NILASAILA INSTITUTE OF SCIENCE AND TECHNOLOGY

SERGARH, BALASORE

LECTURES NOTE ON:- APPLIED CHEMISTRY

SEMESTER: 2nd

PREPARED BY :- MISS ALIVAJYOTI BARIK

LECTURER IN CHEMISTRY, NIST POLYTECHNIC

CONTENT

CHAPTER-1

Atomic Structure, Chemical Bonding and solution

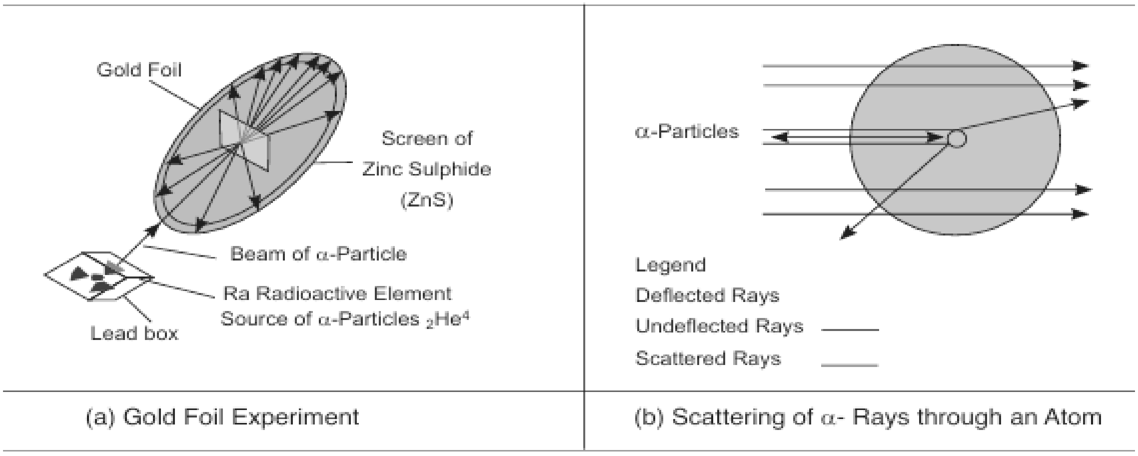
Atomic Structure

Introduction

An atom is the smallest part of the existing universe. To understand the structure and arrangement of the smallest part of matter, thinkers and philosophers from all over the world put forward different theories for explaining the smallest particle of matter. In this unit, we will be learning about basic structure of atom, which is confirmed after performing different experiments.

Rutherford Model of an Atom

In the early 1900, scientists from different countries tried to explain the structure of an atom. J.J. Thomson discovered the presence of electron in an atom in 1897, still he was unable to predict the structure of an atom. J.J Thomson won the Noble Prize of 1906 for the discovery of electrons



(a) Gold Foil Experiment

(b) Scattering of α- Rays through an Atom

(Fig.1.1-Rutherford Experiment))

Rutherford discovered the presence of proton in his famous gold foil experiment. Rutherford used Radium as a source of alpha particles which was placed inside the lead box. A beam of alpha particles bombarded on an ultra-thin gold foil and then the presence of undeflected, scattered and deflected alpha particles were recorded over zinc sulphide (ZnS) screen due to its fluorescent nature as shown in [Fig. 1.1(a)]. He concluded that all of the positive charge and the majority of the mass of the atom must be concentrated in a very small space in the centre of an atom, which he called the nucleus.[Fig. 1.1(b)]. The nucleus is the dense, central core of the atom and is composed of protons and neutrons which contribute nearly all of the mass of the atom. The electrons are distributed around the nucleus and occupy most of the volume of the atom.

Bohr's Theory

Bohr proposed his atomic model to overcome the drawbacks of Rutherford's nuclear model. Bohr's atomic model is based on the following postulates.

- An atom consists of a dense positively charged central part known as the nucleus which is at rest.

- The nucleus contains protons and neutrons combinedly called nucleons.
- The fixed circular path in which electrons revolve around the nucleus is known as orbits or shells.

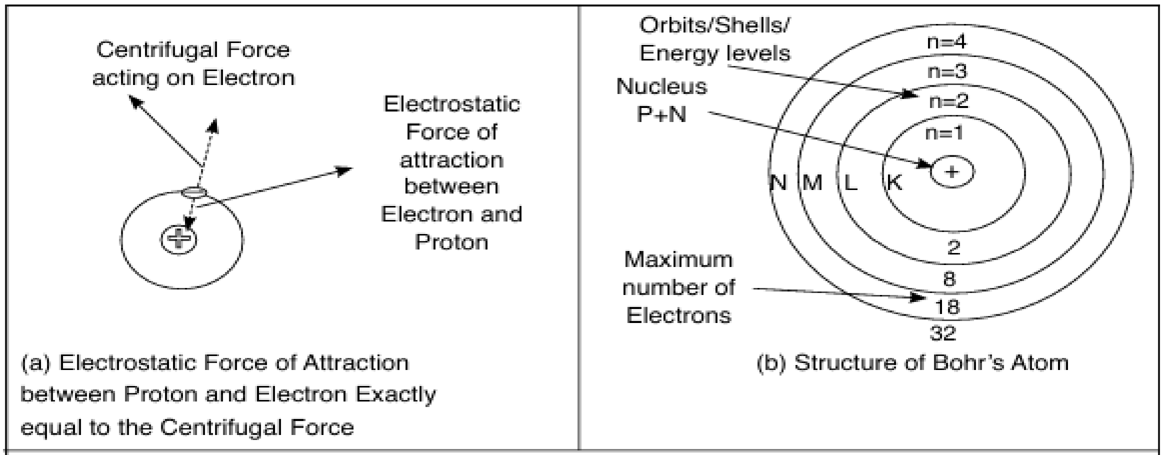
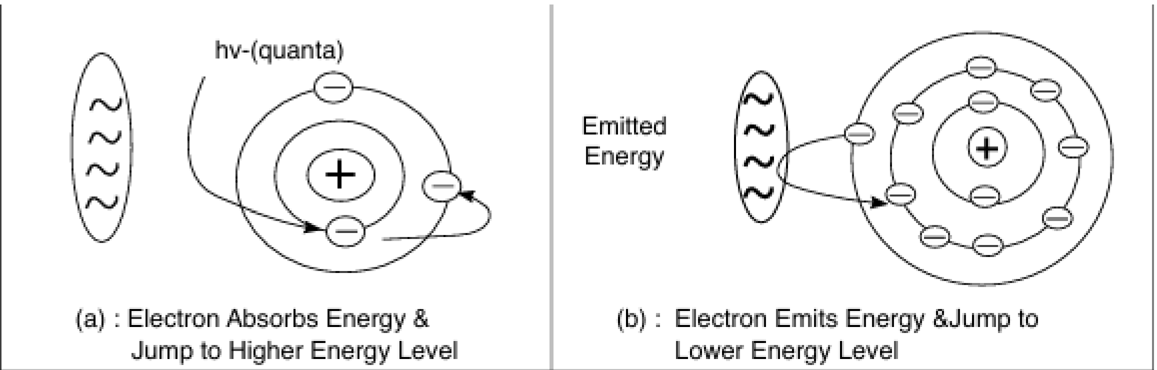


Fig. 1.2 : Bohr's Representation of Forces acting on Electrons and Orbits in an Atom

- Stationary orbits or non-radiating orbits are those orbits in which electrons do not radiate energy i.e. they are permitted to rotate without loss of energy.
- Permitted shells or orbits are those for which the angular momentum of the electron is an integral multiple of $\frac{h}{2\pi}$ i.e. mvr $=n\left(\frac{h}{2\pi}\right)$, where n is a principal quantum number or shell number, momentum is nothing but the product of mass and velocity (mv), r is radius, h is Planks constant $h = 6.626\ x\ 10^{-34} J\ sec$ angular momentum of an electron for n=1, 2, 3, 4…are respectively as $mvr = 1\left(\frac{h}{2\pi}\right), mvr = 2\left(\frac{h}{2\pi}\right), mvr = 3\left(\frac{h}{2\pi}\right), mvr = 4\left(\frac{h}{2\pi}\right)$…
- The shape of orbit is circular. Orbits are designated by K, L, M, N…. or denoted as 1, 2, 3, 4…. from the nucleus as shown in [Fig. 1.2 (b)].
- The maximum capacity to accommodate electrons is given by formula $2n^2$, where n is orbit number.
- The electrostatic force of attraction between the nucleus and electron is exactly balanced by the centrifugal force as shown in [Fig. 1.2 (a)], that is why the electrons do not fall into the nucleus or do not go away from the orbit and hence the atom remains stable.

