CN is 12].

High pressure increases CN and high temperature decreases the CN.

In both ccp and hcp, each sphere is surrounded by 12 adjacent atoms, thus coordination number is equal to 12 in each case. In both these arrangements 74 % space is occupied.

All noble gases have ccp structure except He (hcp structure).

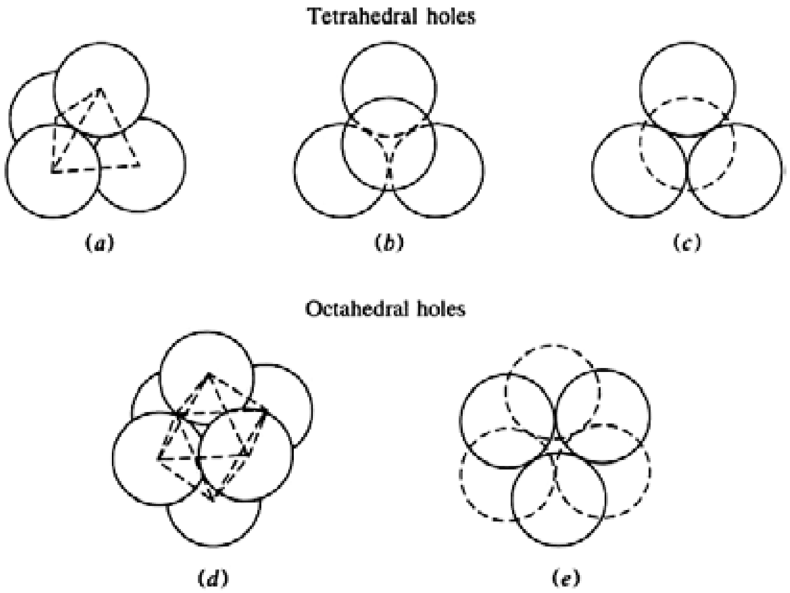
Close packing of atoms in cubic structure = fcc > bcc > sc.

1.6 INTERSTITIAL VOIDS

The vacant space in close packed arrangement is called *void*. 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.



Number of voids

The number of octahedral voids present in a lattice is equal to the number of close packed particles. The number of tetrahedral voids present in a lattice is twice to the number of close packed particles. Thus, if number of close packed spheres is equal to 'N'.

The number of octahedral voids formed = N
And, the number of tetrahedral voids formed = 2N
Therefore, total number of voids formed = 3N

1.7 RADIUS RATIO

For the stability of ionic compound each cation should be surrounded by maximum no. of anions and vice versa. The no. of oppositely charged ions surrounding a particular ion is called its coordination number. As ionic bond is non directional; the arrangement of ions within the ionic crystal is determined by radius ratio

The ratio of radius of cation to that of anion is called as radius ratio .i.e.

$$\textbf{\textit{Radius ratio}} = \frac{Radius\ \ of\ \ cation}{Radius\ \ of\ \ anion}$$

Evidently greater the radius ratio, greater would be the coordination number

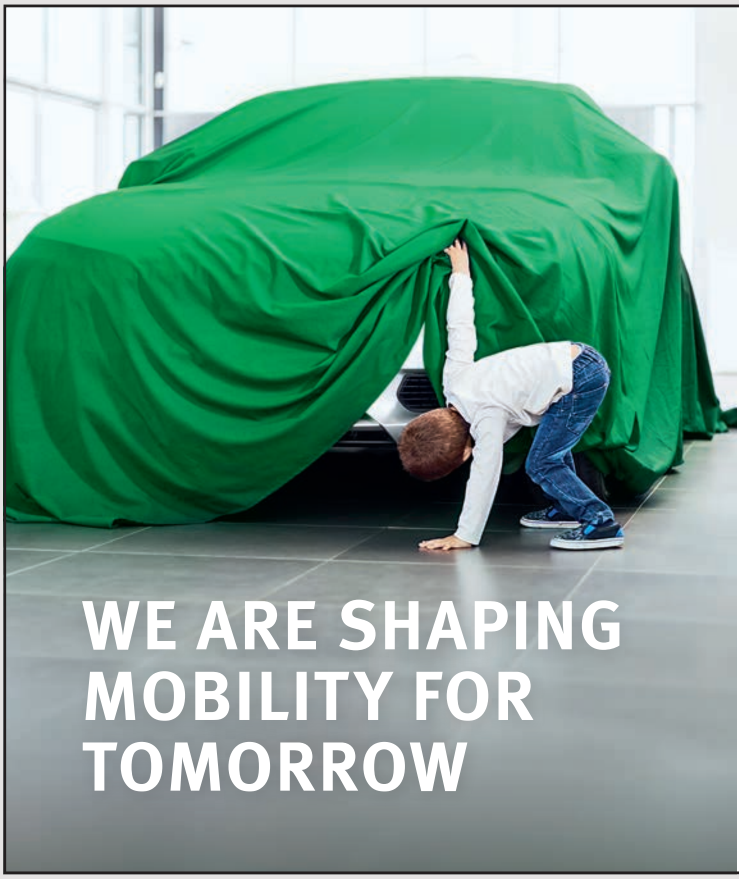
Radius ratio rule: The relationship between radius ratio, coordination number and structural arrangement is called radius ratio rule and is given below

Radius Ratio	Co-ordination no.	Structural arrangement	Example
0.155–0.225	3	Planar Triangular	B_2O_3
0.225–0.414	4	Tetrahedral	ZnS
0.414–0.732	6	Octahedral	NaCl
0.732–1	8	Body – centred cubic	CsCl

Packing Efficiency and Packing fraction

The constituent particles in the solids are closely packed in the crystal lattice. This can be achieved through ccp or hcp mode of packing. In both these types of packing some spaces are left unoccupied in the form of voids.

The fraction of the total space filled by the particles in a solid is called packing fraction.



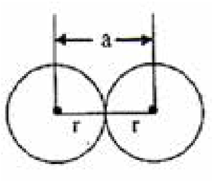
More the packing fraction more is the space occupied by particles and lesser is the empty space due to voids. Packing efficiency can be calculated in different types of voids as

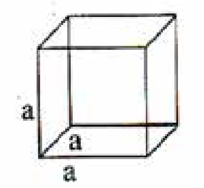
Packing Efficiency of Close Packed Structure: Both ccp and hcp are highly efficient lattice; in terms of packing. The packing efficiency of both types of close packed structure is 74%, i.e. 74% of the space in hcp and ccp is filled. The hcp and ccp structure are equally efficient; in terms of packing. The packing efficiency of simple cubic lattice is 52.4%. And the packing efficiency of body centered cubic lattice (bcc) is 68%

Atomic radius: It is defined as the half of the distance between nearest neighboring atoms in a crystal. It is expressed in terms of length of the edge (a) of the unit cell of the crystal.

a. **Simple cubic structure (S.C.)**

Radius of atom ‘r’ = a/2





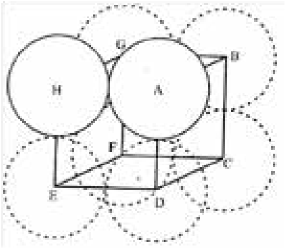
b. **Face centered cubic structure (FCC)**

‘r’ = $\frac{a}{2\sqrt{2}}$

c. **Body centered cubic structure (BCC) ‘r’**

‘r’ = $\frac{\sqrt{3}a}{4}$

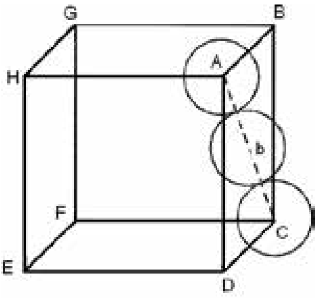
Packing efficiency in simple cubic lattice: In simple cubic lattice, 8 lattice points are on the corners of the cube. Since a simple cubic has only one atom. Let edge length be a then a = 2r, here r is the radius of sphere



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

$$= \frac{\frac{4}{3}\pi r^3}{(2\,r)^3} \times 100 = \frac{\pi}{6} \times 100 = 52.4\%$$

Packing efficiency of Face centered cubic structure



In figure, let cell edge length be 'a' and face diagonal AC = b

In Δ ABC $AC^2 = (DC)^2 + (AD)^2$

Or $(AC)^2 = a^2 + a^2$

Or $(AC)^2 = 2a^2$

Or $AC = \sqrt{2}\,a$ ---------- (i)

If radius of sphere is r, we find $AC = 4r$

From eq (i) $\sqrt{2}\,a = 4r$

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

Volume of the cube = $a^3 = (2\sqrt{2}r)^3 = 16\sqrt{2}r^3$

There are four spheres per unit cell in ccp or fcc structure.

Thus volume of four spheres = $4\times \frac{4}{3}\pi r^3$

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

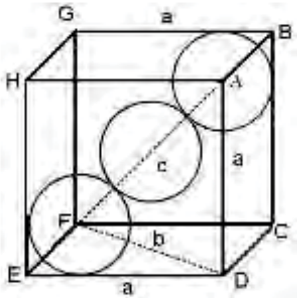
$$\frac{4\times\frac{4}{3}\pi r^3}{16\sqrt{2}r^3} = \times 100$$

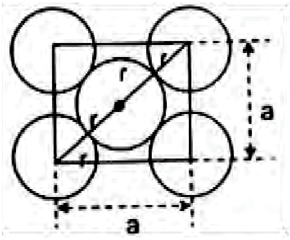
$$= \frac{\pi}{3\sqrt{2}} \times 100$$

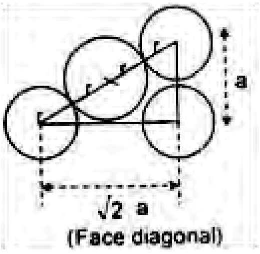
Thus efficiency = 72%

Or Packing fraction =0.72

Packing efficiency of Body Centered Cubic Structure







In figure, let cell edge length be 'a' and face diagonal FD = b , body diagonal AF = c

From ΔEFD $b^2 = a^2 + a^2$

Thus $b^2 = 2\,a^2$ --------- (i)

From ΔAFD $c^2 = a^2 + b^2$

From eq. (i)

$c^2 = a^2 + 2a^2$

Or $c^2 = 3a^2$

$c = \sqrt{3}\,a$ ------------- (ii)

The length of the body diagonal c is equal to 4r. Here r is the radius of the sphere (atom)

From eq. (ii) we get $\sqrt{3}\,a = 4r$

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

There are two spheres per unit cell in bcc

Volume of two sphere $= 2\times \frac{4}{3}\pi r^3$

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

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

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

$$\frac{\sqrt{3}\pi}{6} = \times 100 = 68\ \%$$

Thus efficiency = 68%

Or Packing fraction = 0.68

1.8 DENSITY OF THE UNIT CELL (SOLID)

Consider a cubic unit cell with edge length ‘a’.

Then volume of the unit cell = a^3.

Let ‘M’ be atomic mass of the element in the unit cell (i.e. mass of Avogadro number (N_A) of atoms).

Then mass of one atom = $\frac{M}{N_A}$.

Let the number of particles present per unit cell = z z is also called rank

Then mass of the unit cell = z × $\frac{M}{N_A}$.

Density of the unit cell = $\frac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$

i.e. density (ρ) = $\frac{z\times\frac{M}{N_A}}{a^3}$

Or, $\rho = \frac{z\times M}{a^3 . N_A}$.

1.9 IMPERFECTIONS IN SOLIDS (CRYSTAL DEFECTS)

The deviation from the regular orderly arrangement of particles of a solid is termed as ***imperfections or crystal defects.*** A perfect crystal is one which has same lattice point throughout the crystal which is possible only at 0 K. With rise in temperature some deviation from complete order takes place. The defects in a solid arise due to

- Improper growth of crystal during crystallization
- Impurities
- Temperature

The crystal defects are broadly classified into two groups(A) point defects and(B) 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**.

a. **Point defects:** Point Defects/ Atomic imperfection: Point defects are the irregularities or deviations from ideal arrangement around a point or an atom and occur because of missing atoms, displaced atoms or extra atoms in a crystalline substance.
b. **Line defects**: Line defects are the irregularities or deviations from ideal arrangement in entire rows of lattice points.

Types of 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.**

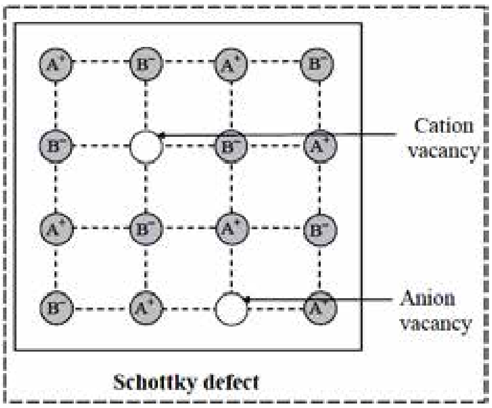
1. **Schottky defect:** It is basically a vacancy defect. This type of defect is characterized by missing equal number of cations and anions from their lattice sites so that the electrical neutrality of the system is maintained

   This type of defect is shown by the compound with

   a. High coordination number
   b. Small difference in size of the positive and negative ions i.e, $\frac{r+}{r-} \approx 1$

Or cations and anions do not differ in size appreciably.

NaCl, KCl, CsCl, AgBr etc. show Schottky defect.



Consequences of Schottky defect

a. Since crystal lattice have lesser number of ions, density of the crystal decreases
b. The presence of a number of ionic vacancies lowers lattice energy or the stability of the crystal
c. The crystal shows electrical conductivity to small extent by ionic mechanism

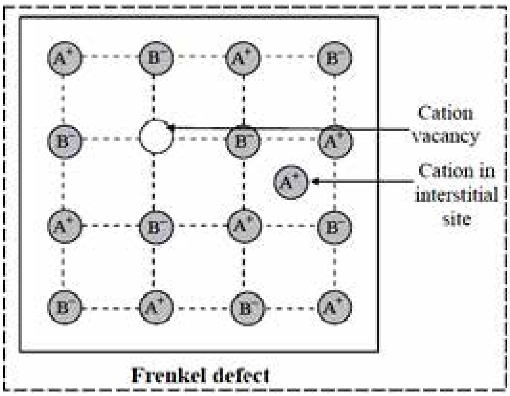
Exampals: NaCl, CsCl, KBr, KCl

In NaCl there are approximately 10^6 Schottky pairs per cm^3 at room temperature. In $1cm^3$ there are about 10^{22} NaCl units. Thus, there is one defect per 10^{16} ions.

3. ***Frenkel Defect*:** This defect is shown by ionic solids. The smaller ion (usually cation) is dislocated from its normal site to an interstitial site. It creates a *vacancy defect* at its original site and an interstitial defect at its new location. Frenkel defect is also called dislocation defect.

   This type of defect is shown by

   a. Compounds having low coordination number because in such compounds the attractive forces, being less, are very easy to overcome and hence the cation can easily move into the interstitial site
   b. Compound having large difference in size of cations and anions. i.e $\frac{r+}{r-}$ is low
   c. Compounds having highly polarizing cations and easily polarizable anions.



Consequences of Frankel defect

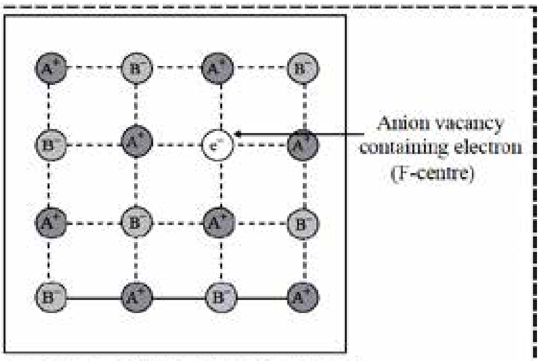
a. Since nothing is lost from crystal as a whole, therefore density of the crystal is not affected
b. The crystal shows electrical conductivity to a small extent by ionic mechanism
c. The closeness of like charges tends to increase the dielecrtic constant of the crystal

> *Note : The number of these two defects in a crystal generally increases with the rise of temperature, hence they are sometimes called as thermodynamic defects*
>
> *AgBr shows both Frenkel and Skhottky defect.*
>
> *Both Frankel and schottky defect explains the conduction of electricity is solids and diffusion in solids*
>
> *Both Frankel and schottky defect maintains the electrical neutrality of a crystal.*

b. **Non-Stoichiometric Defects:** In this type of defect stoichiometry of compound is not maintained. These defects are of two types: (i) metal excess defect and (ii) metal deficiency defect.

1. **Metal Excess Defect:** This type of defect can occur in two ways
   - **By anion vacancies**: In this defect an anion is missing from its lattice site leaving a hole which is occupied by an electron thus maintaining the electrical neutrality.

Explanation: When crystals of NaCl are heated in an atmosphere of sodium vapour, the sodium atoms are deposited on the surface of the crystal. The Cl^- ions diffuse to the surface of the crystal and combine with Na atoms to give NaCl. This happens by loss of electron by sodium atoms to form Na^+ ions. The released electrons diffuse into the crystal and occupy anionic sites .As a result the crystal now has an excess of sodium. The anionic sites occupied by unpaired electrons are called *F-centres* and are responsible for yellow colour to the crystals of NaCl. The colour results by excitation of these electrons when they absorb energy from the visible light falling on the crystals.

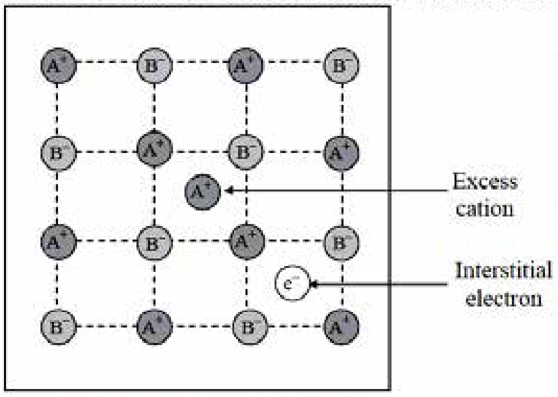


Metal excess defect due to anion vacancy

- **By extra cation:** This type of defect arises if extra positive ion is present in an intersititial site. Neutrality is maintained by the presence of electron in another interstitial site e.g on heating ZnO it loses oxygen and turns yellow.

$$\mathbf{ZnO \xrightarrow[\textit{Heating}]{} Zn^{++} + \frac{1}{2} O_2 + 2e^-}$$

Now there is excess of zinc in the crystal. The excess Zn^{2+} ions move to interstitial sites and the electrons to neighboring interstitial sites.



Metal excess defect due to extra cation

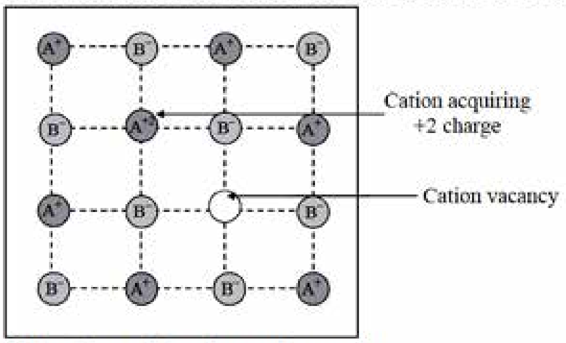
2. ***Metal Deficiency Defect:*** Point defects (in non-stoichiometric crystals) which arise due to the deficiency of positive ions are called **metal deficiency defects**.

Conditions causing metal deficiency defects

Following two conditions cause metal deficiency defects:

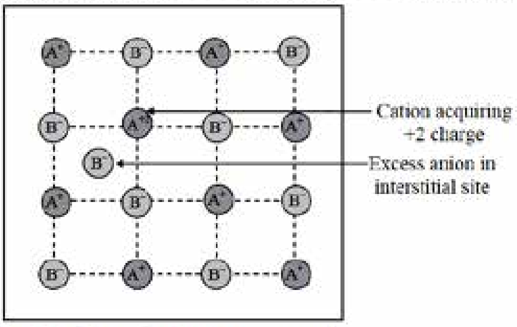
a. Cationic vacancies b. Presence of extra anions at interstitial sites

a. **Cationic vacancies:** This defect occurs if a metal shows variable valency. This defect is caused by the absence of cation from its normal site and presence of cation having higher charge in the adjacent site, thus maintain electrical neutrality e.g. FeO which is mostly found with a composition of $Fe_{0.95}O$. It may actually range from $Fe_{0.93}O$ to $Fe_{0.96}O$. In crystals of FeO some Fe^{2+} cations are missing and the loss of positive charge is made up by the presence of required number of Fe^{3+} ions.



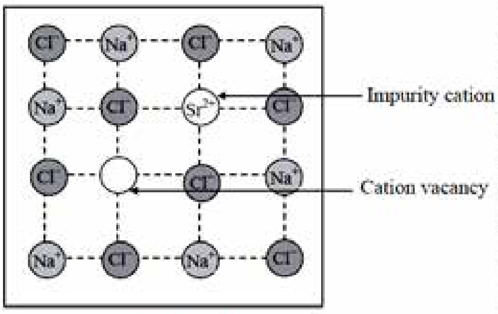
Metal deficiency defect due to cation vacancy

b. **Presence of extra anions at interstitial sites:** When extra anions are present at interstitial sites, the electrical neutrality is maintained due to increase in the charge on the cation. This defect is not commonly observed because negative ions cannot easily occupy interstitial sites due to large size.



Metal deficiency defect due to extra anion

b. ***Impurity Defects:*** If molten NaCl containing a little amount of $SrCl_2$ is crystallized, 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 in number to that of Sr^{2+} ions. Another similar example is the solid solution of $CdCl_2$ and AgCl.



Impurity defect

Electrical Properties

Solids show amazing range of electrical conductivities. Electrical conductivity is the reciprocal of resistivity. Whereas resistivity is the property of solids to resist flow of electricity, conductivity is the property to conduct electricity.

The SI unit of resistivity is ohm meter. Since, conductivity is the reciprocal of resistivity, thus its unit is reciprocal of ohm meter, i.e. ohm^{-1} m^{-1}. Conductivity is generally represented by Greek letter σ (sigma). The SI unit of conductivity is Siemens per meter, i.e. S/m.

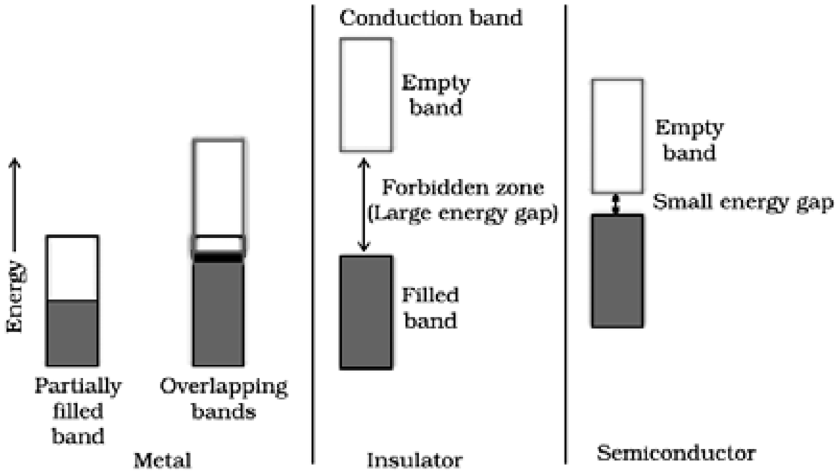
On the basis of magnitude of range of conductivities (from 10^{-20} to 10^{7} ohm^{-1} m^{-1}) solids can be classified into three types.

a. **Conductor:** Solids having range of conductivities from 10^{4} to 10^{7} ohm^{-1} m^{-1} are classified as conductors. Metals are good conductor of electricity. Silver has conductivity in the order of 10^{7} ohm^{-1} m^{-1} is considered as very good conductor.
b. **Insulator:** Solids having range of conductivity from 10^{-20} to 10^{-10} ohm^{-1} m^{-1} are considered as insulators.
c. **Semiconductor:** Solids having intermediate conductivity, i.e. from 10^{-6} to 10^{4} ohm^{-1} m^{-1} are called semiconductors.

1.10 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 orbital, 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.



These are of two types

a. **Intrinsic semiconductors:** Semiconductors which are capable of conducting current only with increase in temperature or when interacted with electromagnetic radiations are called intrinsic semiconductors. This is because certain bonds are broken and released electrons are responsible for the conduction of current.

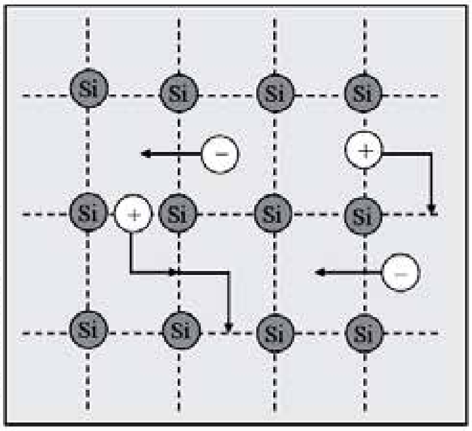
   Pure silicon and germanium have very low conductivities and behave as poor conductors of electricity. They contain completely filled valence band with electrons and an empty conduction band.

   When thermal energy is supplied, some of the electrons are excited from completely filled valence band to empty conduction band. Excitation of electrons results in cleavage of covalent bonds and creation of positive holes.

In presence of an electrical field, electrons move in one direction and positive holes move in other direction. This is known as ***intrinsic semiconductivity*** *of the crystal. The substance is known as* ***intrinsic semiconductor****.*

The electrons move through the interstices of the lattice and the positive holes jump from one bond to another.

Pure silicon and germanium are intrinsic semiconductors.



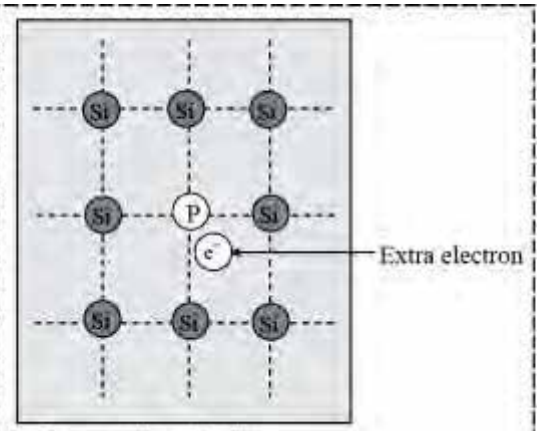
Pure silicon as intrinsic semiconductor

b. **Extrinsic semiconductors:** The conductivity of these intrinsic semiconductors is too low to be of practical use. Their conductivity is increased by adding an appropriate amount of suitable impurity. This process is called doping and the impurity added is called dopant. Doping can be done with an impurity which is electron rich or electron deficient as compared to the intrinsic semiconductor silicon or germanium. Such impurities introduce *electronic defects* in them. Doping can be achieved by

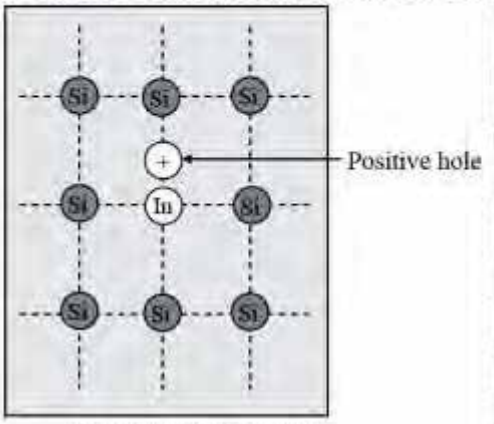
1. By heating the crystal in an atmosphere containing dopant atoms which thereby diffuse into the host crystal.
2. The impurities are added into the molten state of semiconductor.
3. The intrinsic semiconductor is bombarded with ions of impurity atoms.

Extrinsic semiconductors are of two types.

1. **n-type semiconductors**: In silicon crystal each atom forms four covalent bonds with its neighbors when doped with pentavalent impurity like P or As, which contains five valence electrons, they occupy some of the lattice sites in silicon. Four out of five electrons are used in the formation of four covalent bonds with the four neighboring silicon atoms. The fifth electron is extra and becomes delocalized and increases the conductivity of doped silicon. Here the majority charge carriers are electrons, hence silicon doped with electron-rich impurity is called *n*-type semiconductor.
2. **p-type semiconductors**: p-type semiconductor is formed when a trivalent impurity is added to silicon crystal. In this case no. of holes is more as compared to no. of electrons.



n-type semiconductor
(Phosphorus doped silicon semiconductor)



p-type semiconductor
(Indium doped silicon semiconductor)

- In intrinsic or pure semiconductors number of electrons is equal to number of holes.
- In extrinsic (n-type) semiconductor number of electrons is more as compared to number of holes.
- Whereas In p- type semiconductor number of holes is more as compared to number of electrons.
- In intrinsic semiconductor conductivity depends on temperature while as in extrinsic semiconductor conductivity depends on amount of impurity added as well as temperature.

Applications of n-type and p-type semiconductors

Both n-type p-and type semiconductors are used in making electronic components

As diode which is the combination of n-type and p-type semiconductors.

As integrated circuit (ICs).

In photoelectric cell

As transistors, to amplify radio and audio signal

Super conductivity: A substance is said to be superconducting when it offers no resistance to the flow of electricity. Electrical resistance decreases with decreases in temperature and becomes almost zero near the absolute zero. The phenomenon was first discovered by ***Kammerlingh Onnes*** *in* 1913 when he found that mercury becomes superconducting at

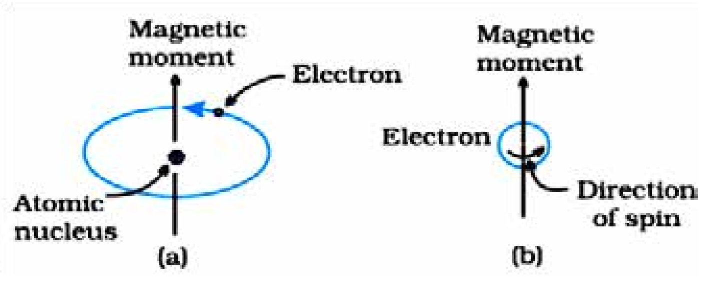
4 K. The temperature at which a substance starts behaving as super conductor is called ***transition temperature***. Most metals have transition temperatures between 2K -5K. Certain organic compounds also become superconducting below 5K. Such low temperature can be attained only with liquid helium which is very expensive.

Certain alloys of niobium have been found to be superconducting at temperature as high as 23 K. Since 1987, many complex metal oxides have been found to possess super conductivity at somewhat higher temperature e.g. $YBa_2Cu_3O_7$ at 90 K

Superconductivity materials have great technical potentials. They can be used in electronics in building magnets, in power transmission and levitation transportation (trains which move in air without rails).

1.11 MAGNETIC PROPERTIES

Every substance has some magnetic properties associated with it. The origin of magnetism in solids originates from two types of motions of electrons in an atom (i) its orbital motion around the nucleus which gives rise to orbital magnetic moment, $\mu = \sqrt{l(l+1)}\,\frac{h}{2\pi}$ (ii) its spin motion around its own axis which gives rise to spin magnetic moment. $\mu = \sqrt{S(S+1)}\,\frac{h}{2\pi}$ or $\mu = \sqrt{n}$ (n+2) BM. Magnitude of this magnetic moment is very small and is measured in the unit called *Bohr magneton,* It is equal to 9.27×10^{-24} A m^2.

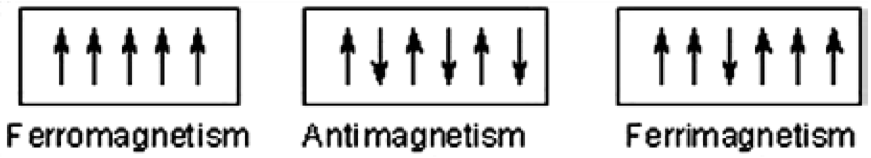


On the basis of their magnetic properties, substances can be classified into following five categories

1. ***Paramagnetism*:** substances which are weakly attracted by a magnetic field are called Paramagnetic substances. They are magnetized in the same direction in a magnetic field. They lose their magnetism in the absence of magnetic field. Paramagnetism is due to presence of one or more unpaired electrons which are attracted by the magnetic field. e.g.O_2, Cu^{2+}, Fe^{3+}, Cr^{3+}

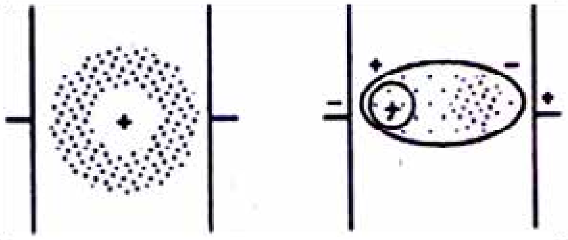
2. ***Diamagnetism*:** Substances which are weakly repelled by a magnetic field are called Diamagnetic substances. They are weakly magnetised in a magnetic field in opposite direction. Diamagnetism is shown by those substances in which all the electrons are paired and there are no unpaired electrons. Pairing of electrons cancels their magnetic moments and they lose their magnetic character. e.g. H_2O, NaCl and C_6H_6.
3. ***Ferromagnetism***: substances which are strongly attracted by a magnetic field and don‘t lose their magnetism even in absence of magnetic field are called ferromagnetic substances. e.g. iron, cobalt, nickel, gadolinium and CrO_2. In solid state, the metal ions of ferromagnetic substances are grouped together into small regions called *domains*. Thus, each domain acts as a tiny magnet. In an unmagnetised piece of a ferromagnetic substance the domains are randomly oriented and their magnetic moments get cancelled. 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 persists even when the magnetic field is removed and the ferromagnetic substance becomes a permanent magnet.

4. ***Antiferromagnetism*:** Substances like MnO showing antiferromagnetism have domain structure similar to ferromagnetic substance, but their domains are oppositely oriented and cancel out each other's magnetic moment
5. ***Ferrimagnetism*:** Ferrimagnetism is observed when the magnetic moments of the domains in the substance are aligned in parallel and anti-parallel directions in unequal numbers .They are weakly attracted by magnetic field as compared to ferromagnetic substances. Fe_3O_4 (magnetite) and ferrites like $MgFe_2O_4$ and $ZnFe_2O_4$ are examples of such substances. These substances also lose ferrimagnetism on heating and become paramagnetic.



- Ferromagnetic, antiferromagnetic and ferrimagnetic substances change into paramagnetic at a particular temperature, due to greater alignment of domains at low temperatures.
- Each ferromagnetic substance has a particular temperature above which no ferromagnetism is observed, known as Curie temperature.

Dielectric properties of solids: Dielectrics or insulators do not conduct electricity because electrons in them are tightly held and are not free to move. On application of electric field polarization takes place and hence dipoles are created. These individual dipoles align in an ordered manner giving crystal a net dipole moment. Such crystals posses the following properties



1. **Piezo electricity:** When mechanical stress is applied on such crystals, electricity is produced due to displacement of ions. The electricity thus produced is called piezoelectricity. And the crystals are called piezoelectric crystals.
   Conversely if electric field is applied on such crystals atomic displacement takes place resulting into mechanical strain.

2. **Pyroelectricity:** Some polar crystals when heated produce a small electric current due to displacement of ions. The electricity thus produced is called pyro electricity.
3. **Ferro electricity:** In some of the piezo electric crystals, the dipoles are permanently aligned even in the absence of electric field. Such crystals are called ferroelectric crystals. e.g barium titanate($BaTiO_3$), sodum potassium tartate (Rochelle salt)
4. **Antiferroelectricity:** In some crystals the dipoles in polyhedra point up and down so that the crystal does not possess net dipole moment. Such crystals are called antiferroelectric .e.g lead zirconate ($PbZrO_3$)

2 SOLUTION

Solution is a homogeneous mixture of two or more substances in a single phase.

It is said to be `binary’ if two substances are present and `ternary’ if three substances are present and `quaternary’ if four substances are being present etc. In a binary solution, the component present in larger amount is called as solvent and the component in smaller amounts is called as solute. Solvent and solute together make a solution.

Solute: component in lesser concentration; **dissolvee**
Solvent—component in greater concentration; **dissolver**
Miscible—When two or more liquids mix (ex. Water and food coloring)
Immiscible—when two or more liquids don’t mix.—they usually layer if allowed setting for a while. (eg. Water and oil)

Components: The substances forming the solution are called components of the solution. On the basis of number of components a solution of two components is called binary solution. In a binary solution, **solvent** is the component which is present in large quantity while the other component is known as **solute**.

Types of Solutions

Following types of solutions are seen on the basis of physical state of solute and solvent.

Type of solution	solute	solvent	Common Examples
Gaseous Solutions	Gas	Gas	Mixture of oxyzen and nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
Liquid Solutions	Gas	Liquid	Oxygen dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Solid Solutions	Gas	Solid	Solution of hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

If water is used as a solvent, the solution is called aqueous solution and if not, the solution is called non-aqueous solution.

Depending upon the amount of solute dissolved in a solvent we have the following types of solutions:

1. **Unsaturated solution:** A solution in which more solute can be dissolved without raising temperature is called an unsaturated solution.
2. **Saturated solution:** A solution in which no solute can be dissolved further at a given temperature is called a saturated solution.
3. **Supersaturated solution:** A solution which contains more solute than that would be necessary to saturate it at a given temperature is called a supersaturated solution.

Expressing Concentration of Solutions

Quantitatively the concentration of solution can be expressed in various ways.

1. **Mass percentage (W/W %):** Amount of solute present in grams dissolved per 100g of solution.

   $$\text{Mass \% of a component} = \frac{\text{Mass of the component in the solution}}{\text{Total mass of solution}} \times 100$$

   e.g If Wa and Wb be the mass of component A and B in a solution , then

   $$\text{Mass \% of a component A} = \frac{Wa}{Wa+Wb} \times 100$$

   $$\text{Mass \% of a component B} = \frac{Wa}{Wa+Wb} \times 100$$

2. **Volume percentage** ***(V/V %)*****:** Volume of solute present in 100ml of solution.

   $$\text{Volume \% of a component} = \frac{\text{Volume of the component}}{\text{Total Volume of solution}} \times 100$$

   e.g. If Va and Vb be the volume of component A and B in a solution, then

   $$\text{Volume \% of a component A} = \frac{Vb}{Va+Vb} \times 100$$

   $$\text{Volume \% of a component B} = \frac{Vb}{Va+Vb} \times 100$$

3. **Mass by volume percentage (W/V %):** It is the amount of solute in grams dissolved in 100 mL of the solution.
4. **Parts per million:** When a solute is present in trace quantities, then concentration is expressed in parts per million (ppm) and is defined as: *Amount of substance present in grams in* 10^6 *gm of solution.*

   $$ppm = \frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 10^6$$

5. **Mole fraction**(χ): Mole fraction of a component in a solution is the ratio of number of moles of the component to the total no. of moles present in a solution. e.g if n_a and n_b be the no. of moles of component A and B in a solution , then

$$\text{Mole fraction of A, } \chi_A = \frac{\text{Number of moles of A}}{\text{number of moles of A+no.of moles of B}}$$

$$= \frac{nA}{nA+nB} \qquad = \frac{\frac{WA}{MA}}{\frac{WA}{MA}+\frac{WB}{MB}}$$

$$\text{Mole fraction of B, } \chi_B = \frac{\text{Number of moles of B}}{\text{number of moles of A+no.of moles of B}}$$

$$= \frac{nB}{nA+nB} \qquad = \frac{\frac{WB}{MB}}{\frac{WA}{MA}+\frac{WB}{MB}}$$

Where W_A, W_B, M_A and M_B are the mass of A, mass of B, Molecular mass of A and Molecular mass of B respectively

For a solution containing *i* no. of components

$$\chi_i = \frac{n1}{n1+n2+n3+\cdots\ldots\ldots ni}$$

- Mole fraction is independent of temperature
- Mole fraction is dimensionless quantity
- The sum of mole fraction of all components in a solution is equal to one

i.e. $\chi_1 + \chi_2 + \chi_3 + \chi_4 + \ldots\ldots\ldots\ldots\ldots\ldots\ \chi_i = 1$

6. **Molarity**: Molarity (*M*) is defined as number of moles of solute dissolved in one liter (or one cubic decimetre) of solution.

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

$$\text{But No. of moles} = \frac{\text{Mass of solute}}{\text{Molecular mass of solute}}$$

Therefore,

$$\text{Molarity} = \frac{\text{Mass of solute}}{\text{Molecular mass of solute}} \times \frac{1000}{\text{Volume of solution (in ml)}}$$

$$M = \frac{nB}{V} \times 1000$$

$$M = \frac{WB \text{ x } 1000}{MB \text{ x } V(ml)}$$

Where , n_B – No. of moles of solute
V – Volume of solution is ml.
W_B – amount of solute
M_B- Molar Mass of solute

- Molarity of solution changes with temperature.

$$\frac{M1V1}{n1} = \frac{M2V2}{n2} \text{ .... (Morality equation or dilution formula)}$$

Here n_1 and n_2 refers to the no. of moles of reactant 1 and 2 respectively in the balances chemical equation.

- If a solution having Morality M_1 and Volume V_1 is mixed with a solution having Morality M_2 and Volume V_2 , than the Morality of resulting solution will be

$$M_3 = \frac{M1V1+M2V2}{(V1+V2)}$$

7. **Molality**: Molality (*m*) is defined as number of moles of solute present per Kg of solvent and is expressed as

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

$$\text{But No. of moles of solute} = \frac{\text{Mass of solute}}{\text{Molecular mass of solute}}$$

$$\text{Therefore, Molality} = \frac{\text{Mass of solute}}{\text{Molecular mass of solute X Mass of solvent in grams}} \times 1000$$

$$m = \frac{\text{WB x 1000}}{\text{MB x WA(gm)}}$$

Where, n_B – No. of moles of solute
W_A – amount of solvent in gm.
W_B – amount of solute
M_B- Molar Mass of solute

- Molality of solution does not change with temperature.

8. **Normality:** Normality is defined as number of gram equivalents of solute dissolved in one litre (or one cubic decimeter) of solution.

$$\text{Normality} = \frac{\text{Number ofgram equivalents of solute}}{\text{Volume of solution in liters}}$$

$$\text{But No. of gram equivalents} = \frac{\text{Mass of solute}}{\text{Equlvalent mass of solute}}$$

Therefore,

$$\text{Normality} = \frac{\text{Mass of solute}}{\text{Equlvalent mass of solute X Volume of solution (in ml)}} \times 1000$$

$$N = \frac{\text{WB x 1000}}{\text{EqWB x V(ml)}}$$

A solution having one gram equivalent of the solute per liter of the solution is called a normal solution.

$$\text{Normality} \times \text{Eq. Weight} = \text{Strength(g/l)}$$

Relationship between Normality and Molarity

As Normality × Eq. Weight = Strength(g/l)

Similarly Molarity × Molecular Weight = Strength (g/l)

Hence Normality × Eq. Weight = Molarity × Molecular Weight

$$\text{Or} = \frac{\text{Normality}}{\text{Molarity}} = \frac{\text{Molecular Weight}}{\text{Eq.Weight}} = \text{n factor}$$

So Normality = n × Molarity

- Normality of solution changes with temperature.
- $\frac{\text{Normality}}{\text{Molarity}}$ = Valency
- $N_1V_1=N_2V_2$……………………………….. (Normality equation or dilution formula)

- If a solution having Normality N_1 and Volume V_1 is mixed with a solution having Normality N_2 and Volume V_2 , then the normality of resulting solution(N_3) will be

  $$N_3 = \frac{N1V1+N2V2}{(V1+V2)}$$

9. **Strength:** Strength of a solution may be defined as weight of solute in gram present per litre of the solution. It is expressed as gram/litre

2.1 SOLUBILITY

Solubility of a Solid in a Liquid

Factors effecting solubility of solid in liquids

Nature of solvent and solute: Every solid does not dissolve in a given liquid. While sodium chloride and sugar dissolve readily in water, naphthalene and anthracene do not. On the other hand, naphthalene and anthracene dissolve readily in benzene but sodium chloride and sugar do not. It is observed that polar solutes dissolve in polar solvents and non polar solutes in nonpolar solvents. In general, a solute dissolves in a solvent if the intermolecular interactions are similar in the two or we may say ***like dissolves like***.

Dissolution: When a solid solute is added to the solvent, some solute dissolves and its concentration increases in solution. This process is known as dissolution.

Crystallization: Some solute particles in solution collide with each other and get separated out of solution. This process is known as crystallization**.**

A stage is reached when the two processes occur at the same rate. Under such conditions, number of solute particles going into solution will be equal to the solute particles separating out and a state of dynamic equilibrium is reached.

Solute + Solvent ⇔ Solution

Effect of temperature: The solubility of a solid in a liquid is significantly affected by temperature changes. According to **Le Chateliers Principle**, if the dissolution process is endothermic ($\Delta H_{sol} > 0$), the solubility should increase with rise in temperature and if it is exothermic ($\Delta H_{sol} < 0$) the solubility should decrease. These trends are also observed experimentally.

Effect of pressure: Pressure does not have any significant effect on solubility of solids in liquids.

Solubility of gases in liquids

The Solubility of gas in liquids is defined as volume of gas in cubic centimeters (cc) which will dissolve in 1 cc of the liquid. This is also called absorption coefficient.

Factors effecting solubility of gas in liquids

Solubility of gas depends on following factors

Nature of gas and the solvent: Some gases like nitrogen, hydrogen, oxygen (non polar) are slightly soluble in water whereas gases like carbon dioxide, ammonia, hydrochloric acid (Polar gases) are highly soluble in water. The higher solubility of these gases is due to their reaction with water.

Effect of temperature: The solubility of gases decreases with increase in temperature because on heating gas is expelled out of the solution. The process of dissolution is exothermic because the gas contracts in volume and energy is released during contraction. According to Le-Chateliers Principle the increase in temperature favors reverse process therefore solubility decreases with increase in temperature

Gas + Liquid ↔ dissolved gas, $\Delta H = -ve.$

Effect of pressure: The effect of pressure on the solubility is given by Henrys law

Henry's Law: It states that

The mass of gas dissolved (m) in a given volume of liquid at constant temperature is directly proportional to the pressure of the gas.

$\mathbf{m \propto p}$

m = K p ……………………… where K is called Henrys constant

The most commonly used form of Henry's law states "***the partial pressure (P) of the gas in vapour phase is proportional to the mole fraction (x) of the gas in the solution***" and is expressed as

p = KH . X Where K_H is the Henry's law constant.

Greater the value of K_H, lower the solubility of the gas. The value of K_H decreases with increase in the temperature. Thus, aquatic species are more comfortable in cold water [more dissolved O_2] rather than Warm water.

Limitations of Henrys law: Henrys law is only applicable if

1. Pressure is low
2. Gas does not undergo compound formation, association, dissociation in the solvent.

Applications

1. In manufacture of soft drinks and soda water, CO_2 is passed at high pressure to increase its solubility.
2. To minimize the painful effects (bends) accompanying the decompression of deep sea divers, O_2 diluted with less soluble Helium gas is used as breathing gas.
3. At high altitudes, the partial pressure of O_2 is less then that at the ground level. This leads to low concentrations of O_2 in the blood of climbers which causes "anoxia".

2.2 VAPOUR PRESSURE

Vapour pressure of a liquid is defined as the pressure exerted by vapours when rate of evaporation is equal to rate of condensation.

Factors effecting vapour pressure: The vapour pressure of liquid depends on the following factors:

1. **Nature of liquid:** Weaker the intermolecular forces, greater the amount of vapour because more molecules can leave the liquid and come into vapour phase.
2. **Temperature:** The vapour pressure of liquid increases with increase in temperature because kinetic energy of molecules increases and hence more molecules leave the surface of liquid and come into vapour phase.

Vapour pressure of solution

- If solute is non volatile solid or liquid, the vapour pressure of solution is equal to partial vapor pressure of solvent in the solution.
- If solute is volatile solid or liquid the vapour pressure will be equal to the sum of partial vapor pressure of solute and that of solvent.

Raoults law and vapour pressure of liquid- liquid solutions

a. **Raoult's law for binary solutions of volatile liquids:** It states that, at a given temperature, for a solution of volatile liquids, the partial vapour pressure of each component is equal to the product of the vapour pressure of the pure component and its mole fraction.

If the solution contains two volatile liquids A & B, then

i.e $P_A = p^0_A X_A$ & $P_B = p^0_B X_B$

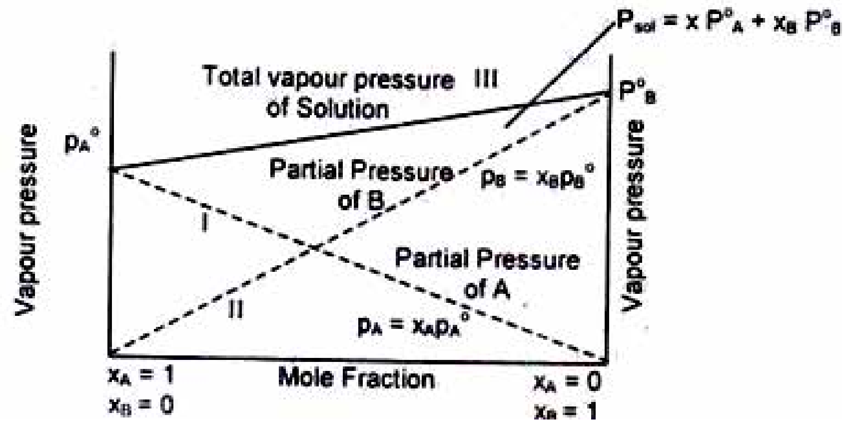
Where → p_A and p_B are the vapour pressures of A and B in solution respectively.

$p^0_A \alpha p^0_B$ are the vapour pressures of A and B in their pure state respectively. x_A and x_B are the mole fractions of A and B in solution respectively.

$P_{total} = P_A + P_B$

$P_{total} = p^0_A X_A + p^0_B X_B$

A plot of P_A or P_B versus the mole fractions X_A and X_B for a solution gives a linear plot as shown:



b. **Raoult's law for solution containing Non–volatile solute:** It states that, at a given temperature, the relative lowering vapour pressure of a solution is equal to the mole fraction of the solute.

Derivation :

We know that, from Raoults law,

$P_{solution} = p_A + p_B$

$P_{solution} = p^0_A X_A + p^0_B X_B$

$P_{solution} = p^0_A X_A + 0$ (Since $p^0_B = 0$, because B is a non-volatile solute)

$P_{solution} = X_A P^0_A$

$\Rightarrow P_{solution} = (1-X_B)\ P^0_A \qquad (\text{Since } X_A + X_B = 1)$

$\Rightarrow P_{solution} = P^0_A - X_B\ P^0_A$

$\Rightarrow P_{solution} - P^0_A = -\ X_B\ P^0_A$

$\Rightarrow (\ P^0_A - P_{solution})\ /\ P^0_A = X_B$

Where , $(\ P^0_A - P_{solution})$ → Lowering of vapour pressure

$(\ P^0_A - P_{solution})/\ P^0_A$ → Relative lowering of vapour pressure.

X_B → Mole fraction of Solute.

Limitations of Raoults law

1. Raoults law is applicable only to ideal and dilute solutions
2. It is not applicable when solute undergoes association or dissociation.

Ideal and Non-Ideal Solutions

a. **Ideal Solutions**: The solution which obeys Raoult's law exactly at all concentration and all temperatures.