Hydrogen Spectrum Explanation Based on Bohr's model of an Atom



(a) : Electron Absorbs Energy & Jump to Higher Energy Level

(b) : Electron Emits Energy &Jump to Lower Energy Level

Fig. 1.3 : Jumping of an Electron after Absorbing and Emitting the Energy

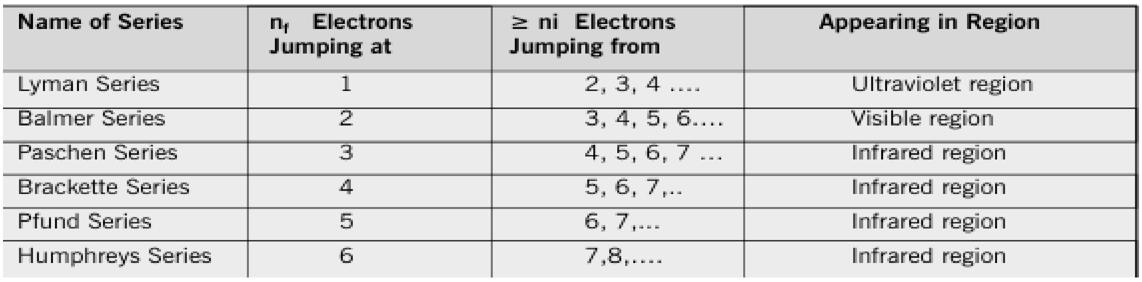
When the electron absorbs energy, the electron moves from the lower energy level to a higher energy level. Jumped electrons are known as excited electrons. As shown in [Fig. 1.3 (a)] when an electron emits energy, electrons jump from a higher energy level to a lower energy level. The emitted energy is the difference of energies between two energy levels i.e. $h\nu$=Energy of electron present in higher energy level - Energy of electron present in lower energy level. Absorbed energy or released energy is in the form of quanta or photon only. The excited electron cannot jump along with high energy to lower energy orbitals. There is a difference in energies when an electron jumps from a higher energy level to a lower one. [Fig. 1.3 (b)]. When an electron emits energy it releases energy in the form of photons. i.e. E= hv. Due to loss of energy, there is a development of spectral lines of different frequencies which shows that distance between two different orbits is not equal. As we move away from the nucleus, the energy of orbits goes on increasing, while the distance between the orbits goes on decreasing. Jumping of the electron from one orbit to another orbit results in the emission of energy known as the transition of the electron. Transition frequency emitted in the form of the photon is given by,

$$\bar{\nu} = \frac{1}{\lambda} = R_H \left[\frac{1}{n_f^2} - \frac{1}{n_i} \right]$$

Where Rh is Rydberg's Constant, ni is initial stationary orbit, nf is final stationary orbit. The wave numbers is reciprocal of the wavelength.

Hence wave number v of photons of the various spectral series are developed as shown in table 1.1 and [Fig. 1.4]. Bohr theory successfully accounts for the spectra of hydrogen and hydrogen like atoms like $He+, Li2+, Be3+, B4+$. Different spectrums are developed due to transition of electron from higher energy level to lower energy level. e.g. Lyman series is a spectral series for the transitions of electron from energy level 2 or 3 or 4 or… to first energy level.

Table 1.1 : Appearance of Hydrogen Spectrum in Different Region



Name of Series	n_f Electrons Jumping at	≥ ni Electrons Jumping from	Appearing in Region
Lyman Series	1	2, 3, 4 ….	Ultraviolet region
Balmer Series	2	3, 4, 5, 6….	Visible region
Paschen Series	3	4, 5, 6, 7 …	Infrared region
Brackette Series	4	5, 6, 7,..	Infrared region
Pfund Series	5	6, 7,…	Infrared region
Humphreys Series	6	7,8,….	Infrared region

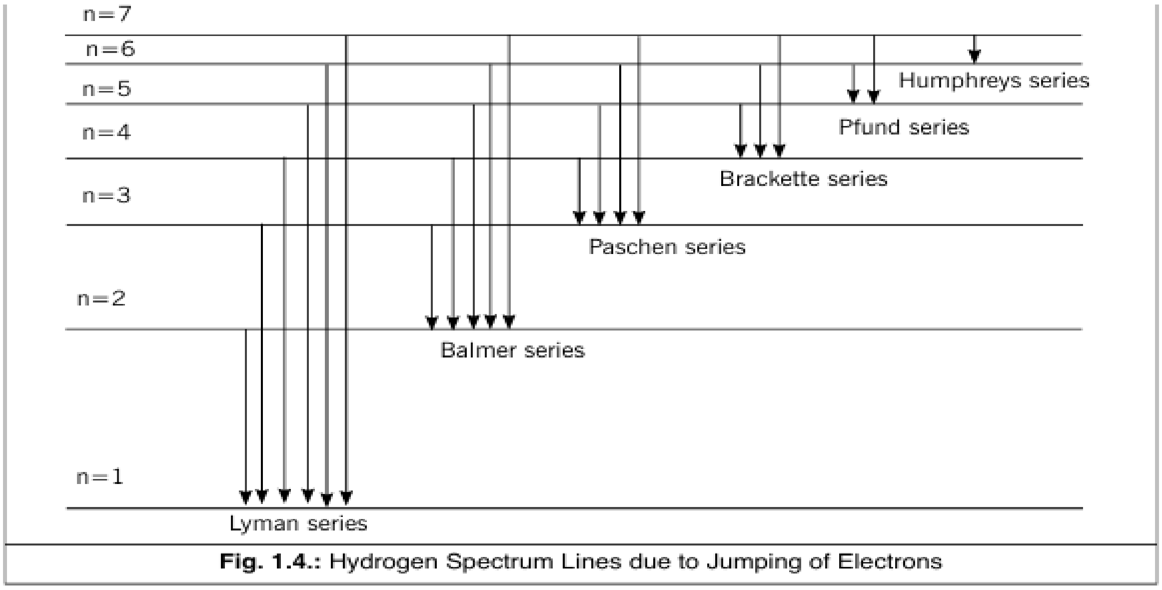


Fig. 1.4.: Hydrogen Spectrum Lines due to Jumping of Electrons

Heisenberg’s Uncertainty Principle

It is not possible to determine precisely the exact position and momentum of moving electron simultaneously. Suppose Δx is uncertainty related to the position of an electron and Δp is the uncertainty related to the momentum of an electron.

Mathematically it is stated as$(\Delta x).(\Delta p) \geq \frac{h}{2\pi}$

when (Δx) is tremendously small we can predict the approximate position of the particle at the same time Δp i.e. uncertainty related to momentum will be more. where Δx is the uncertainty in position and Δp is the uncertainty in momentum (or velocity) of the particle. If the position of the electron is known with high degree of accuracy (Δx is small), then the velocity of the electron will be uncertain [Δp is large]. On the other hand, if the velocity of the electron is known precisely (Δp is small), then the position of the electron will be uncertain(Δx will be large). Heisenberg won the Noble prize in 1932 for the creation of quantum mechanics, the application of which has led to the discovery of the allotropic forms of hydrogen.

Orbital Concept and Shapes of s, p, d and f Orbitals

An orbit, as proposed by Bohr, is a fixed circular path around the nucleus in which an electron moves. A precise description of this path of the electron is impossible according to the Heisenberg uncertainty principle. An atomic orbital thus represents a region in three-dimensional space around the nucleus where there is a maximum probability of finding an electron of specific energy. There are four types of orbitals as follows :

s-Orbital: These orbitals are having spherical and non-directional shape [Fig. 1.5]. Each s orbital can accommodate 2 electrons in the opposite spin. One electron with +1/2 spin, another electron with -1/2 spin. In another way one with upward spin and another with downward spin or one with clockwise spin another with counter-clockwise (anticlockwise spin). Size of 1s is less than 2s orbital; size of 2s is less than 3s orbital.

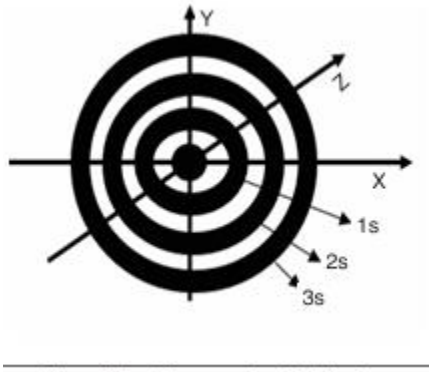


Fig. 1.5 : Shape of s-Orbitals

The empty region between two s-orbitals, where zero per cent probability of finding the electrons is known as the zero electron density region.

p-Orbital: There are three p- sub orbitals (px, py and pz) orbitals having dumb-bell shape [Fig. 1.6]. These orbitals are directional and along the axis orbital. Each p suborbital can accommodate 2 electrons in opposite spin hence the capacity of p orbital is 6 electrons. These sub orbitals are degenerate (having an equal amount of energy). If the lobe of the orbital is sprayed along the x-axis, then that orbital is called px orbital. Similarly if the lobe is sprayed along y-axis then that orbital is called py orbital and if lobe is sprayed along z-axis then that orbital is called pz orbital.

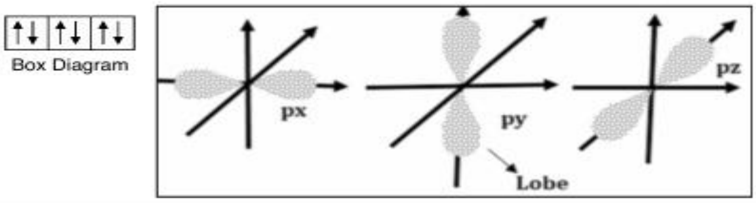


Fig. 1.6 : Dumbbell Shape of p-Orbitals

d-Orbital: There are five d- sub orbitals (dxy, dyz, dxz, $dx2 - y2\ and\ dz2$) orbitals [Fig. 1.7]. d-orbitals are having the double dumb-bell shape or four-lobe planar structure. These orbitals are directional and along the axis orbital (dx2–dy2 and dz2) as well as in between the axis orbitals (dxy, dyz and dxz). Each d sub orbital can accommodate 2 electrons in opposite spin hence the maximum capacity of d orbital to accommodate electrons is 10 electrons.

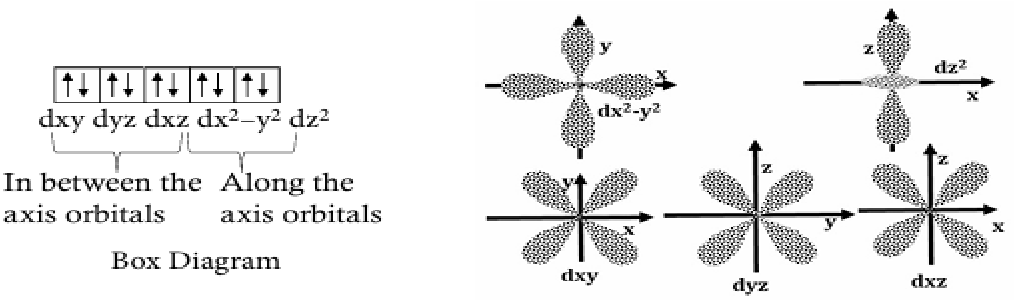


Fig. 1.7 : Double Dumbbell Shape of d-Orbitals

f-Orbital : There are seven f- sub orbitals fx(x2-3y2), fy(3x2-y2),fz(x2-y2),fxz2, fyz2, fz3, fxyz.

f-orbitals are having a complicated shape. Each f-orbital are having seven f-sub orbitals hence capacity to accommodate electrons is 14 electrons.

Quantum Numbers

The Bohr model was a one-dimensional model that used one quantum number to describe the distribution of electrons in the atom. It explains the size of the orbit, which was described by the principal quantum number (n). Schrodinger's model allowed the electron to occupy three-dimensional space. It therefore required set of four quantum numbers, to describe the orbitals in which electrons can be found. Four quantum numbers as principal quantum number(n) give information about main energy level; azimuthal quantum number (l)provides information about sub energy level; magnetic quantum number (m) gives information of orientation of sub-energy level and spin quantum number (ms) gives the direction of spin. These four quantum numbers in an atom give the exact position of the electron, it is just like working of global positioning system (GPS) location or address, we can say that these quantum numbers give the exact location or address of electron.

(A)Principal Quantum Number (n)

- This quantum number is represented by the letter (n).
- This number gives information on the position of the electron as well as the energy associated with the electron.
- The values of 'n' are positive integral numbers as 1, 2, 3, 4…etc. corresponding to K, L, M, N…etc. shells.

(B)Angular Momentum Quantum Number or Azimuthal Quantum Number (l)

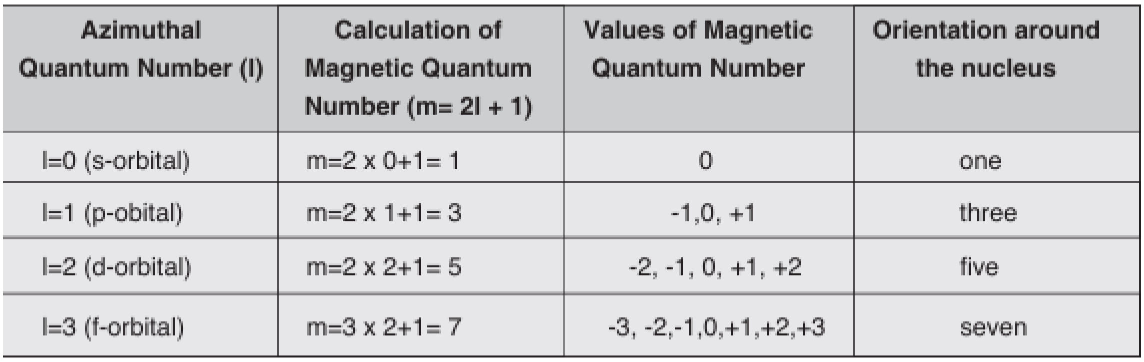
- This quantum number is represented by the letter (l).
- It is used to describe sub-energy level.

- Values of azimuthal quantum numbers are all possible whole numbers from 0 to n-1
  When n=1 thus l=0 (Represents s-orbital)
  When n=2 thus l=0,1 (Represents s and p orbital)
  When n=3 thus l=0,1,2 (Represents s, p and d orbital)
  When n=4 thus l=0,1,2,3 (Represents s, p, d and f orbital)
- Thus various subshells are designated as s, p, d, f according to the value of l=0, 1, 2, 3 respectively.

(C) Magnetic Quantum Number (m)

This quantum number is represented by the letter (m). It is used to describe the orientation of the orbitals. The number of values allowed to m depends on the values of 1. Possible values of m range from –1 through 0 to +1 thus making a total of 2l+1 values. table 1.2

Table 1.2 : Magnetic Quantum Number



Azimuthal Quantum Number (l)	Calculation of Magnetic Quantum Number (m= 2l + 1)	Values of Magnetic Quantum Number	Orientation around the nucleus
l=0 (s-orbital)	m=2 x 0+1= 1	0	one
l=1 (p-obital)	m=2 x 1+1= 3	-1,0, +1	three
l=2 (d-orbital)	m=2 x 2+1= 5	-2, -1, 0, +1, +2	five
l=3 (f-orbital)	m=3 x 2+1= 7	-3, -2,-1,0,+1,+2,+3	seven

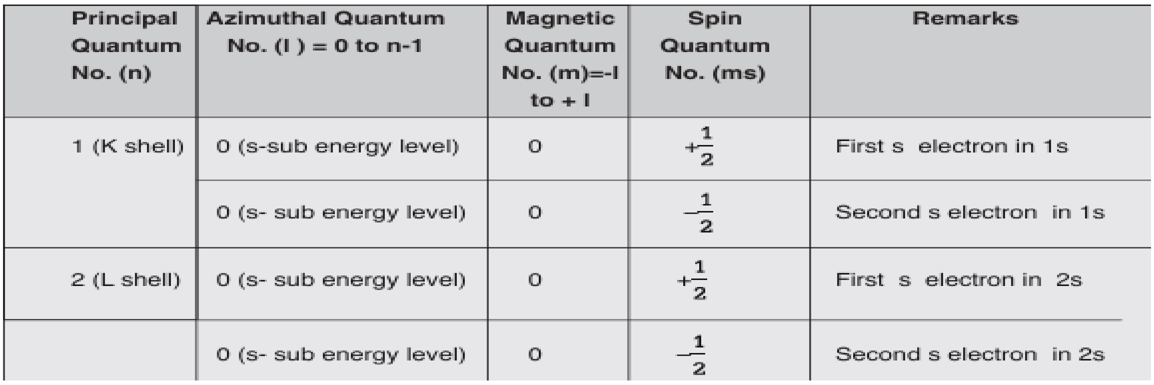
(D) Spin Quantum Number (ms)

This quantum number is represented by (ms). It shows the direction in which the electron is spinning about its own axis. The spin quantum number shows two possible values i.e. clockwise spin as $+\frac{1}{2}$and anticlockwise spin $as -\frac{1}{2}$.

Pauli's Exclusion Principle

No two electrons in a single atom can have same set of four quantum numbers. In an atom two electrons can have a same set of three quantum numbers but they must differ in the value of fourth quantum number table 1.3 The first two electrons in [Ne] gas have the same set of three quantum numbers but differ in spin quantum number i.e. one with $+\frac{1}{2}$ spin and other with $-\frac{1}{2}$ spin.

Table 1.3 : Four Quantum Numbers for First 10 Electrons in [Ne]



Principal Quantum No. (n)	Azimuthal Quantum No. (l) = 0 to n-1	Magnetic Quantum No. (m)=-l to + l	Spin Quantum No. (ms)	Remarks
1 (K shell)	0 (s-sub energy level)	0	$+\frac{1}{2}$	First s electron in 1s
	0 (s- sub energy level)	0	$-\frac{1}{2}$	Second s electron in 1s
2 (L shell)	0 (s- sub energy level)	0	$+\frac{1}{2}$	First s electron in 2s
	0 (s- sub energy level)	0	$-\frac{1}{2}$	Second s electron in 2s

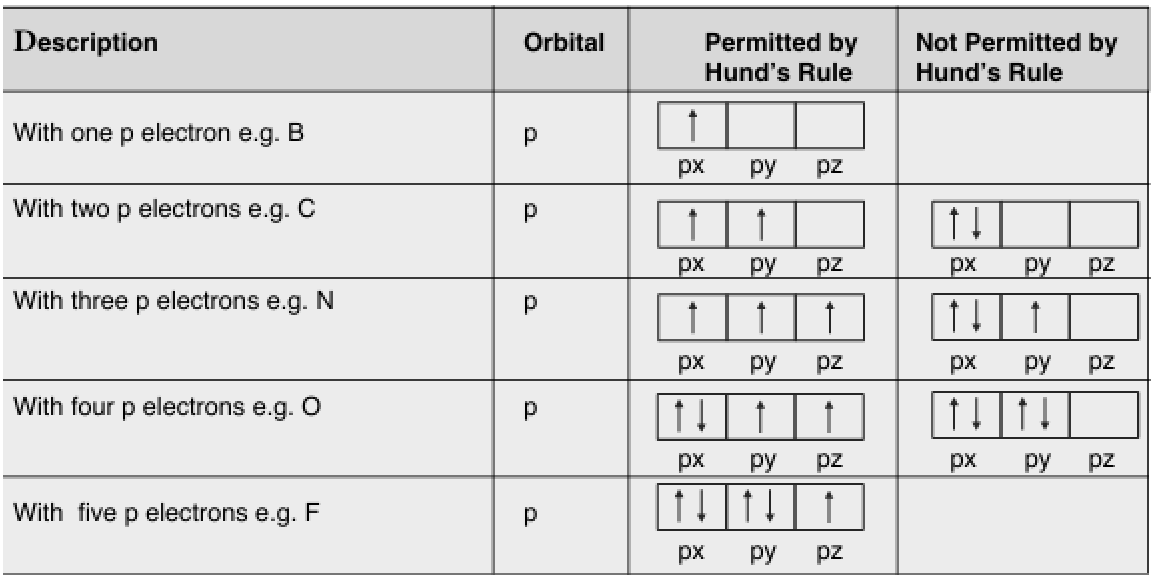
	1 (p- sub energy level)	-1	$+\frac{1}{2}$	First p electron in 2px
	1 (p- sub energy level)	0	$+\frac{1}{2}$	First p electron in 2py
	1 (p- sub energy level)	+1	$+\frac{1}{2}$	First p electron in 2pz
	1 (p- sub energy level)	-1	$-\frac{1}{2}$	Second p electron in 2px
	1 (p- sub energy level)	0	$-\frac{1}{2}$	Second p electron in 2py
	1 (p- sub energy level)	+1	$-\frac{1}{2}$	Second p electron in 2pz

Hund's Rule of maximum multiplicity

When several orbitals with same energy are available, the electrons enters in all orbitals with parallel spin, before pairing in any one orbital.