The ideal solution also has following characteristics:

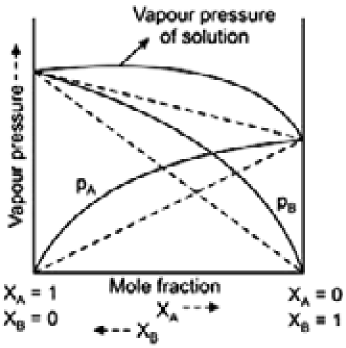
1. It should obey the Raoult's law (Total pressure, P = $p^0_A\ x_A + p^0_B\ x_B$)
2. Heat exchange on mixing is zero ($\Delta H_{mix} = 0$)
3. Volume exchange on mixing is zero ($\Delta V_{mix} = 0$)

b. **Non ideal solutions:** The solutions which do not obey Raoult's law are called non ideal solutions. For these solutions

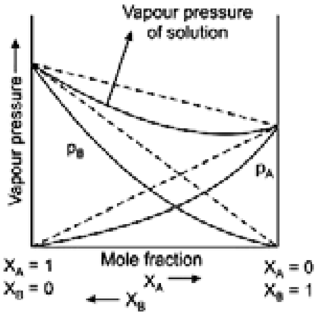
i) $p_A \neq p^0_A\ x_A$ and $p_B \neq p^0_B\ x_B$, ii) Δ H mixing $\neq 0$, iii) Δ V mixing $\neq 0$

Ideal solutions	Non ideal solutions
1. The solutions which obey Raoult's law over the entire range of concentration are known as *ideal solution .i.e.* $P_A = P°_A\ X_A$ $P_B = P°_B\ X_B$ 2. In ideal solution the intermolecular interaction between the components (A-B) is same as found in pure components (i.e A-A and B-B) 3. The enthalpy of mixing of the pure components to form the solution is zero; $\Delta H_{mix} = 0$ 4. . There is no change in volume on mixing the two components to form ideal solutions, $\Delta V_{mix} = 0$ 5. No solution is practically ideal but under very dilute conditions following solutions have been nearly found to be ideal Benzene + Toluene Chlorobemzene + Bromo benzene	1. The solutions which does not obey Raoult's law over the entire range of concentration are known as non *-ideal solution. i.e* $P_A \neq P°_A\ X_A$ $P_B \neq P°_B\ X_B$ 2. In non-ideal solution the intermolecular interaction between the components (A-B) is not same as found in pure components(i.e A-A and B-B interactions) 3. The enthalpy of mixing of the pure components to form the solution is not zero; $\Delta H_{mix} \neq 0$ 4. There is some change in volume on mixing the two components to form non-ideal solutions, $\Delta V_{mix} \neq 0$ 5. The following solutions have been found to be non ideal Ethyl alcohol + Cyclohexane Chloroform + Acetone

Non ideal solution showing positive deviation	**Non ideal solution showing negative deviation**
1. The vapour pressure of these solution is higher than that predicted by Raoults law $P_A > P^{\circ}_A X_A$ $P_B > P^{\circ}_B X_B$ 2. The intermolecular interaction between the components (A-B) is weaker as compared to pure components (i.e A-A and B-B interactions) 3. The Volume change of mixing is positive $\Delta V_{mix} > 0$ 4. The Enthalphy change of mixing is positive $\Delta H_{mix} > 0$ 5. Here minimum boiling azeotropes are formed 6. *Example:* Ethyl alcohol + Cyclohexane	1. The vapour pressure of these solution is lower than that predicted by Raoults law $P_A < P^{\circ}_A X_A$ $P_B < P^{\circ}_B X_B$ 2. The intermolecular interaction between the components (A-B) is stronger as compared to pure components (i.e A-A and B-B interactions) 3. The Volume change of mixing is negative. $\Delta V_{mix} < 0$ 4. The Enthalphy change of mixing is negative. $\Delta H_{mix} < 0$ 5. Here maximim boiling azeotropes are formed 6. *Example:* Chloroform + Acetone



Non ideal solution showing positive deviation



Non ideal solution showing negative deviation

Azeotropes

The binary mixtures having the same composition in liquid and vapour phase and boil at a constant temperature.

Types of Azeotropes

1. **Minimum boiling azeotropes:** The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition.
   Example: Ethanol-water mixture (obtained by fermentation of sugars) on fractional distillation gives a solution containing approximately 95% by volume of ethanol. Once this composition, known as azeotrope composition, has been achieved, the liquid and vapour have the same composition, and no further separation occurs.

2. **Maximum boiling azeotropes:** The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition.
   Example: Nitric acid and water is an example of this class of azeotrope. This azeotrope has the approximate composition, 68% nitric acid and 32% water by mass, with a boiling point of 393.5 K.

Colligative properties

Colligative Properties (Greek *colligatus* = Collected together).

A colligative property may be defined as one which depends on the number of particles in solution and not in any way on the size or chemical nature of the particles.

Consequent to the above definition, each colligative property is exactly related to any other. Thus if one property is measured, the other can be calculated. The colligative properties of dilute solutions are particularly important as these provide valuable methods for finding the molecular weights of the dissolved substances.

Dilute solutions containing non-volatile solute exhibit the following properties:

1. ***Relative Lowering of the Vapour Pressure***
2. ***Elevation of the Boiling Point***
3. ***Depression of the Freezing Point***
4. ***Osmotic Pressure***

1. **Relative lowering of vapour pressure:** When a non-volatile solute is added to solvent the vapour pressure of solution decreases. According to Raoults law the vapour pressure of solution is equal to the product of vapour pressure of solvent and its mole fraction.

We know that for a two component solution A & B

$P_{\text{solution}} = p_A + p_B$

$P_{\text{solution}} = p^0_A X_A + p^0_B X_B$

$P_{\text{solution}} = p^0_A X_A + 0$ (Since $p^0_B = 0$, because B is a non-volatile solute)

$P_{\text{solution}} = X_A P^0_A$

$\Rightarrow P_{\text{solution}} = (1-X_B) P^0_A$ (Since $X_A + X_B = 1$)

$\Rightarrow P_{\text{solution}} = P^0_A - X_B P^0_A$

$\Rightarrow P_{solution} - P^0_A = - X_B P^0_A$

$\Rightarrow (P^0_A - P_{solution}) / P^0_A = X_B$

Where , $(P^0_A - P_{solution}) \rightarrow$ Lowering of vapour pressure

$(P^0_A - P_{solution})/ P^0_A \rightarrow$ Relative lowering of vapour pressure.

$X_B \rightarrow$ Mole fraction of Solute.

Thus Relative lowering of vapour pressure of a solution is equal to mole fraction of non volatile solute in the solution; ***hence it is a colligative property***.

Determination of Molecular mass: The molecular mass of non volatile solute can be calculated from relative lowering of vapour pressure.

$$\frac{P°A-PA}{P°A} = X_B$$

$$But\ X_B = \frac{nB}{nA+nB} = \frac{\frac{WB}{MB}}{\frac{WA}{MA}+\frac{WB}{MB}}$$

Since an ideal solution is dilute in nature ($n_B <<< n_A$), therefore n_B can be neglected in the denominator

$$\frac{P°A-PA}{P°A} = \frac{\frac{WB}{MB}}{\frac{WA}{MA}}$$

$$\frac{P°A-PA}{P°A} = \frac{WB}{MB} \times \frac{MA}{WA}$$

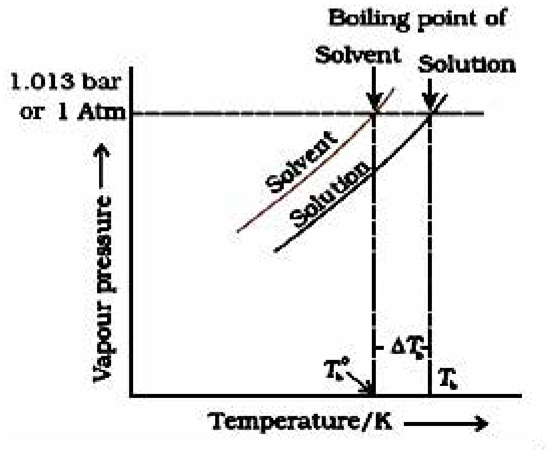
$$\text{Or } M_B = \frac{WB}{\frac{P°A-PA}{P°A}} \times \frac{MA}{WA}$$

Thus molecular mass of solute can be determined if all other values are known.

2. **Elevation in boiling point**:
   The boiling point of a substance may be defined as the temperature at which the vapour pressure of the substance in its liquid phase is equal to the atmospheric pressure. The solution boils at higher temperature than that of solvent and this increase in boiling point on addition of non volatile solute is called elevation in boiling point. This is also illustrated graphically as

Let **T°b** be the boiling point of pure solvent and ***Tb*** be the boiling point of solution. Then increase or elevation in the boiling point is given by

$\Delta T_b = T_b - T^\circ_b$



Experiments have shown that for dilute solutions the elevation of boiling point ΔT_b is directly proportional to the molal concentration of the solute in a solution. Thus

$\Delta T_b \propto m$

$\Delta T_b = K_b \cdot m$ ....(1) here m is molality of solution.

K_b is constant called Boiling Point Elevation Constant or Molal Elevation Constant (Ebullioscopic Constant). The unit of K_b is K kg mol^{-1}.

If m = 1

$\Delta T_b = K_b$

Thus Molal Elevation Constant or Ebullioscopic Constant may be defined as elevation in boiling point of 1 molal solution.

Determination of Molecular mass: The molecular mass of non volatile solute can be calculated by substituting the expression of molality in equation 1.

$$\text{Molality} = \frac{\text{Mass of solute}}{\text{Molecular mass of solute}} \times \frac{1000}{\text{Mass of solvent in grams}}$$

$$m = \frac{WB}{MB} \times \frac{1000}{WA}$$

Where W_B is the weight of solute M_B is the molecular mass of solute and W_A is the weight of solvent.

$$\Delta Tb = K_b \cdot \frac{WB}{MB} \times \frac{1000}{WA}$$

$$\text{Or } M_B = K_b \cdot \frac{WB}{\Delta Tb} \times \frac{1000}{WA}$$

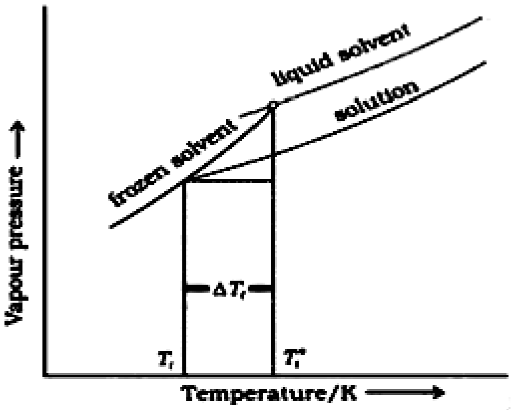
Thus molecular mass of solute can be determined if all other values are known.

3. **Depression of Freezing Point:**
   The freezing point of a substance may be defined as the temperature at which the vapour pressure of the substance in its liquid phase is equal to its vapour pressure in the solid phase. It has been observed that freezing point of solution is always lower than that of pure solvent. This decrease is called depression of Freezing Point.

   As the vapour pressure of solution is lower than that of pure solvent and at freezing point the vapor pressure of solution and solid are equal therefore solution will freeze at a lower temperature as shown in graph.

Let T°_f be the freezing point of pure solvent and T_f be the freezing point of solution. Then decrease or depression in the freezing point is given by

$$\mathbf{\Delta T_f = T^\circ_f - T_f}$$



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

$$\mathbf{\Delta T_f \propto m}$$

$$\mathbf{\Delta T_f = K_f \cdot m} \text{ ....(1)}$$

Where K_f, is constant and its value depends on the nature of the solvent it is also known as Freezing Point Depression Constant or Molal Depression Constant or Cryoscopic Constant. The unit of K_f is K kg mol^{-1}.

Determination of Molecular mass: The molecular mass of non volatile solute can be calculated by substituting the expression of molality in equation 1.

$$\text{Molality} = \frac{\text{Mass of solute}}{\text{Molecular mass of solute}} \times \frac{1000}{\text{Mass of solvent in grams}}$$

$$m = \frac{WB}{MB} \times \frac{1000}{WA}$$

Where W_B is the weight of solute M_B is the molecular mass of solute and W_A is the weight of solvent.

$$\Delta T_f = K_f \cdot \frac{WB}{MB} \times \frac{1000}{WA}$$

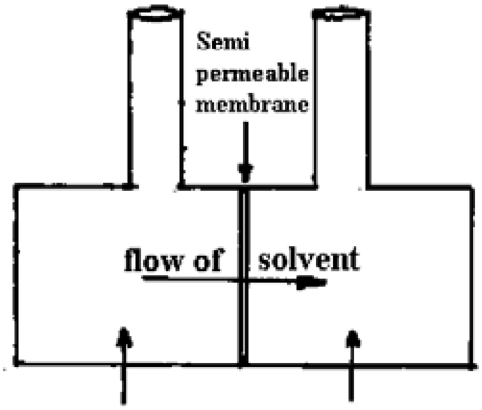
$$\text{Or} \quad M_B = K_f \cdot \frac{WB}{\Delta Tf} \times \frac{1000}{WA}$$

Thus molecular mass of solute can be determined if all other values are known.

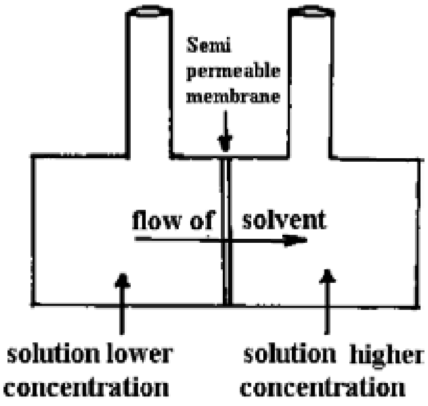
Semi permeable membrane

It is a membrane which allows the solvent molecules, but not the solute molecules, to pass through it. The thin films of the copper ferrocyanide, $Cu_2[Fe(CN)_6]$ deposited in pores of porous porcelain pot is the best semi permeable membrane. Cellulose, cellulose nitrate, animal bladder, etc. are also used as semi permeable membranes.

Osmosis: When a solution is separated from pure solvent by a semi permeable membrane, the solvent molecules pass through the membrane into the solution and dilute it. Similarly, when two solutions of different concentrations are seperated by semipermeable membrane then the direction of flow of solvent molecules is from the solution of lower concentration to the solution of higher concentration. The flow continues till the concentrations of the two solutions become equal.



Osmosis between solvent & solution



Osmosis between 2 solutions of different concentration

Definition of Osmosis

The spontaneous and unidirectional flow of solvent molecules through a semi permeable membrane, into the solution or flow of solvent from a solution of lower concentration to the solution of higher concentration through a semi permeable membrane is called osmosis.

4. **Osmotic Pressure:**
   The flow of the solvent from solvent side to solution side across a semi permeable membrane can be stopped if some extra pressure is applied on the solution. This pressure that must be applied to a solution to prevent osmosis, i.e., to stop the passage of solvent molecules through a semi permeable membrane into the solution is called Osmotic pressure. Osmotic pressure is a colligative property as it depends on the number of solute molecules and not on their identity.

Expression for osmotic pressure: Osmotic pressure (π) is proportional to the molar concentration ***(C)*** of the solution and temperature *T*.

$\pi\ \alpha\ C$……………………..(Boyle Vont Hoff law)

$\pi\ \alpha\ T$……………………..(Gay Lussac law)

Combining above laws

$\pi\ \alpha\ CT$

$\pi = RCT$ where R is gas constant= 0.0821 L atm K^{-1} mol^{-1}

Since $C = \dfrac{\text{number of moles (n)}}{\text{volume (V)}}$

$$\pi = \frac{n}{V} RT$$

$\pi V = nRT$…………………………(1)

This equation is called Vont Hoffs equation for dilute solutions.

Determination of Molecular mass: The molecular mass of non volatile solute can be calculated by substituting the value of n = $\frac{WB}{MB}$ in equation (1)

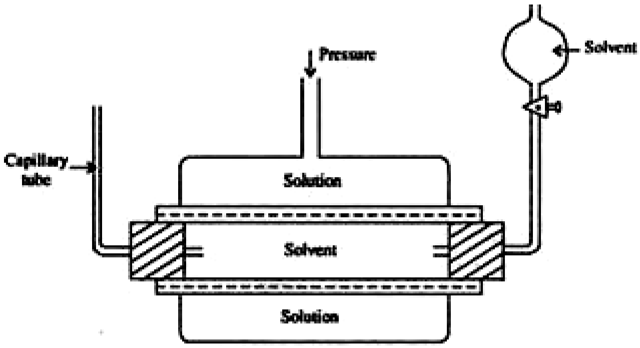
$$\pi V = \frac{WB}{MB} RT$$

$$\text{Or } M_B = \frac{WB}{\pi V} RT$$

where W_B is the weight of solute M_B is the molecular mass of solute. Thus molecular mass of solute can be determined if all other values are known.

Determination of osmotic pressure Berkley and Hartley's method

The method commonly employed for the determination of osmotic pressure is due to Berkley and Hartley (1904). In this method the osmotic pressure is balanced by a counter pressure, which prevents the passage of the solvent into the solution. The apparatus employed, consists of a fine uniformly textured porcelain tube, within the pores of which the semipermeable membrane of copper ferrocyanide is deposited electrolytically. This porcelain tube is fitted into a Gun metal jacket, with liquid tight joint. The outer vessel is provided with an air-tight piston. One end of the porcelain tube is completely filled with water while the outer vessel is filled with the semipermeable membrane in the solution. External pressure, which is measured by a pressure gauge, is applied on the solution by the piston so as to prevent the entrance of water into the solution, which is indicated when the level of water in the capillary tube remains stationary. This pressure measures the osmotic pressure of the solution.

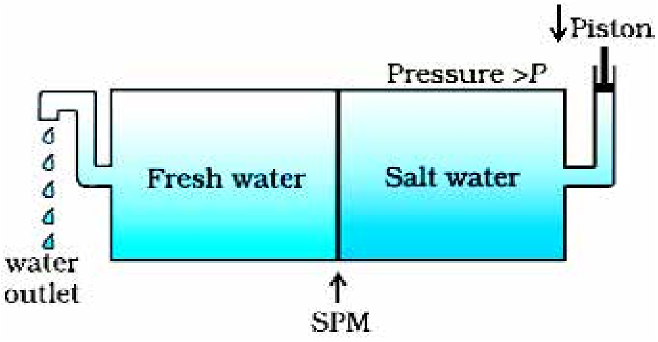


On the basis of osmotic pressure, -the solution can be

1. **Hypertonic solution:** A solution is called hypertonic if its osmotic pressure is higher than that of the solution from which it is separated by a semipermeable membrane. When a plant cell is placed in a hypertonic solution, the fluid from the plant cell comes out and cell shrinks, this phenomenon is called plasmolysis.
2. **Hypotonic solution:** A solution is called hypotonic if its osmotic pressure is lower than that of the solution from which it is separated by a semipermeable membrane.
3. **Isotonic solution:** Two solutions are called isotonic if they exert the same osmotic pressure. These solutions have same molar concentration. 0.91% solution of pure NaCl is isotonic with human RBC"s.

Reverse Osmosis and Water Purification: The direction of osmosis can be reversed if a pressure larger than the osmotic pressure is applied to the solution side. That is, now the pure solvent flows out of the solution through the semi permeable membrane. This phenomenon is called reverse osmosis and is of great practical utility. Reverse osmosis is used in desalination of sea water. A schematic set up for the process is shown in Fig.

When pressure more than osmotic pressure is applied, pure water is squeezed out of the sea water through the membrane. A variety of polymer membranes are available for this purpose.



Abnormal molar mass

We know that all the colligative properties are used for determination of molecular mass. In many cases the substance undergoes association or dissociation and hence the observed value of colligative property or molecular mass is different than expected value.

When the molecular mass of a substance determined by studying any of the colligative property comes out to be different than the the theoretically expected value, the substance is said to show abnormal molecular mass.

Reasons for showing abnormal molecular mass: Abnormal molecular mass is observed in following cases

1. **When the solution is non ideal i.e.** when the solution is not dilute
2. **When the solute undergoes association:** In such cases no. of particles decreases so does the value of any coligative property. Consequently it will lead to increase in the value of calculated molecular mass. e.g. benzoic acid in solution undergoes association to form dimmers
3. **When the solute undergoes dissociation:** In such cases no. of particles increases so does the value of any coligative property. Consequently it will lead to decrease in the value of calculated molecular mass. e.g. NaCl in aq. solution undergoes dissociation.

van't Hoff factor

To account for the extent of dissociation or association, Van't Hoff introduced a factor *i*, known as the van't Hoff factor This factor *i* is defined as ratio of experimental value of colligative property to the calculated value of colligative property

$$i = \frac{\text{Experimental/observed value of colligative property}}{\text{actual/calculated value of colligative property}}$$

$$i = \frac{\text{Normal molecular mass}}{\text{Abnormal molecular mass}}$$

$$i = \frac{\text{Total number of moles of particles after association/dissociation}}{\text{Number of moles of particles before association/dissociations}}$$

In case of association, value of *i* is less than unity while for dissociation it is greater than unity.

If a solute is dissociated or ionized in solution to give 'n' Ions and 'α' is the degree of ionization

Van't Hoff factor $i = 1 + (n - 1)\alpha$

Degree of ionization $\alpha = \frac{i-1}{n-1}$

If a solute associated in solutions 'n' molecules associate and 'α' is the degree of association.

Van't hoff factor $i = 1 + (1/n - 1)\alpha$

Degree of ionization $\alpha = \frac{i-1}{1/n-1}$

Inclusion of van't Hoff factor modifies the equations for colligative properties as follows:

Relative lowering of vapour pressure of solvent $\frac{PA^\circ - PA}{PA^\circ} = i\, X_B$

Elevation of Boiling point, $T_b = i\, K_b\, \mathrm{m}$

Depression of Freezing point, $\Delta T_f = i\, K_f\, \mathrm{m}$

Osmotic pressure of solution, $\prod = i \frac{n}{V} R\, T$

3 ELECTROCHEMISTRY

Electrochemistry is that branch of chemistry which deals with the study of production of electricity from energy released during spontaneous chemical reactions and the use of electrical energy to bring about non-spontaneous chemical transformations.

Importance of Electrochemistry

1. Production of metals like Na, Mg. Ca and Al.
2. Electroplating.
3. Purification of metals.
4. Batteries and cells used in various instruments.

3.1 CONDUCTORS

Substances that allow electric current to pass through them are known as conductors.

Metallic Conductors or Electronic Conductors: Substances which allow the electric current to pass through them by the movement of electrons are called metallic conductors, e.g. Metals.

Electrolytic Conductors or Electrolytes: Substances which allow the passage of electricity through their fused state or aqueous solution by the movement of ions are called electrolytic conductors, e.g., aqueous solution of acids bases and salts.

1. **Strong electrolytes:** The electrolytes that completely dissociate or ionize completely into ions are called strong electrolytes. e.g., HCl, NaOH, K_2SO_4
2. **Weak electrolytes:** The electrolytes that dissociate partially are called weak electrolytes, e.g., CH_3COOH, H_2CO_3, NH_4OH, H_2S, etc.

Metallic conductors (Electronic conductors)	**Electrolytic conductors**
1. The conduction of electricity is due to electrons or holes. Example: Metals	1. Conduction is due to movement of ions Example: Acids bases and their salts
2. No chemical change	2. Under go chemical decomposition
3. Matter is not exchanged	3. Matter is exchanged
4. Electron flow from negative to positive end	4. Ions moves towards oppositely charged electrodes
5. Conduction decreases with rise in temperature	5. Conduction increase with rise in temperature
6. Conductivity depends on nature and structure of metal, number of valence e- per atom and density of the metal.	6. Conductivity depends on nature of electrolyte, size of ions and their solution, nature of solvent, its viscosity and concentration of the electrolyte.

3.2 FACTORS EFFECTING ELECTROLYTIC CONDUCTION

1. **Interionic interaction** (solute- solute interaction): Interaction between ions of the solute is called solute solute interaction or interionic interaction. In general greater the magnitude of Interionic attraction lesser will be electrolytic conduction and vice versa.
2. **Solvation of ions** (solute solvent interaction): The ions of an electrolyte in aqueous solution get surrounded by polar solvent molecules. This physical interaction between solute and the solvent is called salvation. Electrolytic conductance depends on the interaction between solute and solvent. Greater is the magnitude of this interaction lesser is ionic mobility and hence lesser will be conductance.
3. **Viscosity of solvent** (solvent solvent interaction): The Viscosity of solvent depends on solvent solvent interaction. Greater the magnitude of this interaction lesser is the ionic mobility or conductance.
4. **Temperature:** Ionic conductance increases with increase in temperature. This is because with increase in temperature average kinetic energy of ions increases. The interionic interaction, solvation and viscosity decreases with increase in temperature.

3.3 CONDUCTANCE OF ELECTROLYTIC SOLUTION

Like solid conductors, electrolytic solutions also obey Ohm's Law. When a current of I amperes flows through a solution which offers a resistance of R ohms and a potential difference of V volts is applied, then according to ohm's law

$$I = \frac{V}{R}$$

$$\text{or } V = I.\ R$$

Resistance: Resistance is obstruction in the flow of current. It is measured in ohm (Ω). The electrical resistance of substance is directly proportional to its length, l, and inversely proportional to its area of cross section, A. That is,

$$R\ \alpha\ \frac{l}{A}$$

$$\text{or } R = \rho\ \frac{l}{A}$$

Where ρ is constant of proportionality and is called resistivity or specific resistance.

Resistivity or specific resistance: We know that

$$\rho = R\,\frac{A}{l}$$

If A =1cm^2 and l =1cm

Then: $\rho = R$

Therefore specific resistance may be defined as the resistance offered by a conductor of 1cm length and having the area of cross section 1 cm^2. Its SI unit is **ohm-meter** and its value depends on the material of conductor.

Conductance (C): The ease with which current flows through the conductor is called conductance: It is equal to reciprocal of resistance.

$$C = \frac{1}{R} = \frac{1}{\rho} \times \frac{A}{l}$$

The unit of conductance is ohm^{-1} or mho or Siemens (S)

Conductivity or specific conductance (κ): The reciprocal of resistivity of a substance is called conductivity or specific conductance.

$$\kappa = \frac{1}{\rho} = \frac{l}{RA} = \frac{1}{R} \times \frac{l}{A} = \frac{Cl}{A}$$

If A=1cm^2 and l =1cm

Then: $\kappa = C$

Therefore specific conductance or conductivity may be defined as the conductance offered by a conductor of 1cm length and having the area of cross section 1 cm^2 .or simply conductance of 1 cm^3 of solution. Its SI units are ohm^{-1} metre^{-1} and its value does not depend on dimensions of material.

Cell constant: We know that

$$\kappa = \frac{Cl}{A}$$

The quantity $\frac{l}{A}$ is called cell constant denoted by the symbol, *G**.

Thus specific conductance κ = cell constant × conductance

$$= \frac{\text{cell constant}}{\text{Resistance}}$$

Equivalent conductivity: Equivalent conductivity of a solution is defined as conduction power of all the ions produced by dissolving one gram equivalent of an electrolyte. It is denoted by λ_e and is given by

$$\Lambda_e = \frac{\kappa \times 1000}{N}$$

Unit of equivalent conductivity is S cm^2 (g equiv)$^{-1}$.

λ_e values depend on the type of the electrolyte, concentration of the solution and temperature.

Molar conductivity: Molar conductivity of a solution is defined as conduction power of all the ions produced by dissolving one mole of an electrolyte. It is denoted by λ_m. And is given by

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$

Where M is the molar concentration of solution in moles per litre (also called molarity) and κ is the specific conductance.

Units of molar conductivity= $\text{ohm}^{-1}\ \text{cm}^2(\text{mol})^{-1}$

Effect of dilution on specific, equivalent and molar conductance

The specific conductance decreases with increase in dilution because no. of ions per unit volume decreases with increase in dilution. However both equivalent and molar conductance increase with increase in dilution, as both these are the product of specific conductance and volume of solution, since with dilution the decrease in specific conductance is more compensated by increase in volume therefore both equivalent and molar conductance increases with increase in dilution.

Variation of conductivity and molar conductivity with dilution: Both conductivity and molar conductivity change with the concentration of the electrolyte. Conductivity always decreases with decrease in concentration both, for weak and strong electrolytes. This can be explained by the fact that the number of ions per unit volume that carry the current in a solution decreases on dilution.

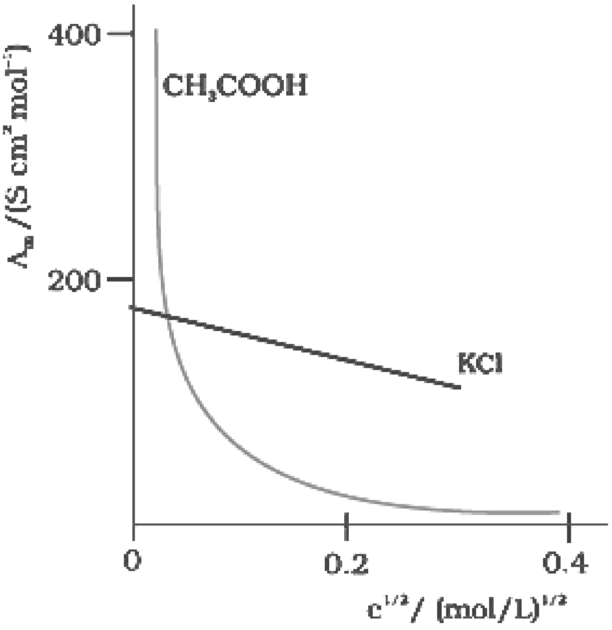
Conductance behavior of strong electrolytes: For strong electrolytes λ_m increases slowly with dilution or decrease in concentration and the molar conductivity of solution at zero concentration or infinite dilution is called its limiting molar conductivity and is represented as λ_m^o. The variation of molar conductivity with increase in dilution for strong electrolytes is given by **Debye Huckel-Onsager equation**

$$\lambda_m = \lambda_m^o - b\sqrt{c}$$

Where λ_m the molar conductivity at concentration c, λ_m^o is the molar conductivity at infinite dilution and b is a constant.

It can be seen that if we plot λ_m against $\sqrt{c}$ we obtain a straight line with intercept equal to λ_m^o and slope equal to '$-b$' at low concentrations but it is not linear for higher concentrations as shown in figure below for strong electrolytes (KCl) .

Conductance behavior of weak electrolytes: from the above figure it is clear that the conductance of weak electrolytes is lower than strong electrolytes for the same concentration, because they are less dissociated. Further the curve obtained shows that there is large increase in conductance with dilution especially near infinite dilution. This can be attributed due to increase in degree of dissociation of weak electrolyte. Further it is clear that λ_m^o for weak electrolytes cannot be determined graphically as the curve doesn't touch zero concentration.



3.4 KOHLRAUSH'S LAW

From a study of the equivalent conductance of different electrolytes at infinite dilution ($\lambda^{\propto}$), Kohlrausch discovered that each ion contributes to the conductance of the solution. In 1875, he enunciated a generalization which is called the **Kohlrausch's Law.**

It states that: ***the equivalent or molar conductance of an electrolyte at infinite dilution is equal to the sum of the equivalent or molar conductance of the component ions.***

The law may be expressed mathematically as:

$$\lambda^{\propto} = \mathbf{n+}\lambda_a + \mathbf{n-}\lambda_c$$

Where λa is the equivalent conductance of the anion and λc *is* that of the cation at infinite dilution. The equivalent conductance of NaCl at infinite dilution at 25°C is found to be 126.45.

The equivalent conductance of Na^+ and Cl^- ion is 50.11 ohm– 1 and 76.34 ohm^{-1} respectively. Thus,

$$\lambda^{\infty}_{(NaCl)} = \lambda_{Cl^-} + \lambda_{Na^+}$$

or 126.45 = 50.11 + 76.34

This is in conformity with the Kohlrausch's Law.

Application of Kohlraush's law

1. **Calculation of λ^∞ for Weak electrolytes:** Weak electrolytes do not ionize to a sufficient extent in solution and are far from being completely ionized even at very high dilution. The practical determination of λ^∞ in such cases is, therefore, not possible. However, it can be calculated with the help of Kohlrausch's law.
   In general

   Λ^∞m for weak electrolyte = Λ^∞m of salt of weak electrolyte (1) + Λ^∞m of strong Acid (2) –Λ^∞m of salt formed by 1 and 2.

   Examples
   1. Λ^∞_m CH_3COOH =Λ^∞_m CH_3COOK + Λ^∞_m HCl - Λ^∞_m KCl
   2. $\Lambda^\infty_m Ba(OH)_2$ = Λ^∞_m $BaCl_2$ +2 Λ^∞_m NaOH - 2Λ^∞_m NaCl
   3. Λ^∞_m NH_4OH = Λ^∞_m NH_4Cl + Λ^∞_m NaOH - Λ^∞_m NaCl

2. **Calculation of degree of dissociation of weak electrolyte (α):** The degree of dissociation of weak electrolyte at concentration c is equal to the ratio of molar conductivity at that concentration (Λ^c_m) to the molar conductivity at infinite dilution (Λ°_m).

Thus $\alpha = \frac{\Lambda_m}{\Lambda_m^\circ}$

Note: this relation is found to hold good for weak electrolytes only.

3. **Calculation of solubility of sparingly soluble salt:** Salts like AgCl, $BaSO_4$ which dissolve to a small extent are called sparingly soluble salts. As they dissolve very little their solutions are considered infinite dilute and their concentration is equal to their solubility.

Thus we have = $\Lambda_m^\circ = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{\kappa \times 1000}{\text{Solubility}}$

Or Solubility = $\frac{\kappa \times 1000}{\Lambda_m^\circ}$

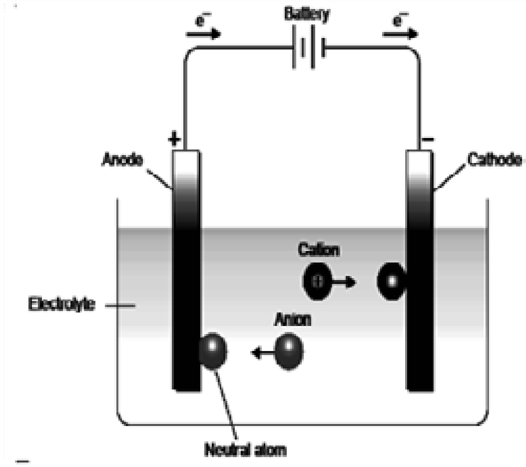
3.5 EECTROCHEMICAL CELL

An electrochemical cell is a device, which is used to convert chemical energy into electrical energy and vise versa. These electrochemical cells are classified into two types as follows.

1. **Electrolytic cell:** These are the electrochemical cells, which are used to convert electrical energy into chemical energy. Eg: Lead acid battery, Nickel cadmium battery etc.
2. **Galvanic or Voltaic cells:** These are the electrochemical cells, which convert chemical energy into electrical energy. Eg. Daniel cell, Dry cell etc.

3.6 ELECTROLYSIS

Water-soluble substances are distinguished as *electrolytes* or *nonelectrolytes.* **Electrolytes are electrovalent substances that form ions in solution which conduct an electric current.** Sodium chloride, copper (II) sulphate and potassium nitrate are examples of electrolytes. Non-electrolytes, on the other hand, are covalent substances which furnish neutral molecules in solution. Their water-solutions do not conduct an electric current. Sugar, alcohol and glycerol are typical non-electrolytes. An electrolyte invariably undergoes chemical decomposition as a result of the passage of electric current through its solution.



The phenomenon of decomposition of an electrolyte by passing electric current through its solution is called Electrolysis (*lysis* = breaking). The process of electrolysis is carried in an apparatus called the **Electrolytic cell.** The cell contains water-solution of an electrolyte in which two metallic rods (called electrodes) are dipped**.** These rods are connected to the two terminals of a battery (source of electricity). The electrode connected to the positive terminal of the battery attracts the negative ions (anions) and is called **anode.** The other electrode connected to the negative end of the battery attracts the positive ions (cations) and is called **cathode.**

Mechanism of electrolysis: How the electrolysis actually takes place, is illustrated in Fig above. The cations migrate to the cathode and form a neutral atom by accepting electrons from it. The anions migrate to the anode and yield a neutral particle by transfer of electrons to it. As a result of the loss of electrons by anions and gain of electrons by cations at their respective electrodes chemical reaction takes place.

Preferential discharge theory: As per this theory if more than one type of ions is attracted towards a particular electrode, then the ion discharged is the ion which requires least energy. The potential at which the ion is discharged or deposited on the appropriate electrode is termed the **discharge** or **deposition potential.**

Or *Discharge potential* *is defined as the minimum potential that must be applied across the electrodes to bring about the electrolysis and subsequent discharge of the ion on the electrode.*

The values of discharge potential are different for different ions. For example, the discharge potential H^+ ions is lower than Na^+ ions when platinum or most of the other metals are used as cathodes. Similarly, discharge potential of Cl^- ions is lower than that of OH^-ions.

Products of electrolysis: In case two or more types of positive and negative ions are present in solution, during electrolysis certain ions are discharged or liberates at the electrodes in preference to others. In general, in such competition the ion, which is stronger oxidizing agent (high value of standard reduction potential), is discharged first at the cathode. The increasing order of deposition of few cations is:

$$\underset{\text{Increasing order of deposition}}{\underline{K^+, Na^+, Ca^{2+}, Mg^{2+}, Al^{3+}, Zn^{2+}, Fe^{2+}, H^+, Cu^{2+}, Ag^+, Au^{3+}}}$$

Similarly the anion, which is stronger reducing agent (low value of standard reduction potential), is liberated first at the anode.

The increasing order of discharge of few anions in

$$\underset{\text{Increasing order of discharge}}{\underline{SO_4^{2-}, NO_3^-, OH^-, Cl^-, Br^-, I^-}}$$

Thus, when an aqueous solution of NaCl containing Na^+, Ca^{2+}, Cl^-, H^+ and OH^- ions is electroysed, H^+ ions are discharged at cathode and Cl^- ions at the anode, i.e., H_2 is liberated at cathode and chlorine at anode.

This can be explained by some examples given below

Electrolysis of molten NaCl

$NaCl \longrightarrow Na^+ + Cl$(in the molten state)

In the electrolytic cell $Cl^–$ ions will move toward the anode and Na^+ ions will move toward the cathode. At the electrodes, the following reactions will take place.

At cathode: $Na^+ + e^- \longrightarrow Na$ (reduction)

At Anode: $Cl^– + e^- \longrightarrow Cl$ (oxidation, primary change)

After the chloride ion loses its electron to the anode, pair of chlorine atoms unites to form chlorine gas, Cl_2.

$Cl + Cl \longrightarrow Cl_2$ (secondary change)

The net effect of the process is the decomposition of NaCl into sodium and chlorine gases. The overall reaction is:

$2NaCl \longrightarrow 2Na + Cl_2$ ………………... (*Decomposition*)

Electrolysis of conc. aqueous solution of NaCl: At anode, Cl^- ions get oxidized in preference to water, although the former has a higher value of standard reduction potential. This is due to over voltage. Thus the electrolysis takes place as follows:

At anode: $2Cl^- \longrightarrow Cl_2 + 2e$ (Oxidation)

At cathode: $2H_2O + 2e^- \longrightarrow H_2 + 2OH$ (Reduction)

Thus, during the electrolysis of aqueous NaCl solution, chlorine gas is evolved at the anode and hydrogen gas at the cathode.

Electrolysis of aqueous copper sulphate solution using platinum electrodes: In this case the electrolysis takes place as follows:

At anode; $H_2O \longrightarrow \frac{1}{2} O_2 + 2H^+ +2e^-$

At cathode; $Cu^{2+} + 2e^- \longrightarrow Cu$

Thus, copper is obtained at the cathode and oxygen gas at the anode.

Electrolysis of aqueous copper sulphate solution using copper electrodes: in this case copper gets deposited at the cathode and an equivalent amount of copper from the anode dissolves into the solution Cu^{2+} ions. This is because the reduction potential of copper is less than that of SO_4^{2-} ions and water. The electrolysis takes place as follows:

At anode: $Cu \longrightarrow Cu^{2+} + 2e^-$

At cathode: $Cu^{2+} + 2e^- \longrightarrow Cu$

Electrolysis of water: pure water is a very weak electrolyte and does not conduct much current. However, electrolysis of water can easily be carried out if a few drops of sulfuric acid are added to it. Addition of sulphuric acid makes water conducting and the electrolysis takes place as follows:

At anode $4OH^- \longrightarrow 2H_2O + O_2 + 4e^-$

At cathode $2H^+ + 2e^- \longrightarrow H_2$

Thus, oxygen gas is liberated at the anode and hydrogen gas at the cathode.

3.7 FARADAY'S LAWS OF ELECTROLYSIS

Michael Faraday studied the quantitative aspect of electrolysis. He discovered that there exists a definite relationship between the amounts of products liberated at the electrodes and the quantity of electricity used in the process. In 1834, he formulated two laws which are known as Faraday's Laws of Electrolysis. These are:

Faraday's First law: *The mass of the substance (W) liberated at the electrodes during the electrolysis is directly proportional to the quantity of electricity (Q) that passes through the electrolyte.*

If m is the mass of substance (in grams) deposited on electrode by passing Q coulombs of electricity, then

$\boldsymbol{W \propto Q}$ .... First law

or $\boldsymbol{W = Z\,Q}$

Where **Z** is the constant, known as the **electrochemical equivalent** of the substance (electrolyte).

We know that $\mathbf{Q} = I \times t$

$$\therefore \quad W = Z \times I \times t$$

If I = 1 ampere and t = 1 second, then

$$W = Z$$

Thus, ***electrochemical equivalent*** *is the mass of substance deposited in gram either by passing one coulomb of charge or by passing one ampere of current for one second.*

The Electrical unit Faraday: One faraday is the quantity of charge carried by one mole of electrons

$\therefore$ 1 F = $1.6\times10^{-19}\times6.023\times10^{23}$ = 96500 coulombs

Or One **Faraday** is the quantity of charge which must be passed in order to deposited or dissolved one gram equivalent of any substance. This is denoted by the symbol **F**.

1 Faraday = 96,500 coulombs = 1 Mole electrons

Also Quantity of electricity = ***n*** x **F**

where *n* is the valency of its ion.

Importance of the First law of Electrolysis

With the help of the first law of electrolysis we are able to calculate:

1. The value of electrochemical equivalents of different substances; and
2. The mass of different substances produced by passing a known quantity of electricity through their solutions.

Faraday's Second law: When the same quantity of charge is passed through different electrolytes, then the masses of different substances deposited at the respective electrodes will be in the ratio of their equivalent masses.

The law can be illustrated by passing same quantity of electric current through three voltameters contianing solutions of H_2SO_4, $CuSO_4$ and $AgNO_3$ respectively.

$$\frac{\textbf{Mass of hydrogen}}{\textbf{Mass of copper}} = \frac{\textbf{Equivalent mass of hydrogen}}{\textbf{Equivalent mass of copper}}$$

$$\textbf{Or } \frac{\textbf{Mass of copper}}{\textbf{Mass of silver}} = \frac{\textbf{Equivalent mass of copper}}{\textbf{Equivalent mass of silver}}$$

$$\textbf{Or } \frac{\textbf{Mass of silver}}{\textbf{Mass of hydrogen}} = \frac{\textbf{Equivalent mass of silver}}{\textbf{Equivalnt mass of hydrogen}}$$

Again according to first law,

$$W = Z \times Q$$

When $Q = 96500$ coulomb, W becomes gram equivalent mass (E).

Thus, $E = Z \times 96500$

Or $Z = \frac{E}{96500}$; $\frac{Z_1}{Z_2} = \frac{E_1}{E_2}$

Quantitative treatment of 2nd law: If same quantity of electricity (say 3F) is passed through solution of Na, Mg and Al.

$\mathbf{Na^{+} + 1e \longrightarrow Na}$

$\mathbf{Mg^{+2} + 2e \longrightarrow Mg}$

$\mathbf{Al^{+3} + 3e \longrightarrow Al}$

Then ratio of no. of moles is given by $n_{Na}: n_{Mg}: n_{Al} = 3$ moles: 1.5 moles: 1 mole and the ratio of weights of substance deposited will be in the order

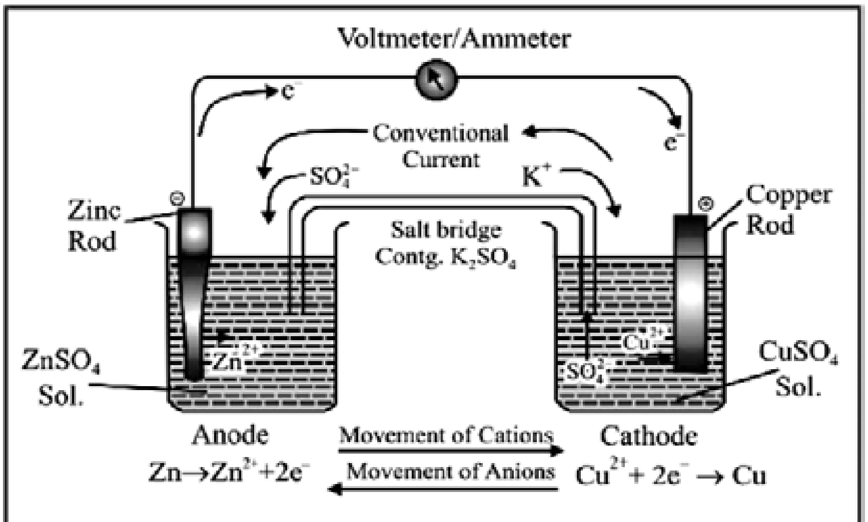
$W_{Na}: W_{Mg}: W_{Al} = E_{Na} : E_{Mg} : E_{Al} = 23 : 12 : 9$

3.8 GALVANIC CELL OR VOLTAIC CELL

A device for producing an electrical current from a chemical reaction (redox reaction) is called Galvanic cell or Voltaic cell in the honor of inventors Galvani and Volta)

A Galvanic cell works on the spontaneous oxidation and reduction reaction in which the transfer of electrons from the substance oxidized to the substance reduced takes place through wire and not directly.

It consists of two half cells, one containing Zn rod dipped in 1M $ZnSO_4$ and other containing Cu rod dipped in 1M $CuSO_4$. The two rods are externally connected by a wire, and internally the two solutions are connected by salt bridge.



Electrochemical cell based on the redox reaction,
$Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$

Working: Zn rod undergoes oxidation giving Zn^{+2} leaving two electrons on the rod.

Oxidation reaction

$$\mathbf{Zn \longrightarrow Zn^{2+} + 2e^-}$$

Electrons given by the Zn rod will flow to copper electrode where they will neutralize some of the copper ions of the solution as shown:

Reduction Reaction

$$\mathbf{Cu^{2+} + 2e^- \longrightarrow Cu}$$

The overall redox reaction is represented as

Over all redox reaction: $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$

The SO_4^{-2} ions will be left and the solution will acquire negative charge; at the same time Zn^{+2} produced from the Zn rod will enter in $ZnSO_4$ solution giving it positive charge. Due to accumulation of charges in two solutions further flow of electrons will stop and hence current stops flowing .This difficulty is overcome by salt bridge

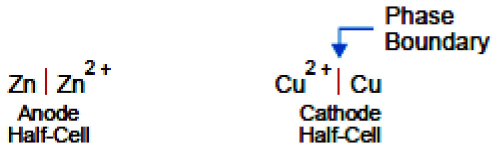
Salt Bridge and its functions: A salt bridge is a U shaped tube containing concentrated solution of an inert electrolyte like KCl, KNO_3, K_2SO_4 or solidified solution of such electrolyte in agar agar or geletine.

The main functions of salt bridge are

1. It completes the electrical circuit by allowing the movement of ions from one solution to other without mixing the two solutions
2. It maintains the electrical neutrality of the solutions of two half cells

Salient features of an electrochemical cell

1. The electrode (Zn) at which oxidation takes place is called anode and the electrode (Cu) at which reduction takes place is called cathode.
2. At Anode(Zn) electrons are produced, it is rich in electrons and therefore is designated as negative pole, where as the cathode (Cu) is in need of electrons for reduction of Cu^{+2} to Cu and therefore is designated as +ve pole.
3. Electrons flow from negative pole to positive pole in external circuit. Conventionally current is said to flow in the opposite direction.
4. As Zn rod undergoes oxidation continuously, its weight keeps on decreasing. However due to reduction of copper ions at copper rod its weight keeps on increasing.
5. Further the concentration of $ZnSO_4$ keeps on increasing in oxidation half cell and that of Copper sulphate keeps on decreasing in reduction half cell with the passage of time.

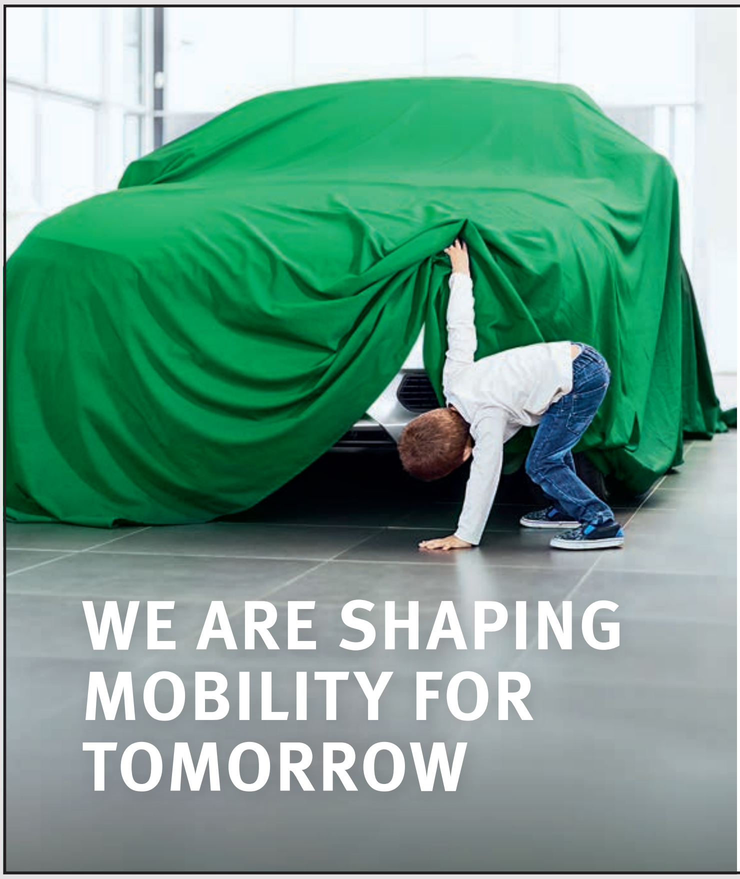


Cell diagram or Representation of a Cell: A cell diagram is an abbreviated symbolic depiction of an electrochemical cell. For this purpose, we will consider that a cell consists of two half-cells. Each half-cell is again made of a metal electrode contact with metal ions in solution.

IUPAC Conventions: In 1953 IUPAC recommended the following conventions for writing cell diagrams. We will illustrate these with reference to Zinc-Copper cell.

1. a **single vertical line** (|) represents a phase boundary between metal electrode and ion solution (electrolyte). Thus the two half-cells in a voltaic cell are indicated as
   It may be noted that the metal electrode in anode half-cell is on the left, while in cathode half-cell it is on the right of the metal ion.
2. A double vertical line (||) represents the salt bridge, porous partition or any other means of permitting ion flow while preventing the electrolyte from mixing.
3. Anode half-cell is written on the left and cathode half-cell on the right.
4. In the complete cell diagram, the two half-cells are separated by a double vertical line (salt bridge) in between. The zinc-copper cell can now be written as

$$\mathbf{Zn_{(s)};\ Zn^{2+}_{(aq)}||Cu^{2+}_{(aq)};Cu_{(s)}}$$



5. The symbol for an **inert electrode,** like the platinum electrode is often enclosed in a bracket.

For example,

$$\mathrm{Mg}\;|\;\mathrm{Mg}^{2+}\;\|\;\mathrm{H}^{+}\;\overset{\text{Inert Electrode}}{|}\;\mathrm{H_2(Pt)}$$

	Electrolytic cell	**Galvanic cell**
1.	Electrical energy is converted into chemical energy	Chemical energy is converted into electrical energy
2.	Anode positive electrode, cathode negative electrode	Anode negative electrode, cathode positive electrode.
3.	Ions are discharged on both the electrodes	Ions are discharged only on the cathode
4.	If the electrodes are inert concentration of the electrolyte decreases when the electric current is circulated	Concentration of the anodic half-cell increases while that of cathodic half-cell decreases when these two electrodes are joined by a wire.
5.	Both the electrodes can be fitted in the same compartment	The electrodes are fitted in different compartments.