Electron pairing in any orbital is not possible until the available orbitals of the same energy from the given subshell contains one electron each. Electrons of different atoms while entering into p-orbital follows Hund's rule as shown in table 1.4

Table 1.4 : Pairing Arrangement of Electrons Permitted by Hund's Rule



Description	Orbital	Permitted by Hund's Rule	Not Permitted by Hund's Rule
With one p electron e.g. B	p	[↑] [ ] [ ] px py pz	
With two p electrons e.g. C	p	[↑] [↑] [ ] px py pz	[↑↓] [ ] [ ] px py pz
With three p electrons e.g. N	p	[↑] [↑] [↑] px py pz	[↑↓] [↑] [ ] px py pz
With four p electrons e.g. O	p	[↑↓] [↑] [↑] px py pz	[↑↓] [↑↓] [ ] px py pz
With five p electrons e.g. F	p	[↑↓] [↑↓] [↑] px py pz	

Aufbau Rule

When several orbitals are available, electron enters into all available orbitals with an increasing amount of energy. i.e. orbitals with lower energy are filled first then electrons enters into higher energy orbitals. 1s<2s<2p<3s<3p<4s<3d<4p<5s<4d<5p<6s<4f<5d<6p<7s<5f<6d<7p<8s.

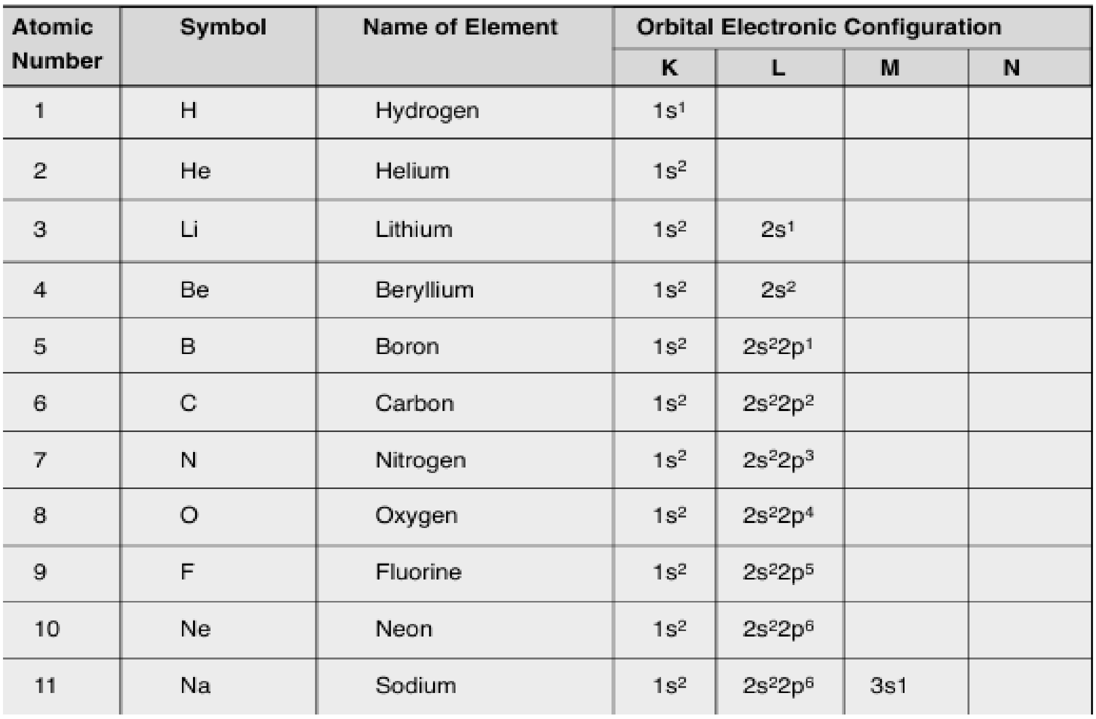
Electronic Configuration

Electronic configuration of 3Li can be written as follows

e.g.3Li 1s2 2s1

In case of lithium first two electrons enter into 1s orbital and after fulfilling the capacity of 1s orbital, the remaining electron enters into 2s orbital. Orbital electronic configuration of the first 11 elements are as shown in table 1.5

Table 1.5 : Orbital Electronic Configuration of Elements up to Atomic No. 11



Atomic Number	Symbol	Name of Element	Orbital Electronic Configuration			
			K	L	M	N
1	H	Hydrogen	$1s^1$			
2	He	Helium	$1s^2$			
3	Li	Lithium	$1s^2$	$2s^1$		
4	Be	Beryllium	$1s^2$	$2s^2$		
5	B	Boron	$1s^2$	$2s^22p^1$		
6	C	Carbon	$1s^2$	$2s^22p^2$		
7	N	Nitrogen	$1s^2$	$2s^22p^3$		
8	O	Oxygen	$1s^2$	$2s^22p^4$		
9	F	Fluorine	$1s^2$	$2s^22p^5$		
10	Ne	Neon	$1s^2$	$2s^22p^6$		
11	Na	Sodium	$1s^2$	$2s^22p^6$	3s1	

CHEMICAL BONDING

Introduction

All matters are composed of atoms. Atoms do not exist in an isolated state in nature. All the naturally occurring elements such as gold, silver, diamond and naturally occurring compound such as water, sodium chloride, CO2 always exists in combination only. Even the variety of compound being prepared synthetically are also having the atoms in a combined state. When two atoms tend to remain together rather than separate from each other, they are said to form a chemical bond with each other. A chemical bond may be defined as an attractive force which holds together the constituent atoms in a molecule.

(A)Lewis Octet Rule:

According to the Lewis Octet rule, atoms of all elements tend to acquire an electronic configuration similar to that of inert gases because it represents the most stable electronic configuration. Valence electrons have a significant role in chemical bonding. All the atoms with unstable or incomplete outer shell have a tendency to gain or lose electrons so as to acquire an electronic configuration of the nearest inert gas in the periodic table. This is called the 'Octet Rule'.

Example : In NH3, Nitrogen atoms has 5 outer electrons. It shares three of these, forming three bonds and attain an Octet. Hydrogen has one electron and by sharing one electron, it attains a stable arrangement of two electrons [Fig. 1.9]

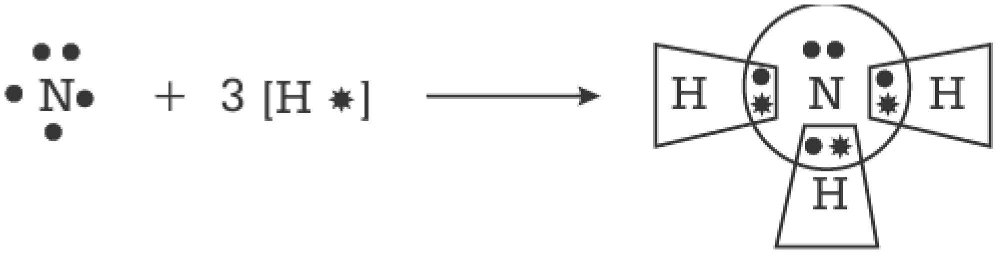


Fig. 1.9 : Lewis Structure of Ammonia

(B) Limitations of Octet Rule

Octet rule is helpful in understanding the structure of most of the organic compounds and second period elements of the periodic table. There are certain exceptions to the octet rule as follows **.**

The shape of the molecules cannot be explained by this. The relative stability and energy of a molecule cannot be explained by this. The octet rule is based on the chemical inertness of noble gases. Some noble gases like Xenon and Krypton combine with oxygen and fluorine to form the number of compounds.

Types of Bonds

Now let us understand the three ways, by which the atoms can acquire a stable electronic configuration by gaining, losing or sharing of electrons. Different types of bonds can also be understood in the following ways:-

1.Inonic bond
2.Covalent bond
3.Metallic bond

Ionic bond

When a bond is formed by complete transference of electrons from one atom to another to complete their outermost orbit by acquiring eight electrons (i,e octet) or two electrons(i.e. duplet) e.g. in case of hydrogen, lithium and hence acquire the stable nearest noble gas configuration, the bond formed is called ionic bond or electrovalent bond.

The chemical bond formed between two or more atoms as a result of the transfer of one or more electrons from electropositive to electronegative atoms is called electrovalent bond. This bond is also called ionic bond or polar bond Ionic bonding results in the formation of two oppositely charged ions, positive ion (cations) and negative ions (anions), which results in a strong attractive force between them termed as ionic or electrovalent bond. Ionic bonds are formed between atoms with large differences in electronegativity. Ionic bond also possess some covalent character.

Formation of NaCl The sodium chloride molecule contains one atom of sodium and one atom of chlorine. Electronic configuration of atoms present in molecular formation are as

${}_{11}$Na- $1s^2\ 2s^2\ 2p^6\ 3s^1$; (2, 8, 1)

${}_{17}$Cl- $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$; (2, 8, 7)

$$\underset{\textit{Sodium atom}}{\underset{2,8,1}{{}_{11}\mathrm{Na}}} \xrightarrow{\qquad} \underset{\textit{Sodium ion (Cation)}}{\underset{2,\,8}{{}_{11}\mathrm{Na}^{+} + 1e^{-}}}$$

Here sodium shows +1 positive electrovalency by loss of one electron and attains [Ne] gas electronic configuration

$$\underset{\textit{Chlorine atom}}{\underset{2,8,7}{{}_{17}\mathrm{Cl} + 1e^{-}}} \xrightarrow{\qquad} \underset{\textit{Chloride ion (Anion)}}{\underset{2,8,8}{{}_{17}\mathrm{Cl}^{-}}}$$

Here chlorine shows -1 negative electrovalency by the gain of one electron and attains [Ar] gas electronic configuration

Due to the loss and gain of one electron, ions are developed which held together by the electrostatic force of attraction. Due to the loss of one electron, sodium attains the nearest inert gas configuration of [10Ne] gas while chlorine attains the nearest [18Ar] gas configuration.

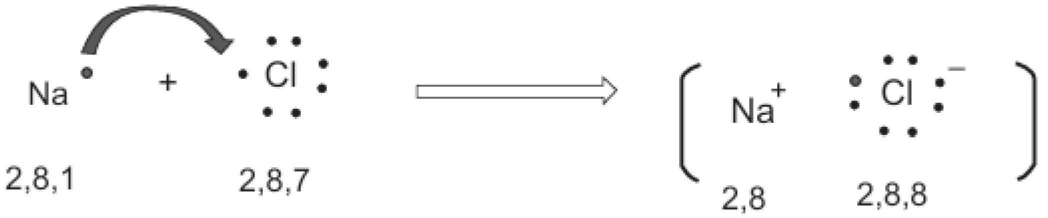


Fig. 1.10 : Electrovalent Bond /Ionic Bond Formation due to Transfer of Electrons

The bond which is formed by loss and gain of electrons or the bond which is formed by transfer of electrons is known as an electrovalent bond or ionic bond [Fig.1.10]. Generally metals are having 1,2,3 electrons in their valence shell, hence they have tendency to lose valence shell electrons and show positive electrovalency. Non-metals are having 5 or 6 or 7 electrons in their valence shell, hence they have tendency to accept electrons and show negative electrovalency.

Covalent Bond

Langmuir refined the Lewis theory by introducing the term covalent bond. Lewis introduced simple symbols to denote the electrons present in the outer shell of an atom known as the valence electrons. These symbols are known as electron-dot symbols and the structure of the compound is known as Lewis dot structure. The dot represents the electrons. Such structures are known as Lewis dot structure. Lewis dot structures provide a picture of bonding in molecules and ions in terms of shared pair of electrons and the octet rule. Electron dot structures of covalent molecules are written with respect to octet rule. According to this rule, all the atoms in the molecule will have eight electrons in their valence shell except the hydrogen atom. Hydrogen will have only two electrons because only two electrons complete its first shell to attain helium configuration. Element of group 17, Cl will share one electron to attain a stable octet, the elements of group 16, O and S will share two electrons, the elements of group 15 will share three electrons and so on.

Conditions for writing the Lewis dot structures

Sharing of an electron pair between the atoms results in the formation of covalent bonds. Each bond consists of two electrons which are contributed by each one of the combining atoms during bond formation as shown in [Fig. 1.11]. Each atom attains octet configuration in its valence shell by mutual sharing of electrons.

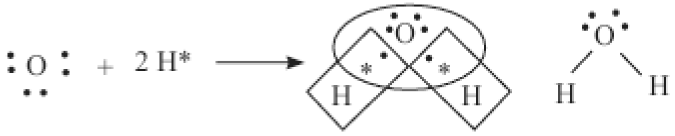


Fig. 1.11 : Lewis Dot Structure

The bond formed between the two atoms by mutual sharing of electrons between them so as to complete their octet or duplets (in case of elements having only one shell) is called covalent bond or covalent linkage and the number of electrons contributed by each atom is known as covalency. Each pair of shared electron is indicated by a line (-). A covalent bond is formed by the equal sharing of electrons from both the participating atoms. The pair of electrons, which are participating in this type of bonding is called shared pair or bonding pair. Covalent bonds are also known as molecular bonds. By sharing bonding pairs, atoms achieve stability in their outer shell, similar to the atoms of noble gases.

Covalent Bonding occurs in two ways

Sharing of electrons between atoms of the same type e.g. Formation of H_2 [Fig. 1.12], Cl_2, O_2, etc. Sharing of electrons between atoms of different type e.g. Formation of CH_4, H_2O, NH_3, etc.

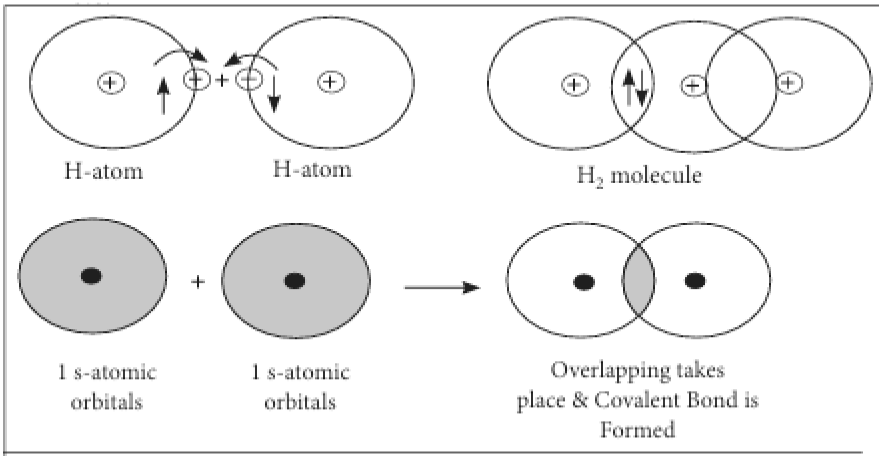


Fig. 1.12 : Formation of Hydrogen Molecule

Covalent Bond in C atom

Covalent Bonding The carbon atom has versatile nature. The carbon atom is able to form so many bonds with so many elements. Each C atom can either donate or accept four electrons to attain stable configuration. The atomic structure of carbon is 6. Its electronic configuration is 2, 4. Donating four electrons from the outermost orbit causes only two electrons left in it. In this case, the carbon atom will become positively charged but still remains unstable. Similarly accepting four electrons from outside will cause carbon atom to become negatively charged. In this situation also C atom remains unstable. From the above explanation, it is inferred that, both the situation leads to the instability of carbon atom. Hence no option is left with C atom, but to share four electrons. Carbon cannot gain or donate electrons, so to complete its nearest noble gas configuration, hence carbon can share all the four valence electrons with other atom and thus forming covalent bonds.

Types of Covalent Bond

Depending upon the number of shared electron pairs, the covalent bond can be classified into single, double and triple covalent bond table 1.18 and [Fig. 1.13].

Table 1.8 : Participation of Electrons in Covalent Bond Formation

Type of Covalent Bond	Name of Molecule as Example	No. of Mutually Shared Electron pair	*Bonding Electrons	**Lone pair of Electrons	Free Electrons
Single	Chlorine Cl_2	1	2	6	12
Double	Oxygen O_2	2	4	4	08
Triple	Nitrogen N_2	3	6	2	04

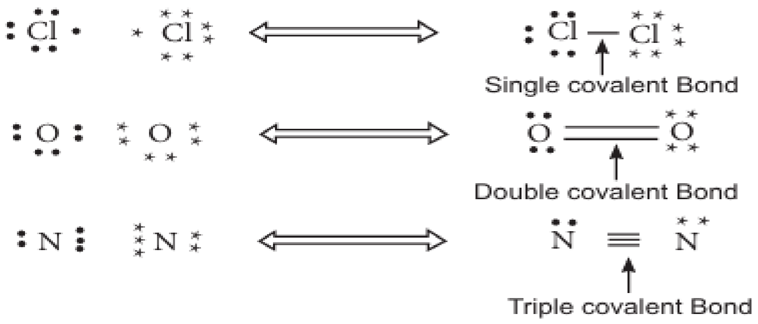


Fig. 1.13 : Types of Covalent Bond

Valence bond theory (VBT)

This theory was proposed by Linus Pauling. The covalent bond is formed by overlapping of valence shell atomic orbital (half- filled) of two different atoms having unpaired electrons. Because of overlapping, there is maximum electron density between the bonding atoms. The greater the overlapping of atomic orbitals, the higher is the strength of the chemical bond, thereby increasing the stability of the resulting molecule.

Features of the Valence Bond Theory

The presence of many unpaired electrons in the valence shell of an atom enables it to form multiple bonds with other atoms. The paired electrons present in the valence shell do not take part in the formation of chemical bonds.