Table: Difference in electroytic cell and galvanic cell

3.9 ELECTRODE POTENTIAL OR SINGLE ELECTRODE POTENTIAL

It is the potential developed at the inter-phase between the metal and the solution, when a metal is dipped in a solution containing its own ions. It is represented as **E.** An electrochemical cell consists of two half-cells. With an open-circuit, the metal electrode in each half-cell transfers its ions into solution. Thus an individual electrode develops a potential with respect to the solution. The potential of a single electrode in a half-cell is called the ***Single electrode potential.*** Thus in a Daniel cell in which the electrodes are not connected externally, the anode Zn/Zn^{2+} develops a negative charge and the cathode Cu/Cu^{2+}, a positive charge. The amount of the charge produced on individual electrode determines its single electrode potential.

The single electrode potential of a half-cell depends on: (*a*) concentration of ions in solution; (*b*) tendency to form ions; and (*c*) temperature

Oxidation electrode potential: it is the tendency of electrode to lose electrons when present in the solution of its own ions and is represented by E_{M/M^+}.

- OEP decreases with increase in concentration of metal ions in solution.
- OEP increases with increase in temperature.

Reduction electrode potential: it is the tendency of electrode to gain electrons when present in the solution of its own ions and is represented by $E_{M^+/M}$

- REP increases with increase in concentration of metal ions in solution.
- REP decreases with increase in temperature.

Measurement of standard electrode potential: The absolute value of electrode potential of single electrode (also called single electrode potential) cannot be determined independently because

1. Oxidation half reaction or reduction half reaction cannot be determined alone
2. Loss or gain of electrons is a relative tendency.

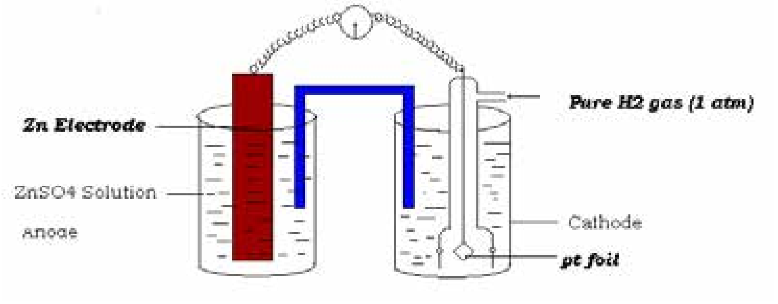
The standard electrode potential can be measured by using some electrode as a reference electrode. The reference electrode chosen is Normal or standard hydrogen electrode (S.H.E or N. H. E)

Determination of standard electrode potential of any electrode: The standard electrode potential of any electrode is determined by connected it with SHE through a wire containing a voltmeter. The potential difference developed as a result of redox reaction is measured with the help of voltmeter. This gives standard electrode potential of that electrode

The direction of flow of current further indicates that weather oxidation or reduction reaction is taking place on the electrode under investigation with respect to hydrogen electrode.

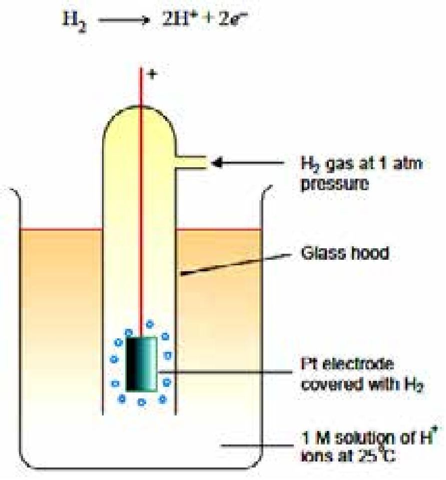
The SHE is coupled with the electrode whose electrode potential is to be determined and the electrode potential of the electrode is determined by fixing the electrode potential and SHE as zero [at all temperatures]

Example: Consider the determination of Single electrode potential of Zinc electrode using Standard Hydrogen electrode. To determine the Single electrode potential of Zinc electrode it is coupled with Standard Hydrogen electrode as follows



Standard hydrogen electrode, SHE or NHE (Reference electrode)

Hydrogen electrode is the primary standard electrode. It consists of a small platinum strip coated with platinum as to adsorb hydrogen gas. A platinum wire is welded to the platinum strip and sealed in a glass tube. The platinum and glass tube is surrounded by an outer glass tube which has an inlet for hydrogen gas at the top and a number of holes at the base for the escape of excess of hydrogen gas. The platinum strip is placed in an acid solution which has H^+ ions concentration I M. Pure hydrogen gas is circulated at one atmospheric pressure. A part of the gas is adsorbed and the rest escapes through holes. The temperature of the cell is maintained at The hydrogen can act as cathode or anode with respect to other electrode.



The reactions taking place are

At anode: $H_{2(g)} \longrightarrow 2H^+ + 2e$; (here con. of H^+ increases in solution)

At Cathode: $2H^+ + 2e \longrightarrow H_{2(g)}$ (here conc. of H^+ decreases in solution).

Thus the electrode is reversible w.r.t to H^+ ions.

By international agreement the standard hydrogen electrode is arbitrarily assigned a potential of exactly ± 0.000 volt.

SHE half reaction	**Electrode potential**
$H_2 \rightarrow 2H^+ + 2e^-$	0.0 V (anode)
$2H^+ + 2e^- \rightarrow H_2$	0.0 V (Cathode)

This electrode is represented as Pt, $H_{2(g)}|\ H^+$ (conc.=c)

- The electrode potential of this electrode is taken to be zero.

EMF of a cell or cell potential or cell voltage

The difference between electrode potential of two electrodes which makes the electrons to flow from the electrode having lower reduction potential to the electrode having higher reduction potential is known as EMF of a cell. It is measured in Volts. The EMF of a cell depends on

1. Nature of reactants 2. Concentration of solution in two half cells 3. Temperature.
The E.M.F of a cell is calculated as
E.M.F. = Reduction potential of cathode + Oxidation potential of Anode
We know that Oxidation potential = - reduction potential,
Therefore the above formula can be modified as
E.M.F. = Reduction potential of cathode – Reduction potential of anode

or **E.M.F. =** $\mathbf{E}_{\text{cathode}} - \mathbf{E}_{\text{anode}}$
or\` **E.M.F =** $\mathbf{E}_{\text{right}} - \mathbf{E}_{\text{left}}$

EMF	Potential difference
1. It is the potential difference beteen two electrodes when no current is flowing in the circuit. 2. It is the maximum voltage that the cell can deliver. 3. It is responsible for the steady flow of current in the cell.	It is the difference of the electrode potentials of the two electrodes when the cell is under operation It is always less than the maximum value of voltage which the cell can deliver. It is not responsible for the steady flow of current in the cell.

Table: Difference between emf and potential difference

Relation between Gibbs free energy change and E.M.F of a cell: The electrical energy produced in a galvanic cell is as a result of decrease in free energy of a cell i.e ,

Electrical energy produced or electrical work done = decrease in free energy of system

Or $\mathbf{W = -\Delta G}$

But **electrical work done = Quantity of electricity flowing** × **E.M.F**

Or $\mathbf{W = Q \times E}$

If n moles of electrons are flowing, then quantity of electricity flowing: $Q = nF$

Therefore $\mathbf{W = nF \times E}$

Hence $\mathbf{-\Delta G = nFE}$

If **E°** is the standard cell potential than standard free energy change **(–ΔG°)** is given by

$$\mathbf{-\Delta G^\circ = nFE^\circ} \text{ ………………… } (1)$$

Further $\mathbf{E^\circ = \frac{2.303RT}{nF} \log Kc}$

Substituting **E°** in equation 1

$$\mathbf{-\Delta G^\circ = nF \frac{2.303RT}{nF} \log K_c}$$

Or $\mathbf{\Delta G^\circ = -\ 2.303RT\log K_c}$

Thus knowing **E°, ΔG°** can be calculated which in turn can be used to calculate equilibrium constant (Kc)

3.10 NERNST EQUATION

Effect of electrolyte concentration and Temperature on the electrode potential: We know experimentally that the potential of a single electrode or half-cell varies with the concentration of ions in the cell. In 1889 Walter Nernst derived a mathematical relationship which enable us to calculate the half-cell potential, E, from the standard electrode potential, **E°,** and the temperature of the cell, this relation known as the **Nernst equation.**

For a general electrochemical reaction of the type

$$\mathbf{aA + bB \longrightarrow cC + dD}$$

the **Nernst equation** can be written as

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

Or $E = E^\circ - \frac{2.303RT}{nF} \log \frac{[C]^c[D]^d}{[A]^a[B]^b}$

Where E° = standard electrode potential
R = gas constant = **8.314 J K^{-1} mol^{-1}**
T = Kelvin temperature
n = number of electrons transferred in the half-reaction
F = Faraday constant = **96500 C**
[ ] = concentration
K = equilibrium constant for the half-cell reaction as in equilibrium law

Calculation of Half-cell potential: For an oxidation half-cell reaction when the metal electrode M gives M^{n+} ion,

$$\mathbf{M \longrightarrow M^{n+} + ne^-}$$

the Nernst equation takes the form

$$E = E^\circ - \frac{2.303RT}{nF} \log \frac{[M^{n+}]}{[M]}$$

The concentration of solid metal **[M]** is equal to one (unity). Therefore, the Nernst equation can be written as

$$E = E^\circ - \frac{2.303RT}{nF} \log [M^{n+}]$$

Substituting the values of R, F and T at 25˚C = 298K, the quantity 2.303 RT/F comes to be 0.0591. Thus the Nernst equation (3) can be written in its simplified form as

$$E = E^\circ - \frac{0.0591}{n} log\,[M^{n+}]$$

Calculation of Cell potential: The Nernst equation is applicable to cell potentials as well. Thus for Danial cell with overall cell reaction

$$Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

$$Ecell = E^\circ cell - \frac{2.303RT}{nF} log \frac{[Zn\,][Cu^{2+}]}{[Cu\,][Zn^{2+}]}$$

Calculation of Equilibrium constant for the cell reaction: The Nernst equation for a cell is

$$Ecell = E^\circ cell - \frac{0.0591}{n} logK$$

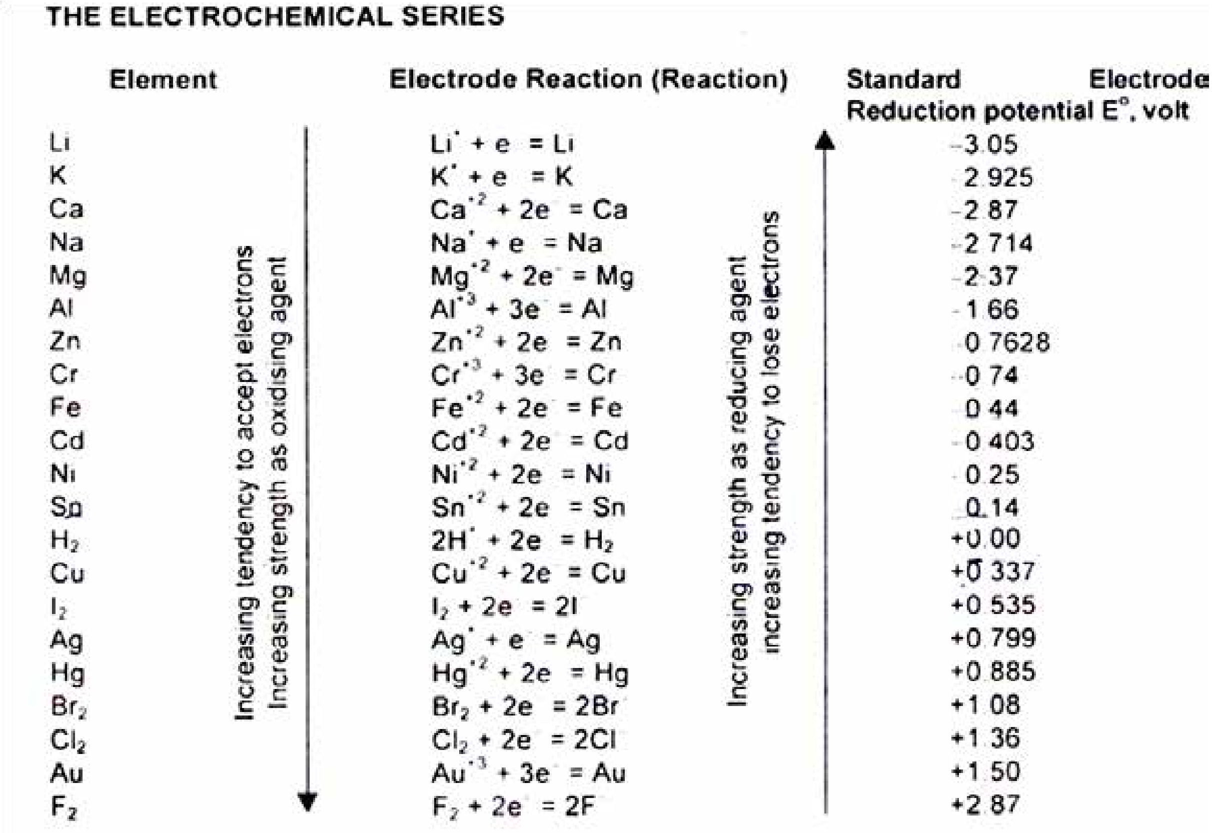
At equilibrium, the cell reaction is balanced and the potential is zero. Thus the Nernst equation may now be written as

$$0 = E°cell - \frac{0.0591}{n} logK$$

$$E°cell = \frac{0.0591}{n} logK$$

Or $$logK = \frac{n\,E°cell}{0.0591}$$

Electrochemical series: the electrochemical series is the arrangement of various electrode systems in the increasing order of their standard reduction potentials.The electrochemical series consisting of some electrode systems along with their half cell reactions is give below



THE ELECTROCHEMICAL SERIES

Element	Electrode Reaction (Reaction)	Standard Electrode Reduction potential E°, volt
Li	$Li^{+} + e = Li$	-3.05
K	$K^{+} + e = K$	-2.925
Ca	$Ca^{+2} + 2e = Ca$	-2.87
Na	$Na^{+} + e = Na$	-2.714
Mg	$Mg^{+2} + 2e^{-} = Mg$	-2.37
Al	$Al^{+3} + 3e = Al$	-1.66
Zn	$Zn^{+2} + 2e = Zn$	-0.7628
Cr	$Cr^{+3} + 3e = Cr$	-0.74
Fe	$Fe^{+2} + 2e^{-} = Fe$	-0.44
Cd	$Cd^{+2} + 2e = Cd$	-0.403
Ni	$Ni^{+2} + 2e = Ni$	-0.25
Sn	$Sn^{+2} + 2e = Sn$	-0.14
H_2	$2H^{+} + 2e = H_2$	+0.00
Cu	$Cu^{+2} + 2e = Cu$	+0.337
I_2	$I_2 + 2e = 2I$	+0.535
Ag	$Ag^{+} + e = Ag$	+0.799
Hg	$Hg^{+2} + 2e = Hg$	+0.885
Br_2	$Br_2 + 2e = 2Br^{-}$	+1.08
Cl_2	$Cl_2 + 2e = 2Cl$	+1.36
Au	$Au^{+3} + 3e = Au$	+1.50
F_2	$F_2 + 2e = 2F$	+2.87

Commercial cells/ Batteries

A battery is combination of one or more than one cells connected in series and the cell that we use as a source of electrical energy is basically a galvanic cell, in which chemical energy of a redox reaction is converted into electrical energy. For an electrochemical cell to be used as a commercial cell it must fulfill the following requirements

1. It should have the compactness, lightness and ruggedness for portability.
2. Its voltage should not drop much during use

The various commercial cells may be classified into the following types

a. **Primary cells:** These cells in which redox reaction occurs only once and the cell becomes dead after some time and cannot be used again. E.g. Dry cell, mercury cell
b. **Secondary cells:** These cells can be recharged by passing an electric current through them and hence can be used over and again e.g. lead storage cell, Ni-Cd cell
c. **Fuel cell:** in these cells electrical energy is produced from the combustion of fuels like H_2, CO, CH_4, hydrogen–Oxygen cell etc.

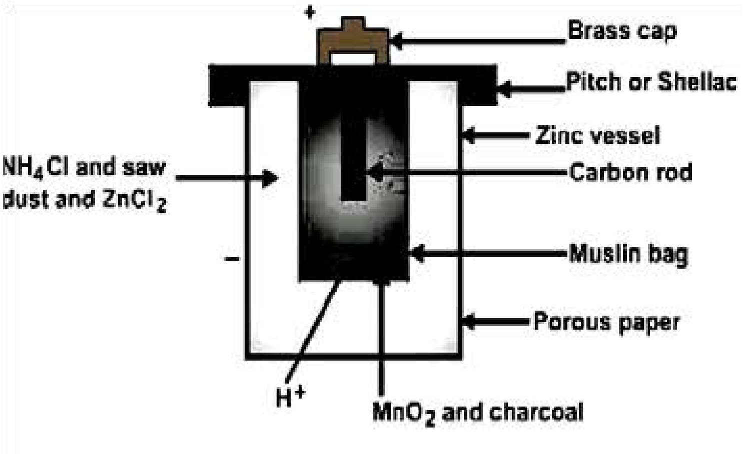
Dry cell: This cell is also known as Leclanche cell after its discoverer and is used commonly in our transistors and clocks etc. it consists of a zinc container that acts as anode and a carbon (graphite) rod which acts as cathode. The carbon rod is surrounded by powdered manganese dioxide and carbon. The space between the electrodes is filled by a moist paste of ammonium chloride (NH_4Cl) and zinc chloride ($ZnCl_2$). The graphite rod is fitted with a metal cap and the cylinder is sealed at the top with a pinch. The Zn container is protected with cardboard to protect it from the atmosphere. The electrode reactions are complex, but they can be written approximately as follows

At Anode: $Zn(s) \longrightarrow Zn^{+2} + 2e^-$

At Cathode: $2MnO_2 + 2NH_4^+ + 2\ e \longrightarrow Mn_2O_3 + 2NH_3 + H_2O$

Overall reasction: $Zn(s) + 2MnO_2 + 2NH_4^+ \longrightarrow Zn^{+2} + Mn_2O_3 + 2NH_3 + H_2O$

In the reaction at cathode, manganese is reduced from the + 4 oxidation state to the +3 state. Ammonia produced in the reaction is not liberated as a gas but combines immediately with Zn^{2+} and Cl^- to form a complex $[Zn\ (NH_3)_2Cl_2]$. The cell has a potential of nearly 1.5 V



Dry cell

Lead storage cell: This is commonly used in automobiles and invertors. It consists of a lead anode and a grid of lead packed with lead dioxide (PbO_2) as cathode. A 38% solution (density =1.30 g/ml) of sulphuric acid is used as an electrolyte. The cell reactions when the battery is in use are given below:

Anode: $Pb_{(s)} + SO_4{}^{2-}{}_{(aq)} \rightarrow PbSO_4(s) + 2e^-$

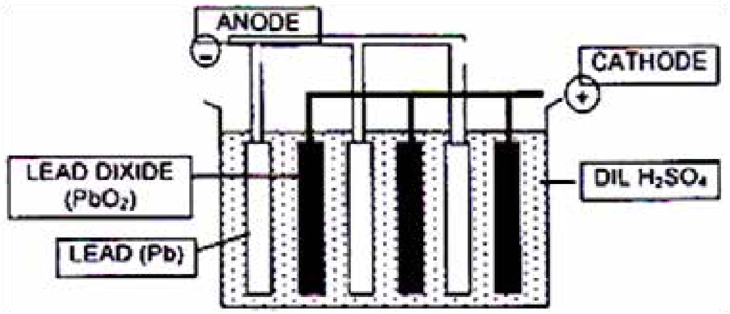
Cathode: $PbO_{2(s)} + SO_4{}^{2-}{}_{(aq)} + 4H^+{}_{(aq)} + 2e \rightarrow PbSO_{4\ (s)} + 2H_2O_{(l)}$

i.e., overall cell reaction consisting of cathode and anode reactions is:

$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4\ (aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$$

As the density of sulphuric acid inside the cell decreases to 1.20 g/ml the battery needs recharging. On charging the battery the reaction is reversed and $PbSO_{4(s)}$ on anode and cathode is converted into Pb and PbO_2, respectively.

Each cell in this battery produces 2.00 Volts.



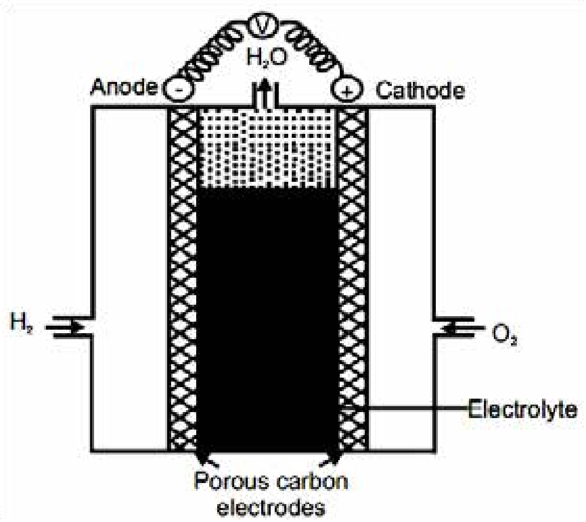
Fuel cell: In these cells electrical energy is produced from the combustion of fuels like H_2, CO, CH_4 etc. One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water. The cell was used for providing electrical power in the Apollo space programme. The water vapors produced during the reaction were condensed and added to the drinking water supply for the astronauts. It consists of porous carbon electrodes containing suitable catalysts incorporated in them. Concentrated NaOH or KOH solution is placed in between them. Hydrogen and Oxygen gases are bubbled through the porous electrodes into the NaOH/ KOH solution.

Anode: $2H_2\ (g) + 4OH^-{}_{(aq)} \rightarrow 4H_2O\ (l) + 4e^-$

Cathode: $O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightarrow 4OH^-{}_{(aq)}$

Overall reaction being: $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

The gaseous materials are consumed and continuously supplied.



Advantages of fuel cell: The main advantages of fuel cell are as

1. Because of continuous supply, such cells never become dead. Such a cell is usually operated at a temperature of 70 – 140 °C and gives a potential of 0.9 V
2. Theoretically fuel cells are expected to have efficiency of 100%. However practically they have efficiency of 60-70%. Still they are superior to thermal power plants which have efficiency of not more than 40%.
3. These cells do not cause any pollution problem.

Difficulties in the construction of fuel cell

1. Providing of contact between the three faces needed in a fuel cell.
2. The corrosiveness of the electrolytes used.
3. High cost of the catalyst needed for the electrode reactions (Pt, Pd, Ag etc)
4. Problem of handling gaseous fuels at low temperature or high pressure.

3.11 CORROSION

The process of slow eating away of metals due to attack of atmospheric gases on the surface of metal resulting into the formation of compounds such as oxides sulphates, carbonates etc is called corrosion.

Thus, **corrosion** *is a process of a deterioration of a metal as a result of its reaction with the environment* surrounding it.

Almost all metals (*except the least active metals such as gold, platinum, and palladium)* are attacked by environment *i.e.,* undergo corrosion. For example, silver tarnishes, copper develop a green coating, lead or stainless steel loses their luster due to corrosion. Corrosion causes enormous damage to buildings, bridges, ships, and many other articles made of iron.

In case of iron, corrosion is called **rusting**. Chemically, rust is hydrated form of ferric oxide, $Fe_2O_3.xH_2O$. Rusting of iron is generally caused by moisture, carbon dioxide and oxygen present in air. It has been observed that rusting takes place when iron is in contact with moist air. *Iron does not rust in dry or in vacuum.*

Mechanism of corrosion: The chemistry of corrosion is quite complex but ***it may be considered essentially as an electrochemical phenomenon*** because it explains the formation of rust on the basis of formation of electrochemical cells on the surface of metal. The following steps are involved

1. At a particular spot of an object made of iron, oxidation takes place and that spot behaves as anode and we can write the reaction
   Anode: $2\ Fe_{(s)} \longrightarrow 2\ Fe^{2+} + 4e^{-}$

Electrons released at anodic spot move through the metal and go to another spot on the metal and reduce oxygen in presence of H^+ (which is believed to be available from H_2CO_3 formed due to dissolution of carbon dioxide from air into water. Hydrogen ion in water may also be available due to dissolution of other acidic oxides from the atmosphere). This spot behaves as cathode with the reaction

Cathode: $\mathbf{O2_{(g)} + 4H^{+}_{(aq)} + 4e^{-} \longrightarrow 2H2O_{(l)}}$

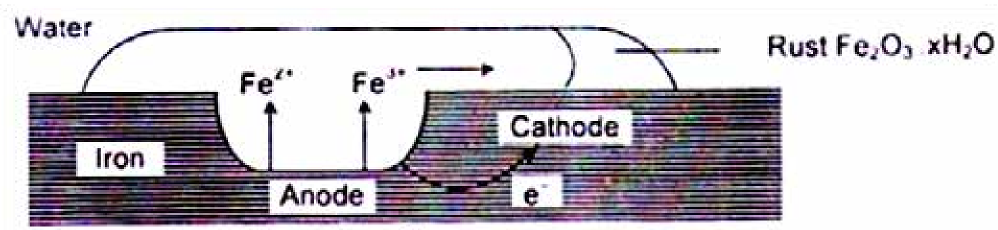
Overall reaction: $\mathbf{2\ Fe_{(s)} + O_{2(g)} + 4\ H^{+}_{(aq)} \longrightarrow 2\ Fe^{2+} + 4\ e^{-} + 2H_2O_{(l)}}$

The ferrous ions formed react with the dissolved oxygen or oxygen from the air to form ferric oxide as

$4\ Fe^{2+} + O_{2(g)} + 4\ H_2O_{(aq)} \longrightarrow Fe_2O_3 + 8H^+$

Ferric oxide than undergoes hydration to form rust as follows

$Fe_2O_3 + xH_2O \longrightarrow Fe_2O_3.xH_2O$



Corrosion of iron

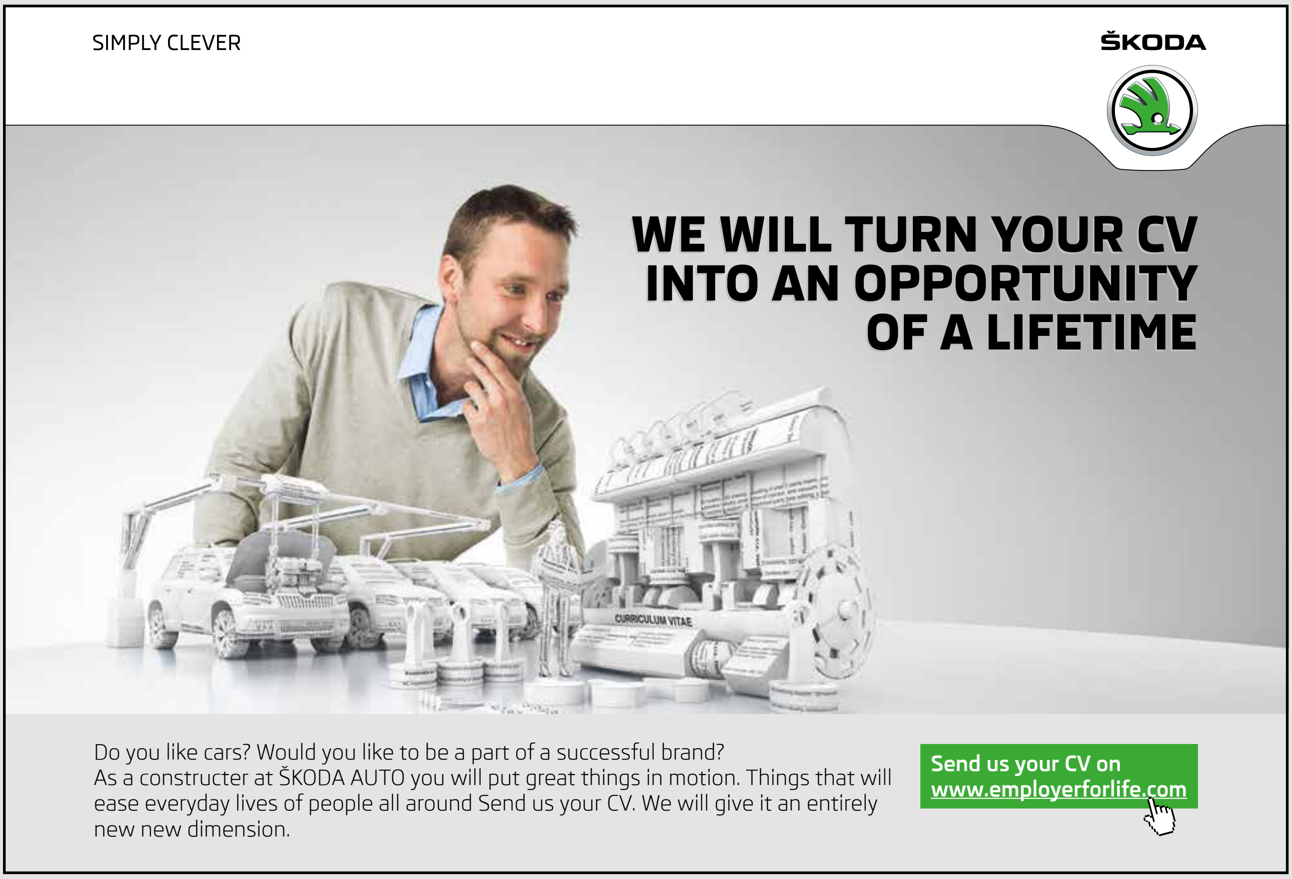
Rust is a non sticking compound i.e it does not stick to the surface. It peels off exposing fresh iron surface for further rusting.

Factors Affecting Corrosion

1. Reactivity of metals
2. Presence of moisture and atmospheric gases like CO_2, SO_2, etc.
3. Presence of impurities
4. Strains in the metal

Rusting of iron can be prevented by the following methods

1. Barrier protection through coating of paints or electroplating.
2. Through galvanization or coating of surface with tin metal.
3. By the use of antirust solutions (bis-phenol).
4. By cathodic protection in which a metal is protected from corrosion by connecting it to another metal that is more easily oxidized.



4 CHEMICAL KINETICS

Chemical Kinetics is the branch of science that deals with rate of reaction, the factors affecting the rate of reaction and mechanism. **Chemical kinetics, also known as** reaction kinetics**, is the study of rates of chemical processes.**

In 1864, **Peter** *Waage and Cato Guldberg pioneered the development of chemical kinetics*

Chemical reaction: A chemical reaction involves breaking of bonds in reactant molecules and making of bonds in product molecules.

A reaction that involves breaking of weak bond(s) is faster than one involving breaking of strong bond at a given temperature. Different reactions differ in respect of the strength of the bonds to be broken and hence they occur at different rates. Reactions which involve less bond rearrangements are generally faster than those which involve considerable bond rearrangements at a given temperature.

4.1 ON THE BASIS OF RATES, THE CHEMICAL REACTIONS ARE BROADLY DIVIDED INTO THREE CATEGORIES

Very fast or Instantaneous reactions: These reactions are so fast that they occur as soon as the reactants are bought together. Generally, these reactions involve ionic species and thus known as ionic reactions. These reactions take about 10^{-14} to 10^{-16} seconds for completion. It is almost impossible to determine the rates of these reactions. Some such examples are:

$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$

$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$

$HCl + NaOH \rightarrow NaCl + H_2O$

Very slow reactions: There are certain reactions which are extremely slow. They may take months together to show any measurable change at room temperature. It is also difficult to study the kinetics of such reactions. Some examples are: Reaction between hydrogen and oxygen at room temperature, Reaction of atmospheric H_2S on basic lead acetate, Reaction between carbon and oxygen etc.

Moderate reactions: Between the above two extremes, there are a number of reactions which take place at moderate and measurable rates at room temperature and it is these reactions which are studied in chemical kinetics. Mostly these reactions are molecular in nature. Some common examples of such type are given below:

Decomposition of hydrogen peroxide: $2H_2O_2 \rightarrow 2H_2O + O_2$

Decomposition of nitrogen pentoxide: $2N_2O_5 \rightarrow 2N_2O_4 + O_2$

Hydrolysis of an ester: $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

Inversion of cane sugar in aqueous solution: $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$

4.2 RATE OF REACTION (AVERAGE RATE OF 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

$$r = \frac{\Delta x}{\Delta t}$$

The **rate of reaction** can be expressed by ***decrease in concentration of reactants*** or by ***increase in concentration of products***.

For a hypothetical reaction $R \longrightarrow P$

The average rate of reaction may be expressed either in terms of decrease in concentration of R (reactants) or in terms of increase in concentration of P (product).

i.e., Rate of reaction = Rate of disappearance of R

$$r = \frac{\text{Decrease in concentration of R}}{\text{Time taken}} = \frac{-\Delta[R]}{\Delta t}$$

Since, $\Delta[R]$ is a negative quantity (as concentration of reactants is decreasing),

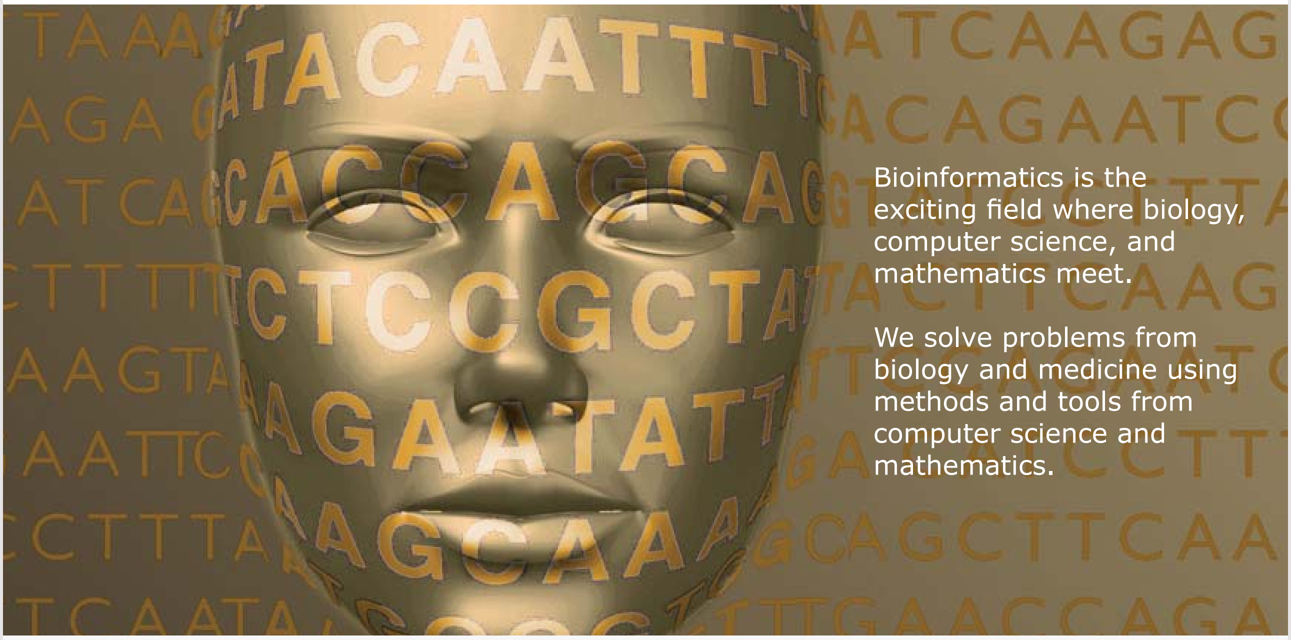
Or, Rate of reaction = Rate of appearance (formation) of P

$$r = \frac{\text{Increase in concentration of } P}{\text{Time taken}} = \frac{+\Delta[P]}{\Delta t}$$

Unit of rate is Mol L^{-1} S^{-1} or atm S^{-1} (For gaseous reaction)

The rate measured over a long time interval is called average rate and the rate measured for an infinitesimally small time interval is called instantaneous rate.

Rate of reaction is not uniform. It goes on decreasing from moment to moment due to decrease in the concentration(s) of reactant(s) with the progress of reaction i.e. with time as shown below by rate V/s time curve.



4.3 INSTANTANEOUS RATE

It is the rate of the reaction at the particular moment of time and measured as a very small concentration change over a very small time interval ($\Delta t \rightarrow 0$).

The rate of change of concentration of any of the reactants or products at a particular instant of time is called the instantaneous rate of the given reaction at that instant.

For a reaction $R \longrightarrow P$

$$\textbf{Instantaneous rate} = \frac{-d[R]}{dt} = \frac{+d[P]}{dt}$$

$$r_{inst.} = \frac{-d[R]}{dt} = -\text{ slope of R}$$

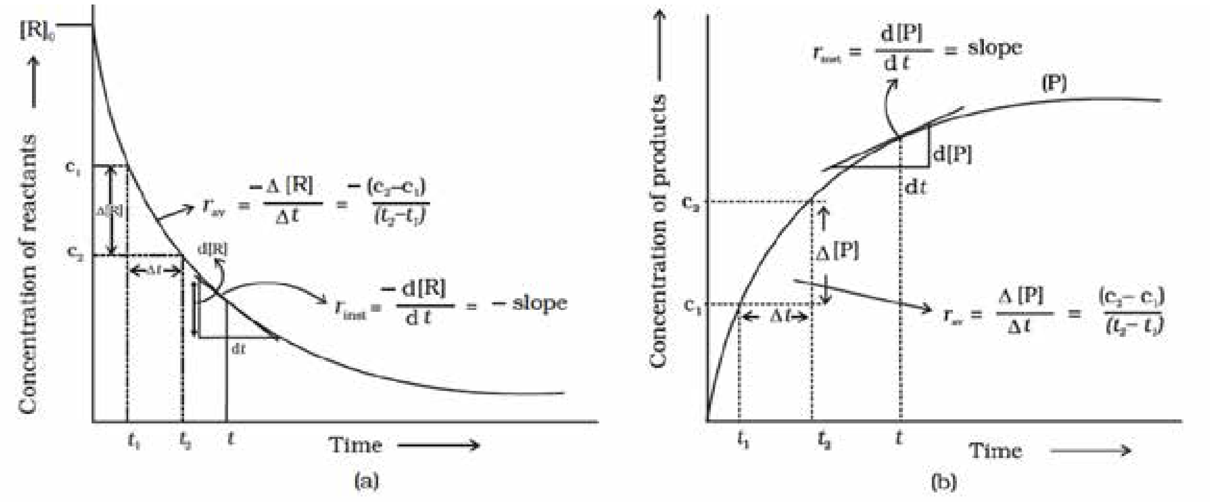
$$r_{inst.} = \frac{+d[P]}{dt} = +\text{ slope of P}$$

For a general chemical reaction

$$aA + bB \rightarrow cC + dD$$

$$R_{av.} = \frac{-1}{a}\frac{\Delta[A]}{\Delta t} = \frac{-1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

$$R_{inst.} = \frac{-1}{a}\frac{d[A]}{dt} = \frac{-1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$$



Rate at the time t = slope of tangent = $\tan \Theta$

> *The concentration change may be positive or negative but the rate of reaction is always positive. The minus sign is always written when required but the plus sign is usually not mentioned.*

Factors influencing reaction rates

There are number of factors which influence the rate of the reaction. These are:

- **Nature of reactants:** the reactions involving polar and ionic substances are quite fast whereas those involving covalent compounds are much slower.
- **Concentration of reactants:** in general, the rate of a reaction increases on increasing the concentration of reactants. This is due to an increase in the probability of molecular collisions.

- **Temperature:** the rate of a reaction usually increases on increasing the temperature. For most of the homogeneous reactions, the rate becomes doubled for each 10 °C rise in temperature.
- **Presence of a catalyst:** a catalyst provides an alternate path with a lower energy barrier and thus enables a larger number of reactant molecules to cross it and to take part in the reaction. Therefore, a catalyst increases the rate of a reaction.
- **Surface area:** if one of the reactants is a solid, the rate of reaction increases with an increase in the surface area of the reactant. An increase in surface area enhances the rate of encounters between the reactant molecules and consequently the rate of reaction increases.

4.4 DEPENDENCE OF RATE OF REACTION ON CONCENTRATION

Law of mass action: In 1864, Guldberg and Waage they postulated a generalization called the **Law of Mass action.** It states that: *the rate of a chemical reaction is proportional to the active masses of the reactants.*

By the term 'active mass' is meant the molar concentration *i.e.,* number of moles per litre. It is expressed by enclosing the formula of the substance in square brackets.

Thus for a chemical reaction,

$$\mathbf{aA + bB \longrightarrow Products}$$

$$\mathbf{Rate \propto [A]^a\ [B]^b}$$

Or $$\mathbf{Rate = k[A]^a\ [B]^b}$$

Where, [A] and [B] molar concentrations of A and B respectively and k is the velocity constant or rate constant or specific reaction rate.

But experimentally, it is observed that the rate of reaction is found to depend upon 'α' concentration terms of A and 'β' concentration terms of B Then,

$$\mathbf{Rate \propto [A]^\alpha\ [B]^\beta}$$

Or $$\mathbf{Rate = k[A]^\alpha\ [B]^\beta}$$ Where $\alpha + \beta$ = **order of reaction**

The above expression is known as **rate law**.

Rate law is defined as the mathematical relationship between rate of a reaction and the concentration of the reactants.

4.5 RATE CONSTANT

The constant ***k*** in the rate law is called the **rate constant**. It is defined as the rate of the reaction when the concentration of each of the reactants is unity.

Rate = k $[1]^{\alpha}$ $[1]^{\beta}$
∴ Rate = k

Unit of rate constant: Units of rate constant or specific reaction rate for nth order reaction is given as

Unit of rate constant= $[\text{concentration}]^{1-n} \times \text{time}^{-1}$

In general, the units of rate constant are **$\text{Mol}^{1-n}\ \text{L}^{n-1}\ \text{S}^{-1}$**, where n represents the sum of powers appearing in the rate law. For a gaseous reaction, units of rate constant will be $atm^{1-n}s^{-1}$

Order of reaction	Units
Zero order	$\text{mol L}^{-1}\ \text{time}^{-1}$
1st order	time^{-1}
2nd order	$\text{mol}^{-1}\text{L time}^{-1}$
3rd order	$\text{mol}^{-2}\text{L}^{2}\text{time}^{-1}$

Characteristics of rate constant

1. It is a measure of the rate of reaction. Higher the value of k, greater is the rate of reaction.
2. A particular reaction has a definite value of k at a particular temperature.
3. The value of rate constant increases with an increase in temperature.
4. It does not depend upon the initial concentrations of reactants.
5. Its units depend upon the overall order of reaction.

Rate of reaction	Reaction rate constant
It is speed with which reactants are converted into products.	It is proportionality constant.
It is measured as the rate of decrease of concentration of reactants or the rate of increase of concentration of products with time.	It is equal to the rate of reaction when the concentration of each of the reactants in unity.
It depends upon the initial concentration of reactants	It is independent of the initial concentration of the reactants and has constant value at fixed temperature.

Table: Difference between rate of reaction and rate constant

4.6 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, -ve or fractional. It is applicable to both elementary and complex reactions.

For a general reaction, **$aA + bB \rightarrow cC + dD$**

Rate = 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.

> *It is to be noted that the order of a reaction is purely an experimental quantity and cannot be known just by seeing the equation. The stoichiometric coefficients present in the balanced chemical equation have nothing to do with the order of the reaction.*

Reactions of different orders and the units of their rate constants

1. **First order reactions:** a reaction of a type A → products is said to be of first order, if its rate law is given by

   Rate = k $[A]^1$

   If the concentration of reactant A is doubled, the rate of reaction also gets double

   Example $PCl_5 \rightarrow PCl_3 + Cl_2; Rate = [PCl_5]^1$

   The units of rate constant for a first order reaction are time^{-1} i.e. s^{-1} , or min^{-1} , or hour^{-1}.

2. **Second order reactions:** a reaction of the type A → products is said to be of second order , if its rate law is given by

   Rate = k $[A]^2$

   When the concentration of reactants is doubled, the rate increases by four times.

   Example $2NO_2 \rightarrow 2NO + O_2; rate = k[NO_2]^2$

The units of rate constant for a second order reaction are conc^{-1}. i.e. mol^{-1} L s^{-1}. For a gaseous reaction the units of k will be atm^{-1} s^{-1}.

3. **Third order reactions:** In such a case, when the concentration is doubled, the rate of reaction increases by eight times.

   The most common third order reactions are of the following type;

   $2A + B \rightarrow$ Products : rate k $[A]^2$ $[B]$

   In this case, the reaction is of order 2 with respect to A

   Order 1 with respect to B.

   The overall order is 2+1 = 3.

   Example $2NO + O_2 \rightarrow 2NO_2; rate = k[NO]^2[O_2]$

   The units of rate constant for a reaction of third order are conc^{-2} time $^{-1}$ i.e. mol $^{-2}$ L^2 s^{-1}. for a gaseous reaction the units will be atm^{-2}s^{-1}.

4. **Zero order reactions:** a reaction A → products is said to be of zero order when its rate law is given by

   Rate =k $[A]^0$ = k

   When the concentration of a reactant is changed, the rate does not change i.e. the reaction proceeds with a constant rate. Some examples of zero order reactions are as follows.

   $$H_2 + Cl_2 \rightarrow 2HCl; rate = k[H_2]^0[Cl_2]^0 = k$$

   $$2NH_3 \rightarrow N_2 + 3H_2; rate = k[NH_3]^0 = k$$

   The units of rate constant for a zero order reaction are conc. Time $^{-1}$ ie.e. mol L^{-1} s$^{-1.}$ For a gaseous reaction the units are atm s^{-1}.

5. **Reaction of fractional order:** some examples of reactions having fractional orders are as follows.

$$CH_3CHO \rightarrow CH_4 + CO; rate = k[CH_3CHO]^{3/2} order = 3/2$$

$$H_2 + Br_2 \rightarrow 2HBr; rate = k[H_2][Br_2]^{1/2} order = 3/2$$

4.7 MOLECULARITY OF A REACTION

It is ***the total number of reacting species which collide 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 uni-molecular reaction.

e.g. Decomposition of ammonium nitrite

$\mathbf{NH_4NO_2 \rightarrow N_2 + 2H_2O}$

If the molecularity of a reaction is 2, it is called bimolecular reaction.

e.g. Decomposition of Hydrogen Iodide

$2HI \rightarrow H_2 + I_2$

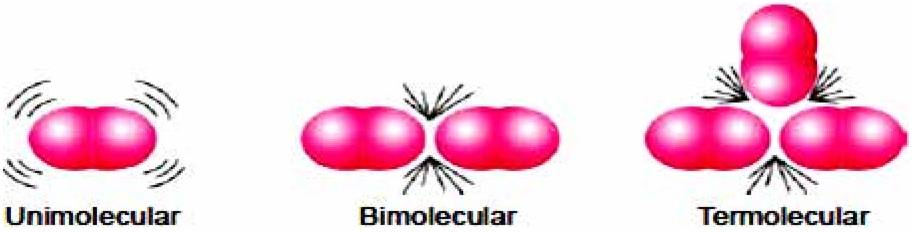
Chemical reactions may be classed into two types

a. Elementary reactions
b. Complex reactions

An **elementary reaction** is a simple reaction which occurs in a single step.

A **complex reaction** is that which occurs in two or more steps.

Molecularity of an Elementary Reaction: *The molecularity of an elementary reaction is defined as: the number of reactant molecules involved in a reaction.*



Thus the molecularity of an elementary reaction is 1, 2, 3, etc., according as one, two or three reactant molecules are participating in the reaction. The elementary reactions having molecularity 1, 2 and 3 are called **unimolecular, bimolecular and trimolecular** respectively. Eg.

Chemical Reaction	Molecularity
$PCl_5 \rightarrow PCl_3 + Cl_2$	Unimolecular
$2HI \rightarrow H_2 + I_2$	Bimolecular
$2SO_2 + O_2 \rightarrow 2SO_3$	Trimolecular

Molecularity of a complex Reaction

Most chemical reactions are complex reactions. These occur in a series of steps. Each step is an elementary reaction. *The stepwise sequence of elementary reactions that convert reactants to products is called the* ***mechanism of the reaction.*** In any mechanism, some of the steps will be fast, others will be slow. A reaction can proceed no faster than its slowest step. Thus the slowest step is the **rate determining step** of the reaction.

Decomposition of H2O2 is an example of a complex reaction.

Overall Reaction $H_2O_2 \rightarrow H_2O + 1/2O_2$

It occurs by the following steps :

Step 1:	$H_2O_2 \rightarrow H_2O + [O]$	Slow
Step 2:	$[O] + [O] \rightarrow O_2$	Fast

Each elementary reaction has its own molecularity equal to the number of molecules or atoms participating in it. It is meaningless to give the molecularity of the overall reaction because it is made of several elementary reactions, each perhaps with a different molecularity. At best could be thought of as: ***The minimum number of reacting particles (molecules, atoms or ions) taking part in the rate-determining step.***

The slowest step is rate-determining. Thus step 1 in the above mechanism is rate-determining and has molecularity '1' which could be considered as the molecularity of the decomposition reaction of H_2O_2.

4.8 MOLECULARITY VERSUS ORDER OF REACTION

The term molecularity is often confused with order of a reaction. The total number of molecules or atoms which take part in a reaction as represented by the chemical equation is known as the **molecularity of reaction.**

The sum of the powers to which the concentrations are raised in the rate law is known as the **order of reaction.**

Molecularity and Order are Identical for Elementary Reactions or Steps

The rate of an elementary reaction is proportional to the number of collisions between molecules (or atoms) of reactions. The number of collisions in turn is proportional to the concentration of each reactant molecule (or atom). Thus for a reaction

$$2A + B \longrightarrow \text{products}$$

$$\textbf{Rate} \propto [\mathbf{A}]\ [\mathbf{A}]\ [\mathbf{B}]$$

$$\textbf{or} \qquad \textbf{Rate} = \boldsymbol{k}\ [\mathbf{A}]^2\ [\mathbf{B}] \qquad\qquad (\textit{rate law})$$

Two molecules of A and one molecule of B are participating in the reaction and, therefore, molecularity of the reaction is 2 + 1 = 3. The sum of powers in the rate law is 2 + 1 and hence the reaction order is also 3. Thus **the molecularity and order for an elementary reaction are equal.**

Moleculariy	**Order of Reaction**
It is the total number of reacting species (molecules, atoms or ions) which bring the chemical change.	It is the sum of powers of molar concentration of the reacting species in the rate equation of the reaction.
It is always a whole number.	It may be a whole number, zero, fractional,
It is a theoretical concept.	It is experimentally determined.
It is meaningful only for simple reactions or individual steps of a complex reaction. It is meaningless for overall complex reaction.	It is meant for the reaction and not for its individual steps
Molecularity is **invariant** for a chemical, equation	Order of a reaction **can change** with the conditions such as pressure, temperature and concentration

4.9 PSEUDO–ORDER REACTIONS

A reaction in which one of the reactants is present in a large excess shows an order different from the actual order. **The experimental order which is not the actual one is referred to as the pseudo order.** Since for elementary reactions molecularity and order are identical, pseudo-order reactions may also be called **pseudo molecular reactions.**

Let us consider a reaction

A + B ——→ products

in which the reactant B is present in a large excess. Since it is an elementary reaction, its rate law can be written as

Rate = k [A] [B]

As B is present in large excess, its concentration remains practically constant in the course of reaction, thus the rate law can be written as

Rate = k' [A]

Where the new rate constant $k' = k$ [B]. Thus the actual order of the reaction is second-order but in practice it will be first-order. Therefore, the reaction is said to have a ***pseudo-first order.***

4.10 METHODS FOR DETERMINATION OF ORDER OF A REACTION

Following methods are used to determine the order of a reaction.