Covalent chemical bonds are directional and are also parallel to the region corresponding to the atomic orbitals that are overlapping. Depending on the type of overlapping of atomic orbitals, sigma bonds (s) and pi bonds (π) are formed. pi bonds are formed from sidewise overlapping, whereas the overlapping along the axis containing the nuclei of the two atoms leads to the formation of sigma bonds.

Sigma Bond(σ)

When a covalent bond is formed by overlapping of half-filled atomic orbitals along the same axis it is called a sigma bond(s). Such type of bond is symmetrical about the line joining the two nuclei, as shown below. [Fig.1.15]. Examples of formation of H2,F2 and HF molecule are shown in [Fig. 1.16, 1.17 and 1.18].

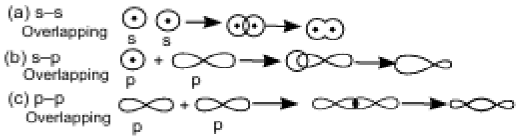


Fig. 1.15 : Orbital Overlap along the Axis

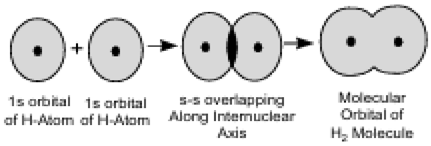


Fig. 1.16 : Formation of H_2 Molecule (s-s Overlapping)

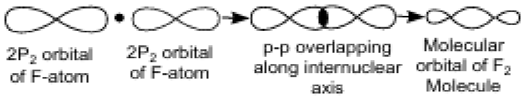


Fig.1.17 : Formation of F_2 Molecule (p-p Overlapping)

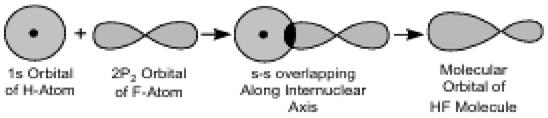


Fig.1.18 : Formation of HF Molecule (s-p Overlapping)

pi-Bond (π)

This type of bond is formed by sideways or lateral overlapping of two half- filled atomic orbitals. [Fig. 1.19]. The strength of a bond depends upon the extent of overlapping of half- filled atomic orbitals. The extent of overlapping is always greater when there is end to end overlapping of orbitals ,than when there is a sideways overlapping of orbitals. Sigma bond is always stronger than pi bonds between the two same groups of atoms. The average distance between the nuclei of two bonded atoms in a molecule is called bond length and the energy required to break one mole of bonds of a particular type in the gaseous state is called bond energy or bond strength. The same amount of energy is released in the formation of 1 mole of a particular bond.

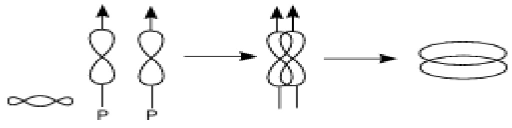


Fig. 1.19 : Orbital Overlap Sidewise

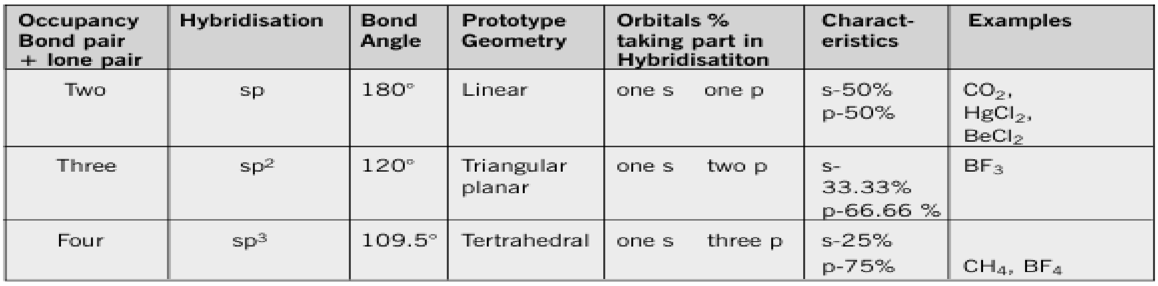
(H) Hybridisation

Hybridisation is hypothetical mixing of atomic orbitals belonging to same atom but having slightly different energies so that redistribution of energy takes place between them, resulting in the formation of new orbitals of equal energies and identical shapes. The new orbitals thus formed are known as hybrid orbitals The hybrid orbitals can be defined as the combination of standard atomic orbitals resulting in the formation of new atomic orbitals. In simple words, hybridisation may be defined as mixing and redistribution of atomic orbitals of more than one type to form new hybrid orbitals.

Important Features of Hybridisation are

- **(A)** Orbitals belonging to the same atom or ion having almost similar energies, get hybridized.
- **(B)** The number of hybrid orbitals formed are equal to the number of atomic orbitals taking part in hybridisation.
- **(C)** Hybridisation takes place to produce equivalent orbitals which give maximum symmetry **.**
- **(D)** Hybrid orbitals form only a sigma bond.

Table 1.10 : Types of Hybridisation



Occupancy Bond pair + lone pair	Hybridisation	Bond Angle	Prototype Geometry	Orbitals % taking part in Hybridisatiton		Charact-eristics	Examples
Two	sp	180°	Linear	one s	one p	s-50% p-50%	CO_2, $HgCl_2$, $BeCl_2$
Three	sp^2	120°	Triangular planar	one s	two p	s-33.33% p-66.66 %	BF_3
Four	sp^3	109.5°	Tertrahedral	one s	three p	s-25% p-75%	CH_4, BF_4

Formation of BF_3 Molecule

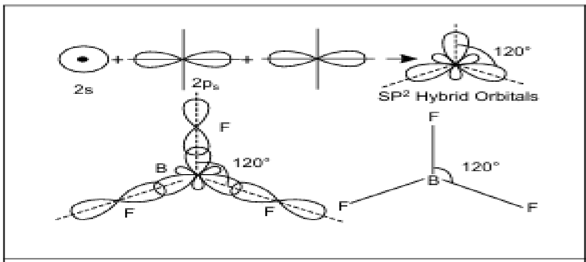


Fig. 1.20: Formation of sp^2 Hybrid Orbitals and Shape of BF_3Molecule

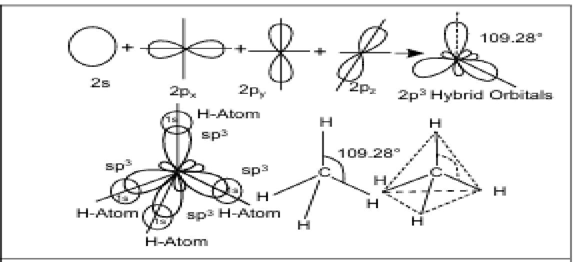


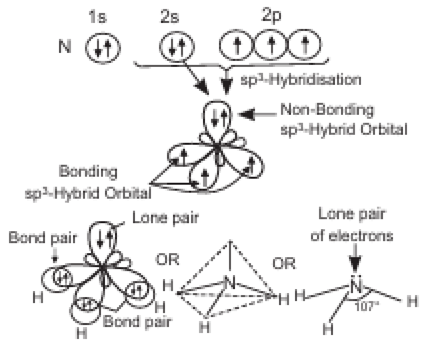
Fig. 1.21 : Formation of sp^3 Hybrid Orbitals and Shape of Methane (CH_4) Molecule

Formation of CH4 Molecule

The atomic number of carbon is 6 Electronic configuration in ground state is 1s2 2s2 2px1 2py1 Electronic configuration in excited state is 1s2 2s1 2px1 2py1 2pz1 One 2s and three 2p orbitals undergo sp3 hybridisation to form four sp3 hybrid orbitals which are arranged tetrahedrally at an angle of 109028‘ to each other. The four sp3 hybrid orbitals overlap with the half-filled 1s orbitals of 4 hydrogen atoms forming CH4. CH4 is a tetrahedral molecule with each H-C-H angle equal to 1090 28‘ [Fig.1.21]

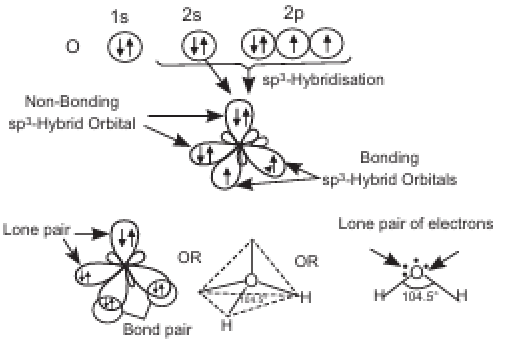
Formation of NH3 Molecule

The atomic number of Nitrogen is 7 Electronic configuration in ground state is 1s2 2s2 2px1 2py1 2pz1 One 2s and three 2p orbitals undergo sp3 hybridisation to form four sp3 hybrid orbitals which are arranged pyramidal at an H-N-H bond angle of 1070. As lone pair –bond pair repulsion is greater than bond pair-bond pair repulsion hence although NH3showing sp3 hybridisation but bond angle get reduced from 1090.28’ to 1070. The three sp3 hybrid orbitals overlap with the half-filled 1s orbitals of 3 hydrogen atoms forming NH3 as shown in in [Fig.1.22].



Formation of ammonia (NH_3) molecule.

Fig. 1.22 : sp^3 Hybridisation - NH_3



Formation of water (H_2O) molecule.

Fig. 1.23 : sp^3 Hybridisation-H_2O

Formation of H2O molecule

The atomic number of Oxygen is 8.

Electronic configuration is 1s2 2s2 2px2 2py1 2pz1.