1. **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,

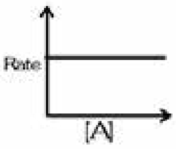
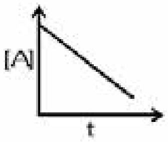
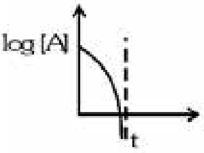
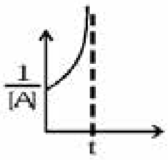
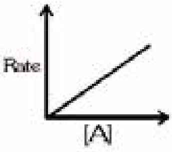
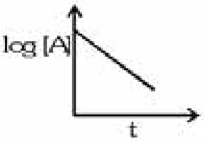
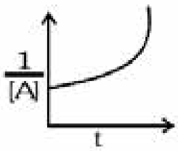
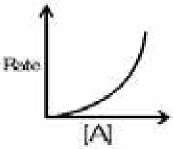
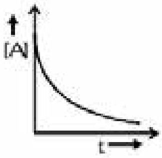
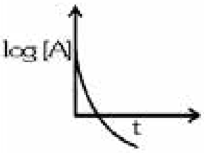
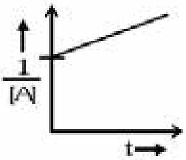
   Rate α $[A]^n$

   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.

Graphs of various orders

Order	Rate vs [A]	[A] vs t	log [A] vs t	$\frac{1}{[A]}$ vs t
Zero order				
First order				
Second order				

2. **Method of integration (Hit and trial method):** The most simple method is the one in which the quantities a, x and t are determined and substituted in the kinetic equations of various orders. The equation, which gives the most constant value for the specific rate constant (k) for a series of time intervals, is the one corresponding to the order of reaction.

3. **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.

Zero Order Reactions (integrated form)

A reaction is said to be of zero order if its rate is independent of the concentration of the reactants, i.e., the rate is proportional to the zeroth power of the concentration of the reactants.

For the reaction **A → products**

to be of zero order,

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^0$$

$$-\frac{d[A]}{dt} = k$$

$$-d[A] = kdt$$

Integrating both sides

$$\int_{[A]o}^{[A]t} d[A] = -k \int_{o}^{t} dt$$

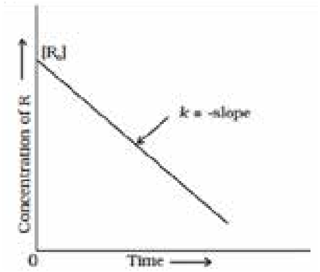
$$[A]_t - [A]_o = -kt \quad .....(i)$$

$$[A]_t = -kt + [A]_0 \quad ..... (ii)$$

Comparing equation (ii) with equation of a straight line

$y = mx + c$

If we plot [A] against t, we get a straight line with slope = –k and intercept equal to $[A]_0$.



Rearranging equation (ii) we get

$$\frac{[A]_o - [A]}{t}$$ --------- (iii) (integrated form of zero order rate equation)

Some photochemical reaction and a few heterogeneous reactions are zero-order reactants. Such reactions are not common.

Characteristics of zero order reaction

The concentration of reactant decreases linearly with time. $[A]_t = [A]_0 - kt$

The time required for the reaction to be complete:

$$\mathbf{t}_{\text{completion}} = \frac{[A]0}{k} = \frac{\text{Initial concentration}}{\text{Rate constant}}$$

The units of k are mol L^{-1} $time^{-1}$.

Half-time or half-life period of a zero order reaction: The half-time of a reaction is defined as the time required reducing the concentration of the reactant to half of its initial value. It is denoted by the symbol $t_{1/2}$. Thus,

For zero order reaction, we know that

$[A] = -kt + [A]_0$

or $-[A] = kt + [A]_0$

or $[A]_0 - [A] = kt$

or $k = \frac{[A]_0 - [A]}{t}$

At half life of reaction, $t = t_{½}$ & $[A] = [A]_o/2$

So $k = \frac{[A]_o - [A]_0/2}{t_{1/2}} = \frac{[A]_o}{2t_{1/2}}$

or $t_{½} = \frac{[A]_0}{2k}$

4.11 FIRST ORDER REACTIONS

A reaction is said to be first order if its rate is determined by the change of one concentration term only.

Consider the reaction A → products

Let $[A]_O$ = Initial Concentration of A

$[A]_t$ = the concentration of A after time t

For the reaction to be of first order

$$Rate = -\frac{d[A]]}{dt} = k[A]$$

$$\Rightarrow \frac{d[A]}{[A]} = -kdt \text{ ……………….(i)}$$

Integrating this equation

$$\int_{[A]_o}^{[A]} \frac{d[A]}{[A]} = -k\int_0^t dt$$

We get

$ln\,[A] - ln[A]_o = -k(t-0)$

Or $ln\frac{[A]}{[A]_o} = -kt$

Or $ln\frac{[A]_o}{[A]} = kt$ ………………….. (ii)

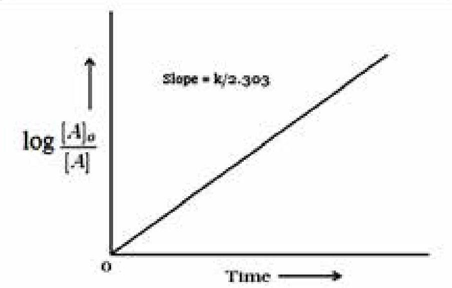
$$log\frac{[A]_o}{[A]} = \frac{kt}{2.303} \text{………………….. (iii)}$$

$$k = \frac{2.303}{t}\,log\frac{[A]_o}{[A]} \text{ ……..…………….... (iv)}$$

On comparing the equation number (ii) with equation of straight line i.e. y= mx +c

We come to know that, If we plot a graph between log $\frac{[A]o}{[A]}$ V/s t,

The slope of line= k/2.303



Unit of rate constant for first order reaction (k) = min^{-1} or s^{-1}

The rate constant of a first order reaction has only time unit. It has no concentration unit.

Half-time or half-life period of a first order reaction

The half-time of a reaction is defined as the time required reducing the concentration of the reactant to half of its initial value. It is denoted by the symbol $t_{1/2}$. Thus,

For first order reaction, we know that

$$k = \frac{2.303}{t} log \frac{[A]_o}{[A]}$$

At half life of reaction,

$t = t_{½}$ & $[A] = [A]_o/2$

So $$k = \frac{2.303}{t} log \frac{[A]_o}{\frac{[A]_o}{2}}$$

$$t_{1/2} = \frac{0.693}{k}$$

Since k is a constant for a given reaction at a given temperature and the expression lacks any concentration term. So ***half-time of a 1st order reaction is a constant independent of initial concentration of reactant.***

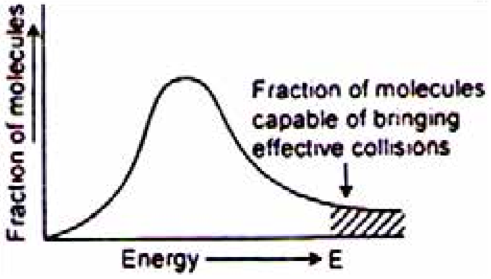
General expression for half life period of a reaction of nth order is $t_{1/2} \propto [A]_O{}^{1-n}$

where n is the order of a reaction (= 0, 1, 2 or 3)

Amount of substance left after n half lives= $-\frac{[A]\circ}{2^n}$

4.12 COLLISION THEORY OF REACTION RATE

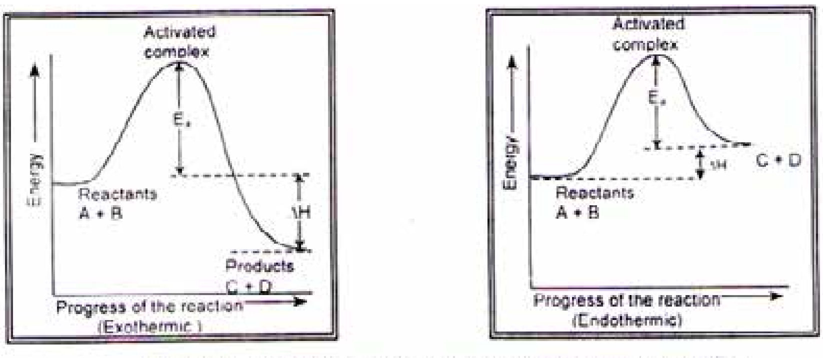
1. A chemical reaction takes place due to collision among reactant molecules. The number of collisions taking place per second per unit volume of the reaction mixture is known as collision frequency (Z). The value of collision frequency is very high, of the order of 10^{25} to 10^{28} in case of binary collisions.
2. Every collision does not bring a chemical change. The collisions that actually produce the products are effective collisions.



Energy Barrier: The minimum amount of energy, which the colliding molecules must possess as to make the chemical reaction to occur, is known as ***threshold energy***. The minimum amount of energy required by reactant molecules to participate in a reaction is called ***activation energy***.

Activation energy = threshold energy – average kinetic energy of reacting molecules.
Threshold energy = initial potential energy of reactant molecules + activation energy.

A collision between high, energy molecules overcomes the forces of repulsion and brings the formation of an unstable molecule cluster, called the **activated complex.** The life span of an activated complex is very small. Thus, the activated complex breaks either into reactants again or new substances, i.e., product. The activation energy (E_a) depends upon the nature of chemical bonds undergoing change and is independent of enthalpies of reactants and products. The energy changes during exothermic and endothermic reactions versus the progress of the reaction are given below:



Activation energy of exothermic and endothermic reaction

Orientation Barrier: Energy alone cannot determine the effectiveness of the collision.

Rate of reaction is directly proportional to the number of effective collisions.

Rate = Collision frequency × fraction of effective collisions × probability factor **= z** × **f** × **p**

Arrhenius Equation (Temperature Dependence of Reaction Rate)

We know that the kinetic energy of a gas is directly proportional to its temperature. Thus as the temperature of a system increases, more and more molecules acquire necessary energy, (greater than E_a) to cause productive collisions. This increases the rate of the reaction.

In 1889, Arrhenius suggested as simple relationship between the rate constant, ***k***, for a reaction and the temperature of the system.

$$\mathbf{K=A\ e}^{-Ea/RT} \quad \ldots\ldots\ldots \quad (1)$$

Where A = a constant known as frequency factor and gives the frequency of binary collisions of reactant molecules per second per liter.

Ea = the energy of activation,
R = gas constant
T = the temperature of the system.
K = the rate constant of the reaction

Taking logarithm on both sides of equation (1), we get

$$\ln k = \ln A\, e^{-Ea/RT}$$

$$\text{or } \ln k = -\frac{Ea}{RT} + \ln A$$

$$\text{Or } 2.303 \log k = -\frac{Ea}{RT} + 2.303 \log A$$

Dividing both sides by 2.303 we get

$$\log k = -\frac{Ea}{2.303RT} + \log A$$

At two temperatures T_1 and T_2 taking log of Arrhenius Equation, we get

$$\log k_1 = -\frac{Ea}{2.303R} \times \frac{1}{T1} + \log A \qquad \text{............(2)}$$

$$\text{And} \quad \log k_2 = -\frac{Ea}{2.303R} \times \frac{1}{T2} + \log A \qquad \text{............(3)}$$

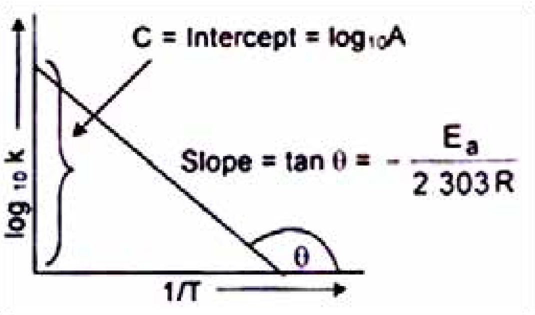
Subtracting Eq. (2) from Eq. (3) and converting the log to the base 10, we get

$$\log_{10}\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

Or

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303\ R}\left[\frac{1}{T}\right] \qquad \text{or} \quad y = m\,x + c$$

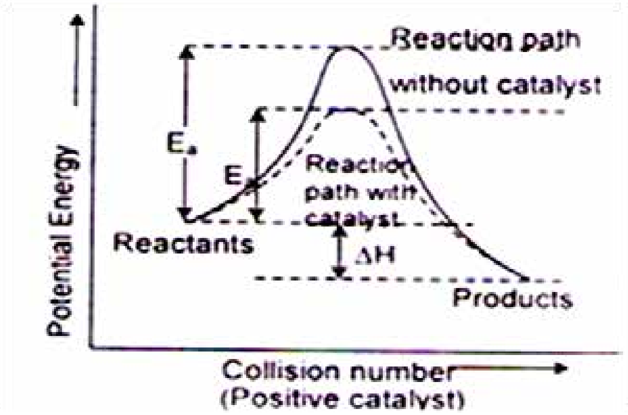
It is equation of straight line with negative slope. On plotting $\log_{10}$ k against [1/T] we get straight line.



In the Arrhenius equation when $T \rightarrow \infty$, then $k = Ae^{0} = A$.

When $E_a = 0, k = A$, then rate of reaction becomes independent of temp.

1. **Presence of a positive catalyst:** The function of a positive catalyst is to lower down the activation energy. The greater the decrease in the activation energy caused by the catalyst, higher will be the reaction rate. In the presence of a catalyst, th reaction follows a path of lower activation energy. Under this condition, a large number of reacting molecules are able to cross over the energy barrier and thus the rate of reaction increases.



2. **Presence of negative catalyst:** A negative catalyst increases the activation energy of reaction by forming a new intermediate of high energy, i.e., by changing the reaction mechanism.

   Due to increases activation energy, some active molecules become inactive, therefore, rate of reaction decreases.

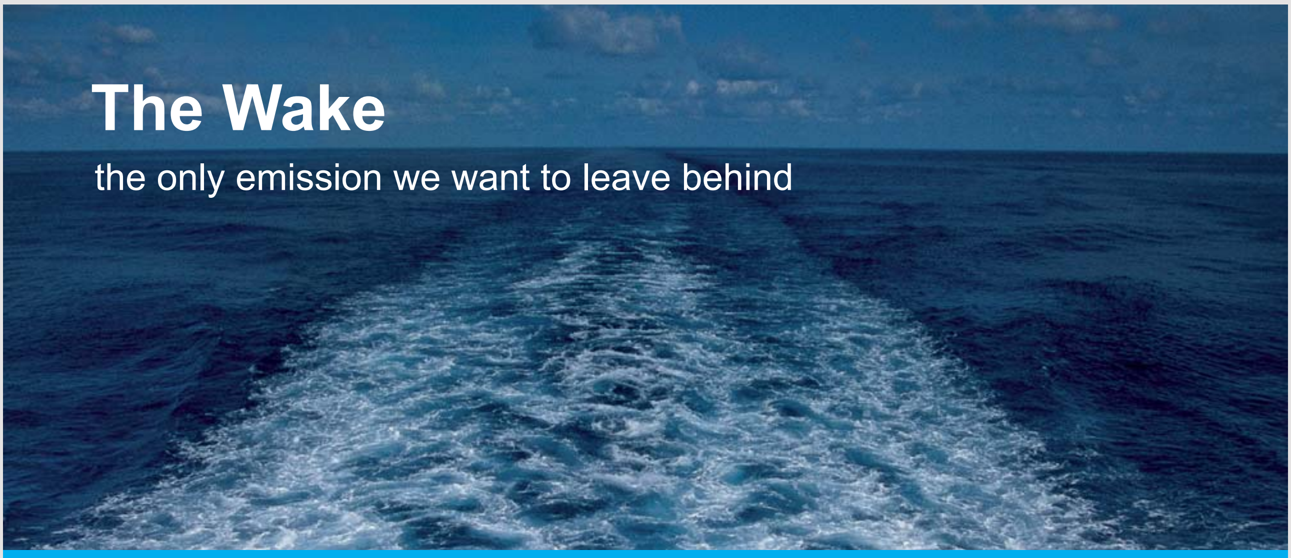
Temperature coefficient: It has been found that generally an increase of temperature increases the rate of reaction. As a rule, an increase of temperature by 10°C doubles the reaction rate. Thus the ratio of rate constants of a reaction at two different temperatures differing by 10 degree is known as ***Temperature Coefficient.***

$$\mu = \text{Temperature coefficient} = \frac{k(t+10)}{kt}$$

The two temperatures generally taken are 35 °C and 25 °C. Thus,

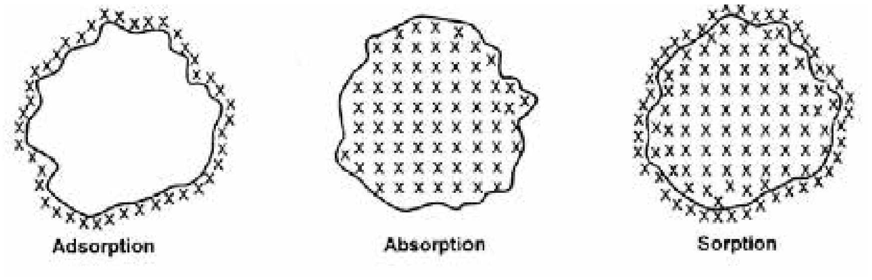
$$\text{Temperature Coefficient} = \frac{k_{35^\circ}}{k_{25^\circ}} = \frac{k_{308}}{k_{298}}$$

Reaction Rates	*How we measure rates.*
Rate Laws	*How the rate depends on amounts of reactants.*
Integrated Rate Laws	*How to calculate amount left or time to reach a given amount.*
Half-life	*How long it takes to react 50% of reactants.*
Arrhenius Equation	*How rate constant changes with temperature.*
Mechanisms	*Link between rate and molecular scale processes.*



5 SURFACE CHEMISTRY

The branch of the Chemistry which deals with the study of surface phenomena is called surface Chemistry.



Adsorption: The phenomenon of increase in concentration of the species on the surface of the solid than in the bulk is called **adsorption.** The solid substance on the surface of which adsorption occurs is called **adsorbent** and the molecular species that get adsorbed on the solid surface due to intermolecular attraction are called **adsorbate.**
The process of removal of an adsorbed substance from the surface of adsorbent is known as **desorption.**

Cause of adsorption: Adsorption arises at the surface of solids as a result of the presence of unbalanced forces at the surface.
Desorption: The reverse process i.e. the removal of adsorbate from the surface is called desorption. Desorption is an endothermic process.
The adsorption of gases on the surface of metals is called **occlusion**.
Sorption: If adsorption and absorption takes place simultaneously, the process is called sorption.

Thermodynamic feasibility of adsorption: For adsorption, ΔH = -ve ΔS = -ve
ΔG = -ve, which is possible only if $\Delta H > T\Delta S$

Competitive adsorption or preferential adsorption: A strong adsorbate gets adsorbed more readily as compared to week adsorbate or in some cases strong adsorbate can displace an already adsorbed week adsorbate from the surface of adsorbant. This is known as Competitive adsorption or preferential adsorption.

Difference between adsorption and absorption

Adsorption	Absorption
1. It is surface phenomena i.e it occurs only at the surface of adsorbent., 2. Here concentration on the surface of adsorbent is different than in the bulk 3. Its rate is high in the beginning than it decreases till equilibrium is attained.	1. It is a bulk phenomena i. e occurs throughout the body of material. 2. Here concentration is same throughout the material 3. Its rate remains same throughout the process

5.1 CLASSIFICATION OF ADSORPTION OF GASES ON SOLIDS

The adsorption of gases on solids has been divided in to two types based on the nature of forces holding the gas molecules to the solids. 1. Physical adsorption (or) Vander waal's adsorption 2. Chemical adsorption (or) chemisorption.

Physical adsorption/ Physisorption	Chemical adsorption / Chemisorption
1. In Physisorption vander Waals'forces operate between adsorbate and adsorbent. 2. It is not specific in nature. Almost all gases are adsorbed on all solids to some extent. 3. It is reversible in nature. 4. It depends on the nature of gas. More easily liquefiable gases are adsorbed readily. 5. Enthalpy of adsorption is low (20-40 kJ mol^{-1}) 6. Low temperature is favorable for adsorption. It decreases with increase of temperature. 7. No appreciable activation energy is needed. 8. It depends on the surface area. It increases with an increase of surface area. 9. It results into multimolecular layers on adsorbent 10.No compound formation takes place	1. In Chemisorption forces operating are similar to that of a chemical bond formation. 2. It is highly specific in nature, and occurs only when there is possibility of compound formation. 3. It is irreversible. 4. It also depends on the nature of gas. Gases which can react with the adsorbent show chemisorption. 5. Enthalpy of adsorption is high (80-400 kJ mol^{-1}) 6. High temperature is favourable for adsorption. It increases with the increase of temperature. 7. High activation energy is sometimes needed. 8. It also depends on the surface area. It too increases with an increase of surface area. 9. It results into unimolecular layer. 10.Surface compound formation takes place.

Factors affecting adsorption

The magnitude of gaseous adsorption depends upon the following factors:

a. **Nature of adsorbate:** Physical adsorption is non-specific in nature and therefore every gas gets adsorbed on the surface of any solid to a lesser or greater extent. However, easily liquefiable gases like NH_3. HCl, CO_2, etc. which have higher critical temperatures are absorbed to greater extent whereas H_2, O_2, N_2 etc. are adsorbed to lesser extent. The chemical adsorption being highly specific, therefore, a gas gets adsorbed on specific solid only if it enters into chemical combination with it.

b. **Nature of adsorbent:** Activated carbon, metal oxides like aluminum oxide, silica gel and clay are commonly used adsorbents. They have their specific adsorption properties depending upon pores.

c. **Specific area of the adsorbent:** The greater the specific area more will be the extent of adsorption. That is why porous or finely divided forms of adsorbents adsorb larger quantities of adsorbate. The pores should be large enough to allow the gas molecules to enter.

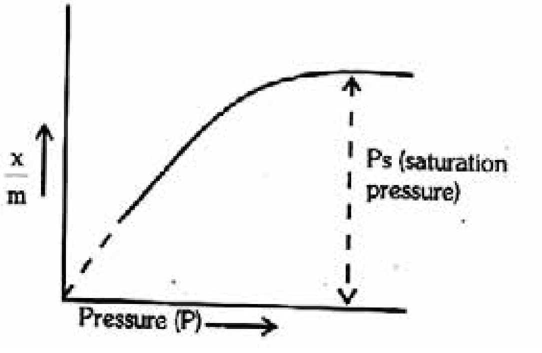
d. **Temperature:-**Adsorption is accompanied by evolution of heat i.e. H is negative, so the rate of adsorption should decrease with rise in temperature. It is found to be so in case of physical adsorption. The effect of temperature is represented by an adsorption isobar.
e. **Activation of adsorbent:-** An adsorbent can be activated either by heating or by bringing it in finely divided state, or by making its surface rough by rubbing. For example charcoal is activated by heating it in vacuum at 1000 °C.
f. **Pressure of the gas:** Physical adsorption increases with increase in pressure.

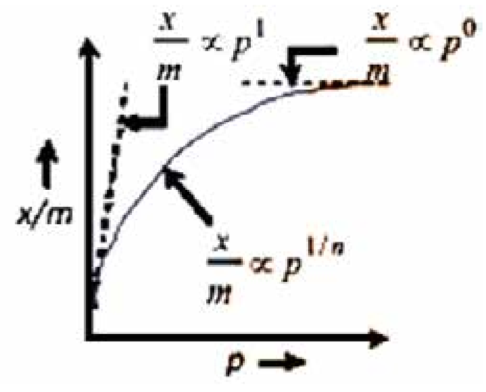
5.2 ADSORPTION ISOTHERM

The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature can be expressed by means of a curve termed as **Adsorption isotherm**

Freundlich adsorption isotherm:

Freundlich, in 1909, gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and pressure at a particular temperature.
The plots of extent of adsorption (x/m) versus pressure at constant temperature is called as adsorption isotherms





1. At low pressures, the graph is a straight sloping and

$$\frac{x}{m} \propto p \qquad \text{or} \qquad \frac{x}{m} = k\,p$$

Where x is the mass of the gas adsorbed on mass *m* of the adsorbent at pressure *p*.

2. At high pressure, the graph becomes independent of pressure,

$$\frac{x}{m} \propto p^0 \qquad \text{or} \qquad \frac{x}{m} = kp^0$$

3. At intermediate pressure, $\frac{x}{m}$ varies with the power of the pressure lying between 0 and 1,

$$\frac{x}{m} \propto p^{\frac{1}{n}} \qquad \text{or} \qquad \frac{x}{m} = kp^{1/n} \text{ ------------ (1)}$$

K and n are constants which depend on the nature of the adsorbent and the gas at a particular temperature

A plot of x/m verses p is shown in figure below;

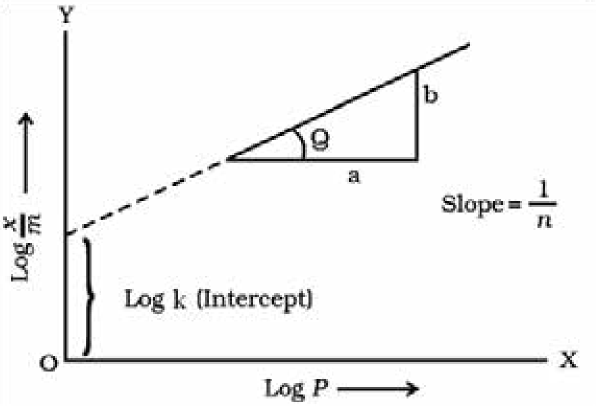
From the figure it is clear that at fixed temperature physical adsorption first increases with increase in pressure at low pressure but becomes independent of pressure at high pressure.

{1/n = 0-1 (Probable range of 1/n = 0.1 to 0.5).

Taking logarithm of Eq. (i)

log x/m= log k + 1/n log P

If we plot a graph between log x/m and log P, we get a straight line.



The slope of the line is 1/n and intercept will be equal to log k.

Freundlich isotherm explains the behavior of adsorption in an approximate manner.

Limitations of *Freundlich adsorption isotherm:* According to Freundlich adsorption isotherm the above graph should be straight line .experimentally it has been found to deviate from linearity at high pressures. Thus it is applicable at low pressures only.

5.3 LANGMUIR ADSORPTION ISOTHERM

The main points of this theory are:-

1. The solid surface consists of a fixed number of adsorption sites where only adsorption of gaseous molecules can take place.
2. Each site can hold only one gaseous molecule. Thus a gas on being adsorbed by solid surface cannot form a layer more than one molecule of thickness i.e. adsorption is uni-molecular.

3. Adsorption is localized and takes place only when gas molecules collide with vacant solid surfaces. Magnitude of adsorption of a gas on a solid goes on increasing with increase in pressure until the entire surface of the solid gets completely covered by a uni-molecular layer of the gas.
4. Thickness of the adsorbed layer is the same as the thickness of the molecule of the adsorbate
5. The gaseous molecules adsorbed at different sites do not interact with each other.
6. Heat of adsorption is the same for all the sites and is independent of pressure and fraction of the adsorbent surface covered.
7. The phenomenon of adsorption involves a dynamic equilibrium and can be represented as:

$$\mathrm{G + S \rightleftharpoons GS}$$

Where, G,S and GS represent the un-adsorbed gaseous molecule, the vacant site on the surface of adsorbent and the adsorbed gaseous molecule respectively

Derivation of Langmuir Adsorption Isotherm: Consider the dynamic equilibrium between free molecules and those adsorbed on the fraction of the solid surface.

The concentration of adsorbed molecules G-S depends only on one factor, namely the number of occupied adsorption sites which in turn is proportional to fraction 'θ' of the surface covered with gaseous molecules. The rate of description or evaporation is proportional to the fraction 'θ' of the surface that is covered with gaseous molecules.

The concentration of vacant sites on the surface of an adsorbent will be directly proportional to fraction of the surface that remains uncovered, i.e. $(1-\theta)$. Therefore, the rate of adsorption or condensation will be proportional to $(1-\theta)$, i.e. the fraction of surface covered. It also depends upon the pressure of the gas as according to the kinetic theory, the number of molecules striking per unit area is proportional to the gas pressure, p.

Rate of adsorption or condensation $\propto (1-\theta)\mathrm{p} = \mathrm{k_1}(1-\theta)\mathrm{p}$

Rate of evaporation $\propto \theta = \mathrm{K_2}\theta$ ....(i)

At equilibrium

$$\mathrm{K_1}(1-\theta)\mathrm{p} = \mathrm{k_2}\theta$$

$$\theta(\mathrm{K_2} + \mathrm{K_1P}) = \mathrm{K_1P}$$

$$\theta = \frac{\mathrm{K_1P}}{\mathrm{K_2+K_1P}} = \frac{(\mathrm{K_1/K_2})\mathrm{P}}{\left(1+\frac{\mathrm{K_1}}{\mathrm{K_2}}\right)\mathrm{P}} = \frac{\mathrm{bP}}{1+\mathrm{bP}} \quad \text{.......(ii)}$$

Where $K_1/K_2 = b$ which is another constant.

Since θ is proportional to the amount of gas adsorbed per unit mass of the adsorbent

$$\frac{x}{m} \propto \theta = K_3\theta \qquad \text{......(iii)}$$

From (ii) and (iii)

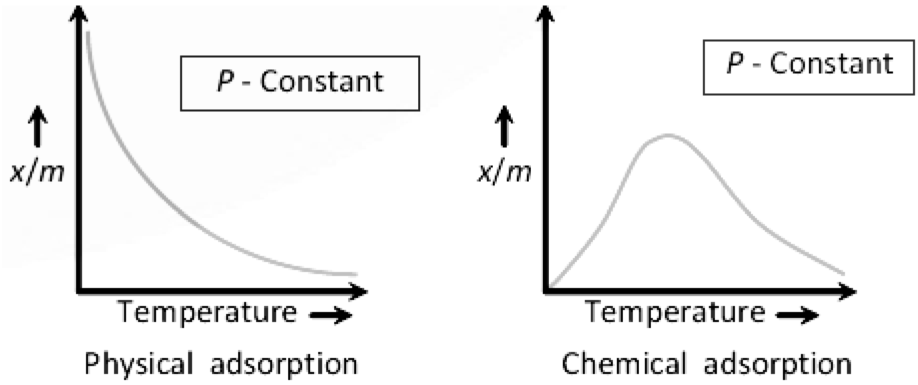
$$\frac{x}{m} = K_3 \frac{bP}{1+bP}$$

This is known as Langmuir adsorption isotherm in which constant a and b depends upon the nature of the gas adsorbed, nature of solid adsorbents and the temperature

As K_3 and b are constant, so their product is also equal to constant say (a)

$\frac{x}{m} = \frac{aP}{1+bP}$ This is known as Langmuir adsorptin isotherm

Adsorption Isobars: These are plots of x/m *V/s* temperature t at constant pressure. For physical and chemical adsorption, they are shown below.



Adsorption Isostere: These are the plot of temperature versus pressure for a given amount of adsorption

Applications of adsorption: The phenomenon of adsorption finds a number of applications. Important ones are listed here:

1. *Production of high vacuum*: The remaining traces of air can be adsorbed by charcoal from a vessel evacuated by a vacuum pump to give a very high vacuum
2. *Gas masks*: Gas mask (a device which consists of activated charcoal or mixture of adsorbents) is usually used for breathing in coal mines to adsorb poisonous gases.

3. *Control of humidity*: Silica and aluminum gels are used as adsorbents for removing moisture and controlling humidity.
4. *Removal of coloring matter from solutions*: Animal charcoal removes colors of solutions by adsorbing colored impurities.
5. *Heterogeneous catalysis*: Adsorption of reactants on the solid surface of the catalysts increases the rate of reaction. e.g. manufacture of ammonia using iron as a catalyst, manufacture of H_2SO_4 by contact process and use of finely divided nickel in the hydrogenation of oils are excellent examples of heterogeneous catalysis.
6. *Separation of inert gases*: Due to the difference in degree of adsorption of gases by charcoal, 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. *Froth floatation process*: A low grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method using pine oil as frothing agent
9. *Adsorption indicators*: Surfaces of certain precipitates such as silver halides have the property of adsorbing some dyes like eosin, fluorescein, etc. and thereby producing a characteristic color at the end point.

5.4 CATALYSIS

Catalyst is a chemical substance which can change the rate of reaction without being used up in that reaction and this process is known as catalysis

Types of catalysts

The catalysts have been divided into different types according to their behavior and pattern of action.

1. **Positive catalyst:** A catalyst which enhances the speed of the reaction is called positive catalyst and the phenomenon is known as positive catalysis. Eg. Decomposition of H_2O_2 in presence of colloidal platinum

   $$2H_2O_2 \xrightarrow{Pt} 2H_2O + O_2$$

2. **Negative Catalyst:** There are certain substances which, when added to the reaction mixture, retard the reaction rate instead of increasing it. These are called negative catalysts or inhibitors and the phenomenon is known as negative catalysis.eg. The decomposition of hydrogen peroxide decreases in presence of glycerine.

   $$2\,H_2O_2 \xrightarrow{\text{Glycerine}} 2\,H_2O + O_2$$

   Promoters and Poisons: Promoters are chemical substances that enhance the activity of a catalyst while poisons decreases the activity of a catalyst

5.5 TYPES OF CATALYSIS

a. **Homogeneous catalysis:** When reactant, product as well as catalyst are in same phase, it is called homogeneous catalyst and type of catalysis is homogeneous catalysis. e.g.

$$2SO_2(g) + O_2(g) \xrightarrow{NO\,(g)} 2SO_3(g)$$

$$2CO(g) + O_2(g) \xrightarrow{NO\,(g)} 2CO_2(g)$$

$$CH_3COOC_2H_5(l) + H_2O(l) \xrightarrow{H^+(aq)} CH_3COOH(l) + C_2H_5OH(l)$$

b. **Heterogeneous catalysis:** When the catalyst is present in different phase than that of the reactant, it is called as Heterogeneous catalyst and this type of catalysis is called Heterogeneous catalysis (Surface catalysis) e.g.

1. Oxidation of sulphur dioxide to Sulphur trioxide in presence of V_2O_5

$$2SO_2(g) + O_2(g) \xrightarrow{V_2O_5} 2SO_3(g)$$

2. Cracking of hydrocarbon in the presence of hydrogen to get lower alkane in presence of Zeolite catalyst.

Characteristics of Catalysts

The following characteristics are generally common to most of the catalytic reactions.

1. The catalyst remains unchanged in mass and in chemical composition at the end of the reaction.
2. Only a small quantity of catalyst is generally needed.
3. A catalyst cannot initiate a reaction. The function of a catalyst is only to alter the speed of the reaction which is already occurring at a particular rate.
4. A catalyst does not alter the position of equilibrium in a reversible reaction.
5. The catalyst is generally specific in its action.

5.6 THEORIES OF CATALYSIS

There are two main theories to explain catalysis.

1. Intermediate compound formation theory
2. Adsorption theory

In general, the intermediate compound formation theory applies to homogeneous catalytic reactions and the adsorption theory applies to heterogeneous catalytic reactions.

The Intermediate Compound Formation Theory

According to this theory, the catalyst first forms an intermediate compound with one of the reactants. The compound is formed with less energy consumption than needed for the actual reaction. The intermediate compound being unstable combines with other reactant to form the desired product and the catalyst is regenerated.

For example, a reaction of the type

$$A + B \xrightarrow{C} AB$$

which occurs in presence of a catalyst C, may take place as

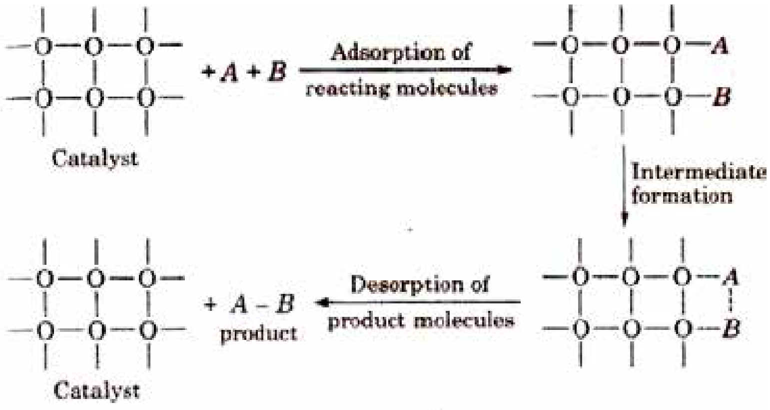
$$A + \underset{\text{Catalyst}}{C} \longrightarrow \underset{\text{Intermediate compound}}{AC}$$

$$AC + B \longrightarrow \underset{\text{Product}}{AB} + \underset{\text{Catalyst}}{C}$$

Adsorption Theory of Heterogeneous Catalysis

The mechanism involves five steps:

1. Diffusion of reactants to the surface of the catalyst
2. Adsorption of reactant molecules on the surface of the catalyst.
3. Occurrence of chemical reaction on the catalyst's surface through formation of an intermediate.
4. Desorption of reaction products from the catalyst surface.
5. Diffusion of reaction products away from the catalyst's surface



Important Features of Solid Catalysts

1. **Activity:** The activity of a catalyst depends upon the strength of chemisorption to a large extent. The adsorption should be reasonably strong but not so strong that they become immobile and no space is available for other reactants to get adsorbed.
2. **Selectivity:** The selectivity of a catalyst is its ability to direct a reaction to yield a particular product.

5.7 ZEOLITES

Zeolites are the naturally occurring or synthetic microporous aluminosilicates. They are used as catalyst in petrochemical industry for cracking of hydrocarbons. The remarkable feature of zeollite is shape selectivity which depends upon pore size of the catalyst.

Zeolites have three-dimensional network silicates in which some silicon atoms are replaced by aluminium atoms generate one negative charge on the aluminosilicate frame work, substitution of x atoms generate x negative charge on aluminosilicate frame work. This charge is neutralized by exchangeable cation M of valency n. The void space which can be greater than 50% of the volume is occupied by molecules of water in the unit cell.

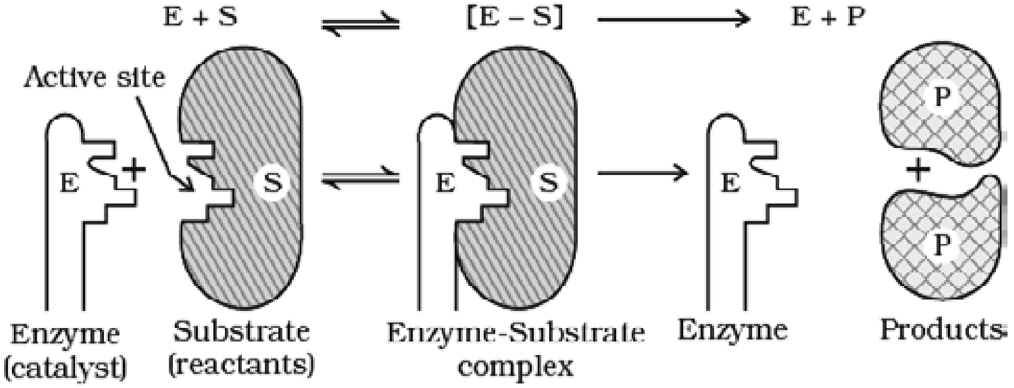
Use of Zeolites

1. $\text{Alcohols} \xrightarrow{\text{ZSM}-5} \text{hydrocarbons}$
   (ZSM 5 = Zeolites Sieve of Molecular Porosity 5)
2. Hydrated Zeolites are used in ion-exchangers in softening of hard water.

5.8 ENZYME CATALYSIS

Enzymes are complex nitrogenous organic compounds which are produced by living plants and animals. They are actually protein molecules of high molecular mass and form colloidal solutions in water. They are also known as biochemical catalysis.

Mechanism of Enzyme Catalysis



Some examples of enzyme catalyzed reactions are:

1. $\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} \xrightarrow{\text{Invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$

2. $\underset{\text{glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$

3. $\underset{\text{starch}}{n(C_6H_{12}O_5)} \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{n(C_{12}H_{22}O_{11})} \xrightarrow{\text{Maltase}} \text{Glucose}$

4. $\underset{\text{Urea}}{NH_2CONH_2} + H_2O \xrightarrow{\text{Urease}} 2NH_3 + CO_2$

5. In stomach, the pepsin enzyme converts proteins into peptides while in intestine, the pancreatic trypsin converts proteins into amino acids by hydrolysis.

Characteristics of Enzyme Catalysis

- **High efficiency:** One molecule of an enzyme may transform one million molecule of reactant per minute.
- **Highly specific nature:** Each enzyme catalyst cannot catalyze more than one reaction.
- **Optimum temperature:** Enzyme catalyst gives higher yield at optimum temperature i.e., at 298-310 K. Human body temperature, i.e., at being 310 K is suited for enzyme catalyzed reactions.
- **Optimum pH:** The rate of an enzyme catalyzed reaction is maximum at optimum pH range 5 to 7.
- **Activators:** Activators like ions such as Na^+, Ca^{2+}, Mn^{2+} help in the activation of enzymes which cannot act on their own strength.
- **Co-enzyme:** Co-enzymes are the substance having nature similar to the enzyme and their presence increases the enzyme activity. Mostly vitamins act as co-enzymes.
- **Effect of Inhibitors:** Inhibitors slow down the rate of enzymatic reaction. The use of many drugs is based on enzyme inhibition action of those drugs in the body

5.9 COLLOIDAL STATE

The foundation of colloid chemistry was laid by an English scientist, Thomas Graham in 1861. The colloidal solutions are intermediate between true solutions and suspensions.

A colloid state is a heterogeneous system in which the size (10Å -1000Å) of particles is such that they can easily pass through the filter paper but not through animal or vegetable membrane.

A colloidal state is heterogeneous system consisting of two phases.

1. **Dispersed phase or Internal phase or discontinuous phase:** It is a component present in small proportion just like a solute present in true solution
2. **Dispersion medium or external phase or continuous phase**: It is a component present in excess just like a solvent present in true solution

Difference between true solution, colloidal state and suspension are as

S.No	Property	True solution	Colloidal state	suspension
1	Particle size	Less than 10^{-9}m or 1nm or 10Å	Between 10^{-9} m to 10^{-7}m or 1nm to 100 nm	More than 10^{-7}m or 100 nm
2	Filterability a. Ordinary filtration b. Ultra filtration	 Not possible Not possible	 Not possible Possible	 Possible possible
3	Settling	Particles don't settle	Particles settle on centrifugation.	Particles settle under gravity.
4	Visibility	Particles are invisible	Scattering of particles observed under ultramicroscope.	Particles visible to a naked eye
5	Diffusion	Diffuse quickly	Diffuse slowly	Don't Diffuse
6	Appearance	Transparent	Translucent	Opaque
7	Nature	Homogenous	Heterogeneous	Heterogeneous
8	Tyndal effect	Does not show	Shows	shows
9	Brownian movement	May or may not show	shows	shows

5.10 CLASSIFICATION OF COLLOIDS

Colloids are classified on the basis of the following criteria

1. **Based on physical state of dispersed phase and dispersion medium:** Depending upon whether the dispersed phase and the dispersion medium are solids, liquids or gases, eight types of colloidal systems are possible shown below. A gas mixed with another gas forms a homogeneous mixture and hence is not a colloidal system.

Dispersed phase	Dispersion medium	Name	Examples
Solid	Gas	Aerosol	Smoke, dust
Solid	Liquid	Sol	Paints
Solid	Solid	Solid sol	Colored glasses, gem stones
Liquid	Solid	Gel	Jellies, cheese
Liquid	Liquid	Emulsion	Milk , hair cream
Liquid	Gas	Aerosol	Fog, mist, cloud
Gas	Solid	Solid foam	Pumice stone, foam, rubber
Gas	Liquid	foam	Whipped cream, froth

2. **Nature of interaction between dispersed phase and dispersion medium:** Depending upon the nature of interaction between the dispersed phase and the dispersion medium, colloidal sols are divided into two categories, namely, lyophilic (solvent attracting) and lyophobic (solvent repelling).If water is the dispersion medium, the terms hydrophilic and hydrophobic are used respectively.

   1. ***Lyophilic colloids***: (or intrinsic colloid) Lyophilic'-liquid-loving. The solutions in which particles of dispersed phase have strong affinity with the dispersed medium are called lyophillic colloids. Such colloidal sols are easily formed by mixing substances like gum, gelatin, starch, rubber, etc., with a suitable liquid (the dispersion medium).These are **reversible** since on evaporating the dispersion medium (e.g water),the residue can easily be again reconverted into colloidal state by addition of liquid solvent. These colloids are quite stable.
   2. ***Lyophobic colloids*:** (or extrinsic colloid) Lyophobic-liquid-hating. The colloids in which particles of dispersed phase have little or no affinity with the dispersed medium are called lyophobic sols. Substances like metals, their sulphides, etc., when simply mixed with the dispersion medium do not form the colloidal sol. Their colloidal sols can be prepared only by special methods. These sols are readily precipitated (or coagulated) on the addition of small amounts of electrolytes, by heating or by shaking and hence, are not stable these sols are also called **irreversible sols**. Lyophobic sols need stabilizing agents for their preservation.

S. No.	Lyophillic colloids	Lyophobic colloids
1.	These are easily prepared and are self stabilized.	These are difficult to prepare and need Small quantities of electrolytes cause precipitation.
2.	Large quantities of electrolytes cause precipitation, small quantities have little effect.	small quantities of other substances for stabilization.
3	Reversible	Irreversible
4	Surface tension is usually lower than that of dispersion medium.	Surface tension is usually same as that of medium.
5	Viscosity is higher than that of dispersion medium.	Almost same as that of dispersion phase.
6	Have higher concentration of dispersed phase.	Have lower concentration of dispersed phase.
7	Cannot be easily detected even with ultramicroscope.	Can be easily detected with ultra-microscope.
8	Do not exhibit Tyndal effect.	Exhibit Tyndall effect
9	Highly solvated.	Not solvated.
10	May or may not migrate in electric field.	Migrate in electric field.

3. **Based on nature of dispersion medium:**

S.No	Dispersion medium	Name of Colloidal Sol
1	Water	Hydrosol/aqua sol
2	Alcohol	Alcosol
3	Benzene	Benzosol
4	Gases	Aerosol

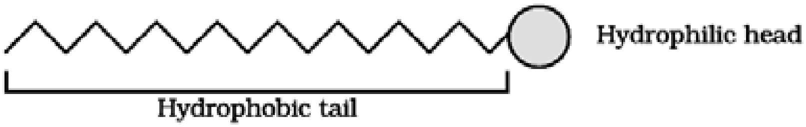
4. **Depending upon the type of the particles of the dispersed phase,**
   a. **Multimolecular colloids:** These are formed by aggregation of large no. of atoms or molecules which generally have diameter less than 1nm, e.g. sols of gold, sulphur etc

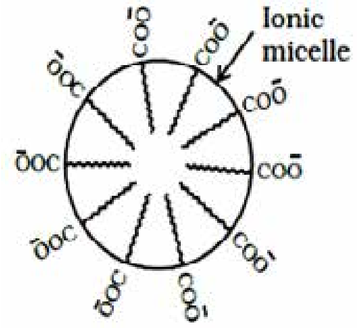
b. **Macromolecular colloids:** in this type of colloidal solution, the particles of dispersed phase are very large in size (macromolecules) e.g. polymers with high molecular mass like rubber, nylon, starch etc. These colloids are quite stable and resemble true solutions in many respects.

c. **Associated colloids:** Substances which at low concentrations behave as normal strong electrolytes, but at higher concentrations exhibit colloidal behavior due to the formation of aggregates are called ***associated colloids*** *or* ***Micelles.***

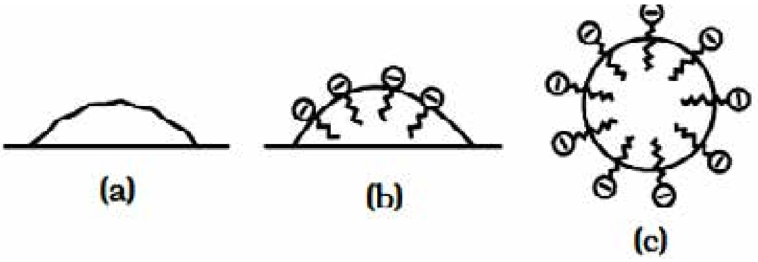
- The minimum concentration above which dispersed phase starts forming micelle is known as ***critical micelle concentration***. (CMC). It is generally 10^{-4} to 10^{-3} mol/lit.
- The minimum temperature above which dispersed phase starts forming micelles is known as ***craft temperature*** (T_k).
- Micelle contains as many as hundred molecules or more.
- Soap solution or detergent acts as good conductors of electricity at low concentration but not at high concentration because at high concentration micelles are formed.

Mechanism of micelle formation: Let us take the example of soap solutions. Soap is sodium or potassium salt of a higher fatty acid and may be represented as $RCOO^-Na^+$ (e.g., sodium stearate $CH_3(CH_2)_{16}COO^-Na^+$, which is a major component of many bar soaps). When dissolved in water, it dissociates into $RCOO^-$ and Na^+ ions. The $RCOO^-$ ions, however, 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, therefore, present on the surface with their COO^-groups in water and the hydrocarbon chains R staying away from it and remain 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 with their hydrocarbon chains pointing towards the centre of the sphere with COO^- part remaining outward on the surface of the sphere. An aggregate thus formed is known as **ionic micelle**. These micelles may contain as many as 100 such ions.





Cleansing action of soaps: Soap when applied on an oily/greasy skin surface along with water hydrophobic alkyl part penetrates into oil/grease, whereas $–COO^-$ remains in water. This disparity leads to the formation of micelle above CMC. Each micelle possess negative charge and repels its neighboring micelle are easily washed away by water.

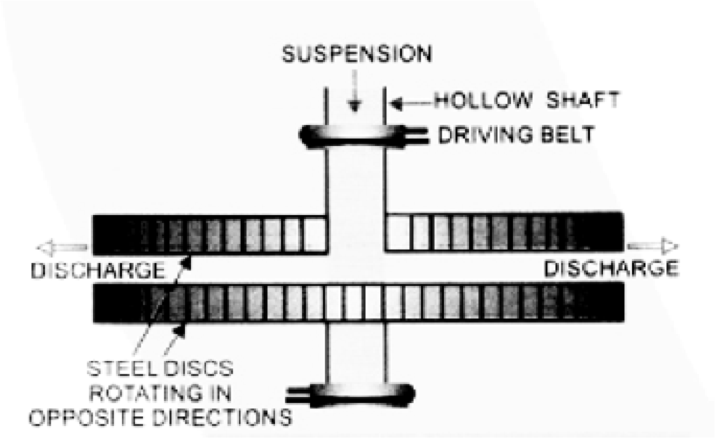


(a) Grease on cloth (b) Stearate ions arranging around the grease droplet and (c) Grease droplet surrounded by stearate ions (micelle formed)

5.11 PREPARATION OF COLLOIDS

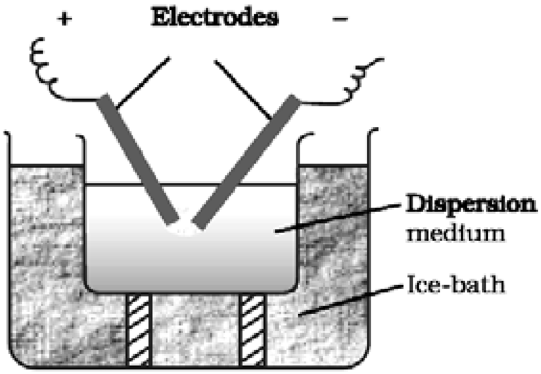
1. **Preparation of lyophilic sols:** The colloidal solutions of lyophilic colloids like starch, glue, gelatin etc., can be readily prepared by dissolving these substances in water either in cold or on warming.
2. **Preparation of lyophobic sols:** Lyophobic sols are prepared by special methods. These methods fall into two categories.
    1. Dispersion methods: By splitting coarse aggregates of a substance into a colloidal size.
    2. Condensation methods: By aggregating very small particles into the colloidal particles.

a. **Dispersion methods or disintegration method/ physical methods:**
    1. ***Mechanical Disintegration:*** The mechanical disintegration is carried in a machine called as colloidal mill which consists of two steel discs with a little gap in between and capable of rotating in opposite directions at high speed. A suspension of substance in water is introduced into the mill, where these are reduced to colloidal size particles.



2. ***Electrical disintegration or Bredig's Arc method:*** In this method, electric arc is struck between electrodes of the metal immersed in the dispersion medium.

   The intense heat produced vaporizes the metal, which then condenses to form particles of colloidal size. This process involves dispersion as well as condensation. Colloidal sols of metals such as gold, silver, platinum, etc., can be prepared by this method.



3. ***Peptization:*** The process of converting a precipitate into colloidal sol by shaking it with dispersion medium in the presence of a small amount of electrolyte is called peptization. The electrolyte used for this purpose is called peptizing agent. This method is applied, generally, to convert a freshly prepared precipitate into a colloidal sol.

   Cause of peptization*:* During peptization, the precipitate adsorbs one particular type of the ions of the electrolyte on its surface and gets dispersed due to electrostatic repulsions. This gives particles of colloidal size.

b. **Condensation or aggregation methods:**
This method involves joining together of large no. of small particles to form particles of colloidal size. It involves following methods.

1. ***Double decomposition:*** A colloidal solution of arsenious sulphide is obtained by passing H_2S through a dilute solution of arsenious oxide in water.

   $As_2O_3 + 3H_2S \rightarrow As_2S_3$(colloidal sol) $+ 3H_2O$

2. ***By Reduction*:** Colloidal solutions of metals can be obtained by reduction of their salts with a suitable reducing agent.

   $2AuCl_3 + 3SnCl_2 \rightarrow 2Au$ (Colloidal sol) $+3SnCl_4$

3. ***By oxidation:*** Colloidal solution of sulphur can be obtained by passing H_2S gas through solution of an oxidizing agent like nitric acid, bromine water etc

   $Br_2 + H_2S \rightarrow S$ (Colloidal sol) $+ 2HBr$

4. ***By hydrolysis:*** Many Salt solutions are readily hydrolyzed and form colloidal solutions. e.g colloidal sols of ferric hydroxide is obtained by boiling solutions of ferric chloride.

   $FeCl_3 + 3H_2O \rightarrow Fe(OH)_3$ (Colloidal sol) $+ 3HCl$

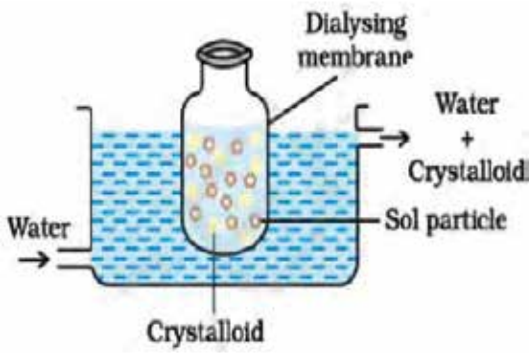
5.12 PURIFICATION OF COLLOIDAL SOLUTIONS

Colloidal solutions when prepared contain excessive amount of electrolytes and some other soluble impurities, while the presence of traces of electrolyte is essential for their stability but larger quantities can coagulate it. ***The process used for reducing the amount of impurities to a requisite minimum is known as purification of colloidal solution***. It is carried out by the following methods

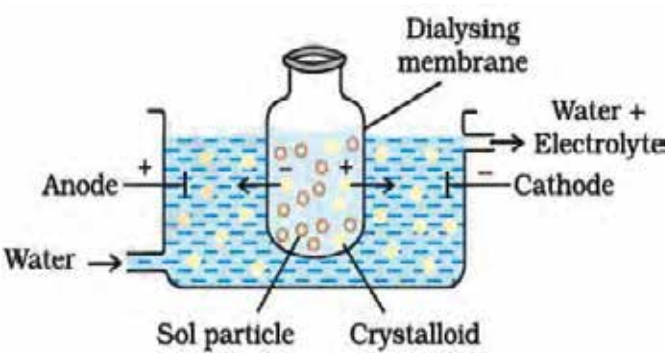
Dialysis: *it is the process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane.*

Principal: it is based on the principal that the particles (ions or smaller molecules) of a true solution can pass through animal membrane (bladder) or parchment paper or cellophane sheet but not the colloidal particles; the apparatus used for this purpose is called dialyzer.

It consists of a bag of suitable membrane containing the colloidal solution which is suspended in a vessel through which fresh water is continuously flowing. The molecules and ions diffuse through membrane into the outer water and pure colloidal solution is left behind.



Dialysis



Electro-dialysis

1. ***Electro-dialysis*:** The process of dialysis is quite slow. It can be made faster by applying an electric field only if the dissolved substance in the impure colloidal solution is an electrolyte. The process is then named electro dialysis.

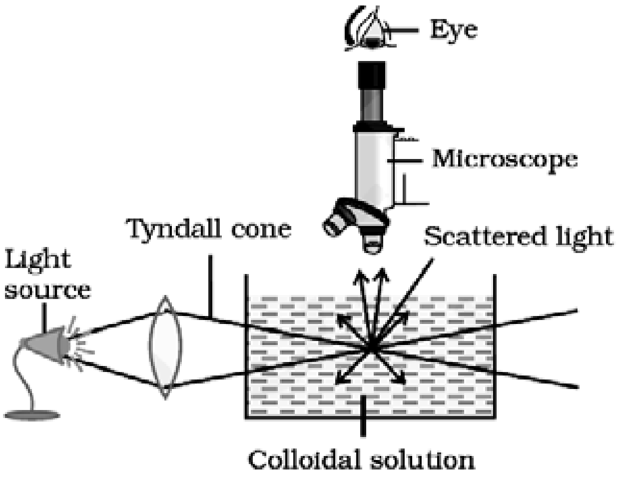
> *The most important application of dialysis is in the purification of blood in the artificial kidney machine. The dialysis membrane permits small particles of excess ions and waste products to pass through where as colloid sized particles such as hemoglobin do not pass through.*

2. **Ultra filtration:** Ultra filtration is the process of separating the colloidal particles from the solvent and soluble solutes present in the colloidal solution by specially prepared filters, which are permeable to all substances except the colloidal particles. Colloidal particles can pass through ordinary filter paper because the pores are too large. However, the pores of filter paper can be reduced in size by impregnating with **colloidon** solution (*which is 4% solution of nitrocellulose in a mixture of alcohol and ether*) to stop the flow of colloidal particles.. An ultra-filter paper may be prepared by soaking the filter paper in a colloidon solution, hardened by formaldehyde and then finally drying it. By using the solution of different concentration a series of graded ultrafilters can be obtained. Ultra filtration is a slow process. To speed up the process, pressure or suction is applied.

5.13 PROPERTIES OF COLLOIDAL SOLUTIONS:

1. ***Colligative properties***: Colloidal particles being bigger aggregates, the number of particles in a colloidal solution is comparatively small as compared to a true solution. Hence, the values of colligative properties (osmotic pressure, lowering in vapour pressure, and depression in freezing point and elevation in boiling point) are of small order as compared to values shown by true solutions at same concentrations.
2. ***Optical properties (Tyndall effect):*** if a beam of light is passed through a colloidal solution placed in a dark room, the path of beam gets illuminated with a bluish light due to scattering of light by colloidal particles. This phenomenon is called Tyndall effect and illuminated path of light is called Tyndall cone. Tyndall effect is observed only when the following two conditions are satisfied.

   (i) The diameter of the dispersed particles is not much smaller than the wavelength of the light used; and (ii) The refractive indices of the dispersed phase and the dispersion medium differ greatly in magnitude.



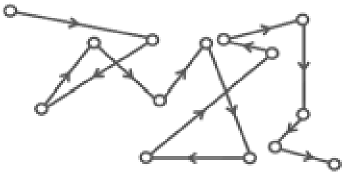
Note: Tyndall effect has helped to confirm the heterogeneous nature of colloidal solution.

Some examples of Tyndall effect are

a. Blue color of sky and sea water.
b. Visibility of tails of comets and twinkling of stars.
c. Visibility f projector path and circus light.
d. Visibility of sharp ray of sunlight passing through a slit in dark room.

3. ***Mechanical properties**: **(Brownian movement)***: When colloidal solutions are viewed under a powerful ultra microscope, the colloidal particles appear to be in a state of continuous zig-zag motion all over the field of view. This motion is known as Brownian movement. ***Thus Brownian movement may be defined as continuous Zig Zag movement of colloidal particles in a colloidal solution***. This motion is independent of the nature of the colloid but depends on the size of the particles and viscosity of the solution. Smaller the size and lesser the viscosity, faster is the motion.

   Cause of Brownian movement: the molecules of dispersion phase (colloidal particles) are being constantly hit by the dispersion medium which are in constant motion like the molecules of gas, thereby making the colloidal particles to to move in Zig Zag motion.



Importance of Brownian movement

1. Brownain movement opposes the force of gravity and does not allow the colloidal particles to settle down.Thus it is responsible for the stability of colloidal solutions.
2. It has also helped in the determination of Avogadro's number

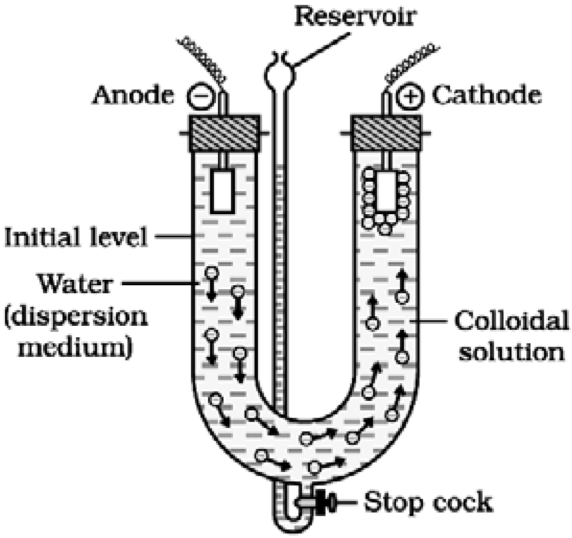
4. **Electrical properties /*Charge on colloidal particles* (stability of colloidal sols):** Colloidal particles always carry an electric charge. The nature of this charge is same on all the particles in a given colloidal solution and may be either positive or negative while the dispersion medium has an equal but opposite charge. The system as a whole is electrically neutral. The presence of equal and similar charges on colloidal particles is largely responsible in providing stability to the colloidal solution, because the repulsive forces between charged particles having same charge prevent them from coalescing or aggregating when they come closer to one another and hence the particles do not settle down.

   Origin of charge on colloidal particles: The charge on the sol particles is due to following reasons.

1. Due to electron capture by sol particles during electro dispersion of metals,
2. Due to preferential adsorption of ions from solution
3. Due to formulation of electrical double layer.

The electrical properties of colloids can also be explained by **electrical double layer theory.** According to this theory, a double layer of ions appear at the surface of solid. The ion preferentially adsorbed is held in fixed part and imparts charge to colloidal particles. Above the fixed layer a second layer consists of both the types of charges. The net charge on the second layer (diffused part) is exactly equal to that on the fixed part. The existence of opposite sign on fixed and diffuse parts of double layer leads to appearance of a difference of potential, known as **Zeta potential** or **electrokinetic potential.** Now when electric field is employed the particles move and we have electrophoresis.

Electrophoresis: When electric potential is applied across two platinum electrodes dipping in a colloidal solution, the colloidal particles move towards one or the other electrode. *This movement of colloidal particles under an applied electric potential is called electrophoresis or cataphoresis*. Positively charged particles move towards the cathode while negatively charged particles move towards the anode**.**



Electro-osmosis: *Electro osmosis may be defined as the phenomena in which in which molecules of dispersion medium are allowed to move under the influence of electric field whereas colloidal particles are not allowed to move.*

5. ***Coagulation or precipitation or Flocculation**: This process involves coming together of colloidal particles so as to change into large sized particles which ultimately settle as a precipitate or float on a surface. Coagulation is brought about by addition of electrolytes, when electrolyte is added to a colloidal solution; the particles of sol take up the oppositely charged ions and thus get neutralized. The neutral particles thus accumulate and form particles of large size which settle down.*

Flocculation value: The minimum concentration of an electrolyte in millimoles per litre of the electrolyte solution which is required to cause the coagulation or flocculation of colloidal sol is called **Flocculation value.**

Greater the coagulation power of effective ion, lower will be the flocculaiton value o the electrolyte containing the effective ion.

Therefore, Flocculation value $\propto \frac{1}{\text{Coagulating power}}$

Hardy Schulze Rule: Different electrolytes are known to have different coagulation values. The coagulation behaviour is governed by **Hardy Schulze** rule according the which:

1. The ion having opposite charge to sol particles cause coagulation and
2. Coagulation power of an electrolyte depend on the valancy of ion i.e., greater the valancy more is the coagulating power.

The decreasing order of flocculation value of electrolytes for a –ve sol is

$\mathbf{NaCl > BaCl_2 > AlCl_3 > SnCl_4}$

and the decreasing order of flocculation value of electrolytes for a +ve sol is

$\mathbf{KCl > Na_2SO_4 > Na_3PO_4 > K_4[Fe(CN)_6]}$

Flocculation value is inversely proportional to valency of oppositely charged ion

The coagulation of the lyophobic sols can be carried out in the following ways:

1. *By electrophoresis*: The colloidal particles move towards oppositely charged electrodes, get discharged and precipitated.
2. *By mixing two oppositely charged sols*: when oppositely charged sols are mixed in almost equal proportions, they neutralise their charges and get partially or completely precipitated. Mixing of hydrated ferric oxide (+ve sol) and arsenious sulphide (–ve sol) bring them in the precipitated forms. This type of coagulation is called mutual coagulation.

3. *By boiling*: When a sol is boiled, the adsorbed layer is disturbed due to increased collisions with the molecules of dispersion medium. This reduces the charge on the particles and ultimately leads to settling down in the form of precipitate.
4. By persistent dialysis: On prolonged dialysis, traces of the electrolyte present in the sol are removed almost completely and the colloids become unstable and ultimately coagulate.
5. By addition of electrolyte: when electrolyte is added to a colloidal solution; the particles of sol take up the oppositely charged ions and thus get neutralized. The neutral particles thus accumulate and form particles of large size which settle down.

5.14 PROTECTIVE COLLOIDS

Lyophobic sols of metals are unstable and are easily precipitated by addition of electrolytes. However addition of small amount of *lyophilic colloid* prevents them from coagulation. *This process of protecting the lyophobic colloidal solution from coagulation by previous addition of some lyophilic colloid is known as protection and the lyophilic colloids thus used are known as protective colloids*. The protective action of lyophilic colloid is due to covering up of the particles of lyophobic colloid by those of lyophilic colloid.

5.15 GOLD NUMBER

In order to measure the protective powers of hydrophilic colloids, term **gold number** is used. *It is defined as the number of milligrams of the protective colloid required to just prevent the coagulation of 10 mL of red gold sol when 1 mL of 10% solution of sodium chloride is added to it.* Lower is the value of gold number greater is the protective power.

The gold numbers of a few protective colloids are given below

Gelatin	0.005–0.01
Casein	0.01–0.02
Egg albumin	0.10–0.2
Gum Arabic	0.15–0.25

Goldnumber is inversely proportional to protective power

5.16 EMULSIONS

These are liquid-liquid colloidal systems, i.e., the dispersion of finely divided droplets in another liquid. If a mixture of two immiscible or partially miscible liquids is shaken, a coarse dispersion of one liquid in the other is obtained which is called **emulsion**. Generally, one of the two liquids is water.

There are two types of emulsions.

1. Oil dispersed in water (O/W type),
2. Water dispersed in oil (W/O type).

In the first system water acts as dispersion medium. Examples of this type of emulsions are milk and vanishing cream. In milk, liquid fat is dispersed in water.

In the second system oil acts as dispersion medium. Common examples of this type are butter and cream.

Emulsions of oil and water are unstable and sometimes they separate into two layers on standing. For the stabilization of an emulsion, a third component called **emulsifying agent** is usually added. The emulsifying agent forms an interfacial film between suspended particles and the medium. The principal agents for O/W emulsions are proteins, gums, natural and synthetic soaps, etc. For W/O emulsions, the principal emulsifying agents are heavy metal salts of fatty acids, long chain alcohols, lampblack, etc.

Emulsions can be diluted with any amount of the dispersion medium. On the other hand, the dispersed liquid when mixed forms at once a separate layer. The droplets in emulsions are often negatively charged and can be precipitated by electrolytes. They also show Brownian movement and Tyndall effect. Emulsions can be broken into constituent liquids by heating, freezing, centrifuging, etc.

Properties of emulsions

S.No.	Property	Water in oil	Oil in water
1	Dispersed phase	Water	Oil
2	Dispersion medium	Oil	Water
3	Examples	Butter, cold cream, cod liver oil	Milk, face creams, butter, creams
4	Viscosity	More than water	Slightly more than water
5	Appearance	Oily, opaque and translucent	Watery, opaque and translucent
6	Electrical conductivity	Very low	Nearly equal to water.
7	Dilution Test	More oil added is soluble but not water	More water added is soluble but not oil
8	Spreading test	Spreads easily on an oily layer.	Spreads readily on watery layer
9	Dye test: Adding of oil soluble dye like methylene blue	Dye dissolved giving a bright coulor	Dye remains insoluble in the form of colored droplets.

Role of Emulsions

1. Cleaning action of soaps and detergents.
2. Milk, cream, butter are all emulsions and are important constituents of our food
3. Various cosmetics as cold cream, body lotions are emulsions.
4. Digestion of fats in intestine is through emulsification.
5. Various oily drugs are administered as emulsions for fast assimilation.

5.17 GELS

Gels are colloidal systems in which liquids are dispersed phase and solids act as dispersion medium. Gels may shrink by losing some liquid held by them. This is known as **Synereises** or **Weeping.** Some gels are known to liquefy on shaking and reset on being allowed to stand. This reversible sol-gel transformation is called thixotropy.

Gels are of two types

1. **Non elastic.** They are irreversible i.e., when dehydrate these change into powder which cannot be change back by addition of water.
2. **Elastic.** These are reversible i.e. these can be changed back into original form even after dehydration.

6 GENERAL PRINCIPLES & PROCESSES OF ISOLATION OF METALS

Elements occur in nature in two states: Native state and combined state. When the metals are in the elementary form they are said to be in their native state. Eg: Au, Ag, Cu, Pt etc.

When the metals are found in the form of their compounds, they are in the combined state.

In the combined state the metals are found in the crust of the earth as oxides, carbonates, sulphides, silicates, Phosphates etc.

Minerals: A naturally occurring material in which a metal or its compound occurs is called a mineral. **OR**

The chemical substances in the earth's crust obtained by mining are called **Minerals**.

Every mineral cannot be used for its extraction.

Ores: A mineral from which a metal can be extracted economically and conveniently is called an **ore**.

All ores are minerals but all minerals are not ores.

Some important ores

Metal	Ore	Composition
Potassium	Sylvine	KCl
Calcium	Gypsum, Limestone	$CaSO_4.2H_2O$, $CaCO_3$
Sodium	Rock salt	NaCl
Magnesium	Magnesite, Dolomite	$MgCO_3$, $MgCO_3.CaCO_3$
Aluminium	Bauxite, Diaspore, Kaolinite(a form of clay)	$Al_2O_3.2H_2O$, $Al_2O_3.H_2O$ $Al_2(OH)_4.Si_2O_5$
Titanium	Rutile, Ilmenite	TiO_2, $FeTiO_3$
Zinc	Zinc blende or sphalerite, Calamine Zincite	ZnS $ZnCO_3$ ZnO
Iron	Haematite Iron Pyrite(Fool's gold) Magnetite	$Fe_2O_3.xH_2O$ FeS_2 Fe_3O_4
Tin	Cassiterite or tin stone	SnO_2
Chromium	Chromite	$FeCr_2O_4$
Manganese	Pyrolusite	MnO_2
Lead	Galena	PbS
Copper	Chalcopyrite(copper pyrites) Malachite Cuprite	$CuFeS_2$ $Cu(CO_3).Cu(OH)_2$ Cu_2S
Mercury	Cinnabar	HgS
Silver	Argentite	Ag_2S
Gold	Native metal	Au

Gangue or Matrix: Ores are invariably found in nature in contact with rocky materials. These rocky or earthy impurities accompanying the ores are termed as ***gangue** or **matrix.***

OR Impurities associated with ores are called **gangue** or **matrix**.

Extraction of Metals

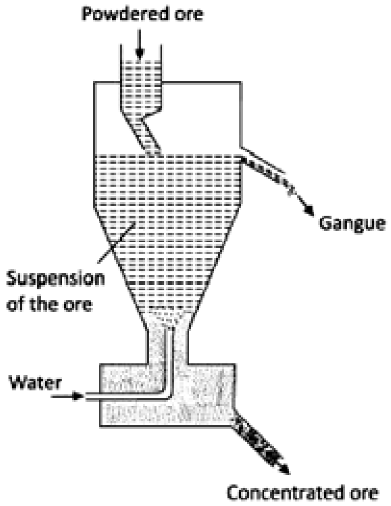
The process of extracting the metals from their ores and refining them is called ***metallurgy.*** The steps involved in metallurgy are called the **metallurgical operations.**

The choice of the process depends upon the nature of the ore and the type of the metal. The metal content in the ore can vary depending upon the impurities present and chemical composition of the ore. Some common steps involved in the extraction of metals from their ores are:

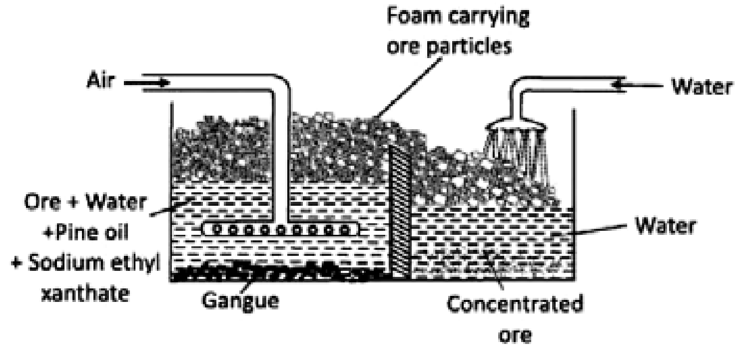
1. *Crushing and pulverization*
2. *Concentration or dressing of the ore*
3. *Calcination or roasting of the ore*
4. *Reduction of metal oxides to free metal*
5. *Purification and refining of metal*

1. **Crushing and Pulverization:** The ore is generally obtained as big rock pieces. These big lumps of the ore are crushed to smaller pieces by using ***jaw crushers*** and *grinders*. It is easier to work with crushed ore. The big lumps of the ore are brought in between the plates of a crusher forming a jaw. One of the plates of the crusher is stationary while the other moves to and fro and the crushed pieces are collected below. The crushed pieces of the ore are then pulverized (powdered) in a stamp mill. The heavy stamp rises and falls on a hard die to powder the ore. The powdered ore is then taken out through a screen by a stream of water.
2. **Concentration or Dressing of the Ore:** *Removal of gangue from ore is called Concentration, Dressing or Benefaction of ore.*
   Generally, the ores are found mixed with earthy impurities like sand, clay, lime stone etc.
   The unwanted impurities present in ore are called ***gangue or matrix.***
   The process of removal of gangue from powdered ore is called concentration or ore dressing.
   There are several methods for concentrating the ores. The choice of method depends on the nature of the ore. Some important methods are:

   a. **Hydraulic Washing/Gravity Separation/Levigation:** In this method, the light (low specific gravity) earthy impurities are removed from the heavier metallic ore particles by washing with water. It is therefore, used for the concentration of heavier oxide ores, like haematite (Fe_2O_3) tinstone (SnO_2) and gold (Au). In this method, the powdered ore is agitated with water or washed with a strong current of water. The heavier ore settles down rapidly in the grooves and the lighter sandy and earthy materials (gangue particles) are washed away.



Froth Floatation Process: The finely divided ore is introduced into water containing small quantity of oil (e.g. Pine Oil). The mixture is agitated violently with air a froth is formed which carries away along with it the metallic particles on account of the surface tension forces. The froth is transferred to another bath where gangue-free ore settles down.



The froth can be stabilised by the addition of stabilisers (aniline or cresols).

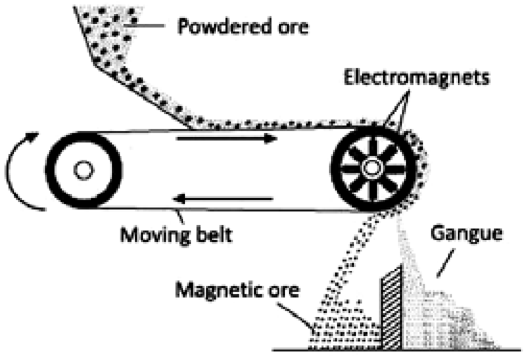
Activator: They activate the floating property of one of the component of the ore and help in the separation of different minerals present in the same ore ($CuSO_4$ is used as activator.

Depressants: These are used to prevent certain types of particles from forming the froth with air bubbles, e.g., NaCN can be used as a depressant in the separation of ZnS and PbS ores. KCN is another depressant.

Collectors: It increases the non-wettability of ore particles by water, e.g., pine oils, xanthates and fatty acids.

b. **Electro Magnetic Separator*:*** A magnetic separator consists of a belt moving over two rollers, one of which is magnetic. The powdered ore is dropped on the belt at the other end. Magnetic portion of the ore is attracted by the magnetic roller and falls near to the roller while the non-magnetic impurity falls farther off.

   Separation of transition metal ores such as Magnetite (Fe_3O_4), Pyrolusite (MnO_2) and Chromite (FeO,Cr_2O_3) from unwanted gangue can be performed by this method.



c. **Chemical Method (Leaching):** Leaching is the process in which the ore is concentrated by chemical reaction with a suitable reagent which dissolves the ore but not the impurities, e.g., bauxite is leached with a hot concentrated solution of NaOH which dissolves aluminium while other oxides (Fe_2O_3, TiO_2, SiO_2), remain undissolved and noble metals (Ag and Au) are leached with a dilute aqueous solution of NaCN or KCN in the presence of air.

$$\underset{\text{Bauxite}}{Al_2O_3 . 2H_2O} + NaOH \longrightarrow \underset{\text{Sodium meta aluminate}}{2\ NaAlO_2} + 3H_2O \quad \text{or } [NaAl(OH)_4]$$

$$\underset{\text{Argentite}}{Ag_2S} + 4NaCN \longrightarrow \underset{\text{Sodium.argento cyanide}}{2Na[Ag(CN)_2]} + Na_2S$$

3. **Conversion to Oxides (oxidation of ore):**
   a. **Calcination:** It is a process of heating the ore in a limited supply of air below its melting point. The process involves

   - removal of impurities,
   - removal of moisture,
   - removal of volatile impurities,
   - the impurities like sulphur, phosphorous, arsenic are removed as their oxides,
   - Decomposition of any carbonate ore into oxide.

Expulsion of CO_2 from carbonate

$$ZnCO_3 \longrightarrow ZnO + CO_2$$

$$CaCO_3.MgCO_3 \longrightarrow CaO + MgO + 2CO_2$$

Removal of water of hydration

$$Al_2O_3.2H_2O \longrightarrow Al_2O_3 + 2H_2O$$

$$Fe_2O_3.xH_2O \longrightarrow Fe_2O_3 + xH_2O$$

b. **Roasting:** It is the process of heating the ore in the excess supply of air below its melting point. This process is employed when oxidation of the ore is required. As a result of roasting,

- moisture is driven away,
- volatile impurities are removed,
- the impurities like sulphur, phosphorous, arsenic are removed as their oxides,
- the ore undergoes oxidation to form metal oxide or sulphate.

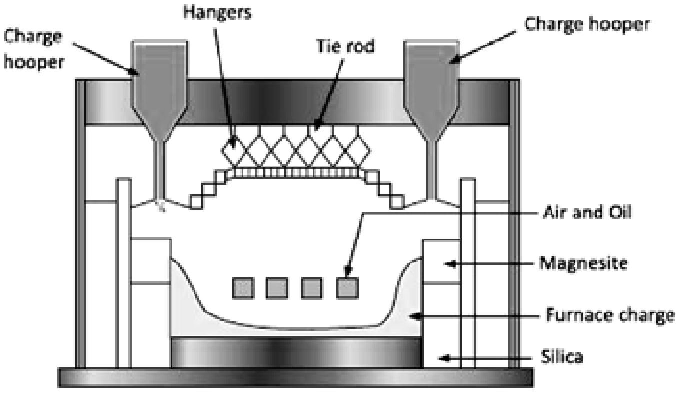
$$2PbS + 3O_2 \longrightarrow 2PbO + 2SO_2$$

$$2ZnS + 3O_2 \longrightarrow 2ZnO + SO_2$$

$$2Cu2S + 3O_2 \longrightarrow 2Cu2O + 2SO_2$$

It is advantageous to roast a sulphide ore to the oxide because metal oxides can be reduced to metal more easily than sulphides.

Both calcinations and roasting processes are carried out in a special type of furnace called reverberatory furnace. The SO_2 *gas produced during roasting is utilized in manufacturing sulphuric acid (*H_2SO_4*)*



A section of a modern reverberatory furnace

4. **Reduction(or electronation):** After the preliminary treatment, the ore may be subjected to reduction process by any one of the following methods depending upon its nature.

Smelting (Reduction with carbon): In this process, the roasted or calcined ore is mixed with suitable quantity of coke or charcoal (which acts as a reducing agent) and is heated to a high temperature above its melting point. During melting an additional reagent is also added to the ore to remove the impurities still present in the ore. This additional reagent is called flux. Flux combines with the impurities to form a fusible product called slag.

Flux + gangue ——→ Slag.

Acidic fluxes like silica, borax etc are used when the gangue is basic such as lime or other metallic oxides like MnO, FeO, etc

Basic fluxes like CaO, lime stone ($CaCO_3$), magnesite ($MgCO_3$), hematite (Fe_2O_3) etc are used when the gangue is acidic like silica, P_4O_{10} etc.

The selection of flux depends upon the nature of impurities. If impurities are acidic in nature, the flux is basic,i.e., lime (CaO). On the other hand, for basic impurities, an acidic flux, silica (SiO_2) is used. For example,

$$\underset{\text{Acidic impurity}}{P_4O_{10}} + \underset{\text{Basic flux}}{6\,CaO} \longrightarrow \underset{\text{Slag}}{2Ca_3(PO_4)_2}$$

$$\underset{\text{Basic impurity}}{CaO} + \underset{\text{acidic flux}}{SiO_2} \longrightarrow \underset{\text{Slag.}}{CaSiO_3}$$

The metal oxide, during the reduction process gets reduced to metal.

$$Fe_2O_3 + 3C \xrightarrow{823K} 2Fe + 3CO$$

$$ZnO + C \xrightarrow{1600K} Zn + CO$$

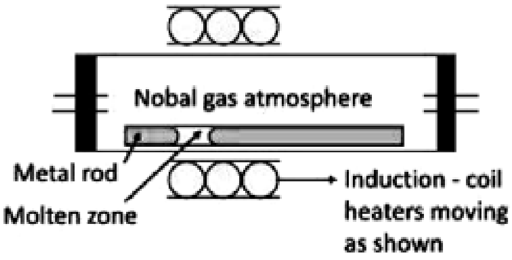
$$SnO_2 + 2C \xrightarrow{1473\text{-}1573K} Sn + 2CO.$$

The process of reduction with Carbon is carried out in the blast furnace

Reduction of metal oxide involves heating of metal in presence of suitable reagent Coke or $CO_{2.}$

5. **Refining of metals:** The metals obtained by the application of above reduction methods from the concentration ores are usually impure. The impure metal is thus subjected to some purifying process known as refining in order to remove undesired impurities. Various processes for this are:

Zone refining (Fractional crystallization): This method is employed for preparing extremely pure metals. This method is based upon the principle that when a molten solution of the impure metal is allowed to cool, the pure metal crystallizes out while the impurities remain in the melt. For example, Germanium, Silicon and Gallium for being used in semiconductors are purified by this method.



Electro-refining: In this method, the impure metal is converted into a block which forms the anode while cathode is a rod or plate of pure metal. These electrodes are suspended in an electrolyte which is the solution of a soluble salt of the metal usually a double salt of the metal. When electric current is passed, metal ions from the electrolyte are deposited at the cathode in the form of pure metal while an equivalent amount of metal dissolves from the anode and goes into the electrolyte solution as metal ion. The soluble impurities present in the crude metal anode go into the solution while the insoluble impurities settle down below the anode as anode mud.

Cupellation: It is used for refining of metals containing impurities of other metals e.g. traces of lead are removed from silver by heating impure silver with a blast of air in a **Cupel** (an oval shaped pan made up of bone ash) in which lead is oxidized to lead oxide (PbO) and being volatile PbO escapes leaving behind pure silver.

Poling: Poling is used for refining of such metals which contain impurities of its own oxide. In this process, the molten impure metal is stored with green wooden poles. At the high temperature of the molten metal, wood liberates methane which reduces the oxide of the metal to free metal.

$$3Cu_2O + CH_4 \longrightarrow 6Cu + 2H_2O + CO$$

Van-Arkel Method: In this method, the metal is converted into its volatile unstable compound such as iodide leaving behind the impurities. The unstable compound thus formed is decomposed to get the pure metal.

$$Ti(s) + 2I_2(s) + \xrightarrow[540K]{} TiI_4(g) \xrightarrow[Ti(s)]{1700K} Ti + 2I_2(g)$$

Extraction of Aluminium

Important Ores of Aluminium: Bauxite: $Al_2O_3 \times 2H_2O$ Cryolite: Na_3AlF_6

Feldspar: $K_2OAl_2O_3.6SiO_2$ or $KAlSi_3O_8$ Mica: $K_2O \times 3Al_2O_3.6SiO_2.2H_2O$

Corundum: Al_2O_3 Alumstone or Alunite: $K_2SO_4.Al_2(SO_4)_3.4Al(OH)_3$

Flow sheet for extraction of aluminium

Bauxite $Al_2O_3.2H_2O$

↓

Concentration of ore is done by leaching .Bauxite is treated with NaOH .Following reaction takes place:-

Al_2O_3 +2NaOH + 3 H_2O $\longrightarrow$ 2 Na [Al (OH) $_4$] and impurities of Fe_2O_3, TiO2 &SiO_2 are removed.

↓

Na [Al $(OH)_4$] ,then reacts with CO_2 then pure Alumina is obtained.

$Na[Al(OH)_4] + 2CO_2 \rightarrow Al_2O_3.xH_2O + 2NaHCO_3$

↓

Electrolytic reduction of pure alumina takes place in iron box (cathode) with cryolite (Na_3AlF_6) & fluorspar CaF_2.Graphide rods act as anode. Following reactions take place:-

At cathode:- $Al^{3+} + 3e \rightarrow Al$, At Anode:- $2O^{2-} \rightarrow O_2 + 4e$

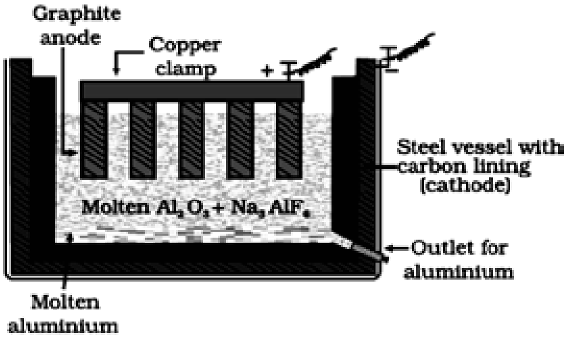
↓

By this process 98.8% pure Aluminum is obtained.

Refining of Aluminium: Electrolysis of fused pure alumina (Hall & Herolt Method)

The graphite rods dipped in pure aluminium and Cu–Al alloy rod at the bottom in the impure aluminium work as conductors. On electrolysis, aluminium is deposited at cathode from the middle layer and equivalent amount of aluminium is taken up by the middle layer from the bottom layer (impure aluminium). Therefore, aluminium is transferred from bottom to the top layer through middle layer while the impurities are left behind. Aluminium thus obtained is 99.98% pure.

The addition of cryolite (Na_3AlF_6) and fluorspar (CaF_2) makes alumina a good conductor of electricity and lowers its Fusion temperature from 2323 to 1140 K. the reaction taking place during electrolysis.



$AlF_3 \longrightarrow Al^{3+} + 3F^-$
At cathode: $Al^{3+} + 3e^- \longrightarrow Al$
At the same time, Al_2O_3 dissociates into Al^{3+} and O^{2-}.

Since 'O' is below F in the electronegativity series, O^{2-} ions are selectively discharged at the anode as oxygen.

$2\ Al_2O_3 \longrightarrow 4\ Al^{3+} + 6\ O^{2-}$

At anode: $6\ O^{2-} \longrightarrow 3\ O_2 + 12\ e^-$

The oxygen liberated at anode combines with carbon of anode to form CO and CO_2 so anode, which burn away have to be replaced periodically. Molten Al collects at the bottom of cell (99% pure)

6.1 EXTRACTION OF IRON

Important Ores of Iron: Hematite Fe_2O_3 (red oxide of iron) Limonite $Fe_2O_3 \times 3H_2O$ (hydrated oxide of iron) Magnetite Fe_3O_4 (magnetic oxide of iron)

Flow sheet for extraction of iron

Iron ore(Magnetite Fe_3O_4) (Haematite Fe_2O_3)

↓

Concentration is done by Gravity separation followed by magnetic separation

↓

Calcination &Roasting i.e. Ore+Air+Heat$\rightarrow$Moisture,CO_2,SO_2, As_2O_3 removed And FeO oxidized to Fe_2O_3

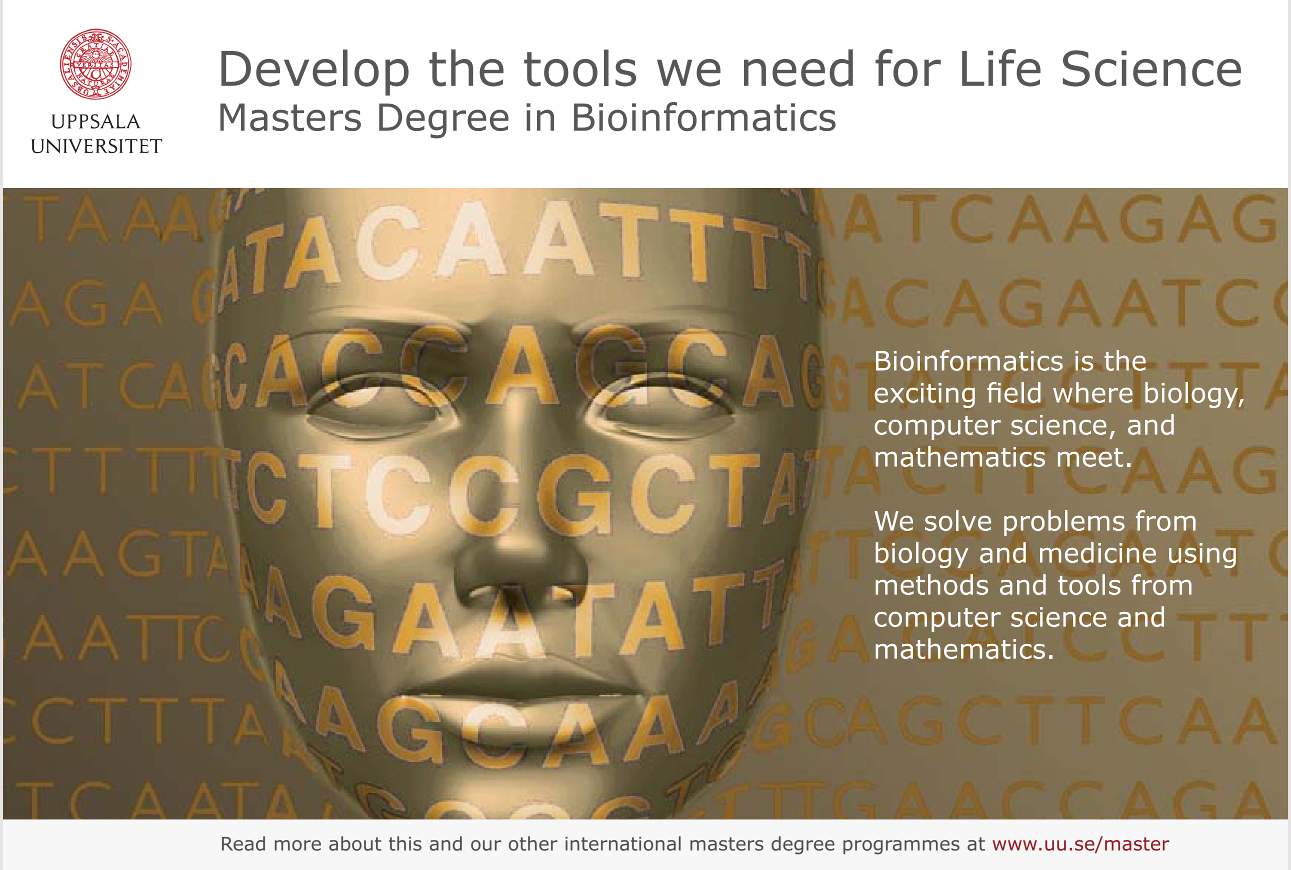
↓

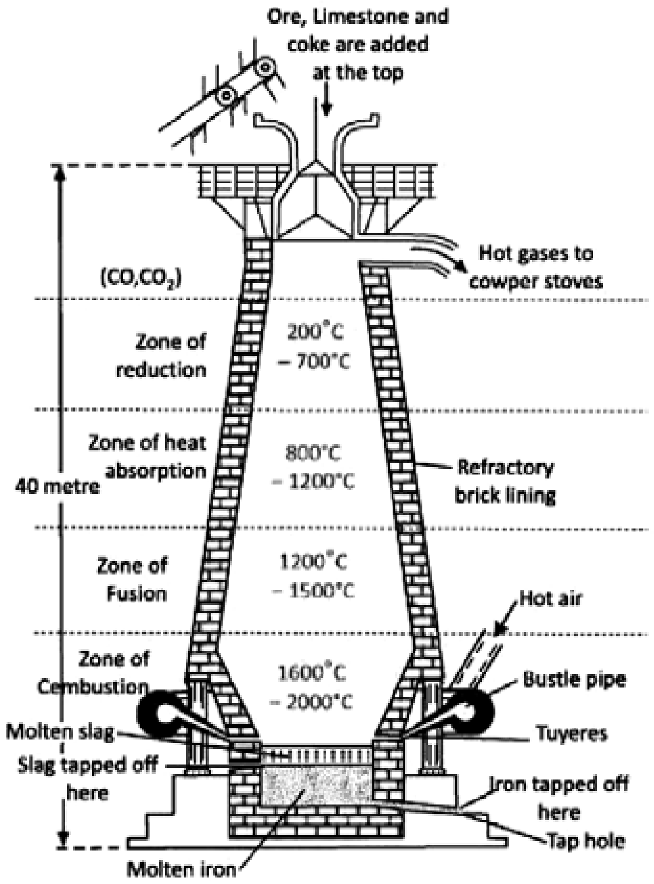
Smelting of charge i.e. mixture of ore, coke & $CaCO_3$ takes place in long BLAST FURNACE. Following reaction take place at different zones:-

(shown below)

↓

Pig iron is obtained, which is re-melted and cooled then cast iron is obtained





Pig Iron: - It contains Fe 93-95%, Carbon 2.5-5%, and Impurities 3%.

Cast Iron: - It contains Fe 99.5-99.8%, Carbon 0.1-0.2% Impurities 0.3%.

Spongy iron: - Iron formed in the zone of reduction of blast furnace is called spongy iron. It contains impurities of C, Mn , Si, etc.

Varieties of Iron

Pig or Cast Iron

» Most impure form

» 2.5 – 5 % carbon and other impurities like Mn, Si, S and P

» It is hard and Brittle, hence cannot be moulded by hammering

Wrought Iron

» Purest form of iron

» 0.1-2.5% carbon

» It is ductile soft and maleable

Steel

» It is between pig iron and wrought iron

» 0.25 to 2% carbon

Extraction of Copper

Ores of Copper: Copper glance (chalcocite): Cu_2S Copper pyrites (Chalcopyrites): $CuFeS_2$, Malachite $Cu(OH)_2 .CuCO_3$ Cuprite or Ruby copper: Cu_2O Azurite : $Cu(OH)_2 \times 2CuCO_3$

Flow sheet for extraction of copper

Copper Pyrites $CuFeS_2$

↓

Concentration is done by Froth floatation process

Powdered ore + water + pine oil + air → Sulphide ore in the froth

↓

Roasting in presence of air. following reactions take place:-

$S + O_2 \rightarrow SO_2$, $4As + 3O_2 \rightarrow 2As_2O_3$, $2CuFeS_2 + O_2 \rightarrow Cu_2S + 2FeS + SO_2$

↓

Smelting in small blast furnace of a mixture of Roasted ore, coke, and silica.

$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$, $FeO + SiO_2 \rightarrow FeSiO_3$(slag)

↓

A mixture of Cu_2S, FeS & silica is obtained from blast furnace known as Copper matte

↓

Bessemerisation of copper matte is done in Bessemer converter in presence of air. Following reactions take place:-

$2FeS + 3O_2 \rightarrow 2FeO + 2SO_2$, $FeO + SiO_2 \rightarrow FeSiO_3$ (slag),

$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$, $2Cu_2O + 2Cu_2S \rightarrow 6Cu + SO_2$

↓

Melted copper is cooled, and then SO_2 is evolved. such copper is known as BLISTER COPPER (98%Cu+2% impurities)

↓

Electrolytic refining

Anode = impure copper

Cathode = pure copper

Electrolyte = $CuSO_4 + H_2SO_4$

↓

Pure copper at cathode = 99.9% pure

Extraction of zinc

Important ores of Zn:- Zinc blende - ZnS, Calamine- $ZnCO_3$, and Zincite – ZnO. ZnS is commercially important ore of Zn. Various stages involved in the extraction of Zn from ZnS are as following:-

1. ***Concentration of ore:-***It is concentrated by Froth flotation process followed by gravity separation process.
2. ***Roasting:-*** The concentrated ore is roasted in presence of air. Following reactions take place.

   $$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2$$

   The mass obtained during roasting is porous and is called porous ***clinker.***
3. ***Reduction of ZnO to Zn: -*** ZnO is made into bricketts with coke and clay and heated at 1163K.Zn formed distills off and is collected by rapid cooling of zinc vapours.

   $$ZnO + C \rightarrow Zn + CO$$

4. ***Purification:-***Zinc is purified by electrolytic refining. In this process, Impure Zinc is anode and cathode is of pure thin sheet of Zinc. The electrolyte is $ZnSO_4$ solution containing a little of dil.H_2SO_4. On passing electric current, pure zinc get deposited at the cathode.

7 P BLOCK ELEMENTS

The group number 13 to 18, in which the last electrons or the valence electrons enter in the *p*-orbital are called the *p*-block elements. The general electronic configuration of *p*-block elements is $ns^2\ np^{1-6}$

Nitrogen family

Commonly Called as **Pnicogens** and their Compounds are **Pnictides**:

The elements of group 15: nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi) having general electronic configuration $ns^2\ np^3$, are known as the nitrogen family. The *s*-orbital in these elements is completely filled and *p*-orbitals are half-filled, making their electronic configuration extra stable.

Electronic configuration of nitrogen family

Element	N	P	As	Sb	Bi
Config.	$[He]2s^22p^3$	$[Ne]3s^23p^3$	$[Ar]\ 3d^{10}4s^24p^3$	$[Kr]4d^{10}5s^25p^3$	$[Xe]4f^{14}5d^{10}6s^26p^3$

General properties of nitrogen family

Atomic and ionic radii: Covalent and ionic radii increase down the group. There is appreciable increase in covalent radii from N to P. However, from As to Bi only a small increase in covalent radius is observed due to presence of completely filled *d* or *f*-orbitals in heavy elements.

Ionization enthalpy: Ionization enthalpy goes on decreasing down the group due to the increase in atomic size. Due to the stable electronic configuration with half filled *p*-orbital, group 15 elements have higher ionization energy than group 16 elements. Also due to the smaller size of the elements, the group 15 elements have higher ionization energy than group 14 elements.

Oxidation states: The common oxidation states are +3, +5, –3. The tendency to show –3 oxidation state decreases down the group due to increased size and hence decreased electronegativity. The stability of +5 oxidation state decreases whereas stability of +3 oxidation state increases due to inert pair effect. Nitrogen and phosphorus with oxidation states from +1 to +4 undergo oxidation as well as reduction in acidic medium. This process is called disproportionation.

For example: $3HNO_2 \rightarrow HNO_3 + H_2O + 2NO$

Anomalous properties of nitrogen

Nitrogen differs from the rest of the members of this group due to its smaller size, high electronegativity, 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 pπ-pπ multiple bonds with itself and with other elements like C and O. Other elements of this group do not form pπ-pπ 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 *dπ*– pπ bond or *dπ*–*dπ* bond, While Phosphorus and arsenic can form *dπ*–*dπ* bond with transition metals and with C and O.

Chemical properties of nitrogen family

Reactivity towards hydrogen: Form hydrides of formula EH_3

Structure pyramidal

Bond angle decreases down the group due to decrease in electro negativity.

Stability decreases due to increase in size.

Reducing character increases due to decrease in stability. NH_3 is a mild reducing agent while BiH_3 is strongest.

Basic character decreases in the order: $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.

Reactivity towards oxygen

Form two types of oxides of the formula: E_2O_3 and E_2O_5. The oxide in the higher oxidation is more acidic than that of lower oxidation state. Acidic character decreases down the group.

N_2O_3, P_2O_3 = Acidic

As_2O_3, Sb_2O_3 = Amphoteric

Bi_2O_3 = Basic oxide

Reactivity towards halogens

They form halides of the formula: EX_3 and EX_5.

Nitrogen does not form pentahalide due to absence of the d orbitals.

Pentahalides are more covalent than trihalides.

All trihalides except those of nitrogen are stable.

Among nitrogen halides only NF_3 is stable.

Trihalides except BiF_3 are predominantly covalent.

Reactivity towards metals

All the group 15 elements react with metals to form binary compounds in –3 oxidation state.

Ninitrogen (N_2)

Preparation: N_2 is produced commercially by the liquefaction of air followed by fractional distillation. Liquid N_2 distills out first leaving behind liquid oxygen.