One 2s and three 2p orbitals undergo sp3 hybridisation to form four sp3 hybrid orbitals which are arranged in ‘V’ shape The two sp3 hybrid orbitals overlap with the half-filled 1s orbitals of 2 hydrogen atoms forming H2O molecule which contains two lone pair and two bond pair of electrons. As repulsion between Lone pair - lone pair > lone pair - bond pair > bond pair - bond pair (L.P-L.P>L.P.-B.P.>B.P.-B.P.) hence although H_2O showing sp3 hybridisation but shows bond angle as 104045’ as shown in [Fig. 1.23].

Formation of BeCl2 molecule

The atomic number of Beryllium is 4. Electronic configuration is 1s2 2s2 in ground state Electronic configuration in excited state 1s2 2s1 2px1 One 2s and one 2px orbital mix to from two sp hybrid orbital 1s orbital of two hydrogen combines with two sp orbital of Be to form H-Be-H bond angle of 1800 with linear geometry and sp hybridisation.

Molecular Orbital Theory

Characteristic of molecules their relative bond strength, paramagnetic and diamagnetic nature may be explained by another approach known as Molecular orbital theory.

It says that when two atomic orbitals combine or overlap, they lose their identity and form new orbitals.

The new orbitals formed are called molecular orbitals.

Coordinate Bond (A)

Introduction

It is a special type of covalent bond in which both the shared electrons are contributed by one atom only. This bond is also called a dative Bond or dipolar bond. They are formed in reactions that involve two non-metals such as a hydrogen atom or during bond formation between metals ions and ligands.(Ligand is an ion or molecule attached to a metal atom by coordinate bonding.) Co-ordinate covalent bonds can help in formation of complex organic molecules.

Characteristic Features of Coordinate Bond

The atom that shares an electron pair from itself is known as the donor. While the other atom which accepts these shared pair of electrons from the donor is known as a receptor or acceptor.

The bond is represented with an arrow , pointing towards the acceptor from the donor atom. [Fig. 1.24].

Each atom gets stability after sharing of electron pair.

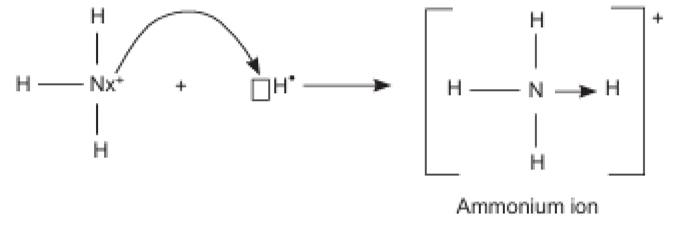


Fig. 1.24 : Co-ordinate Bonding in NH_4^+

Properties of Coordinate Compounds

Coordinate compounds have lower melting and boiling points than ionic compounds Some of these compounds exhibit isomerism.

It is called a directional bond because sharing of electrons takes place in a definite direction.

It is weaker than ionic bonding.

Hydrogen bonding

When a molecule with hydrogen atom is linked to a highly electronegative atom (like F,O or N),the electronegative atom attracts the shared pair of electrons more and so this end of the molecule becomes slightly negative while the other end (i.e., H-end) becomes slightly positive. The negative end of one molecule attracts the positive end of the other, thus a weak hydrogen bond is formed between them. This bond is called Hydrogen bond .

It is represented by dotted lines(---)as shown here:-

$$\overset{+\delta}{H}-\overset{-\delta}{X}----\overset{+\delta}{H}-\overset{-\delta}{X}----\overset{+\delta}{H}-\overset{-\delta}{X}$$

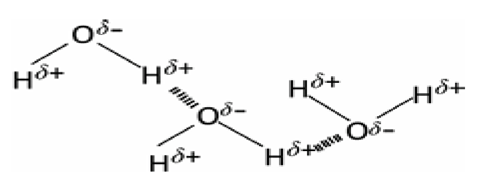


Fig. 1.25 : H Bonding in Water Molecule

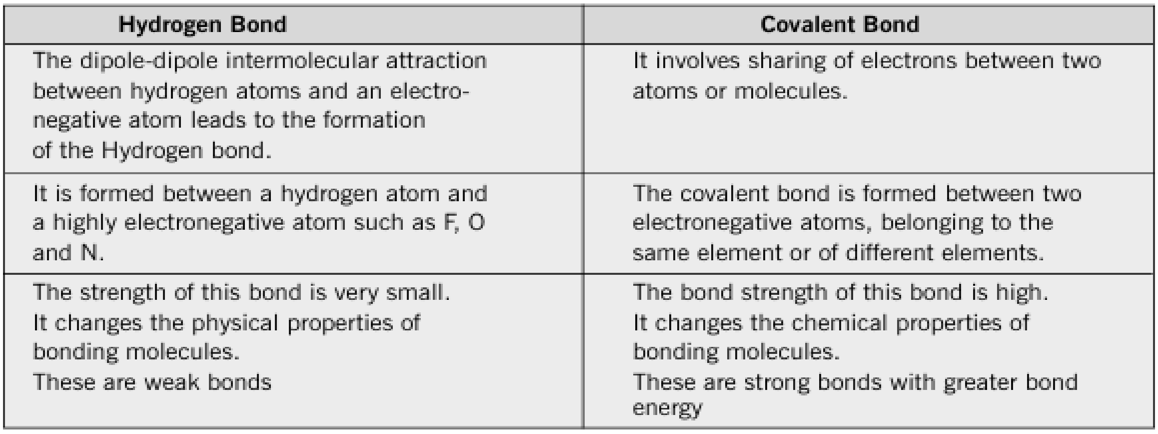
Due to hydrogen bonding, an H-atom link with the two highly electronegative atoms simultaneously, one by a covalent bond and the other by a hydrogen bond. Thus it forms a Hydrogen bridge. For example, in water molecules (H_2O), hydrogen is covalently bonded to the more electronegative oxygen atom. The dipole-dipole interactions between the hydrogen atom of one water molecule and the oxygen atom of another H_2O molecule give rise to hydrogen bonding in water [Fig. 1.25] The hydrogen bond is weak. The strength of the hydrogen bond is in-between the weak van der waals and the strong covalent bonds. If we press two ice cubes over each other, they unite to form one cube due to hydrogen bonding.

Hydrogen Bonding in Water Molecule

In water, each oxygen atom is linked to four H-atoms, two by covalent bonds & two by H-bonds. Each water molecule is linked to four water molecules tetrahedrally by H-bonds. Water has a maximum density at 277 K. At 273 K, there is sufficient hydrogen bonding present in the water molecules (or ice). Ice has a lower density than water. In the case of solid ice, the hydrogen bonding gives rise to a cage-like structure of water molecules, as each water molecule is linked to four water molecules tetrahedrally. When ice melts, this cage-like structure collapses and the molecules come closer to each other. Thus, for the same mass of water, the volume decreases and hence density increases. Therefore, ice has a lower density than water at 273 K. That is why ice floats on water. On heating, the hydrogen bonds start breaking and start coming together resulting in the decrease of volume and increase of density. This goes on up to 277 K. After 277 K, the increase in volume due to the expansion of liquid water becomes much more than the decrease in volume due to the breaking of H bonding. After 277 K, there is a net increase of volume on heating, which means a decrease in density. Hence, the density of water is maximum at 277 K.

Ice also has relatively high freezing and boiling point due to its hydrogen bonds. These are stronger than Vander Waals forces therefore more energy is needed to break the hydrogen bonds, resulting in higher freezing and boiling points.

Table 1.11 : Difference between Hydrogen Bond and Covalent Bond



Hydrogen Bond	Covalent Bond
The dipole-dipole intermolecular attraction between hydrogen atoms and an electro-negative atom leads to the formation of the Hydrogen bond.	It involves sharing of electrons between two atoms or molecules.
It is formed between a hydrogen atom and a highly electronegative atom such as F, O and N.	The covalent bond is formed between two electronegative atoms, belonging to the same element or of different elements.
The strength of this bond is very small. It changes the physical properties of bonding molecules. These are weak bonds	The bond strength of this bond is high. It changes the chemical properties of bonding molecules. These are strong bonds with greater bond energy

Anomalous properties of Water and Ammonia

These are strong bonds with greater bond energy Water is a liquid whereas H2S, H2Se and H2Te are all gases at ordinary temperature. In water, hydrogen bonding causes linkages in the water molecules which result in the boiling point of water than that of the other compounds. Because of strong intermolecular hydrogen bonding, H2O, HF & NH3 exist as associated molecules. Therefore, their melting and boiling point are much higher than those of the corresponding hydrides in their respective groups. Ammonia has a higher boiling point than PH3 because there is hydrogen bonding in NH3 but not in PH3. Hydrogen bonding is responsible for ammonia's remarkably high solubility in water.

Metallic bond

Giant structures of atoms are arranged in a regular pattern inside the metals. The electrons of the outer shells of the metal atoms are delocalised, and are free to move through the whole structure. This sharing of delocalised electrons results in strong metallic bonding. [Fig.1.27].

Collective sharing of a sea of valence electrons between several positively charged metal ions is known as Metal bonding. In other words, metallic bonding is the sharing of many detached electrons between many positive ions, where the electrons act as a "glue" giving the substance a definite structure.