In the laboratory, dinitrogen is prepared by treating an aqueous solution of ammonium chloride with sodium nitrite.

$NH_4Cl\ (aq) + NaNO_2\ (aq) \rightarrow N_2\ (g) + 2H_2O\ (l) + NaCl\ (aq)$

Small amounts of NO and HNO_3 formed as impurities can be removed by passing the gas through aqueous H_2SO_4 containing $K_2Cr_2O_7$.

$(NH_4)_2Cr_2O_7 \rightarrow N_2 + 4\ H_2O + Cr_2O_3$

Very pure nitrogen can be obtained by the thermal decomposition of sodium or barium azide

$Ba\ (N_3)_2 \rightarrow Ba + 3N_2$

1. By heating a mixture of NH_4Cl and $NaNO_2$. N_2 is collected by the downward displacement of water.

$$NH_4Cl + NaNO_2 \xrightarrow{\Delta} NH_4NO_2 + NaCl ;$$

$$NH_4NO_2 \xrightarrow{\Delta} N_2\uparrow + 2H_2O$$

2. By treating an aqueous solution of ammonium chloride with sodium nitrate. It is laboratory method of preparation.

$$NH_4Cl_{(aq)} + NaNO_{2(aq)} \longrightarrow N2(g) + H_2O_{(l)} + NaCl_{(aq)}$$

3. By heating ammonium dichromate:

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2\uparrow + 4H_2O + Cr_2O_3$$

4. By oxidation of ammonia
5. By reaction of ammonia with calcium hypochlorite or Br_2

$$4NH_3 + 3Ca(OCl)_2 \xrightarrow{\Delta} 3\ CaCl_2 + 2N_2 + 6H_2O$$

6. By passing ammonia over heated cupric oxide or PbO :

$$2NH_3 + 3CuO \xrightarrow{\Delta} N_2\uparrow + 3Cu + 3H_2O$$

7. Very pure nitrogen;

$$Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2$$

Sodium azide also gives N_2 on heating.

Industrial methods of preparation

1. **From liquefied air:** The B.P of N_2 is –196 °C and that of oxygen is –183 °C and hence they can be separated by fractional distillation.
2. **From producer gas from furnaces:** Producer gas is a mixture of CO and N_2. When the mixture of CO and N_2 is passed over heated CuO, the CO gas is oxidized to CO_2 which is absorbed in alkalis & N_2 remains which is collected in gas cylinders.

Physical Properties

1. N_2 is a colorless, odorless gas insoluble in water.
2. It is non-polar covalent and neutral molecule.
3. It is neither combustible nor a supporter of combustion.

Chemical Properties

4. It is absorbed by heated Mg and Al. The nitrides formed thus react with water to form NH_3.

$$3Mg + N_2 \longrightarrow Mg_3N_2\ (+\ 6H_2O) \longrightarrow 3Mg(OH)_2 + 2NH_3\uparrow$$

$$2Al + N2 \longrightarrow 2AlN\ (+\ 6H_2O) \longrightarrow 2Al\ (OH)_3 + 2NH_3\uparrow$$

5. Reaction with H_2: At 200 atm and 500 °C, and in the presence of iron catalyst and molybdenum promoter, N_2 combines with H_2 reversibly to form ammonia. The process is called **Haber's Process** and is the industrial method of manufacturing ammonia. The reaction is exothermic.

   $N_2 + 3H_2 \longrightarrow 2NH_3$

6. Reaction with oxygen: When air free from CO_2 and moisture is passed over an **electric arc at about 2000 K**, nitric oxide is formed. This reaction is endothermic.

   $N_2 + O_2 \longrightarrow 2NO$

7. Reaction with CaC_2 and BaC_2: At 1100 °C, these carbides react with N_2 forming $CaCN_2$ and $Ba(CN)_2$ respectively.

   $CaC_2 + N_2 \xrightarrow{\Delta} CaCN_2$ (nitrolim, a fertilizer) + C

   $BaC_2 + N_2 \xrightarrow{\Delta} Ba(CN)_2$

   $CaCN_2$ reacts with H_2O in the soil to produce NH_3 gas. NH_3 gas is converted (by the nitrating bacteria present in soil) into nitrates.

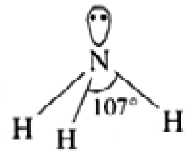
   (The nitrates are readily absorbed by the plants and meet their requirement of the element nitrogen.)

   Uses: Some important uses of dinitrogen are as follows:
   Liquid N_2 is used as a refrigerant
   It is used to provide inert atmosphere in iron and steel industry
   It is used in the manufacture of HNO_3 and NH_3.

Ammonia(NH3)

Ammonia molecule is trigonal pyramidal with nitrogen atom at the apex. It has 3 bond pairs and 1 lone pair. N is sp^3 hybridized.

Ammonia is highly soluble in water and is weakly basic.



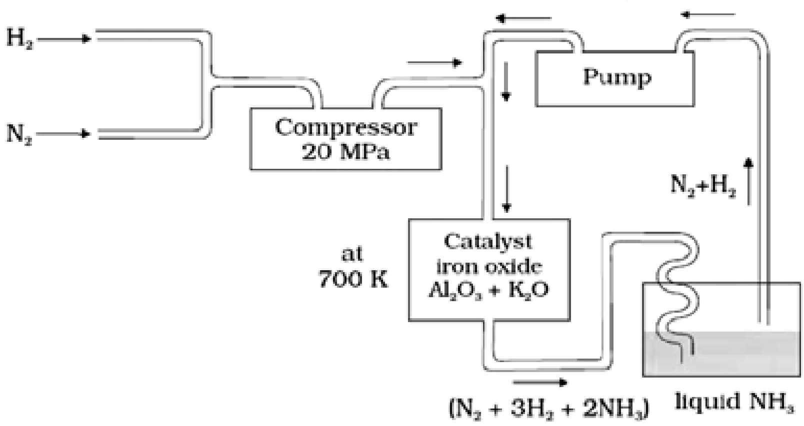
$NH_3(aq) + H_2O(l) \rightleftarrows NH_4^+(aq) + OH^-(aq)$

Preparation: Ammonia (NH_3) is manufactured on the commercial scale by Haber's process.

$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)\ \Delta_f H^\circ = -46.1 kJ\ mol^{-1}$

Pressure = 200×10^5 Pa Temperature = 773 K

Catalyst = Iron oxide with small amounts of K_2O and Al_2O_3



Flow chart of Habers process

In laboratory, ammonia is prepared by

1. By the action of any base or alkali on any ammonium salt:

   $NH_4Cl + NaOH \rightarrow NaCl + H_2O + NH_3$

   $(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3\uparrow + Na_2SO_4 + 2H_2O$

   $NH_4NO_3 + NaOH \longrightarrow NH_3\uparrow + NaNO_3 + H_2O$

   $(NH_4)_3PO_4 + 3NaOH \longrightarrow 3NH_3\uparrow + Na_3PO_4 + 3H_2O$

   $(NH_4)_2SO_4 + CaO \longrightarrow 2NH_3\uparrow + CaSO_4 + H_2O$

   This is a general method and is used as a test for ammonium salts.

2. By the hydrolsis of metal nitrides like AlN or Mg_3N_2.

   $AlN + NaOH + H_2O \longrightarrow NaAlO_2 + NH3$

3. From organic amides: When an organic amide is heated with NaOH solution ammonia is evolved.

   $CH_3CONH_2 + NaOH \longrightarrow CH_3COONa + NH_3\uparrow$

Properties

Ammonia is a colorless gas with pungent smell. It is highly soluble in water because of its ability to form inter molecular hydrogen bond with water. Liquid ammonia has high melting and boiling points because of inter molecular hydrogen bonding. 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.

$$NH_{3\ (g)} + H_2O_{(l)} \rightarrow NH_4{}^+{}_{(aq)} + OH^-{}_{(aq)}$$

As a weak base, it precipitates the hydroxides of many metals from their salt solutions.

For example,

$$2FeCl_{3\ (aq)} + 3NH_4OH_{\ (aq)} \rightarrow Fe_2O_3.xH_2O_{\ (s)} + 3NH_4Cl_{\ (aq)}$$

$$ZnSO_{4\ (aq)} + 2NH_4OH_{\ (aq)} \rightarrow Zn(OH)_{2\ (S)} + (NH_4)_2SO_{4\ (aq)}$$

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 Cu^{2+}, Ag^+ etc. So it is used for the detection of these metal ions.

$$Cu^{2+}{}_{(aq)} + 4\ NH_{3(aq)} \rightarrow [Cu(NH_3)_4]^{2+}{}_{(aq)}$$

(blue) (deep blue)

$$Ag^+{}_{(aq)} + Cl^-{}_{(aq)} \rightarrow AgCl_{\ (S)}$$

(colourless) (white ppt)

$$AgCl + 2NH_{3\ (aq)} \rightarrow [Ag\ (NH_3)_2]Cl_{\ (aq)}$$

(white ppt) (colourless)

Uses: Some important uses of ammonia are:
It is used as a refrigerant
It is used in the manufacture of nitric acid,
It is used in the production of nitrogenous fertilizers.

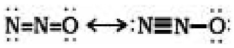
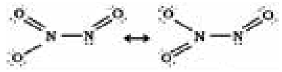
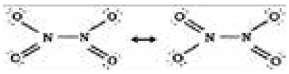
Oxides of nitrogen

Nitrogen forms a total of five oxides from +1 oxidation state to +5 oxidation state. The five oxides of nitrogen are: N_2O, NO, N_2O_3, NO_2 or N_2O_4, N_2O_5. All these oxides of nitrogen exhibit *pπ-pπ* multiple bonding between nitrogen and oxygen.

The following table gives the brief information of various oxides of nitrogen:

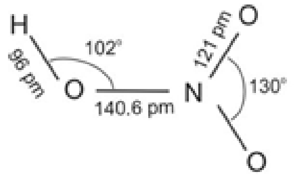
Name	Formula	Colour	Remarks
Nitrous oxide	N_2O	Colourless(g)	Neutral, + 1 oxidation state
Nitric oxide	NO	Colourless(g)	Neutral, + 2 oxidation state
Dinitrogen trioxide	N_2O_3	Dark blue (s)	Acidic, + 3 oxidation state
Nitrogen dioxide	NO_2	Brown (g)	Acidic, + 3 oxidation state
Dinitrogen tetroxide	N_2O_4	Colourless (s)	Extensively dissociated to NO_2 as gas and partly dissociated as liquid, acidic, +4 oxidation state
Dinitrogen pentoxide	N_2O_5	Colourless (s)	Unstable as gas; ionic solid NO_2^+, NO_3^-, acidic, +5 oxidation state

Structure of oxides of nitrogen

Formula	Oxidation state	Resonance structure	Common Methods of preparation
N_2O	+1		$NH_4NO_3 \xrightarrow{Heat} N_2O+2H_2O$
NO	+2		$2NaNO_2+2FeSO_4+3H_2SO_4 \rightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O+2NO$
N_2O3	+3		$2NO+N_2O_4 \xrightarrow{250K} 2N_2O_3$
NO_2	+4		$2Pb(NO_3)_2 \xrightarrow{673K} 4NO_2+ 2PbO$
N_2O_4	+4		$2NO_2 \underset{Heat}{\overset{Cool}{\rightleftharpoons}} N_2O_4$
N_2O_5	+5		$4HNO_3+P_4O_{10} \rightarrow 4HPO_3+2N_2O_5$

Nitric acid, HNO_3

Nitric acid is the most important oxoacid formed by nitrogen. It is a colourless liquid. In the gaseous state, HNO_3 exists as a planar molecule with the structure as shown below:



Preparation

Nitric acid is manufactured by the catalytic oxidation of ammonia in Ostwald process.

$$4NH_3(g) + 5O_2(g) \xrightarrow[500\,K]{PtRh} 4N0(g) + 6H_2O(g)$$
$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$
$$3NO_2(g) + H_2O(1) \rightarrow 2HNO_3(aq) + NO(g)$$

In laboratory, nitric acid can be prepared by the heating $NaNO_3$ or KNO_3 with conc. H_2SO_4
$MNO_3 + H_2SO_4 \rightarrow MHSO_4 + HNO_3$

Like $KNO_3 + H_2SO_4 \rightarrow KHSO_4 + HNO_3$

$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3$

Properties: It is a colorless liquid.

Laboratory grade nitric acid contains ~ 68% of the HNO_3 by mass and has a specific gravity of 1.504.

In aqueous solution, nitric acid behaves as a strong acid giving hydronium and nitrate ions.

$$HNO_3(aq) + H_2O(l) \rightarrow H_3O^+(aq) + NO_3^-(aq)$$

Concentrated HNO_3 is a strong oxidizing agent and attacks most metals except noble metals. Cr, Fe and Al do not dissolve in conc. HNO_3 due to the formation of a passive film of oxide on the surface.

The oxidizing action of HNO_3 is depends on its concentration and the nature of the reducing agent. The principal product of reduction of HNO_3 is NO when it is dilute but NO_2 when it is concentrated.

For example:

$3Cu + 8HNO_3\ (dil) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

$Cu + 4HNO_3\ (conc) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

Brown ring test for the detection of nitrates: Addition of dilute ferrous sulphate solution (Fe^{2+}) to an aqueous solution containing nitrate ion, and then carefully adding concentrated sulphuric acid along the sides of the test tube results in the formation of a brown colored complex $Fe[(H_2O)_5(NO)]SO_4$

$NO_3^- + 3Fe^{2+} + 4H^+ \rightarrow NO + 3Fe^{3+} + 2H_2O$

$[Fe(H_2O)_6]^{2+} + NO \rightarrow \underset{\text{(brown)}}{[Fe\ (H_2O)_5\ (NO)]^{2+}} + H2O$

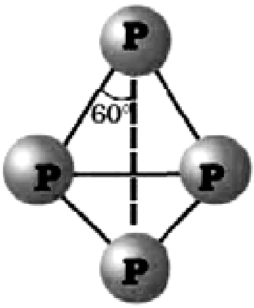
Uses: Some important uses of nitric acid are:

1. HNO_3 is used in the manufacture of fertilizers.
2. It is used in the formation of explosives, dynamites, TNT, etc.
3. It is also used in the etching of metals.

Phosphorus

Phosphorus is an essential constituent of elements and plants. It has many allotropic forms, the important ones are:
White phosphorus
Red phosphorus
Black phosphorus

Properties of white phosphorus or yellow phosphorus (P_4)

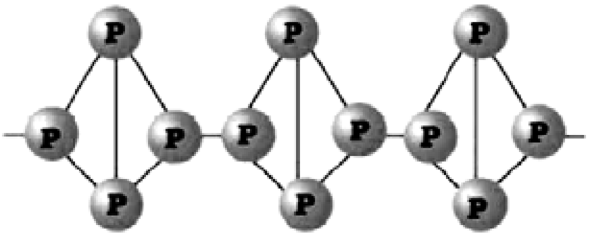


It is white-to-transparent
Soft waxy solid
Its density is 1.8 g/cc at 20°C.
Its mp and bp are 44°C and 287°C respectively.
It is soluble in CS_2 but insoluble in water
It glows in dark due to slow oxidation producing yellowish-green light. This phenomenon is called phosphorescence

$P_4 + 5O_2 \rightarrow P_4O_{10}$

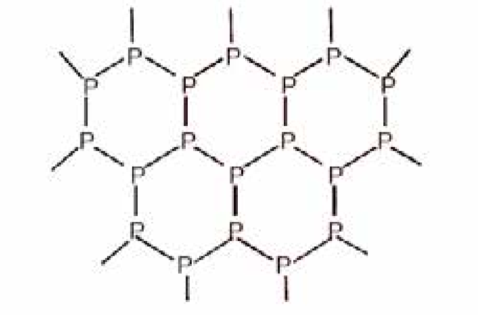
White phosphorus is poisonous
It turns yellow after some time; so is called yellow phosphorus
It undergoes oxidation in the presence of air which slowly raises its temperature and due to its low ignition temperature (~ 30°C) after a few moments it catches fire spontaneously. Due to this reason, it is stored under water.
More reactive than the other solid phases due to the angular strain in the P_4 molecule
Discrete tetrahedral P_4 molecules

Properties of Red phosphorus



Prepared by heating white phosphorus at 573K in an inert atmosphere
It is a red crystalline solid
Having a density of 2.2 g/cc
Does not dissolve in liquid CS_2
It does not catch fire at room temperature because its ignition temperature is 260°C.
It is a polymeric substance forming linear chains like this.
Odourless, nonpoisonous and insoluble in H_2O
Less reactive than white phosphorus
Higher meltng point and density
Polymeric structure consisting of chains of P_4 units linked together

Properties of Black phosphorus



Prepared by heating white phosphorus at 200 °C under high pressure
It does not burn in air up to 400 °C.
It is a conductor of electricity and is insoluble in CS_2
Prepared by heating white phosphorus at 200 °C under high pressure
It has two forms- α-black phosphorus and β-black phosphorus.
Thermodynamically most stable, i.e., least reactive
It has an opaque monoclinic or rhombohedral crystal

Uses: Some important uses of phosphorus are:
It is used in the manufacture of fertilizers and food grade phosphates.
Elemental P is used the manufacture of organo-phosphorus compounds used as pesticides.

Phosphine (PH_3)

Phosphine is a highly poisonous, colourless gas and has a smell of rotten fish
Preparation: Phosphine is prepared by the reaction of calcium phosphide with water or dilute HCl

$Ca_3P_2 + 6H_2O \rightarrow 2PH_3 + 3Ca(OH)_2$

$Ca_3P_2 + 6HCl \rightarrow 2PH_3 + 3CaCl_2$

Properties

It is insoluble in water and is a weaker base than ammonia. Like ammonia, it gives phosphonium compounds with acids.

For example: $PH_3 + HBr \rightarrow PH_4Br$

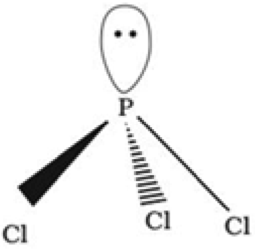
PH_3 is non-inflammable when pure but becomes inflammable owing to the presence of P_2H_4 or P_4 vapours.
In water, PH_3 decomposes in the presence of light to give red phosphorus and H_2.

Phosphorus halides

Phosphorus forms two types of halides, PX_3 (X = F, Cl, Br, I) and PX_5 (X = F, Cl, Br).

Phosphorus trichloride, PCl_3

It is a colorless oily liquid.



Preparation

It is obtained by passing dry chlorine over heated white phosphorus or by the action of thionyl chloride with white phosphorus.

$$P_4 + 6Cl_2 \rightarrow 4PCl_3$$

$$P_4 + 8\,SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$$

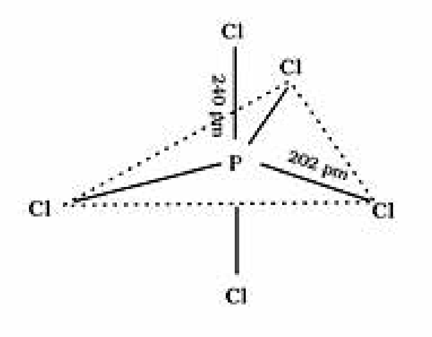
Properties: It has a pyramidal shape, in which phosphorus is sp^3 hybridized.
It gets hydrolysed in the presence of moisture.

$$PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$$

Phosphorus pentachloride, PCl_5

In gaseous and liquid phases, it is molecular and has a trigonal pyramidal structure. There are 2 kinds of bond lengths, 3 equatorial and 2 axial bonds.

In solid state exists as $[PCl_4]^+[PCl_6]^-$ containing tetra and hexa-coordinated phosphorous species.



Preparation

Phosphorus pentachloride is prepared by the reaction of white phosphorus with excess of dry chlorine or can be prepared by the action of SO_2Cl_2 on phosphorus.

$PCl_3 + Cl_2 \rightarrow PCl_5$

$P_4 + 10Cl_2 \rightarrow 4PCl_5$

$P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10\ SO_2$

Properties

PCl_5 is a yellowish white powder and in moist air, it hydrolyses to $POCl_3$ and finally gets converted to Phosphoric acid.

PCl_5 exist as PCl_5 molecule in gaseous or liquid state.

In the solid state it exists as an ionic solid, $[PCl_4]^+$ $[PCl_6]^-$ in which the cation, $[PCl_4]^+$ is tetrahedral and the anion, $[PCl_6]^-$ is octahedral.

PCl_5 reacts with organic compounds.

$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$

$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

Finely divided metals on heating with PCl_5 give corresponding chlorides.

$2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$

$Sn + 2PCl_5 \rightarrow SnCl_4 + 2PCl_3$

Hydrolysis:

$PCl_5 + H_2O \rightarrow POCl_3 + 2HCl$

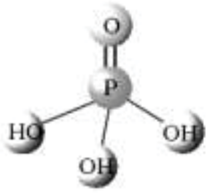
$PCl_5 + 3H_2O \text{ (excess)} \rightarrow H_3PO_3 + 2HCl$

Oxoacids of Phosphorus: Phosphorus forms a number of oxoacids. The important oxoacids of phosphorus with their formulas and the presence of some characteristic bonds in their structures are given in Table below

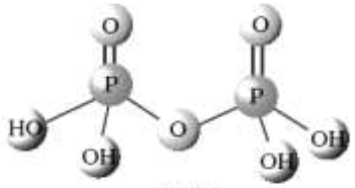
Name	Formula	Oxidation state of Phosphorus	Characteristic bonds and their number
Hypophosphorous (Phosphinic)	H_3PO_2	+1	One P – OH Two P – H One P = O
Orthophosphorous	H_3PO_3	+3	Two P – OH One P – H One P = O
Pyrophosphorous	$H_4P_2O_5$	+3	Two P – OH Two P – H Two P = O
Hypophosphoric	$H_4P_2O_6$	+4	Four P – OH Two P = O One P – P
OrthoPhosphoric	H_3PO_4	+5	Three P – OH One P = O
Pyrophosphoric	$H_4P_2O_7$	+5	Four P – OH Two P = O One P – O – P
Metaphosphoric	$(HPO_3)_n$	+5	Three P – OH Three P = O Three P – O – P

**Exists in polymeric forms only.*

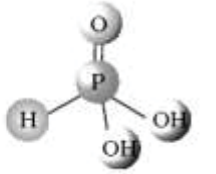
The compositions of the oxoacids are interrelated in terms of loss or gain of H_2O molecule or O-atom. The structures of some important oxoacids are given below:



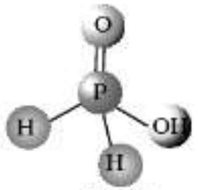
H_3PO_4
Orthophosphoric acid



$H_4P_2O_7$
Pyrophosphoric acid

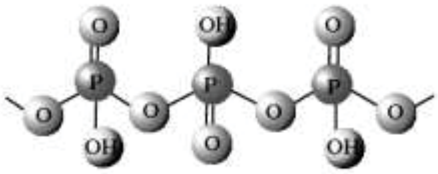


H_3PO_3
Orthophosphorous acid



H_3PO_2
Hypophosphorous acid

Cyclotrimetaphosphoric acid, $(HPO_3)_3$



Polymetaphosphoric acid, $(HPO_3)_n$

Oxygen family

The elements of group 15: oxygen (O), sulphur (S), selenium(Se), tellurium (Te) and polonium (Po) having general electronic configuration ns^2np^4, are known as the oxygen family. All these elements collectively are also known as chalcogens. Polonium is a radioactive element.

Element	Oxygen	Sulfur	Selenium	Tellurium	Polonium
Config.	$[He]2s^22p^4$	$[Ne]3s^23p^4$	$[Ar]\ 3d^{10}4s^24p^4$	$[Kr]4d^{10}5s^25p^4$	$[Xe]4f^{14}5d^{10}6s^26p^4$

General properties of oxygen family

Atomic and ionic radii: Due to increase in the number of shells, atomic and ionic radii increase from top to bottom in the group.

Ionization enthalpy: Due to the increase in size of the atoms the ionization enthalpy decreases down the group. IE1of group 16 elements is less than the IE_1 of group 15. This is because group 15 elements have extra stability due to half-filled *p*-orbitals.

Electron gain enthalpy: Due the compact nature of oxygen, it has less electron gain enthalpy than sulphur. After sulphur, the electron gain enthalpy decreases down the group.

Electronegativity: The electronegativity decreases down the group. This implies that the metallic character increases down the group from oxygen to polonium.

Melting and boiling point: The melting and boiling point increases with increase in atomic number down the group.

Oxidation states: Group 16 elements show −2, +2, +4, +6 oxidation states. The stability of −2 oxidation state decreases down the group due to increase in atomic size and decrease in electronegativity. O shows only −2 oxidation state except when it combines with the most electronegative F with which it shows positive oxidation states. S shows + 6 only with O and F.

Anomalous behavior of oxygen

Oxygen forms strong hydrogen bonding in H_2O which is not found in H_2S. H_2O is a liquid while H_2S is a gas, because in water due to the small size and high electronegativity of O, strong hydrogen bonding is present there.

Also, the maximum covalency of oxygen is four, whereas in a case of other elements of the group, the valence shells can be expanded and covalency exceeds four.

Reasons for the anomalous behaviour of oxygen are:

Small size and high electronegativity

Absence of d-orbitals

Reactivity towards hydrogen: All the elements of Group 16 form hydrides of the type H_2E

(E = S, Se, Te, Po).

Thermal stability: Thermal stability of group 16 elements decreases down the group.

$$H_2O > H_2S > H_2Se > H_2Te > H_2Po$$

This is because the H-E bond length increases down the group, hence the bond dissociation enthalpy decreases down the group.

Acidic nature: Due to the decreasing bond dissociation enthalpy, acidic character of group 16 elements increases down the group.

$$H_2O < H_2S < H_2Se < H_2Te$$

Reducing character: The reducing character also decreases down the group due to the decreasing bond dissociation enthalpy.

$$H_2O < H_2S < H_2Se < H_2Te < H_2Po$$

Reactivity towards oxygen: All group 16 elements form oxides of the type EO_2 and EO_3 Reducing character of dioxides decreases down the group. Acidity also decreases down the group. Besides EO_2 type, sulphur, selenium and tellurium also form EO_3 type oxides. Both types of oxides are acidic in nature.

Reactivity with halogens: Elements of Group 16 form a large number of halides of the type, EX_2 EX_4 and EX_6, where X is a halogen. The stability of halides decreases in the order

$F^- > Cl^- > Br^- > I^-$. This is because E-X bond length increases with increase in size. Among hexa halides, hexafluorides are the most stable because of steric reasons. Dihalides are *sp*^{3} hybridized and have tetrahedral geometry.

Oxygen

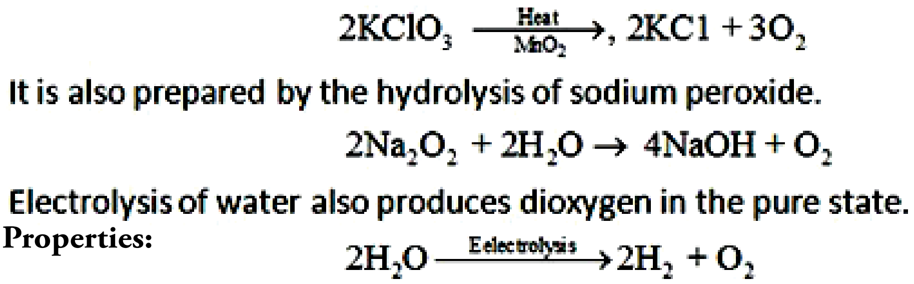
Oxygen is the first element of Group 16 with the electronic configuration of $1s^2$ $2s^2$ $2p^4$ in the ground state. Oxygen has two allotropes: dioxygen (O_2) and trioxygen or ozone (O_3).

Dioxygen (O_2)

Oxygen usually exists in the form of dioxygen.

Preparation

Dioxygen is prepared in the laboratory by thermal decompositions of oxygen rich compounds such as $KClO_3$,



$$2KClO_3 \xrightarrow[MnO_2]{Heat}, 2KCl + 3O_2$$

It is also prepared by the hydrolysis of sodium peroxide.

$$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$$

Electrolysis of water also produces dioxygen in the pure state.

$$2H_2O \xrightarrow{Eelectrolysis} 2H_2 + O_2$$

Properties:

Properties

Oxygen is a colorless, odorless and is a highly reactive tasteless gas.

Due to the presence of $p\pi - p\pi$ bonding, O_2 is a discrete molecule and intermolecular forces are weak van der Waals forces, hence, O_2 is a gas.

Dioxygen combines with metals and non-metals to form binary compounds called oxides.

Examples are:

$$2Ca + O_2 \rightarrow 2CaO$$

$$P_4 + 5O_2 \rightarrow P_4O_{10}$$

Some compounds are catalytically oxidized

For example

$$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$$

$$SO_2 + O_2 \xrightarrow{V_2O_5} SO_3$$

Uses

Dioxygen is used in making steel.It is used in the production of oxygen containing organic chemicals.

Dioxygen is also used for sewage treatment, river revival and paper pulp bleaching.

It is used as an oxidizer in underwater diving and in space shuttles.

Oxygen combines with majority of the elements of the periodic table to forms oxides (O^{2-}).

Simple Oxides

There are three types of oxides:

1. **Acidic oxides:** Oxides of non- metals are usually acidic in nature. For example, SO_2 combines with water to give H_2SO_3, an acid.

   $$SO_2 + H_2O \rightarrow H_2SO_3$$

2. **Basic oxides:** Metallic oxides are mostly basic in nature. Basic oxides dissolve in water to give basic solution. For example, CaO combines with water to give $Ca(OH)_2$, a base.

   $$CaO + H_2O \rightarrow Ca(OH)_2$$

3. **Amphoteric oxides:** Some metallic oxides show characteristics of both acidic as well as basic oxides. Such oxides are known as amphoteric oxides. For example, Al_2O_3 reacts with acids as well as alkalies

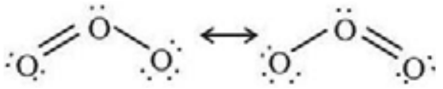
   $$Al_2O_3 + 6HCl + 9H_2O \rightarrow 2\ [Al(H_2O)_6]^{3+} + 6\ Cl^-$$
   Base Acid

$Al_2O_3 + 6NaOH + 3H_2O \rightarrow 2Na_3[Al(OH)_6]$

Acid Base

Ozone (O_3)

Ozone is an allotropic form of oxygen. Ozone has angular structure with a bond angle of about 117°. Both O = O bonds are of equal bond length due to resonance.



Preparation

It is formed when dioxygen is irradiated with UV light or silent electric discharge.

$3O_2\ (g) \rightarrow 2O_3\ (g)\ \Delta H^\circ = +142\ KJ/mol$

Properties

Ozone is a pale blue gas with a characteristic pungent odor.

Ozone is diamagnetic in nature.

It is the second most powerful oxidizing agent after fluorine. It liberates oxygen gas when acting as an oxidizing agent.

$2Fe^{2+} + O_3 + 2H^+ \rightarrow 2Fe^{3+} + H_2O + O_2$

$PbS + 4O_3 \rightarrow PbSO_4 + 4O_2$

Depletion of ozone layer

Thinning of the ozone layer is termed as depletion of ozone layer. The depletion of ozone layer in the stratosphere is caused by the presence of chlorofluoro carbons. CFCs decomposed by UV radiation to produce chlorine which reacts with ozone and this causes a decrease in the concentration of ozone at a rate faster than its formation from dioxygen. Another cause of depletion of ozone layer is the release of nitrogen oxides into the stratosphere by supersonic jet aero-planes.

$$NO + O_3 \rightarrow NO_2 + O_2$$

Sulphur (S)

Sulphur forms many 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.

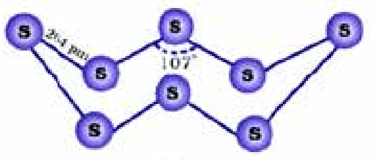
a. Yellow Rhombic (α - sulphur)
b. Monoclinic (β- sulphur)

$$\alpha-\text{Sulphur} \underset{\text{below 369 K}}{\overset{\text{above 369 K}}{\rightleftharpoons}} \beta-\text{Sulphur}$$

At 369 K both forms are stable. S_8 puckered shape in both forms and has crown shape.

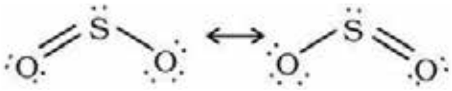
1. **Rhombic sulphur (α-sulphur):** It is prepared by evaporating the solution of roll sulphur in CS_2. It is insoluble in water but readily soluble in CS_2.
2. **Monoclinic sulphur (β-sulphur):** It is prepared by melting rhombic sulphur in a dish and cooling, till a crust is formed. Two holes are made 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 369 K both the forms are stable. This temperature is called **transition temperature**.

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)

The molecule of SO_2 is angular. It is a resonance hybrid of the two canonical forms:



Preparation

Sulphur dioxide is formed together with a little (6-8%) sulphur trioxide when sulphur is burnt in air or oxygen:

$$S\ (g) + O_2(g) \rightarrow SO_2(g)$$

In the laboratory it is readily generated by treating a sulphite with dilute sulphuric acid.

$$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + SO_2$$

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).

$$SO_2(g) + H_2O(l) \rightleftarrows H_2SO_3(aq)$$

With sodium hydroxide solution, it forms sodium sulphite, which then reacts with more sulphur dioxide to form sodium hydrogen sulphite.

$$2NaOH + SO_2 \rightarrow Na_2SO_3 + H_2O$$

$$Na_2SO_3 + H_2O + SO_2 \rightarrow 2NaHSO_3$$

SO_2 is oxidised to sulphur trioxide by oxygen in the presence of vanadium pentoxide (V_2O_5) catalyst.

$$2SO_2 + O_2 \rightarrow 2SO_3$$

Moist sulphur dioxide behaves as a reducing agent. It converts iron(III) ions to iron(II) ions and decolorizes acidified potassium permanganate(VII) solution (This is used as a test for SO_2).

$$2Fe^{3+} + SO_2 + 2H_2O \rightarrow 2Fe^{2+} + SO_4^{2-} + 4H^+$$

$$5\ SO_2 + 2MnO_4^- + 2H_2O \rightarrow 5\ SO_4^{2-} + 4H^+ + 2Mn^{2+}$$

Uses

SO_2 is used in refining petroleum and sugar

It is used in bleaching wool and silk

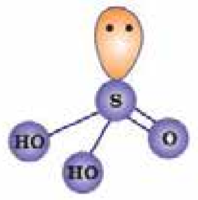
It is also used as a disinfectant and preservative.It is used in the manufacture of sulphuric acid, sodium hydrogen sulphite and calcium hydrogen sulphite.

Oxoacids of sulphur

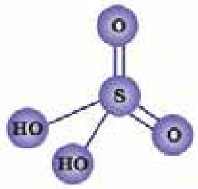
Sulphur forms variety of oxoacids. All oxoacids of sulphur are dibasic.

Sulphur forms a number of oxoacids such as H_2SO_3, $H_2S_2O_3$, $H_2S_2O_4$, $H_2S_2O_5$, $H_2S_xO_6$

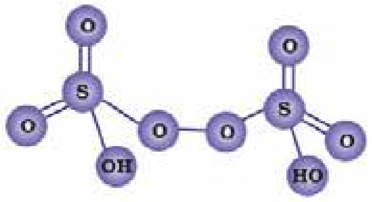
(x = 2 to 5), H_2SO_4, $H_2S_2O_7$, H_2SO_5, $H_2S_2O_8$. Some of these acids are unstable and cannot be isolated. They are known in aqueous solution or in the form of their salts. Structures of some important oxoacids are shown in figure given below



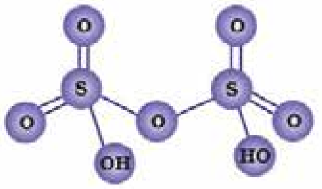
Sulphurous acid (H_2SO_3)



Sulphuric acid (H_2SO_4)



Peroxodisulphuric acid ($H_2S_2O_8$)



Pyrosulphuric acid (Oleum) ($H_2S_2O_7$)

Sulphuric acid (H_2SO_4)

Manufacture

Sulphuric acid is manufactured by the **Contact Process** which involves three steps:

1. Burning of sulphur or sulphide ores in air to generate SO_2.

   $\mathbf{S + O_2 \rightarrow SO_2}$

2. Conversion of SO_2 to SO_3 by the reaction with oxygen in the presence of a catalyst (V_2O_5)

   $\mathbf{2SO_2 + O_2 \rightarrow 2SO_3}$

3. Absorption of SO_3 in H_2SO_4 to give *Oleum* ($H_2S_2O_7$).

   $\mathbf{SO_3 + H_2SO_4 \rightarrow H_2S_2O_7}$

4. Dilution of oleum with water gives H_2SO_4 of the desired concentration.

   $\mathbf{H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4}$

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.

$$H_2SO_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + HSO_4^-$$

$$HSO_4^-(aq) + H_2O(l) \rightarrow H_3O^+(aq) + SO_4^{2-}$$

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.

$2\ MX + H_2SO_4 \rightarrow 2\ HX + M_2SO_4$ (where X = F, Cl, NO_3 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.: $C_{12}H_{22}O_{11} + H_2SO_4 \rightarrow 12C + 11H_2O$

Hot concentrated sulphuric acid is a moderately strong oxidizing agent. It oxidizes both metals and nonmetals and the acid itself reduces to SO_2.

$Cu + 2\ H_2SO_4\ (conc.) \rightarrow CuSO_4 + SO_2 + 2H_2O$

$S + 2H_2SO_4\ (conc.) \rightarrow 3SO_2 + 2H_2O$

$C + 2H_2SO_4\ (conc.) \rightarrow CO_2 + 2SO_2 + 2H_2O$

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.

Halogen Family

Group 17 elements are fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At) are collectively known as halogens and are having the general electronic configuration of ns^2, np^5.

Element	F	Cl	Br	I	At
Config.	$[He]2s^2 2p^5$	$[Ne]3s^2 3p^5$	$[Ar] 3d^{10} 4s^2 4p^5$	$[Kr]4d^{10} 5s^2 5p^4$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^5$

Atomic and ionic radii: The halogens have the smallest atomic radii in their respective periods due to maximum effective nuclear charge. Atomic and ionic radii increase down the group due to the addition of a new shell at each step.

Ionisation enthalpy: Due to their small size halogens have little tendency to lose electron. Thus they have very high ionisation enthalpy. Ionisation enthalpy decreases down the group due to the increase in atomic size.

Electron gain enthalpy: Electron gain enthalpy of halogens is very high as they are short of only one electron to attain noble gas configuration. Electron gain enthalpy becomes less negative as we move down the group. However F has less electron gain enthalpy than Cl due to its small size and high electron density.

Electronegativity: Electronegativity decreases down the group. F is the most electronegative element in the periodic table.

Melting and boiling point: The melting and boiling points increases down the group.

Bond dissociation enthalpy: Bond dissociation enthalpy decreases as we move down the group. F_2 has less ΔH_{diss} than Cl_2 due to small size and strong lone pair-lone pair repulsion.

Colour: All halogens exhibit colour due to the absorption of radiations in visible region of light due to which the electrons get excited to higher energy levels.

For example, F_2 has yellow, Cl_2 has greenish yellow, Br_2 has red and I_2 has violet colour.

Oxidation state: The most common oxidation state of halogens is –1. Cl, Br, I also shows positive oxidation states of +1, +3, + 5, + 7. F does not show positive oxidation states due to non-availability of *d*-orbitals.

Reactivity: All halogens are highly reactive and the reactivity decreases down the group.

Anomalous behavior of fluorine

Fluorine is anomalous in many properties like, ionization enthalpy, electronegativity that are higher than expected from the regular trends among the halogens. Its ionic and covalent radii, melting and boiling points, and electron gain enthalpy is quite lower than expected.

Reasons for the anomalous behavior of oxygen are:
Small size and highest electronegativity
Low F-F bond dissociation enthalpy
Absence of d-orbitals

Reactivity towards hydrogen: All halogens reacts with H_2 to form hydrogen halides (HX) and the reactivity towards H_2 decreases down the group

Acidic strength: As the size of X increases and the strength of H–X bond decreases down the group, acidic strength dectreses down the group

$HF < HCl < HBr < HI$

Stability: As the bond dissociation enthalpy decreases down the group so the stability of hydrogen halides also decreases from HF to HI.

$HF > HCl > HBr > HI$

Boiling point: Due to the increase in size of halogens the van der Waals forces increases down the group resulting in the increase in boiling point from HCl to HI. HF has the highest boiling point due to the presence of strong intermolecular H bonding

$HCl < HBr < HI < HF$

Ionic character: Due to the decrease in electronegativity down the group the ionic character of hydrogen halides also decreases down the group.

$F > HCl > HBr > HI$

Dipole moment: Due to the decrease in electronegativity down the group the dipole moment of hydrogen halides also decreases down the group.

$HF > HCl > HBr > HI$

Reducing power: As the bond dissociation enthalpy decreases, so it becomes easier to give out the hydrogen atom causing the reducing power to increase from HF to HI.

$HF < HCl < HBr < HI$

Reactivity towards metals: Halogens react with metals to form metal halides of the form MX, where M is a monovalent metal.

Ionic character: Due to the decrease in electronegativity down the group the ionic character of metal halides also decreases down the group

$MF > MCl > MBr > MI$

Chlorine (Cl)

Preparation: It can be prepared by any one of the following methods:

1. By heating manganese dioxide with concentrated hydrochloric acid.

$MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$

Conc. HCl can be replaced by a mixture of common salt and concentrated H_2SO_4

$4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$

2. By the action of HCl on potassium permanganate.

$2KMnO_4 + 16HCl \rightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$

Manufacture of chlorine

1. **Deacon's process**: By oxidation of hydrogen chloride gas by atmospheric oxygen in the presence of $CuCl_2$ (catalyst) at 723 K

   $4HCl+O_2 \longrightarrow 2Cl_2 +2H_2O$

2. **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 odor. It is soluble in water.

It reacts with a number of metals and non-metals to form chlorides.

$2Al + 3Cl_2 \rightarrow 2AlCl_3$
$P_4 + 6Cl_2 \rightarrow 4PCl_3$
$2Na + Cl_2 \rightarrow 2NaCl$
$S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$
$2Fe + 3Cl_2 \rightarrow 2FeCl_3$

With excess ammonia, chlorine gives nitrogen and ammonium chloride whereas with excess chlorine, nitrogen trichloride (explosive) is formed.

$8NH_3 \text{ (excess)} + 3Cl_2 \rightarrow 6NH_4Cl + N_2$

$NH_3 + 3Cl_2 \text{ (excess)} \rightarrow NCl_3 + 3HCl$

With cold and dilute alkalies chlorine produces a mixture of chloride and hypochlorite but with hot and concentrated alkalies it gives chloride and chlorate.

$$2NaOH\text{ (cold and dilute)} + Cl_2 \rightarrow NaCl + NaOCl + H_2O$$

$$6\ NaOH\text{ (hot and conc.)} + 3Cl_2 \rightarrow 5NaCl + NaClO_3 + 3H_2O$$

With dry slaked lime it gives bleaching powder.

$$2Ca(OH)_2 + 2Cl_2 \rightarrow CaOCl_2 + CaCl_2 + 2H_2O$$

Chlorine reacts with hydrocarbons and gives substitution products with saturated hydrocarbons and addition products with unsaturated hydrocarbons in presence of UV.

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

$$C_2H_4 + Cl_2 \longrightarrow C_2H_4Cl_2$$

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.

1. It oxidises ferrous to ferric, sulphite to sulphate, sulphur dioxide to sulphuric acid and iodine to iodic acid.

   $2FeSO_4 + H_2SO_4 + Cl_2 \rightarrow Fe_2(SO_4)_3 + 2HCl$
   $Na_2SO_3 + Cl_2 + H_2O \rightarrow Na_2SO_4 + 2HCl$
   $SO_2 + 2H_2O + Cl_2 \rightarrow H_2SO_4 + 2HCl$
   $I_2 + 6H_2O + 5Cl_2 \rightarrow 2HIO_3 + 10HCl$

2. It is a powerful bleaching agent; bleaching action is due to oxidation.

   $Cl_2 + H_2O \rightarrow 2HCl + [O]$

   Coloured substance + [O] → Colourless substance

It bleaches vegetable or organic matter in the presence of moisture. Its bleaching action is permanent.

Uses: It is used

1. for bleaching wood pulp, bleaching cotton and textiles,
2. in the extraction of gold and platinum
3. in the manufacture of dyes, drugs and organic compounds such as CCl_4, $CHCl_3$, DDT, refrigerants, etc.
4. in sterilizing drinking water and
5. 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 by heating sodium chloride with concentrated sulphuric acid.

$2 NaCl + H_2SO_4 + Heat \rightarrow Na_2SO_4 + HCl$

Properties

HCl is a colourless gas with pungent odour.
It is extremely soluble in water, $HCl + H_2O \rightarrow H_3O^+ + Cl^-$
It decomposes salts of weaker acids, $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$
When treated with NH_3, it gives white fumes of NH_4Cl, $NH_3 + HCl \rightarrow NH_4Cl$
3HCl : $1HNO_3$ is called aqua regia, which is used for dissolving noble metals.

$$Au + 4\,H^+ + NO_3^- + 4Cl^- \rightarrow AuCl_4^- + NO + 2\,H_2O$$

Uses

Hydrogen chloride is used in medicine and as a laboratory reagent.

It is used in the manufacture of chlorine, NH_4Cl and glucose.

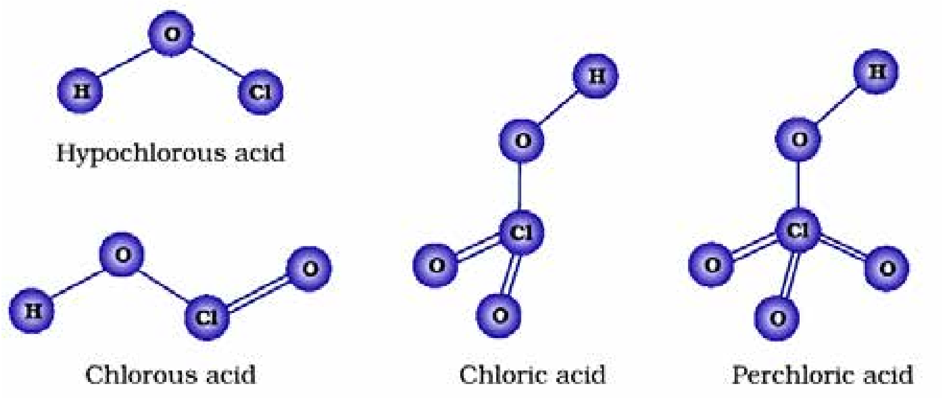
Oxoacids of halogens

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 $HClO_4$). Other halogen form several oxoacids as given in the following table:

Halic (I) acid (Hypohalous acid)	**HOF (Hypofluorous acid)**	**HOCl (Hypochlorous acid)**	**HOBr (Hypobromous acid)**	**HOI (Hypoiodous acid)**
Halic (III) acid (Halous acid)	– –	HOClO (chlorous acid)	– –	– –
Halic (V) acid (Halic acid)	– –	HOClO2 (chloric acid)	HOBrO2 (bromic acid)	HOIO2 (Iodic acid)
Halic (VII) acid (Perhalic acid)	– –	HOClO3 (perchloric acid)	HOBrO3 (perbromic acid)	HOIO3 (periodic acid)

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.

Properties

These are all covalent molecules and are diamagnetic in nature. They are volatile solids or liquids except Cl-F 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:

Type	Examples	Structure
AX	ClF, BrF, IF, BrCl, BrI	Linear
AX_3	ClF_3, BrF_3, IF_3, ICl_3, IBr_3 etc.	Bent T-shaped
AX_5	ClF_5, BrF_5, IF_5	Square pyramidal
AX_7	IF_7	Pentagonal Bipyramidal

Uses: These compounds can be used as non aqueous solvents. Interhalogen compounds are very useful fluorinating agents.

Noble gases

Group 18 elements: helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe) and radon (Rn) having the electronic configuration $ns^2\ np^6$, are named as noble gases. All these are gases and chemically unreactive.

Element	He	Ne	Ar	Kr	Xe	Rn
Config.	$1s^2$	$[He]2s^22p^6$	$[Ne]3s^23p^6$	$[Ar]\ 3d^{10}4s^24p^6$	$[Kr]4d^{10}5s^25p^6$	$[Xe]\ 4f^{14}5d^{10}6s^26p^6$

General properties of noble gases

Atomic radii: Atomic radii of noble gases increase down the group due to the addition of a new shell at each step.

$$He < Ne < Ar < Kr < Xe < Rn$$

Ionisation enthalpy: They have very high ionization enthalpy because of completely filled orbitals. Ionization enthalpy decreases down the group because of increase in size.

Atomic radii => $He < Ne < Ar < Kr < Xe < Rn$

Thus Ionisation enthalpy => $He > Ne > Ar > Kr > Xe > Rn$

Electron gain enthalpy: Because of stable electronic configuration, noble gases have no tendency to accept the electron and therefore, have large positive values of electron gain enthalpy.

Melting and boiling point: Due to the weak dispersion forces they have low melting and boiling point.

Xenon-fluorine compounds: Xenon forms three binary fluorides, XeF_2, XeF_4 and XeF_6 .

Preparation

$$\mathrm{Xe(g) + F_2(g) \xrightarrow{673K, 1bar} XeF_2(s)}$$

$$\text{(Xenon in excess)}$$

$$\mathrm{Xe(g) + 2F_2(g) \xrightarrow{873K, 7bar} XeF_4(s)}$$

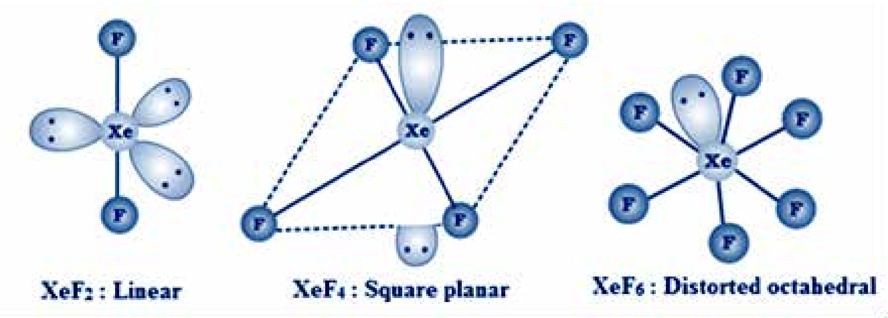
$$\text{(1:5 ratio)}$$

$$\mathrm{Xe(g) + 3F_2(g) \xrightarrow{573K, 60-70bar} XeF_6(s)}$$

$$\text{(1:20 ratio)}$$

Properties

XeF_2 is linear, XeF_4 is square planar and XeF_6 is distorted octahedral.



XeF_2 : Linear

XeF_4 : Square planar

XeF_6 : Distorted octahedral

XeF_2, XeF_4 and XeF_6 are colorless crystalline solids

They are readily hydrolyzed

$$2XeF_2(s) + 2H_2O(l) \rightarrow 2Xe(g) + HF(aq) + O_2(g)$$

They react with fluoride ion acceptors to form cationic species and fluoride ion donors to form fluoroanions.

$$\mathbf{XeF_2 + PF_5 \rightarrow [XeF]^+ + [PF_6]^-}$$

$$\mathbf{XeF_4 + SbF_5 \rightarrow [XeF_3]^+ [SbF_6]^-}$$

$$\mathbf{XeF_6 + MF \rightarrow M^+ [XeF_7]^-}$$

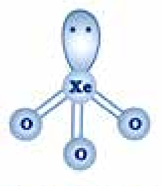
[Where, M = Na, K, Rb or Cs]

Xenon-oxygen compounds

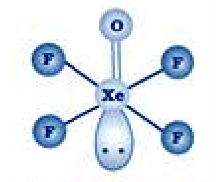
Xenon forms some important compounds with oxygen like XeO_3, $XeOF_4$ XeO_2F_2.

Preparation

Various xenon-oxygen compounds are prepared as follows:



XeO_3 : Pyramidal



$XeOF_4$: Square pyramidal

$$6XeF_4 + 12H_2O \rightarrow 4Xe + 2XeO_3 + 24HF + 3O_2$$

$$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$$

Partial Hydrolysis $XeOF_4$

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2\ HF$$

Partial Hydrolysis also gives XeO_2F_4

$$XeF_6 + 2H_2O \rightarrow XeO_2F_4 + 4HF$$

Properties

XeO_3 is a colorless explosive solid having a trigonal pyramidal structure.

$XeOF_4$ is a colorless volatile liquid with a square pyramidal

Uses of inert gases

Helium is used

Gas cooled Nuclear reactors
In filling balloons for meteorological observations
In the oxygen mixture of deep sea divers
In inflating aero-plane tyres
Used to provide an inert atmosphere in melting and welding of easily oxidizable metals

Neon is used

In discharge tubes and fluorescent bulbs used for advertising purposes
In beacon lights for the safety of air navigators as the light can easily pass through the fog for a clear view.

Argon is used

To provide an inert atmosphere in high-temperature metallurgical processes (arc welding of metals or alloys)
For filling electric bulbs
In the laboratory for handling substances that are air-sensitive.
Xenon and Krypton are also used in light bulbs.

8 D-AND F-BLOCK ELEMENTS

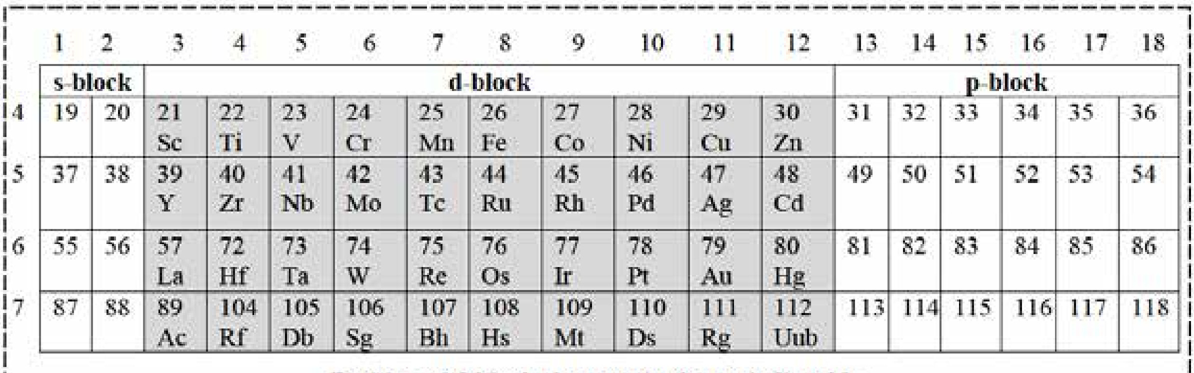
The elements in which the last electron enters the (n-1) d subshell where ‘n’ is the outermost shell, are called **d-block elements.**

Their general valence or outer electronic configuration is $(n-1)\ d^{1-10}\ ns^{0-2}$

Position of d-block elements in the periodic table

1. The d-block elements are situated in between s- and p-block elements, i.e., these elements are located in the middle part of the periodic table.
2. d-block elements are also called transition elements as they show transition in the properties from the most electropositive s-block elements to the less electropositive p-block elements.

Transition elements *are defined as those elements which have partly or incompletely filled (n-1) d-subshell in their elementary state or in any of their common oxidation states.*



	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	s-block		d-block										p-block					
4	19	20	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31	32	33	34	35	36
5	37	38	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49	50	51	52	53	54
6	55	56	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81	82	83	84	85	86
7	87	88	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Uub	113	114	115	116	117	118

Position of d-block elements in the periodic table

Classification of d-block elements: The long form of periodic table contains four series of transition elements, known as transition series.

Four transition series are 3d, 4d, 5d and 6d series wherein orbitals of (n- 1)th main shell gets filled.

a. The 3d series contains the elements from Sc (Z = 21) to Zn (Z = 30) belonging to the 4th period.
b. The 4d series contains the elements from Y (Z = 39) to Cd (Z = 48) belonging to the 5th period.
c. The 5d series begins with La (Z = 57) and contains elements from Hf (Z = 72) to Hg (Z = 80) belonging to the 6th period.
d. The 6d series begins with Ac (Z = 89) and contains elements from Rf (Z = 104) to Uub (Z = 112) belonging to the 7th period.

The 3d, 4d, 5d and 6d series of the d-block elements correspond to the filling of 3d, 4d, 5d and 6d orbitals of the (n-1)th main shell. The last electron enters the (n- 1) d-orbital.

d-block elements are present from group 3 to group 12.

Electronic configuration of transition elements: 3d series of d-block elements

3d series or First Row Transition Series (Sc to Zn)				
Elements	**Symbols**	**Atomic Number**	**Expected electronic configuration**	**Observed electronic configuration**
Scandium	Sc	21	[Ar] $3d^1$ $4s^2$	[Ar] $3d^1$ $4s^2$
Titanium	Ti	22	[Ar] $3d^2$ $4s^2$	[Ar] $3d^2$ $4s^2$
Vanadium	V	23	[Ar] $3d^3$ $4s^2$	[[Ar] $3d^3$ $4s^2$
Chromium	Cr	24	[Ar] $3d^4$ $4s^2$	[Ar] $3d^5$ $4s^1$
Manganes	Mn	25	[Ar] $3d^5$ $4s^2$	[Ar] $3d^5$ $4s^2$
Iron	Fe	26	[Ar] $3d^6$ $4s^2$	[Ar] $3d^6$ $4s^2$
Cobalt	Co	27	[Ar] $3d^7$ $4s^2$	[Ar] $3d^7$ $4s^2$
Nickel	Ni	28	[Ar] $3d^8$ $4s^2$	[Ar] $3d^8$ $4s^2$
Copper	Cu	29	[Ar] $3d^9$ $4s^2$	[Ar] $3d^{10}$ $4s^1$
Zinc	Zn	30	[Ar] $3d^{10}$ $4s^2$	[Ar] $3d^{10}$ $4s^2$

[Ar] = $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$

Q. Why does chromium and copper show abnormal electronic configuration?

Ans: ^{24}**Cr (Expected):** $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $\mathbf{3d^4}$ $\mathbf{4s^2}$
(Actual): $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $\mathbf{3d^5}$ $\mathbf{4s^1}$

^{29}**Cu (Expected):** $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $\mathbf{3d^9}$ $\mathbf{4s^2}$
(Actual): $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $\mathbf{3d^{10}}$ $\mathbf{4s^1}$

Explanation

1. The energy difference between the 3d and 4s orbital is very low.
2. The d-orbital being degenerate, acquires more stability when it is half-filled ($3d^5$) or completely filled ($3d^{10}$).
3. Due to the inter-electronic repulsion, one electron from the 4s orbital is transferred to the 3d orbital thus acquiring more stable electronic configuration.

8.1 CHARACTERISTICS OF TRANSITION ELEMENTS

1. Transition elements are metals and thereby they show metallic properties such as ductility, malleability, electrical conductivity, high tensile strength and metallic luster.
2. Except mercury which is liquid at room temperature, other transition elements have typical metallic structures.
3. Their compounds generally contain unpaired electrons; hence they are paramagnetic in nature and form colored compounds.
4. They show variable oxidation states.
5. They have tendency to form large number of complexes.
6. They have higher densities as compared to the metals of groups 1 and 2 (s-block).
7. They are heavy metals with higher melting and boiling point as well as higher heats of vaporization.
8. Transition elements are less reactive than s-block elements due to their higher ionization energy.
9. Most of the transition metals such as Mn, Ni, Co, Cr, V, Pt, etc., and their compounds are used as catalysts.
10. They have good thermal and electrical conductivity.
11. They form alloys with different metals.
12. They form interstitial compounds with elements such as H_2, boron, carbon, nitrogen, etc.
13. They form organometallic compounds.

8.2 GENERAL TRENDS IN PROPERTIES OF TRANSITION ELEMENTS

Atomic radii: The atomic radii are intermediate between those of s-and p- block elements. The Following trends are observed:

a. The atomic radii of elements of a particular series decrease with increase in atomic number but this decrease in atomic radii become small after midway.

Reason- The atomic radii decreases in the beginning because of increase in atomic no., the nuclear charge goes on increasing progressively, but the electrons enter the penultimate shell and the added d-electrons screen the outermost s-electrons. The shielding effect is small so that net electrostatic attraction between the nuclear charge and outermost electrons increases.

Consequently atomic radius decreases. As the no. of d-electrons increase the screening effect increases. This neutralizes the effect of increased nuclear charge due increase in atomic number and consequently atomic radius remains almost unchanged after chromium.

b. At the end of each period, there is slight increase in atomic radii.

Reason- This is because of increased electron-electron repulsions between the added electrons in the same orbital which exceeds the attractive forces due to increased nuclear charge.

Therefore, electron cloud expands and size increase.

c. The atomic radii increase while going down the group.

Reason – The atomic radii of second transition series is larger than that of first transition series because of increase in no. of outermost shell.

The third transition series have nearly the same radii as metals of second transition series. This is because of lanthanide contraction. This is associated with the interventions of 4f-orbitals which are filled before 5d-series. 4f- orbital have poor screening effect, this results in regular decrease in atomic radii which compensates the expected increase in atomic size with increase in atomic no.

Ionic Radii: The ionic radii follow the same trend as atomic radii. Since metals exhibit different oxidation states, radii of ions also differ. The ionic radii decrease with increase in nuclear charge.

Metallic character: All transition elements are metals. They have high density, hardness, high melting point, boiling point & high tensile strengths, ductility, high, thermal and electrical conductivity and luster.

Reason – The metallic character is due to their relatively low ionization enthalpies and number of vacant orbitals in the outermost shell. The hardness of these metals suggests the presence of strong bonding due to overlap of unpaired electrons between different metal atoms. Therefore, they exhibit high enthalpy of atomization. Enthalpy of atomization is maximum in the middle indicates unpaired electrons are particularly favorable for strong atomic interaction, hence, maximum enthalpy of atomization.

Density: All metals have high density. Within a period, the densities vary inversely with atomic radius that is densities increase along a period. Also densities increase upon descending down the group.

Reason: Atomic volumes of transition elements are low because electrons are added in (n-1) d subshell and not in **ns** subshell. Therefore, increased nuclear charge is partly screened by the d-electrons and outer electrons are strongly attracted by the nucleus. Moreover, electrons are added in inner orbital. Consequently, densities of transition metals are high.

Melting and boiling points: The transition metals have high melting point & boiling point. The melting point & boiling point of metals rise to a maximum value and then decrease with increase in atomic number. However, Mn and Tc have abnormally low melting point & boiling point.

Reason – The high melting point & boiling point is due to strong metallic bonds between the atoms of these elements. The metallic bond is formed due to interaction of electrons in the outermost orbital.

The strength of bonding depends on the number of outer most unpaired electrons. Greater is the number of valance electrons, stronger is the metallic bonding and consequently, melting point is high.

Therefore metallic strength increase up to the middle till d^5 configuration and then decreases with the decrease in availability of unpaired d- electrons (from Fe onwards). Therefore, m.p decreases after the middle because of increase in pairing of electrons.

The dip in the curve in Mn and Tc is due to the fact that Mn has stable electronic configuration ($3d^5\ 4S^2$). As a result 3d electrons are more tightly held by Mn atomic nucleus and this reduces delocalization of electrons resulting in weaker metallic bonding.

Color: Many ionic and covalent compounds of transition elements are colored (In contrast those of s and p block are generally white). Color arises when a compound is able to absorb some wavelength in the visible region of the spectrum. The color of the compound is then that of the transmitted light i.e. the complementary color to the color of the light absorbed. Ions having d^{10} or d^0 configuration are usually colorless. Thus $ZnSO_4$ and TiO_2 are colorless because in $Zn^{2+}(d^{10})$ and $Ti^{4+}(d^0)$ it is not possible to promote electrons within the *d*-level. Another reason for color can be charge transfer from one atom to another as occurs in MnO_4^- (intense purple).

Oxidation States: Transition metals exhibit a larger number of oxidation states in their compound.

Reason - This is because of participation of inner (n -1)d electrons in addition to outer ns electrons because the energies of ns and (n -1)d electrons are almost equal.

The elements which gave the greatest number of oxidations states occur in or near the middle of the series. eg. Mn ; oxidation states from + 2 to +7

The lesser number of oxidation states at the extreme ends is either due to too few electrons to loose or share or too many d electrons, hence fewer orbital are available in to available to share electrons with others, thus higher valence cannot be attained. eg. Cu can have oxidation state of +1& +2, Zn can have oxidation state of +2 only

Oxidation state of first row transition elements

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
21	22	23	24	25	26	27	28	29	30
$3d^14s^2$	$3d^24s^2$	$3d^34s^2$	$3d^54s^1$	$3d^54s^2$	$3d^64s^2$	$3d^74s^2$	$3d^84s^2$	$3d^{10}4s^1$	$3d^{10}4s^2$
+2 +3	+2 +3 +4	+2 +3 +4 +5	+2 +3 +4 +5 +6	+2 +3 +4 +5 +6 +7	+2 +3 +4 +6	+2 +3 +4	+2 +3 +4	+1 +2	+2

a. Except Sc, the most common oxidation state of first row transition elements is +2 which arises due to loss of 4s- electrons. This means 3d–orbitals are more stable and lower in energy than 4s- orbital. As a result electrons are first removed from 4s- orbital.
b. Zinc shows oxidation state +2 in which no d-electrons are involved.
c. Within a group, maximum oxidation state increases with atomic number. For example in group 8 , Fe shows +2 and +3 but Rutheniun and Osmium form compounds in +4, +6 and + 8 oxidation state.
d. In + 2 and + 3 oxidation state, bonds formed are ionic and in the compounds of higher oxidation state bonds are covalent.

Transition elements show low oxidation states in some compounds or complexes having ligands such as CO. For example: in $Ni\ (CO)_4$, Ni has zero oxidation state.

Trends in stability of higher oxidation states

The highest oxidation state is generally shown among halides and oxidation.

a. Transition metals react with halogens at high temp as they have high activation energies. High temp is required to start the reaction but heat of reaction is sufficient to continue.
Order of reactivity: $F_2 > Cl_2 > Br_2 > I_2$

b. In general elements of I transition series enact in low oxidation state.
c. Since florine is the most electronegative element, the transition elements show high oxidations states with fluorine.
d. The highest oxidation states are found in TiX_4.
e. The +7 oxidation states are not shown by simple halides.
f. V^{+5} is shown by VF_5 only. Other halides form oxo halides like VOX_3.
g. Fluorides are unstable in their low oxidation state. eg V forms VX_2 (X = C1,Br or I) Cu can form CuX (X=Cl ,I) Cu (II) halides are known except the iodide.
h. The ability of oxygen to stabilize the highest oxidation state is exhibited in their oxides.

The highest oxidation state of an element is equal to its group number. For example Sc in Sc_2O_3 is +3 and is a member of group 3. Mn shows oxidation state equal to +7 in Mn_2O_7. Mangnese forms highest oxidation state fluorides as MnF_4 whereas the highest oxide is Mn_2O_7.Tthis is due to tendency of oxygen to form multiple bonds. In the covalent oxide Mn_2O_7, each Mn is tetrahedrally surrounded by oxygen atoms and has Mn-O-Mn Bridge. Tetrahedral structures are also known for MnO_4^{-2} and ions like V (V), Cr(VI), Mn(VI) and Mn(VII).

Magnetic Properties: The magnetic properties of a substance are determined by the number of unpaired electrons in it. There are two main types of substances.

1. **Paramagnetic substances:** The paramagnetic character arises because of the presence of unpaired electrons. Paramagnetic substances are the substances which are attracted by magnetic field.
2. **Diamagnetic Substances:** Diamagnetic character arises because of the absence of unpaired electrons. Diamagnetic substances are the substances which are repelled by the magnetic field.

Most of the transition elements and their compounds are paramagnetic and are attracted by magnetic field. Greater the number of unpaired electrons in the substance greater is the paramagnetic character.

The magnetic character of a substance is expressed in terms of magnetic moment (μ). The magnetic moment can be calculated using the relation

$\mu = \sqrt{n(n+2)}$ BM (Bohr Magneton)

n = number of unpaired electrons

Larger the value of magnetic moment, the greater is the paramagnetic character. In addition to paramagnetic and diamagnetic substance, there are a few substances such as iron which are highly magnetic as compared to ordinary metals. These substances are called ferromagnetic substances.

Interstitial Compounds: Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. These are compounds of indefinite structure and proportions. It is mostly due to the variable valency of transition elements. Sometimes, non stoichiometry is caused by defects in the solid structures. Transition metals form number of interstitial compounds, in which they take up atoms of small size e.g. H, C and N in the vacant spaces in their lattices. The presence of these atoms results in decrease in malleability and ductility of the metals but increases their tensile strength.

Formation of alloys: Transition metals form alloys with each other. This is because they have almost similar size and the atoms of one metal can easily take up positions in the crystal lattice of the other. For example Alloys of Cr-Ni, Cr-Ni-Fe, Cr-V-Fe, Mn-Fe.....etc.

Complex formation: The cations of d-block elements have strong tendency to form complexes with certain molecules (e.g. CO, NO, NH_3....etc) or ions (e.g. F^-, Cl^-, CN^-....etc) called ligands. Their tendency to form complexes is due to two reasons.

1. Small size and high positive charge density.
2. Presence of vacant (n-1)d orbitals which are of appropriate energy to accept lone pair and unshared pair of electrons from the ligands for bonding with them. Examples of some complex compounds are,$[Cu(NH_3)_4]^{2+}$, $[Ag(NH_3)_2]^+$, $[Fe(CN)_6]^{4-}$,.... etc.

Ionization enthalpy: It *is defined as the amount of energy required to remove the outermost electron completely from a gaseous atom in its ground state.*

The ionization enthalpies of transition elements are higher than the ionization enthalpies of s-block elements and lower than the ionization enthalpies of p-block elements. This is due to the trends in atomic radii and nuclear charge. Due to an increase in nuclear charge which accompanies the filling of the inner *d* orbitals, there is an increase in ionisation enthalpy along each series of the transition elements from left to right.

Some exceptions observed in ionization enthalpies are

a. Cr and Cu have high I.E. This is attributed to their half filled (d^5) and completely (d^{10}) electronic configuration.
b. The value of second I.E. for zinc is low because ionization involves removal of an electron resulting in stable $3d^{10}$ configuration.
c. The trend in third I.E. shows high value for Mn^{+2} and Zn^{+2} because of stable $3d^5$ and $3d^{10}$ electronic configurations.
   Similarly, IE_3 for Fe is less than IE_3 for Mn because of stable $3d^5$ in Fe.

Catalytic Properties: Most of the transition metals and their compounds are used as catalyst. The catalytic activity of transition metals is due to the following reasons.

1. They show a variety of oxidation states and thereby can form intermediate products with various reactants.
2. They are also capable of forming interstitial compounds which can adsorb and activate the reacting species. Some examples of catalyst are
   1. Iron / molybdenum act as catalyst in the synthesis of ammonia by Haber's Process.
   2. Vanadium pentoxide (V_2O_5) is used for catalytic oxidation of SO_2 to SO_3
   3. $TiCl_4$ is employed as a catalyst in the manufacture of polythene.

Some Important Compounds of Transition Elements

Preparation and properties of KMnO4

Preparation: This is the most important and well known salt of permanganic acid and is prepared from the pyrolusite ore. It is prepared by fusing pyrolusite ore either with KOH or K_2CO_3 in presence of atmospheric oxygen or any other oxidizing agent such as KNO_3. The fused mass turns green with the formation of potassium manganate, K_2MnO_4.

$$2MnO_2 + 4KOH + O_2 \longrightarrow 2K_2MnO_4 + 2H_2O$$

$$2MnO_2 + 2K_2CO_3 + O_2 \longrightarrow 2K_2MnO_4 + 2CO_2$$

The fused mass is extracted with water and the solution is now treated with a current of chlorine or ozone or carbon dioxide to convert manganate into permanganate.

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$

$$2K_2MnO_4 + H_2O + O_3 \longrightarrow 2KMnO_4 + 2KOH + O_2$$

$$3K_2MnO_4 + 2CO_2 \longrightarrow 2KMnO_4 + MnO_2 + 2K_2CO_3$$

Commercially it is prepared by fusion of MnO_2 with KOH followed by electrolytic oxidation of manganate.

$$MnO_4^{2-} \text{ (green)} \longrightarrow MnO_4^{-} \text{ (purple)} + e^-$$

In the laboratory, a manganese (II) ion salt is oxidised by peroxodisulphate to permanganate

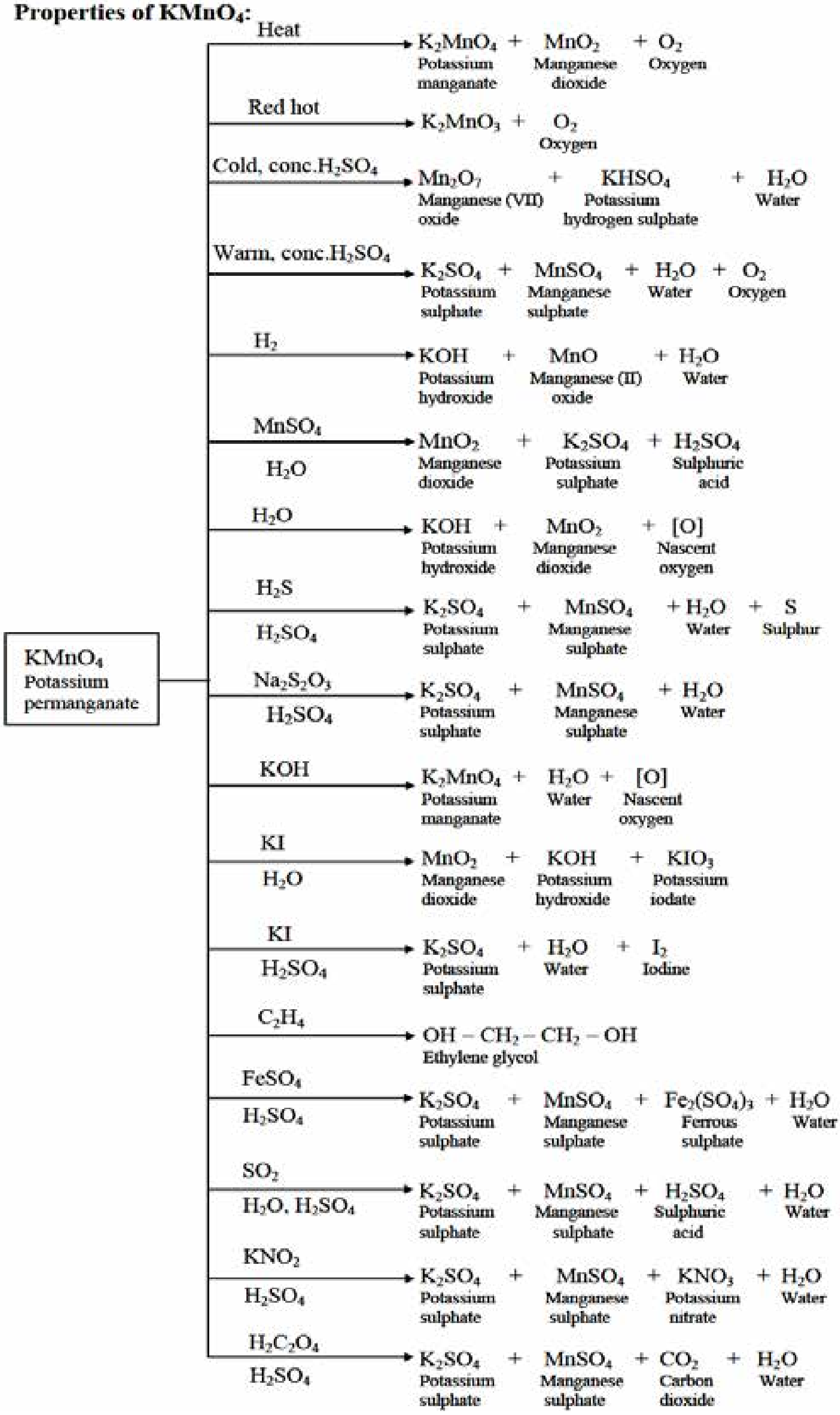
$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \longrightarrow 2MnO_4- + 10SO_4^{2-} + 16H^+$$

Properties

a. **Physical:** It is purple coloured crystalline compound. It is moderately soluble in water at room temperature.

b. **Chemical:**

- **Properties of $KMnO_4$:**



Preparation and properties of K2Cr2O7

Preparation

$K_2Cr_2O_7$ is prepared from chromite ore ($FeO.Cr_2O_3$) which is also known as chrome iron ore. The following steps are involved:

Step I: Concentration of ore: In a hydraulic classifier, powdered chromite ore is washed with water current. The lighter gangue is washed away with water current. The heavier chromite ore is settled at the bottom.

Step II: Conversion of chromite ore into sodium chromate (Roasting)

$$4FeO.Cr_2O_3 + O_2 \longrightarrow 2Fe_2O_3 + 4Cr_2O_3$$

$$[2Cr_2O_3 + 4Na_2CO_3 + 3O_2 \longrightarrow 4Na_2CrO_4 + 4CO_2] \times 2$$

$$4FeO.Cr_2O_3 + 8Na_2CO_3 + 7O_2 \longrightarrow 2Fe_2O_3 + 8Na_2CrO_4 + 8CO_2$$

Addition of limestone makes the mass porous and aids easier oxidation.

Step III: Conversion of sodium chromate into sodium dichromate

$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

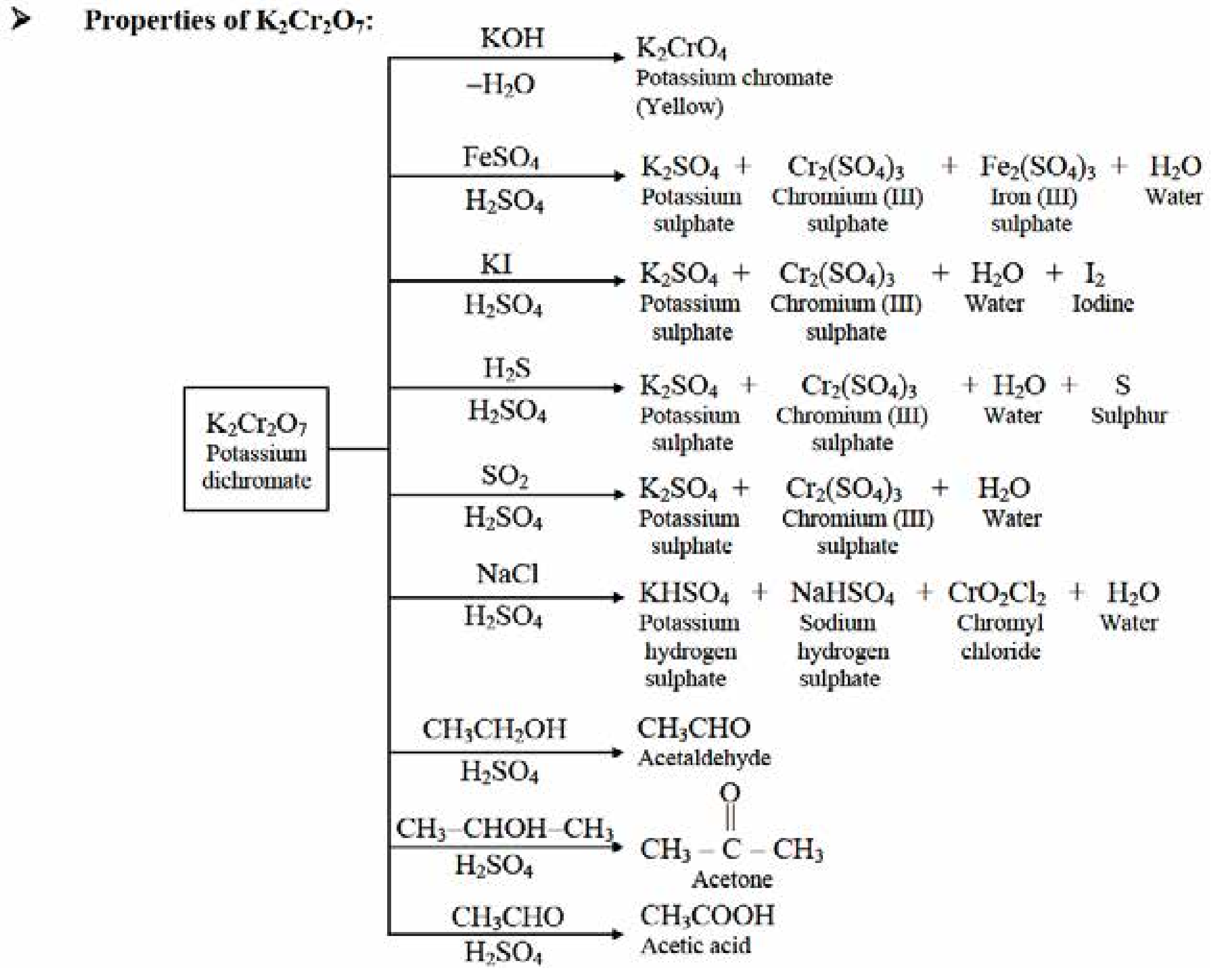
Step IV: Conversion of sodium dichromate into potassium dichromate

$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$

Orange red crystals of potassium dichromate are obtained by crystallization. These crystals are further purified by re-crystallization. Sodium chloride (being more soluble than potassium dichromate) remains in the solution.

Properties

a. **Physical:** It is orange-red colored crystalline compound. It is moderately soluble in cold water but freely soluble in hot water. It melts at 398°C.
b. **Chemical:**

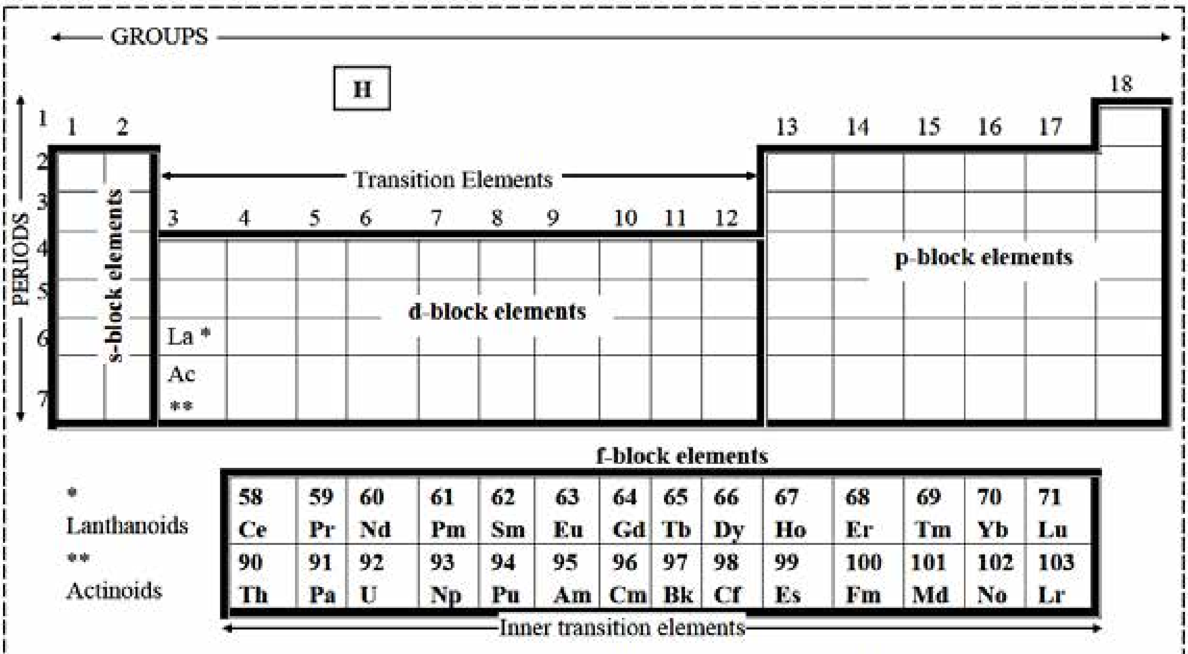


8.3 INNER TRANSITION ELEMENTS OR F-BLOCK ELEMENTS

The elements in which the last electron enters into (n-2) f-subshell of the atoms are called ***f-block elements.*** In these elements, the last electron enters in to the prepenultimate (n-2) shell (called Antepenultimate shell).The general valence electronic configuration is: $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$.

The last electron in the f-block elements enters into (n-2) f-orbitals, i.e., inner to the penultimate energy level and they form a transition series within the transition series (d-block elements). Hence, the f-block elements are known as inner transition series.

1. There are two series of inner transition elements:
    a. Lanthanoids (atomic number 58-71) ------- (4f-block elements)
    b. Actinoids (atomic number 90-103) -------- (5f-block elements)



Position of lanthanoids in the periodic table

Lanthanides: *The series involving the filling of 4f-orbitals following lanthanum La (Z = 57) is called* ***lanthanide series.*** *The elements present in this series are called* ***lanthanides.*** There are fourteen elements in this series starting with cerium, Ce(Z = 58) and ending with Lutetium, Lu(Z = 71). These elements are represented by the general symbol Ln. The name 'lanthanide' has been derived from 'lanthanum' which is the prototype of lanthanide.

Actinides: *The series of elements from Thorium (Z = 90) to Lawrencium (Z = 103) in which 5f orbitals are progressively filled are called* ***actinides****.*

The elements are called actinides because many physical and chemical properties are similar to actinium which is the prototype of the actinides.

Electronic configuration of lanthanum and 4f-series of f-block elements

The 4f-series includes elements from cerium (Ce) to lutetium (Lu). The electronic configuration of these elements can be expressed in terms of its nearest inert gas Xe (Z = 54). Electronic configuration of Xe (Z = 54) = $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$

Therefore, general electronic configuration of 4f-series is $[Xe]\ 4f^{1-14}\ 5d^{0-1}\ 6s^2$.

Lanthanum has electronic configuration $[Xe]4f^0\ 5d^1\ 6s^2$. It does not have any 4f electrons.

Element	**Symbol**	**Atomic Number**	**Expected electronic configuration**	**Observed electronic configuration**
Lanthanum	La	57	[Xe] $4f^0\ 5d^1\ 6s^2$	[Xe] $4f^0\ 5d^1\ 6s^2$
Cerium	Ce	58	[Xe] $4f^1\ 5d^1\ 6s^2$	[Xe] $4f^2\ 5d^0\ 6s^2$
Praseodymium	Pr	59	[Xe] $4f^2\ 5d^1\ 6s^2$	[Xe] $4f^3\ 5d^0\ 6s^2$
Neodymium	Nd	60	[Xe] $4f^3\ 5d^1\ 6s^2$	[Xe] $4f^4\ 5d^0\ 6s^2$
Promethium	Pm	61	[Xe] $4f^4\ 5d^1\ 6s^2$	[Xe] $4f^5\ 5d^0\ 6s^2$
Samarium	Sm	62	[Xe] $4f^5\ 5d^1\ 6s^2$	[Xe] $4f^6\ 5d^0\ 6s^2$
Europium	Eu	63	[Xe] $4f^6\ 5d^1\ 6s^2$	[Xe] $4f^7\ 5d^0\ 6s^2$
Gadolinium	Gd	64	[Xe] $4f^7\ 5d^1\ 6s^2$	[Xe] $4f^8\ 5d^0\ 6s^2$
Terbium	Tb	65	[Xe] $4f^8\ 5d^1\ 6s^2$	[Xe] $4f^9\ 5d^0\ 6s^2$
Dysprosium	Dy	66	[Xe] $4f^9\ 5d^1\ 6s^2$	[Xe] $4f^{10}\ 5d^0\ 6s^2$
Holmium	Ho	67	[Xe] $4f^{10}\ 5d^1\ 6s^2$	[Xe] $4f^{11}\ 5d^0\ 6s^2$
Erbium	Er	68	[Xe] $4f^{11}\ 5d^1\ 6s^2$	[Xe] $4f^{12}\ 5d^0\ 6s^2$
Thulium	Tm	69	[Xe] $4f^{12}\ 5d^1\ 6s^2$	[Xe] $4f^{13}\ 5d^0\ 6s^2$
Ytterbium	Yb	70	[Xe] $4f^{13}\ 5d^1\ 6s^2$	[Xe] $4f^{14}\ 5d^0\ 6s^2$
Lutetium	Lu	71	[Xe] $4f^{14}\ 5d^1\ 6s^2$	[Xe] $4f^{14}\ 5d^0\ 6s^2$

Mnemonic:

Lazy **C**ollege **P**rofessors **N**ever **P**repare **S**uperior **G**raduates
To **D**ramatically **H**elp **E**xecutives **T**rim **Y**early **L**osses.

Oxidation states of lanthanides

1. All lanthanoids exhibit a common stable oxidation state of +3.
2. In addition, some lanthanoids show +2 and +4 oxidation states also.
3. These are shown by those elements which by doing so attain the stable f^0, f^7 or f^{14} configurations i.e., empty, half-filled and completely filled 4f sub-shells. **eg.** Ce and Tb exhibit +4 oxidation states, Eu and Yb exhibit +2 oxidation states, while La, Gd and Lu exhibit only +3 oxidation states.

Lanthanoid contraction

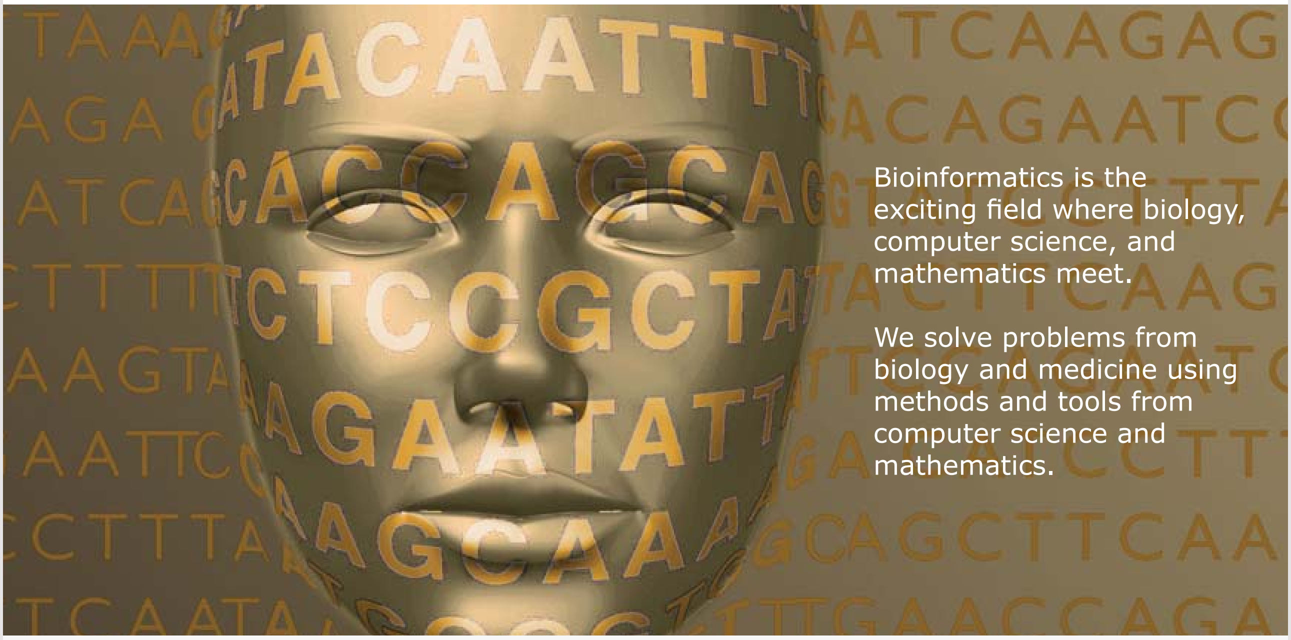
The atomic and ionic radii of lanthanoids show gradual decrease with increase in atomic number. It is known as ***Lanthanoid contraction****.*

There are 14 Lanthanoids from Ce to Lu. In Lanthanoids, after Lanthanum (La), the electrons are added to prepenultimate shell i.e., 4f - subshell.

For each electron, one proton is also added to the nucleus of the atom of the element. Hence from Ce to Lu as atomic number increases, nuclear charge increases, therefore nuclear attraction increases. As atomic number increases, atomic volume or radius decreases as observed with all the elements along the period.

But in case of Lanthanoids, this decrease in atomic volume or radius is comparatively very small.

This is explained in terms of Lanthanoid contraction.



Causes of the lanthanoid contraction

The nuclear positive charge increases by +1, when the atomic number increases by 1. An electron is added in the partly filled 4f orbital.

The shielding of 4f electrons is less effective than the shielding of 5d electron as 4f orbital is more diffused in shape than 5d orbital.

Thus, greater effective nuclear charge is experienced with the increase in the atomic number. This results in slight pull of the valence shell towards the nucleus.

Thus, the atomic and ionic radii decrease slightly with increase in the atomic number, thereby causing lanthanoid contraction.

In a given lanthanoid series, atomic radii decrease by 10 pm and the ionic radii decrease by 18 pm.

Thus, the extent of decrease is very small.

Effects of lanthanoid contractio:

1. **Decrease in basicity:**
   a. The size of Ln^{3+} cation decreases with increase in the atomic number, due to lanthanoid contraction. This decreases the ionic character of M-OH bond and gradually increases the covalent character of M-OH bond.
   b. Therefore the basic strength of the corresponding hydroxides decreases from $La(OH)_3$ to

   $Lu(OH)_3$. Thus, $La(OH)_3$ is most basic and $Lu(OH)_3$ is least basic.

   Note: *As per **Fajan's principle**, "With increase in the size of cation, the tendency of the hydroxide to dissociate, increases. This increases the strength of base."*

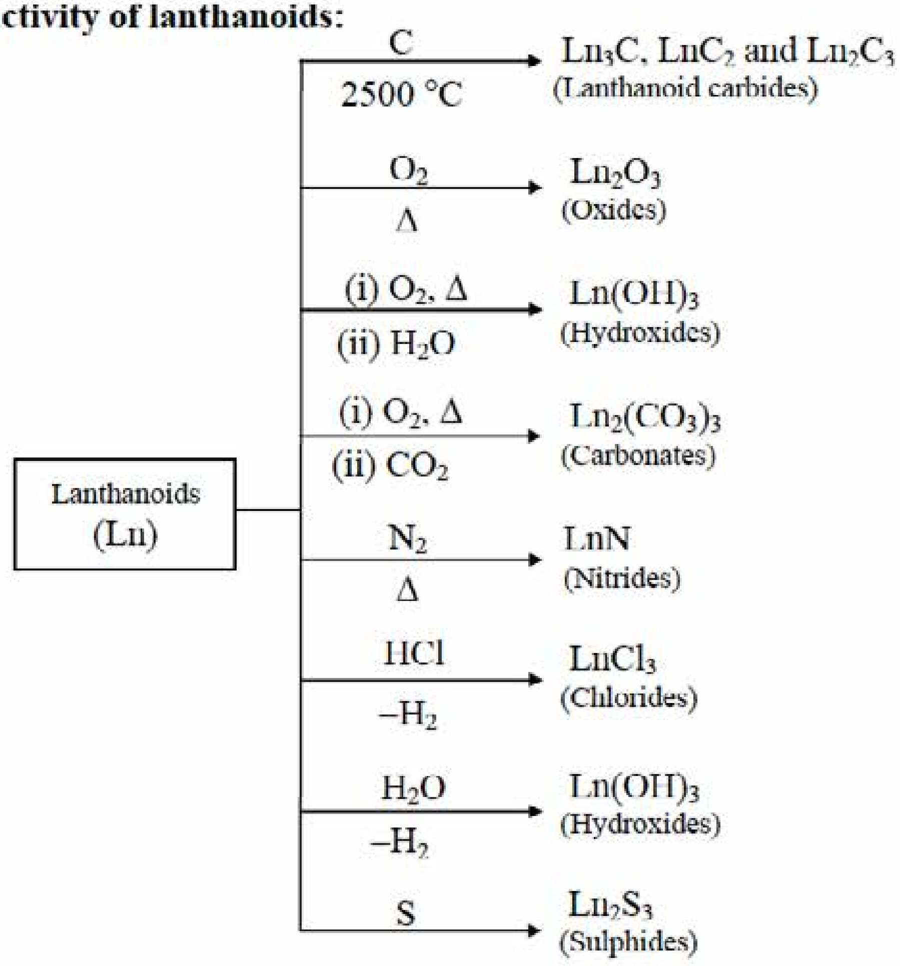
2. **Ionic radii of post lanthanoids:**
   a. There is a regular increase in size from Sc to Y to La. But after the lanthanoids, the increase in radii from second to third transition series almost vanishes.
   b. Pairs of elements such as Zr–Hf (group 4), Nb–Ta (group 5), Mo–W (group 6) and Tc-Re (group 7) possess almost same size. These pairs of elements are called '**chemical twins**'. The properties of these elements are also similar. So due to lanthanoid contraction, elements of second and third series resemble each other.

3. **Similarity among lanthanoids:** Lanthanoids show very small change in radii so their chemical properties are quite similar. Thus it is very difficult to separate the elements in pure state.

Uses of lanthanoids

1. Lanthanoids do not find any use in the pure state. The most important use of lanthanoids is in the production of alloy steels to improve the strength and workability of steel.
2. Their oxides (**eg.** La_2O_3) are used in glass industry, for polishing glass and for making coloured glasses for goggles as they give protection against UV light and as phosphor for television screens and similar fluorescing surfaces. Mixed oxides of lanthanoids are used as catalysts in petroleum cracking.
3. Because of their paramagnetic and ferromagnetic properties, their compounds are used in making magnetic and electronic devices.
4. Ceric sulphate is a well known oxidizing agent in volumetric analysis.

➤ Chemical reactivity of lanthanoids:



Electronic configuration of actinium and 5f-series of f-block elements

1. The 5f-series includes elements from thorium (Th) to lawrencium (Lr).The electronic configuration of these elements can be expressed in terms of Rn (Z = 86).
2. Electronic configuration of Rn (Z=86) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2\ 5p^6\ 5d^{10}\ 5f^{14}\ 6s^2\ 6p^{6}$’
3. Therefore, General electronic configuration of actinoids : [Rn] $5f^{1-14}\ 6d^{0-1}\ 7s^2$
4. The electronic configuration of actinium (Z = 89) is [Rn] $5f^0\ 6d^1\ 7s^2$. It does not contain any 5f electron.
5. Thorium (Z = 90) has expected electronic configuration [Rn] 5f1 6d1 7s2 and observed electronic configuration [Rn] $5f^0\ 6d^2\ 7s^2$. This can be explained on the basis of extra stability of empty 5f orbital. The electrons are successively added to 5f subshell.

Element	Symbol	Atomic Number	Electronic configuration (Expected)	Electronic configuration (Observed)
Actinium	Ac	89	[Rn] $5f^0\ 6d^1\ 7s^2$	[Rn] $5f^0\ 6d^1\ 7s^2$
Thorium	Th	90	[Rn] $5f^1\ 6d^1\ 7s^2$	[Rn] $5f^0\ 6d^2\ 7s^2$
Protactinium	Pa	91	[Rn] $5f^2\ 6d^1\ 7s^2$	[Rn] $5f^2\ 6d^1\ 7s^2$
Uranium	U	92	[Rn] $5f^3\ 6d^1\ 7s^2$	[Rn] $5f^3\ 6d^1\ 7s^2$
Neptunium	Np	93	[Rn] $5f^4\ 6d^1\ 7s^2$	[Rn] $5f^4\ 6d^1\ 7s^2$
Plutonium	Pu	94	[Rn] $5f^5\ 6d^1\ 7s^2$	[Rn] $5f^6\ 6d^0\ 7s^2$
Americium	Am	95	[Rn] $5f^7\ 6d^0\ 7s^2$	[Rn] $5f^7\ 6d^0\ 7s^2$
Curium	Cm	96	[Rn] $5f^7\ 6d^1\ 7s^2$	[Rn] $5f^7\ 6d^1\ 7s^2$
Berkelium	Bk	97	[Rn] $5f^8\ 6d^1\ 7s^2$	[Rn] $5f^9\ 6d^0\ 7s^2$
Californium	Cf	98	[Rn] $5f^9\ 6d^1\ 7s^2$	[Rn] $5f^{10}\ 6d^0\ 7s^2$
Einsteinium	Es	99	[Rn] $5f^{10}\ 6d^1\ 7s^2$	[Rn] $5f^{11}\ 6d^0\ 7s^2$
Fermium	Fm	100	[Rn] $5f^{11}\ 6d^1\ 7s^2$	[Rn] $5f^{12}\ 6d^0\ 7s^2$
Mendelevium	Md	101	[Rn] $5f^{12}\ 6d^1\ 7s^2$	[Rn] $5f^{13}\ 6d^0\ 7s^2$
Nobelium	No	102	[Rn] $5f^{14}\ 6d^0\ 7s^2$	[Rn] $5f^{14}\ 6d^0\ 7s^2$
Lawrencium	Lr	103	[Rn] $5f^{14}\ 6d^1\ 7s^2$	[Rn] $5f^{14}\ 6d^1\ 7s^2$

Oxidation states of actinoids

1. Actinoids have variable oxidation states ranging from +2 to +7 due to availability of 5f, 6d and 7s orbitals.
2. The common oxidation state of actinoid elements is +3. +3 oxidation state is formed by loss of two 7s and one 5f or 6d electrons.
3. With increase in atomic number, +3 oxidation state becomes more and more stable.
4. Beside +3 oxidation state, actinoids show +2, +4, +5, +6 and +7 oxidation states.

5. Actinoids exhibit large number of variable oxidation states because all the electrons in 5f, 6d and 7s orbitals can take part in bond formation due to very small energy gap between these orbitals.
6. Actinoids have more compounds in +3 oxidation state than in +4 oxidation state. However, compounds of actinoids in +3 and +4 oxidation states have tendency to undergo hydrolysis.

Comparison of Lanthanides and Actinides: Both show close resemblance because these involve filling of f-subshells. Both have coloured ions, low electronegativity, high reactivity and show magnetic properties. However, these also differ from each other as shown in the following table.

	Lanthanoids	Actinoids
1	In lanthanoids, last differentiating electron occpies 4f orbital.	In actinoids, last differentiating electron occupies 5f orbital.
2	They are the elements of first inner transition series.	They are the elements of second inner transition series.
3	They are present in period 6.	They are present in period 7.
4	Most of lanthanoids (with exception of promethium) occur in nature.	Most of actinoids (with exception of uranium and thorium) are prepared in laboratory.
5	Most of lanthanoids (with exception of promethium) are non-radioactive.	All the actinoids are radioactive.
6	Lanthanoids do not form oxo cation.	Actinoids form oxo cation such as UO_2^{2+}, PuO^{2+}, UO^+
7	4f orbitals in lanthanoids have higher binding energy.	5f orbitals in actinoids have lower binding energy.
8	Contraction in atomic and ionic radii is relatively less in lanthanoids	Contraction in atomic and ionic radii is relatively greater in actinoids due to poor shielding of 5f electrons.
9	Lanthanoids shows +2, +3 and +4 oxidation states.	Actinoids show +3, +4, +5, +6, +7 oxidation states.
10	Lanthanoids have less tendency to form complexes.	Actinoids have greater tendency to form complexes.
11	Some ions of lanthanoids are coloured.	Most of the ions of actinoids are deeply coloured
12	Lanthanoid hydroxides are less basic in nature.	Actinoid hydroxides are more basic in nature.

9 COORDINATION COMPOUNDS

Salt: A salt is formed by the neutralization of an acid by a base. There are different types of salts. They are:-

a. Simple salt
b. Molecular (or) addition compounds

a. **Simple salt:** A simple salt is formed by the neutralization of an acid by a base.
$KOH + HCl \rightarrow KCl + H_2O$
Normally, a simple salt ionizes in water and produces ions in solution. The solution of the simple salt exhibits the properties of its component ions.

b. **Molecular (or) addition compounds:** When solutions containing two (or) more simple stable compounds in molecular proportions are allowed to evaporate, crystals of new substances are obtained. These substances are termed molecular (or) addition compounds.
   1. **Double salts:** The molecular compounds which dissociate in solution into its constituent ions are known as double salt. These are molecular compounds which are formed by the evaporation of solution containing two (or) more salts in stoichiometric proportions. Double salts retain their properties only in solid state.

      These are also called as ***lattice compounds.***

      Example

      $K_2SO_4. Al_2(SO_4)_3.24H_2O$ Potash alum
      It dissociates in solution
      $K_2SO_4. Al_2(SO_4)_3.24H_2O \rightarrow 2K^+ + 2Al^{3+} + 4SO_4^{2-} + 24H_2O$
      $FeSO_4. (NH_4)_2\ SO_4.6H_2O$ Mohr's salt
      It dissociates in solution
      $FeSO_4. (NH_4)_2\ SO_4.6H_2O \rightarrow Fe^{+2} + 2NH_4^+ + 3SO_4^{2-} + 6H_2O$
      Thus double salts give the test of all their constituent ions in solution.

   2. **Coordination (or complex) compounds:** The molecular compounds, which do not dissociate into its constituent ions in solution, are called coordination compounds. Coordination compound is 'a compound formed from a Lewis acid and a Lewis base'.

When $CuSO_4.4NH_3$ is dissolved in water there is no evidence for the presence of Cu^{2+} ions (or) NH_3 molecules. This is because a new ion $[Cu(NH_3)_4]^{2+}$ is formed in which NH_3 molecules are directly linked with the metal ion

$$CuSO_4 + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} + SO_4^{2-}$$

Thus, a co-ordination compound is a molecular compound that is formed by combination of two (or) more simple stable compounds and retains its identity in the solid as well as in dissolved state.

The properties of coordination compounds are totally different from their individual constituents.

Example

$$Fe(CN)_2 + 4KCN \rightarrow Fe(CN)_2.4KCN \rightleftarrows 4K^+ + Fe(CN)6^{4-}$$

Thus we see that in the above compound the individual ions lose their identity. Such compounds are termed as coordination compounds or complex compounds. Their aqueous solution does not contain simple ions; instead the complex ion remains intact.

A coordination compound may consist of a

- Simple cation and complex anion, for example, $K_4[Fe(CN)_6]$
- Complex cation and simple anion $[Pt(NH_3)_5Cl]Br_3$
- Complex cation and complex anion, for example, $[Ag(NH_3)_2][Ag(CN)_2]$.

The ions $[Fe(CN)_6]^{2-}$, $[Pt(NH_3)_5Cl]^{4+}$, $[Ag(NH_3)_2]^+$ and $[Ag(CN)_2]^-$ are the complex ions. A complex ion is an electrically charged radical formed by the union of a metal cation with one or more neutral molecules or anions.

A co-ordination compound very often (but not always) contains a complex ion.

For example $[NiCO_4]$ is a neutral co-ordination compound and has no complex ion.

9.1 TERMS USED IN COORDINATION CHEMISTRY

Lewis Acid: All electron acceptors are Lewis acids.

Lewis Base: All electron donors are Lewis bases.

Coordination entity: A coordination entity constitutes a central metal atom or ion bonded to a fixed number of ions or molecules. Example: in $K_4[Fe(CN)_6]$, $[Fe(CN)_6]^{4-}$ represents coordination entity.

Central atom/ion: In a coordination entity, the atom/ion to which a fixed number of ions/groups are bound around it (in a definite geometrical arrangement) is called the central atom or ion. Example: in $K_4[Fe(CN)_6]$, Fe^{2+} is the central metal ion.
These central atoms/ions are also referred to as **Lewis acids**.

Ligands: The ions, atoms or molecules bound to the central atom/ion in the coordination entity are called ligands. Ligand may be negative, neutral or positively charged.
The "***donor atom***" is the atom in the ligand, which attaches to the central metal ion.

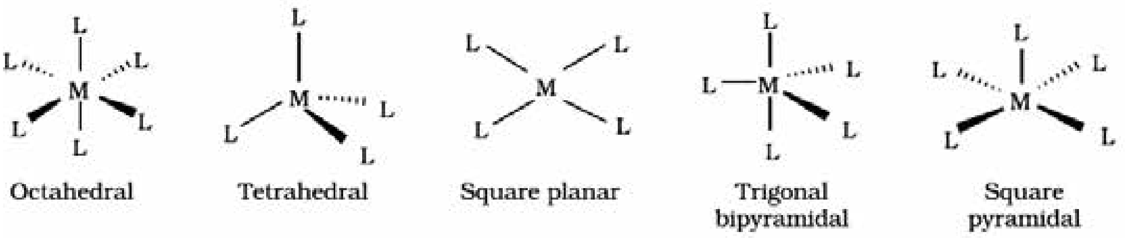
Coordination Number or ligancy: The coordination number of the central atom/ion is determined by the number of sigma bonds between the ligands and the central atom/ions i.e. the number of ligand donor atoms to which the metal is directly attached. For example, in the complex ions, $[PtCl_6]^{2-}$ and $[Ni(NH_3)_4]^{2+}$ the coordination number of Pt and Ni are 6 and 4 respectively.

Pi bonds, if formed between the ligand and the central atom/ion, are not counted for this purpose.

Complex ion	Ligand	Coordination number
1. $[Fe(CN)_6]^{3-}$	CN	6
2. $Ni(CO)_4$	CO	4
3. $Ni(NH_2CH_2CH_2NH_2)_3]^{2+}$	$NH_2CH_2CH_2NH_2$	6
4. $[Co(H_2O)_2(NH_3)_4]^{2+}$	H_2O and NH_3	6

Coordination sphere: The central atom/ion and the ligands attached to it are enclosed in square bracket and are collectively termed as the **coordination sphere**. The ionizable groups are written outside the bracket and are called **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^+.

Coordination polyhedron: The spatial arrangement of the ligand atoms which are directly attached to the central atom/ion defines a coordination polyhedron about the central atom. The most common coordination 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.



Shapes of different coordination polyhedra (M represents the central atom/ion and L, a unidentate ligand.)

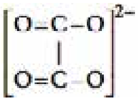
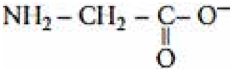
9.2 DENTICITY

The number of ligating (linking) atoms present in a ligand is called the **denticity** of the ligand.

Types of ligands

a. ***Unidentate ligand*:** When a ligand is bound to a metal ion through a single donor atom, the ligand is said to be **unidentate. Example:** Cl^-, H_2O or NH_3 etc.

b. ***Didentate or bidentate***: When a ligand can bind through two donor atoms it is said to be **didentate.** For example $H_2NCH_2CH_2NH_2$ (ethane-1,2-diamine),

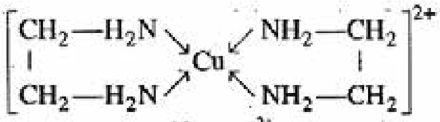
 (oxalate) and  $NH_2-CH_2-\underset{\underset{O}{\|}}{C}-O^-$ (glycenate) etc.

c. ***Polydentate:*** When several donor atoms are present in a single ligand, the ligand is said to be **polydentate**. Ethylenediaminetetraacetate ion ($EDTA^{4-}$) is an important hexadentate ligand. It can bind through two nitrogen and four oxygen atoms to a central metal ion.

d. **Chelating ligand:** When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion and forms a closed or cyclic ring structure it is said to be a **chelating** ligand.

The complexes, thus fonned are called **chelates.** The word chelate has been derived from the Greek word *chele* meaning claw.

The complex formed by Cu^{2+} ion with ethylenediamine is an example of a chelate.



$[Cu(en)_2]^{2+}$

e. ***Ambidentate ligand***: These are the monodentate ligands which can ligate through two different sites, e.g., NO_2^- can ligate through N ($–NO_2$) or through O (–ONO)
SCN⁻ can ligate through S (–SCN) or through N (–NCS)

f. ***Bridging ligand*: A ligand which attaches to more than one metal ion at a time.**

Oxidation Number of Central Atom: The charge of the complex if all the ligands are removed along with the electron pairs that are shared with the central atom is called oxidation number of central atom. e.g., $[Cu(CN)_4]^{3-}$, oxidation number of copper is +1, and represented as Cu(I).

Complex ion or coordination entity: It is an electrically charged species in which central metal atom or ion is surrounded by number of ions or neutral molecules.

1. **Cationic complex entity:** It is the complex ion which carries positive charge. e.g., $[Pt(NH_3)_4]^{2+}$
2. **Anionic complex entity:** It is the complex ion which carries negative charge. e.g., $[Fe(CN)_6]^{4-}$

9.3 TYPES OF COMPLEXES

1. **Homoleptic complexes:** Complexes in which the metal atom or ion is linked to only one kind of donor atoms, are called homoleptic complexes e.g., $[Co(NH_3)_6]^{3+}$
2. **Heteroleptic complexes:** Complexes in which the metal atom or ion is linked to more than one kind of donor atoms are called heteroleptic complexes e.g., $[Co(NH_3)_4CI_2]^+$
3. **Labile and inert complexes:** Complexes in which the ligand substitution is fast are known as labile complexes and in which ligand substitution is slow, are known as inert complexes.

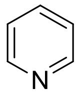
IUPAC Naming of Complex Compounds

The general rules laid down by IUPAC for naming coordination compounds are as follows:

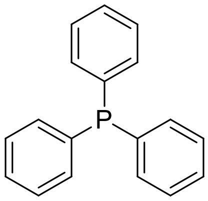
1. While naming a coordination compound the positive ion (cation) is named first followed by the negative ion (anion), for example, in $K_4[Fe(CN)_6]$ potassium is named first followed by the complex ion. Similarly in $[Co(NH_3)_5]Cl_3$ the cation $[Co(NH_3)_5]^{3+}$ is named before the anion Cl^{-}.

2. *Naming of coordination sphere:* While naming the coordination sphere, the ligands are named first followed by the central metal ion. The ligands are written in alphabetical order regardless of the charge on them. For example, in $[Co(NH_3)_5Cl]^{2+}$, ammonia is written before chloride, followed by the metal. If the complex ion contains more than one metal atom then it is indicated by using the prefixes di, tri and so on; for example, $[Re_2 Cl_8]^{2-}$ is named as octachloridodirhenate(III).
3. *Naming of ligands*
    1. *Negative ligands* (end in o): The names of negative ligands ending in 'ide', 'ite' and 'ate' respectively, are changed to end in 'ido', 'ito' and 'ato', respectively. Certain simple ligands which were earlier represented as fluoro, chloro, bromo, iodo, hydroxo, cyano, oxo, etc. are now fluorido, chlorido, bromido, hydroxido, hydrido, cyanido, oxido, etc, (IUPAC recommendations for inorganic nomenclature 2005)
    2. *Positive ligands (end in -ium):*
    NO^+ nitrosonium
    NO_2^+ nitronium
    $NH_2NH_3^+$ hydrazinium

3. *Neutral ligands (named as such)*
   $NH_2CH_2CH_2NH_2$ ethylenediamine



pyridine



triphenylphosphine

However, there are several exceptions in naming neutral ligands. For example

H_2O aqua
NH_3 ammine
NO nitrosyl
CO carbonyl
O_2 dioxygen
N_2 dinitrogen

The names of ligands in accordance with IUPAC recommendations 2005 are given in table below

Formula	**Ligand name**
Cl^-	Chlorido
Br^-	Bromido
CN^-	Cyanido
H^-	Hydrido
F^-	Fluorido
OH^-	Hydroxido
I^-	Iodido
NO_3^-	Nitrato
O^{2-}	Oxido
S^{2-}	Sulphido
CO_3^{2-}	Carbanato
NO_2^-	Nitrito-κN
ONO^-	Nitrito-κO
NCS^-	Thiocyanato-κN
SCN–	Thiocyanato-κS
H_2O	Aqua
NH_3	Ammine
CO	Carbonyl
$C_5H_5^-$	Cyclopentadienyl
C_5H_5N	Pyridine
$NH_2CH_2CH_2NH_2$	Ethylenediamine
$C_2O_4^{2-}$	Oxalato
$H_2NCH_2COO^-$	Glycinato

Table: Common ligands and their names

4. *Order of naming ligand:* In case of the coordination sphere consisting of more than one ligand, then the ligands are named in alphabetical order (ignoring numerical prefixes) without separation by hyphen irrespective of the charge on them, for example, $[Co(NH_3)_4Cl(NO_2)]^+$ the ligands are named in the order ammine, chlorido and nitro. Similarly in the complex $K_3[Fe(CN)_5NO]$ the ligands are named in the order cyanido followed by nitrosyl.
5. *Indicating the number of ligand:* Two, three, four, five and six ligands are represented by using the prefixes di, tri, tetra, penta and hexa, respectively. If the ligand itself includes the prefix di, tri and tetra, then the prefix bis, tris and tetrakis are used for two, three and four ligands with the ligand name in parentheses. For example, two ethylenediamine will be represented as bis(ethylenediamine).
6. *Indicating central metal atom:*For cationic and neutral complexes, the central metal ion is written as such but for anionic complexes *'ate'* is suffixed to the name of the metal.

   For example, $K[Pt(NH_3)Cl_5]$ potassium amminepentachloridoplatinate(IV).

For anionic complexes, the Latin names of the metals are generally used as shown in table below.

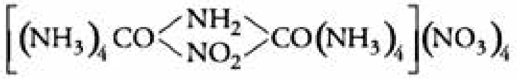
Cu	Cuperate	Zn	Zincate
Al	Aluminate	Cr	Chromate
Sn	Stannate	Co	Cobaltate
Ni	Nickelate	Au	Aurate
Ag	Argentate	Pb	Plumbate
Rh	Rhodate	Fe	Ferrate
Mn	Manganate	B	Borate

Table: Names of some metal atoms in anionic complexes

7. *Oxidation number of the central metal atom:* The ligand name is followed by the name of central metal atom with the oxidation number in parentheses in roman numerals following the metal atom without a gap between the two.

For example $[Co(NH_3)_5Cl]Cl_2$ pentaamminechloridocobalt(III) chloride (The Roman numeral **III** in parentheses indicates the oxidation number of cobalt)

8. *Bridging ligand:* Bridging ligands are preceded by the Greek letter μ(mu), which is repeated before the name of each different kind of bridging group, for example,



$$\left[(NH_3)_4CO\begin{matrix}\diagup NH_2 \diagdown\\ \diagdown NO_2 \diagup\end{matrix}CO(NH_3)_4\right](NO_3)_4$$

μ-amido-μ-nitrobis(tetraamminecobalt(III) nitrate.

In case of ambidentate ligands, which have more than one donor atom, the letter κ is used to indicate the atom of ligation.

For example if the thiocyanato ion coordinates with the metal ion through N atom (NCS)– it is written as thiocyanato – κN and if it coordinates through the S atom it is expressed as thiocyanato – κS.

Similarly NO_2^- is written as nitrito – κN for ligation through N atom as in $M - NO_2^-$ and as nitrito – κO for ligation through O atom as in $M - ONO^-$.

$[Zn(NCS)_4]^{2+}$ tetrathiocyanato – κN – zinc(II) since the ligand is attached to central metal atom through N atom.

Note: the κ terminology has only been recently introduced. Earlier coordination through N was indicated by isothiocyanato and coordination through S was indicated by thiocyanato. However, the old terminology is still widely used.

The above-mentioned rules are further illustrated by the examples given below.

1. $[Co(NH_3)_6]Cl_3$	hexaamminecobalt(III)chloride
2. $[CoCl(NH_3)_5]^{2+}$	pentaamminechloridocobalt(III)
3. $[CoCl.CN.NO_2(NH_3)_3]$	triamminechloridocyanidonitrito-κN-cobalt(III)
4. $[Cd(SCN)_4]^{2+}$	tetrathiocyanato-κS-cadmium(II)
5. $K_4[Fe(CN)_6]$	potassium hexacyanidoferrate(II)
6. $K_4[Fe(CN)_5NO]$	potassium pentacyanidonitrosylferrate(II)
7. $Fe(C_5H_5)_2$	bis(cyclopentadienyl)iron(II)
8. $[Pt(py)_4][PtCl_4]$	tetrapyridineplatinum(II)tetrachloridoplatinate(II)
9. $[Cr(en)_3]Cl_3$	tris(ethylenediamine)chromium(III)chloride
10. $[CuCl_2(CH_3NH_2)_2]$	dichloridobis(methylamine)copper(II)
11. $[Co(H_2O)_6]Cl_3$	hexaaquacobalt(III) chloride

12. $K_2[PtCl_6]$	potassium hexachloroplatinate(IV)
13. $[Pt(NH_3)_2Cl_4]$	diamminetetrachloroplatinum(IV)
14. $[Co(en)_2Cl_2]Cl$	dichlorobis(ethylenediamine)cobalt(III) chloride.
15. $[Co(H_2NCH_2CH_2NH_2)_3]_2(SO_4)_3$	tris (ethane-l,2-diamine)cobalt(III) sulphate
16. $[Ag(NH_3)_2]$ $[Ag(CN)_2]$	diamminesilver(I) dicyanoargentate(I)

Effective Atomic Number (EAN)

This concept was proposed by Sidgwick.

It can be defined as the resultant number of electrons with the metal atom or ion after gaining electrons from the donor atoms of the ligands.

EAN = Z – ON of metal + (2 × CN)

(Where, Z = atomic number of metal atom

ON = oxidation number of metal and CN = coordination number of complex)

The complexes, in which the EAN of the central atom equals the atomic number of the next noble gas, are found to be extra stable.

Complex	Central metal ion	Atomic number of central metal ion	Electrons on metal ion	Electrons gained by coordination	EAN	Atomic number of next noble gas
$[Fe(CN)_6]^{4-}$	Fe^{2+}	26	26 – 2=24	6 × 2 =12	36	36 (Kr)
$[Co(NH_3)_6]3^+$	Co^{3+}	27	27 – 3=24	6 × 2 =12	36	36 (Kr)
$[Ni(CO)_4]$	Ni	28	28 – 0=28	4 × 2 =8	36	36 (Kr)
$[Cu(CN)_4]^{3-}$	Cu^+	29	29 – 1=28	4 × 2 =8	36	36 (Kr)
$[Pd(NH_3)_6]^{4+}$	Pd^{4+}	46	46 – 4=42	6 × 2 =12	54	54 (Xe)
$[Cd(NH_3)_4]^{2+}$	Cd^{2+}	48	48 – 2=46	4 × 2 =8	54	54 (Xe)
$[Pt(NH_3)_6]^{4+}$	Pt^{4+}	78	78 – 4=74	6 × 2 =12	86	86 (Rn)
$[Pt(NH_3)_4Cl_2]^{2+}$	Pt^{4+}	78	78 – 4=74	6 × 2 =12	86	86 (Rn)

Table: Complexes that follow EAN rule

Complex	Central metal ion	Atomic number of central metal ion	Electrons on metal ion	Electrons gained by coordination	EAN	Atomic number of nearest noble gas
$[Cr(NH_3)_6]^{3+}$	Cr^{3+}	24	24 − 3 =21	6 × 2 =12	33	36 (Kr)
$[Ni(en)_3]^{2+}$	Ni^{2+}	28	28 − 2 =26	6 × 2 =12	38	36 (Kr)
$[Ni(NH_3)_6]^{2+}$	Ni^{2+}	28	28 − 2 =26	6 × 2 =12	38	36 (Kr)
$[CuCl_2]^-$	Cu^+	29	29 − 1 =28	2 × 2 =4	32	36 (Kr)
$[Ag(NH_3)_2]^+$	Ag^+	47	47 − 1 =46	2 × 2 =4	50	54 (Xe)
$[Pt(NH_3)_4]^{2+}$	Pt^{2+}	78	78 − 2 =76	4 × 2 =8	84	86 (Rn)

Table: Complexes that do not follow EAN rule

9.4 BONDING IN COORDINATION COMPOUNDS

Werner's Theory

Alfred Werner (**considered as the father of coordination chemistry**) studied the structure of coordination complexes such as $CoCl_3.6NH_3$ and $CuSO_4.4NH_3$ in 1893.
His painstaking work of twenty years in this field won him the Nobel Prize for chemistry in 1913. The main postulates of his theory are:

a. Each metal in coordination compound possesses two types of valencies:
   1. Primary valency or principal valency: This is ionizable, non-directional valency and corresponds to the oxidation state of the metal ion.
   2. Secondary valency: This is directional, non-ionizable valency and it corresponds to the coordination number of the metal ion under consideration.

For example in a simple salt $CuSO_4$, the primary valency of copper is two, that is, copper forms two ionic bonds.

Similarly in the complex $[Cu(NH_3)_4]SO_4$ which ionizes as $[Cu(NH_3)_4]^{2+}$ and SO_4^{2-}; copper again has a primary valency of two as this compound also has two ionic bonds. But is this complex copper has secondary valancy of four, i.e. it forms four secondary bonds with four NH_3.

b. Primary valencies are satisfied by anions only. The number of primary valencies depends upon the oxidation state of the central metal. It may change from one compound to other. These are represented by dotted lines between central metal atom and anion.

c. Secondary valencies are satisfied only by electron pair donor, the ions or the neutral species. These are represented by thick lines.
For example

d. Each metal has a fixed number of secondary valencies also referred as coordination number. The coordination number depends mainly on the size and the charge on the central atom. The maximum number of ions or molecules that the central atom can hold by secondary valencies is known as coordination number.

e. The ions attached to primary valencies possess ionizing nature whereas the ions attached to secondary valencies do not ionise when the complex is dissolved in a solvent.

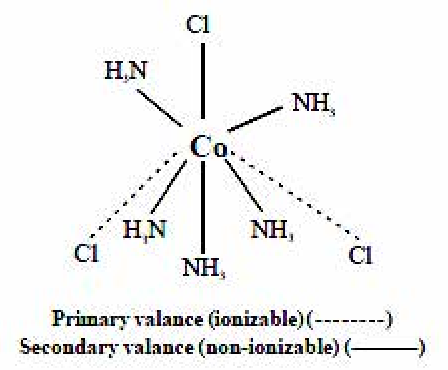
f. Every central ion tends to satisfy its primary as well as secondary valencies.

g. The secondary valencies are directional and are directed in space about the central metal ion. The primary valencies are non directional.

For further illustration let us discuss some examples

a. **$CoCl_3.6NH_3$** This compound on ionization gives three chloride ions. Thus primary valency is satisfied by $3Cl^-$ ions. It has six secondary valencies satisfied by 6 NH_3 molecules.

b. **$CoCl_3$.$5NH_3$:**This compound on ionization gives two chloride ions ∴Primary valency is two and is satisfied by 2 Cl^-. Secondary valency is six ($5NH_3$ & one Cl^-) this Cl^- ion exhibits dual character



Valence bond theory (VB Theory)

Valence bond theory, primarily the work of Linus Pauling regarded bonding as characterized by the overlap of atomic or hybrid orbitals of individual atoms.

The postulates of valence bond theory

1. The central metal atom/ion makes available a number of vacant orbitals equal to its coordination number.
2. These vacant orbitals form covalent bonds with the ligand orbitals.
3. A covalent bond is formed by the overlap of a vacant metal orbital and filled ligand orbitals. This complete overlap leads to the formation of a metal ligand, σ (sigma) bond.
4. A strong covalent bond is formed only when the orbitals overlap to the maximum extent. This maximum overlapping is possible only when the metal vacant orbitals undergo a process called 'hybridisation'. A hybridised orbital has better directional characteristics than an unhybridised one.

The following table gives the coordination number, orbital hybridisation and spatial geometry of the more important geometrics.

Coordination number	Types of hybridization	Geometry
2	sp	Linear
4	sp^3	Tetrahedral
4	dsp^2	Square planner
6	d^2sp^3	Octahedral
6	sp^3d^2	Octahedral

Magnetic moment: A species having atleast one unpaired electron is said to be paramagnetic. It is attracted by an external field. The paramagnetic moment is given by the following spin-only formula.

$$\mu_s = \sqrt{n(n+2)} \text{ BM}$$

μ_s= spin-only magnetic moment

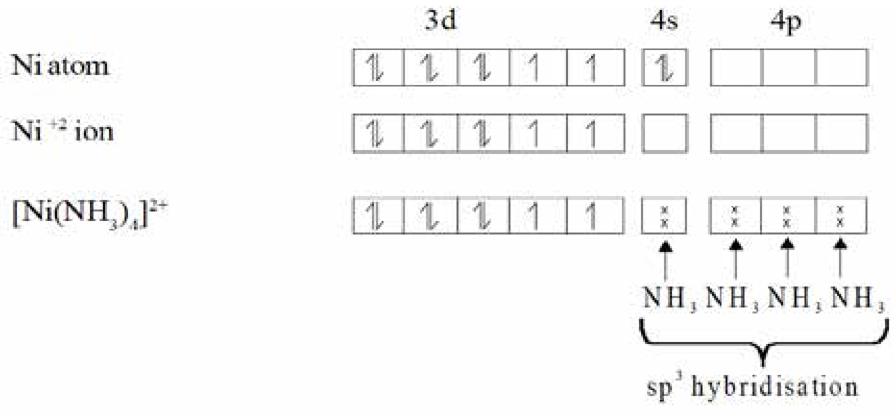
n = number of unpaired electrons
BM = Bohr magneton, the unit which expresses the magnetic moment. When the species does not contain any unpaired electron, it is diamagnetic.

Number of unpaired electrons	Spin-only moment (BM)
1.	$\sqrt{1(1+2)} = \sqrt{3} = 1.73$
2.	$\sqrt{2(2+2)} = \sqrt{8} = 2.83$

Applications of valence bond theory

1. Nickel atom

   Outer electronic configuration $3d^8\ 4s^2$



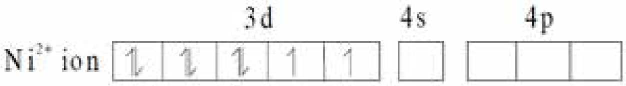
Number of unpaired electrons = 2

$$\therefore \quad \mu_s = \sqrt{2(2+2)} = 2.83\,BM$$

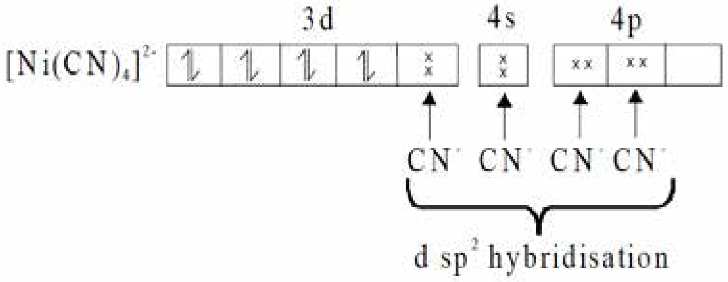
Since the hybridisation is sp^3, the geometry of the molecule is tetrahedral.

2) $[Ni(CN)_4]^{2-}$

Another possible geometry for the 4 coordinated complex is the square planar configuration involving dsp^2 hybridisation.



The ligand CN^- is a powerful ligand. Hence it forces the unpaired electrons to pair up in d orbitals. Hence this complex ion does not contain unpaired electrons. It is diamagnetic.

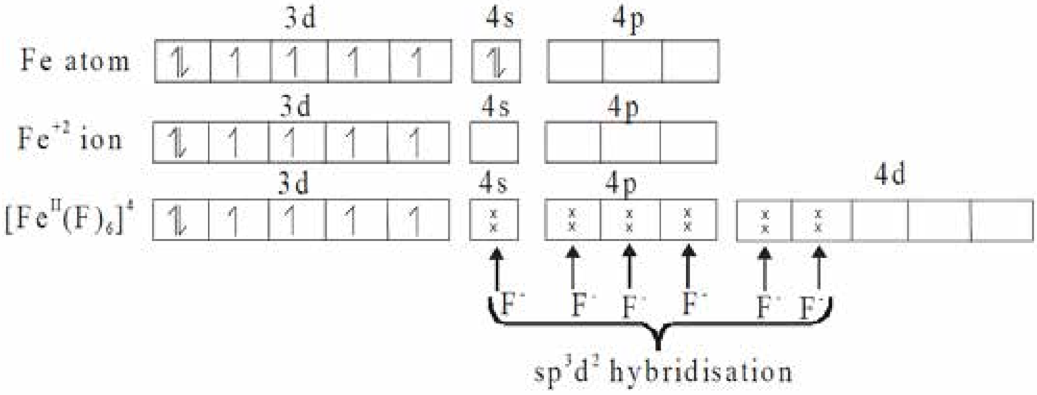


The geometry of the molecule is square planar.

Octahedral complexes

1) Fe atom

Outer electronic configuration $3d^6 \quad 4s^2$

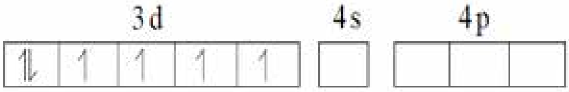


Number of unpaired electron = 4

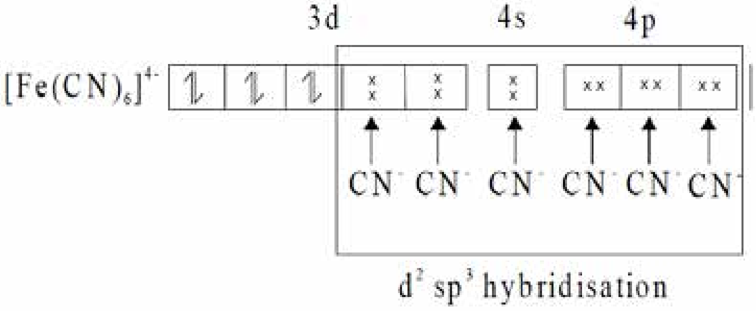
$$\therefore \quad \mu_s \sqrt{4(4+2)} = \sqrt{24} = 4.90\,\text{BM}$$

The molecule is paramagnetic. The geometry of the molecule is octahedral.

2) Fe^{+2} ion



In $[Fe(CN)_6]^{4-}$ complex the CN^- ligand is a powerful ligand, it forces the unpaired electrons in 3d level to pair up inside. Hence the species has no unpaired electron. The molecule is diamagnetic.



The molecular geometry is octahedral.

Limitations of Valence Bond Theory

1. The representation of bonding given by valence bond theory is essentially qualitative in nature.
   It offers no explanation to the electronic spectra and color of coordination compounds, their stabilities, reactivities or mechanism of reactions.
2. Valence bond theory considers that the magnetic moments of complexes are due to the magnetic field generated by the spin of electrons. It does not take into account the orbital motion of electrons. This is the reason why the experimental values differ from those predicted on the basis of valence bond theory. The correct magnetic moment is the sum of μ_{spin} and $\mu_{orbital}$.
3. According to valence bond theory the square planar complexes of Cu(II) as in $[Cu(NH_3)_4]^{2+}$ have dsp^2 hybridization in which the d orbital is vacated by the promotion of unpaired 3d electron to $4p_z$ orbital. According to this explanation the square Cu(II) complexes should easily oxidize to Cu(III) complexes because removal of electron from 4pzorbital would be easy.
   But the oxidation of $[Cu(NH_3)_4]^{2+}$ to $[Cu(NH_3)_4]^{3+}$ does not occur at all.
4. VBT fails to explain why a metal forms inner orbital complexes and at other times it forms outer orbital complexes. For instance, [Co(NH3)4]3+ is diamagnetic and an inner orbital complex, whereas $[CoF_6]^{3-}$ is paramagnetic and an outer orbital complex .

5. Octahedral complexes (d^2sp^3 or sp^3d^2 hybridization), tetrahedral (sp^3) or square planar (dsp^2 hybridization) of complexes of d1, d2, d3 and d9 ions have the same number of unpaired electrons, hence merely on the basis of unpaired electrons it is difficult to predict the geometry and hybridization of these complexes.
6. VBT lays too much stress on central metal ion and the role of ligand is not properly emphasized.

Crystal field theory

This theory was proposed by H. Bethe and van Vleck in 1930. Orgel in 1952 applied this theory to coordination compounds. In this theory, ligands are treated as **point charges** in case of anions and **dipoles** in case of neutral molecules.

The five d-orbitals are classified as

1. Three d-orbitals i.e., dxy, dyz and dzx are oriented in between the coordinate axes and are called t_{2g} – orbitals. (ii) The other two d-orbitals, i.e., d x^2 - y^2 and d z^2 oriented along the x – y and z axes are called e_g – orbitals.
   Due to approach of ligands, the five degenerate d-orbitals split. Splitting of d-orbitals depends on the nature of the crystal field.
   [The energy difference between t_2g and e_g level is designated by Δ and is called **crystal field splitting energy.**]

   By using spectroscopic data for a number of coordination compounds, having the same metal ions but different ligand, the crystal field splitting for each ligand has been calculated. A series in which ligand are arranged in order of increasing magnitude of crystal field splitting, is called **spectrochemical series**.

Spectrochemical series: $I^- < Br^- < SCN^- < Cl^- < S^{2-} < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < edta^{4-} < NH_3 < en < NO_2^- < CN^- < CO$

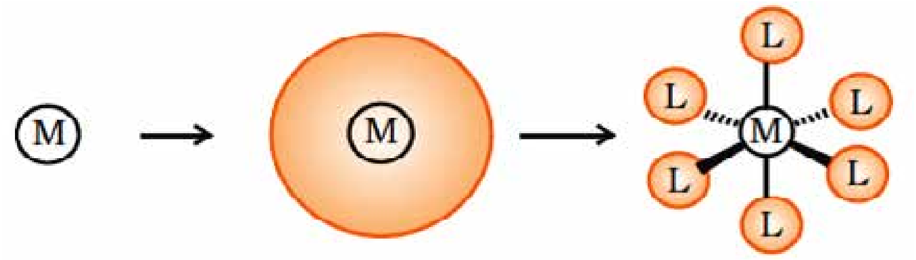
Crystal field splitting in octahedral complex: In case of octahedral complexes, energy separation is denoted by Δo (where subscript o is for octahedral).

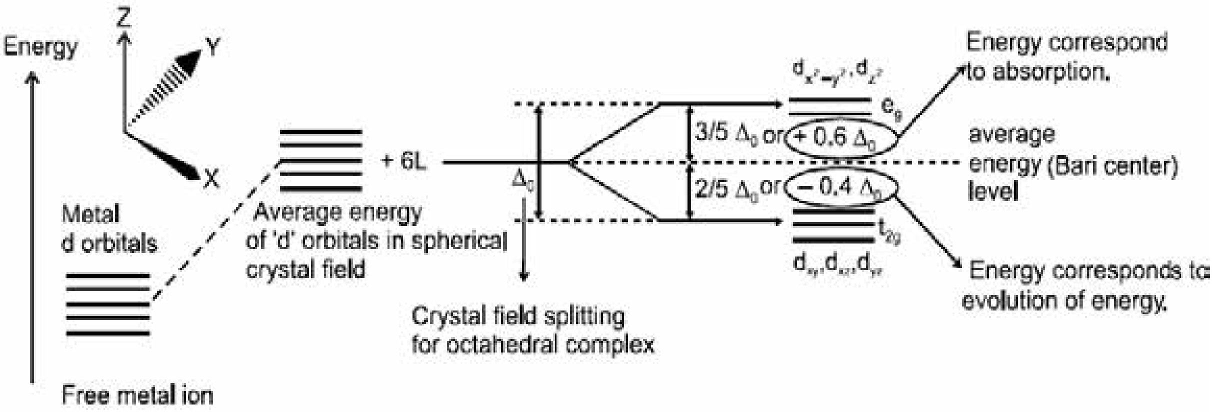
In octahedral complexes, the six-ligands approach the central metal ion along the axis of d x^2 -y^2 and d z^2orbitals.

Energy of e_g set of orbitals > energy of t_{2g} set of orbitals.

The energy of e_g orbitals will increase by (3/5) Δ_o and t_{2g} will decrease by (2/5) Δ_o.

1. If $D_o < P$, the fourth electron enters one of the e_g orbitals giving the configuration $t_{2g}^{3} e_g^{1}$. (where, P = energy required for e- pairing in an orbital). ***Ligands for which $\Delta_o < P$ are known as weak field ligands and form high spin complexes.***
2. If $D_o > P$, it becomes more energetically favourable for the fourth electron to occupy a t_{2g} orbital with configuration $t_{2g}^{4} eg^{0}$. ***Ligands which produce this effect are known as strong field ligands and form low spin complexes.***



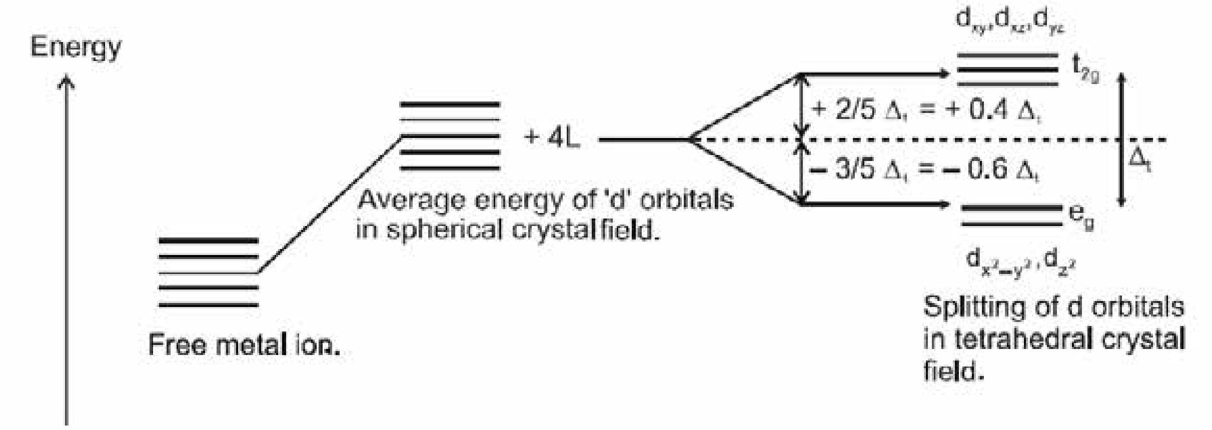


Crystal field splitting in tetrahedral coordination entities: In tetrahedral complexes, four ligands may be imagined to occupy the alternate corners of the cube and the metal ion at the center of the cube.

Energy of t_{2g} set of orbitals > Energy of e_g set of orbitals.

In such complexes d –orbital splitting is inverted and is smaller as compared to the octahedral field splitting.

Orbital splitting energies are so low that pairing of electrons is not possible so these are high spin complexes. $\Delta_t < \Delta_o$ $\Delta_t \cong \mathbf{4/9}\Delta_o$



Limitations of crystal field theory

1. CFT lays emphasis only on the metal orbitals and ignores the ligand orbitals. In the metal orbitals also it considers only the metal d orbitals. It does not take into account other orbitals like the s, p_x, p_y and p_z orbitals. Neither does it consider the p orbitals of the ligand. Hence all properties of complexes dependent on the p- ligand orbitals cannot be explained by CFT;
   CFT does not consider p-bonding in complexes.
2. CFT is unable to explain the relative strengths of ligands. For example CFT offers no explanation as to why H2O is a stronger ligand than OH^-.
3. CFT considers the interaction between metal and ligand as purely ionic. It does not take into account the covalent character of metal ligand bonds.
4. CFT is unable to explain the p-bonding in complexes despite its frequent occurrence.

Isomerism in Coordination Compounds

Compounds that have the same chemical formula but different structural arrangements are called isomers and the phenomenon is called isomerism.

Coordination compounds exhibit the following types of isomerism:

1. **Structural Isomerism:**
   The isomers which have same molecular formula but different structural arrangement of atoms or groups of atoms around the central metal ion are called structural isomers.
   a. **Ionisation isomerism**: The compounds which have same molecular formula but give different ions in solution are called ionisation isomers. In this type of isomerism the interchange of groups occurs within or outside the co-ordination entity. The counter ion itself is a ligand in such type of isomers.

   Ex: i. $[Co(NH_3)_4ClBr]Cl$ and $[Co(NH_3)_4Cl_2]Br$

   $[Co(NH_3)_4ClBr]Cl$ → Tetramminebromochlorocobalt(III) chloride

   $[Co(NH_3)_4Cl_2]Br$ → tetramminedichlorocobalt(III) bromide

   2. $[CoBr(NH_3)_5]SO_4$ and $[CoSO_4(NH_3)_5]Br$

   $[CoBr(NH_3)_5]SO_4$ → Pentamminebromocobalt (III) sulphate

   $[CoSO_4(NH_3)_5]Br$ → Pentamminesulphatocobalt(III)bromide

b. **Hydrate isomerism:** The compounds which have the similar molecular formula but differ in the number of water molecules present as ligands or as molecules of hydration are called hydrate isomers.

- This isomerism is similar to that of ionization isomerism.

Ex : $[CrCl_3(H_2O)_3]$, $[CrCl(H_2O)_5]Cl_2.H_2O$ and $[CrCl_2(H_2O)_4]Cl.2H_2O$

c. **Co-ordination isomerism:** The type of isomerism occurs in compounds containing both cationic and anionic entities and the isomers differ in the distribution of ligands in the co-ordination entity of cationic and anionic parts. Ex: i) $[Co(NH_3)_6]$ $[Cr(CN)_6]$ and $[Cr(NH_3)_6]$ $[Co(CN)_6]$ ii) $[Cu(NH_3)_4]$ $[PtCl_4]$ and $[Pt(NH_3)_4]$ $[CuCl_4]$

d. **Linkage isomerism:** The compounds which have the same molecular formula but differ in the mode of attachment of a ligand to the metal atom or ion are called linkage isomers.
Ex: **(A)** $[Co(ONO)(NH_3)_5]Cl_2$ and **(B)** $[Co(NO_2)(NH_3)_5]Cl_2$

Pentaamminenitritocobalt(III) chloride Pentaamminenitrocobalt (III) chloride

In complex ‘A’ oxygen atom of NO_2^- is the electron pair donar and in B nitrogen atom of NO_2^- is the electron pair donar. NO_2^- is ambidentate ligand.

2. **Stereoisomers:**

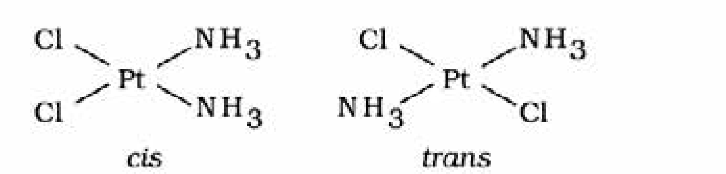
The isomers which have the same position of atoms or groups but they differ in the spatial arrangements around the central atom.
Stereoisomerism is of two types (a) Geometrical isomerism and (b) Optical isomerism.

a. **Geometrical isomerism:** This kind of isomerism gives rise to two kinds of isomers, namely cis and trans isomer.
Cis isomer: When two ligands of same type occupy adjacent positions in co-ordination sphere of the central atom then it is called as cis isomer.

Trans isomer: When two ligands of same type occupy opposite positions to each other in co-ordination sphere of the central atom then it is called as trans isomer.

Geometrical isomerism in complexes with coordination number 4

1. Tetrahedral complexes do not show geometrical isomerism.
2. Square planar complexes of formula [MX_2L_2] (X and L are unidentate) show geometrical isomerism. The two X ligands may be arranged adjacent to each other in a cis isomer, or opposite to each other in a trans isomer, e.g.,

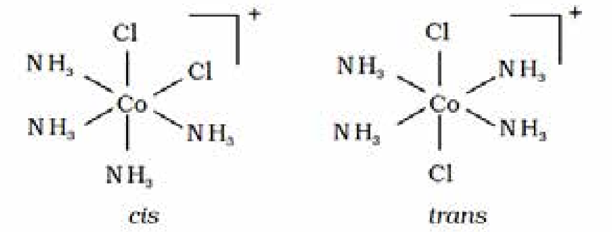


Geometrical isomers (cis and trans) of Pt [NH_3]$_2$$Cl_2$]

3. Square planar complex of the type [MABXL] (where A, B, X, L, are unidentate ligands) shows three isomers, two cis and one trans. e.g., [Pt(NH_3) (Br)(Cl)(Py)].

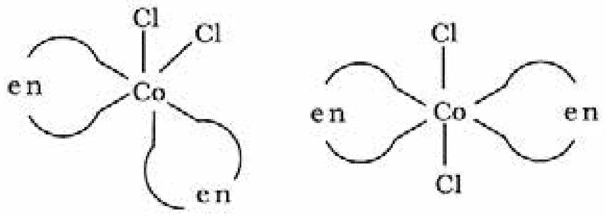
Geometrical isomerism in complexes with coordination number 6

Octahedral complexes of formula [MX_2L_4], in which the two X ligands may be oriented cis or trans to each other, e.g., [Co(NH_3)$_4$$Cl_2$)]$^+$



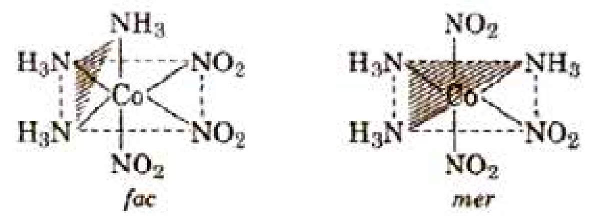
Geometrical isomers (cis and trans) of [Co(NH_3)$_4$$Cl_2$]$^+$

Octahedral complexes of formula [$MX_2(AA)_2$], where X are unidentate ligands and (AA) are bidentate ligand form cis and trans isomers, e.g., [CoC1$_2$(en)$_2$]$^+$



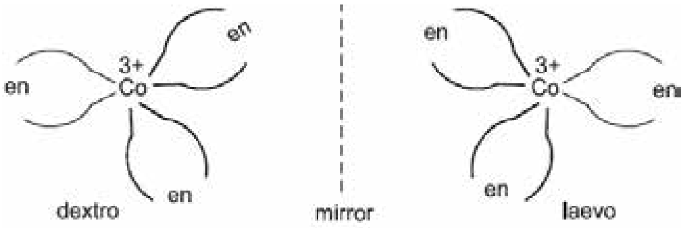
Geometrical isomers (cis and trans) of [$CoCl_2(en)_2$]

The facial (fac) and meridional (mer) isomers: In octahedral complexes of formula [MA_3X_3], if three donor atoms of the same ligands occupy adjacent positions at the corners of an octahedral face, it is known as facial (fac) isomer, when the positions are around the meridian of the octahedron, it is known as meridional (mer) isomer. e.g., [Co ($(NH_3)_3(NO_2)_3$]



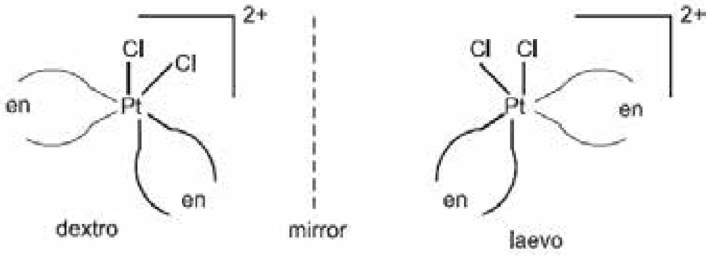
b. **Optical Isomerism:** Optical isomers are mirror images that cannot be superimposed on one another. These are called as *enantiomers*. The molecules or ions that cannot be superimposed are called *chiral*. The two forms are called *dextro (d)* and *laevo (l)* depending upon the direction in which they rotate the plane of polarized light. Optical activity is determined by a polarimeter in which *dextro (d) compound* rotates the plane polarized light to the right, and *laevo (l) compound* rotates it to the left.

When the coordination compounds have same formula but differ in their ability to rotate directions of the plane of polarised light, these are said to exhibit optical isomerism and the molecules are optical isomers. Optical isomerism is common in octahedral complexes involving didentate ligands. For example, [$Co(en)_3]^{3+}$ has *(d)* and *(l)* forms as given below.



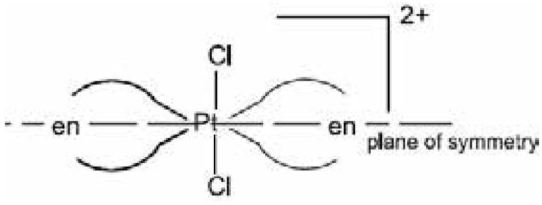
d and ℓ of [$Co(en)_3]^{3+}$

Cis-isomer of [$PtCl_2(en)_2]^{2+}$ show optical isomerism as shown below because of the absence of plane of symmetry as well as centre of symmetry.



d and ℓ of cis-[$PtCl_2(en)_2]^{2+}$

But trans isomer of $[PtCl_2(en)_2]^{2+}$ does not show optical isomerism.



Tetrahedral complex: Optical isomerism is expected in tetrahedral complexes of the type [Mabcd] analogous to tetrahedral carbon atom.

Uses of coordination compounds

1. **Dyes and Pigments:** Coordination compounds have been used from the earliest times as dyes and pigments, for example madder dye which is red, was used by the ancient Greeks and others. It is a complex of hydroxyanthraquinone. A more modern example is the pigment copper phthalocyanine, which is blue.
2. **Analytical Chemistry:** The coordination compounds used for various purpose, in the laboratary are as follows.
   a. **Colour Tests**: Since many complexes are highly coloured they can be used as colourimetric reagents e.g. formation of red 2,2'-bipyridyl and 1,10-phenanthroline complexes as a test for Fe^{2+}
   b. **Gravimetric Analysis**: Here chelating ligands are often used to form insoluble complexes e.g. $Ni(DMG)_2$ and $Al(oxine)_3$.
   c. **Complexometric Titrations and Masking Agents**: An example of this is the use of EDTA in the volumetric determination of a wide variety of metal ions in solution, e.g. Zn^{2+}, Pb^{2+},Ca^{2+},Co^{2+},$Ni^{2+,}Cu^{2+,}$ etc. By careful adjustment of the pH and using suitable indicators, mixtures of metals can be analysed, e.g. Bi^{3+}in the presence of Pb^{2+}. Alternatively, EDTA may be used as a masking agent to remove a metal ion which would interfere with the analysis of a second metal ion present.
3. **Extraction of Metals:** Sometimes certain metals can be leached from their ores by formation of stable complexes e.g. Ag and Au as complexes of cyanide ion.
4. **Bio-Inorganic Chemistry:** Naturally occurring complexes include haemoglobin, chlorophyll, vitamin B_{12} etc. Therapeutic chelating agents are used as antidotes for heavy metal poisoning. EDTA and other complexing agents have been used to speed the elimination of harmful radioactive and other toxic elements from the body. (E.g. Pb^{2+}). In these cases a soluble metal chelate is formed.

5. **Chemotherapy:** An example here is the use of cis-$Pt(NH_3)_2Cl_2$ as an anti-tumour drug.
6. **Synthetic detergents:** Synthetic detergents containing chelating agents such as tripolyphosphate. The chelating agent sequesters hard-water cations, rendering them incapable of interfering with the surfactant.