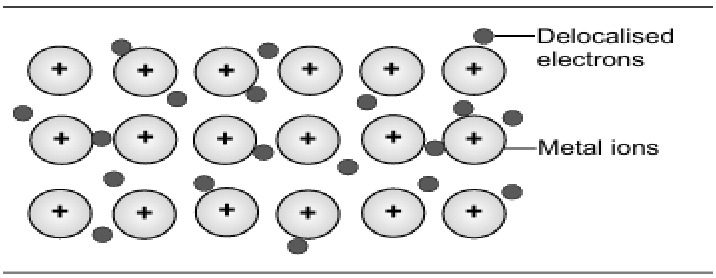


Fig. 1. 27 : Delocalised Electrons in Metallic Bond

Characteristic properties due to Metallic bonds

High electrical and thermal conductivity Highly malleable and ductile Metallic lustre High melting and boiling points.

Factors responsible for the Strength of Metallic Bonds

If the number of delocalised electrons increases, the stronger will be the bond. If the magnitude of the charge on metal cation increases, the stronger the force of attraction between the electron sea and the cations. If the ionic radius of cation is smaller, the greater the effective nuclear charge acting on the electron sea.

Table 1.12 : Difference between Metallic Bond and Ionic Bond

Metallic Bond	Ionic Bond
Metallic bonds are formed when a rigid, definite lattice of metal cations share a sea of delocalized valence electrons.	It involves the transfer of electrons between two chemical species. They arise from a difference in the electro negativities of the bonded atoms.

SOLUTION

Introduction

For chemical analysis of different compounds and engineering materials and also for the preparation of many chemical compounds required in variety of industries, we need to comprehend in depth the preparation of solutions of different concentration. In this unit we shall be learning about preparation of solutions of different strength e.g. normal solution, molar solution, ppm solution etc.

The Idea of Solute, Solvent and Solution

For understanding the concept of solute, solvent and solution, let us consider the example of Sodium Chloride. NaCl salt is added into the water to form NaCl solution. In this case, we can call NaCl as a solute, water as the solvent and a mixture of salt and water as solution [Fig.1.28]. Now let us understand the definition of the three terms.

Solute : Substance added to the solvent in small quantity is known as solute.

Solvent : A substance present in a large quantity to dissolve solute, is known as a solvent.

Solution : Homogeneous mixture of solute and solvent is known as a solution.

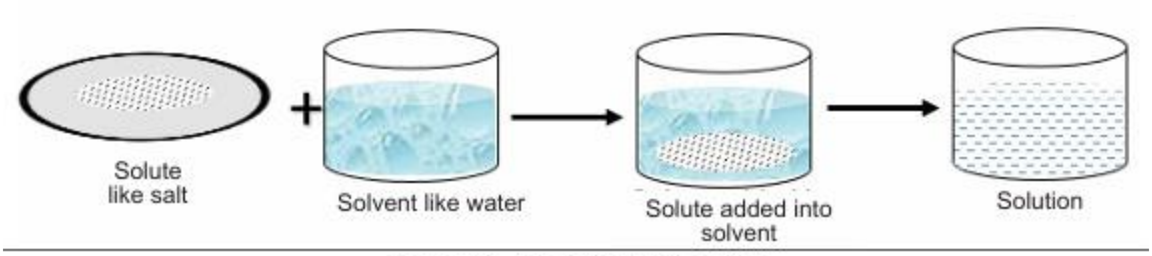


Fig. 1.28 : Solute-Solvent-Solution

Methods to Express the Concentration Solution

The solution can be of varying concentration depends upon the amount of solute added to it.

Fig.1.29 : Concentration of Solution

Let us consider two solutions containing NaCl as a salt. Beaker ‘A’ contains 5.85 g of NaCl while beaker ‘B’ contains 58.5 g of NaCl. If we test this two beakers we can feel that the beaker ‘B’ is much more saltier as compared with beaker ‘A’. In terms of concentration, we can say that solution in beaker ‘B’ is having a higher concentration of salt as compared with the solution in beaker ‘A’ [Fig.1.29]. There are various methods to express the concentration of the solution, some of them are as follows.

Molarity

Number of moles of solute dissolves in one litre of solution known as molar solution. A solution in which 1 mole (equal to molecular weight) of compound solute is dissolved in the solvent and diluted up to 1000 ml thus we get 1 molar solution. In the above example solution in beaker ‘B’ is a 1 molar NaCl solution (11Na23 and 17Cl35.5). We can also calculate the number of moles of substance from given molarity as :

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{The volume of solvent in L}}$$

Hence, Number of moles of solute=Molarity Volume of solute

Parts Per Million (ppm)

Parts per million is defined as the mass ratio of parts of solute to one million gram of sample ppm is a dimensionless quantity because it is a ratio of two quantities of the same unit.

$$\text{ppm} = \frac{\text{grams of solute}}{10^6 \text{grams of solution}}$$

It is also expressed as

$$\text{Hardness in terms of } CaCO_3 = (\text{strength of salt in mg/L}) \times \frac{\text{The Chemical Equivalent of } CaCO_3}{\text{Chemical Equivalent of Dissolved Salt}}$$

Mass Percentage :

Percentage mass fraction of sample present in the entire mass

$$\text{Mass percentage solute} = \frac{\text{mass of solute}}{\text{mass of an entire sample}} \times 100\%$$

$$\text{Mass percentage sovent} = \frac{\text{mass of solvent}}{\text{mass of an entire sample}} \times 100\%$$

Volume Percentage :

The percentage volume fraction of solute to the total volume of solution.

$$\text{Volume percentage} = \frac{\text{Volume of solute}}{\text{total volume of solution}} \times 100\%$$

Mole Fraction :

Fraction of moles of solute or solvent to the moles of solution (i.e. moles of solute and moles of solvent).

$$\text{Mole fraction solute (or solvent)} = \frac{\text{Moles of solute (or solvent)}}{\text{moles of solution}}$$

CHAPTER-2

WATER

Introduction

Water is everywhere on the earth, i.e. above the earth, in the air, in the clouds, on the earth's surface in the form of rivers, oceans, ice, plants, and living organisms. Water is extremely crucial for the proper functioning of the human body. Infact, about 60 percent of the human body is made up of water while blood consists of 90 percent water. Water lubricates the joints, forms an integral part of saliva and mucus and most importantly carries oxygen to different parts of the body through the blood. It also provides a cushion for the brain, spinal cord, and other sensitive tissues, keeps the skin healthy, regulates body temperature, helps in digestion, flushes out waste, maintains functioning of the kidneys, helps maintain blood pressure, and dissolves vital minerals and nutrients in the body.

Graphical Representation of Water Distribution on the Earth

Different pie charts are helpful to understand the existence and distribution of available water on the earth. Fig. 2.1 represents a pie chart of earth water. Out of total existing water,only 3% of water is freshwater, while the remaining 97% of water is saline or seawater. Fig. 2.2, shows the percentage distribution of freshwater. Almost 99% of it is locked up in ice and the ground; only a slight 1% of all is surface water. Fig. 2.3 shows the breakdown of surface freshwater. 69% of this water is locked up in ice, and another 21% is found in lakes. Soil moisture contains 3.8% water, the atmosphere contains 3% water and swamp and marshes have 2.6% water. Rivers account for a small percentage of fresh water i.e. 0.49%, large portion of which is available for living organisms.

Fig.2.1 Earths Water

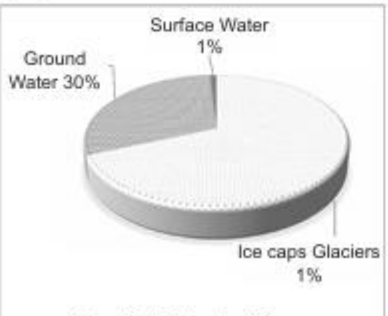


Fig. 2.2 Fresh Water

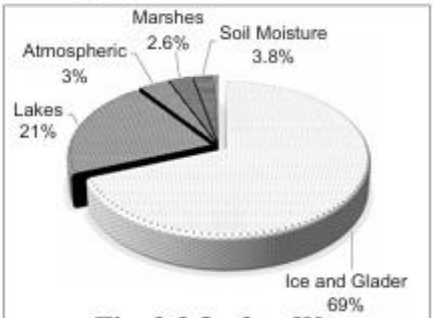


Fig. 2.3 Surface Water

Classification of Soft and Hard Water

(a) Soft Water

Water that produces lather easily on shaking with soap solution is called soft water. Soap is sodium or potassium salt of higher fatty acids. When soap is mixed with soft water,the lather is produced due to stearic acid and sodium stearate.

$$C_{17}H_{35}COONa + H_2O \longrightarrow C_{17}H_{35}COOH + NaOH$$

Sodium Stearate   Stearic Acid
(Soap)

$$C_{17}H_{35}COONa + C_{17}H_{35}COOH \longrightarrow \text{Lather}$$

Soap   Stearic Acid

(b)Hard water

Water that does not produce lather with soap solution readily, but forms a white curd i.e. white scum is called hard water. Soap is a mixture of sodium or potassium salt of higher fatty acids. Soap is soluble in water and forms salty end and fatty end, which helps cleanse action. When water combines with soap, it creates lather, due to which it has cleansing property. When water containing dissolved salts like magnesium and calcium is mixed with soap, insoluble salts of magnesium and calcium salts are obtained.

Salt causing Water Hardness

Natural water is usually contaminated by different types of impurities i.e. dissolved, suspended and biological which might restrict its usefulness.

The hardness of water is mainly due to the presence of different salts in a dissolved state. Hardness is basically of two types

A) Temporary Hardness
B) Permanent Hardness

(A) Temporary Hardness

Hardness of water which can be removed by mere boiling is known as temporary hardness. Such hardness is caused by the presence of dissolved bicarbonates of magnesium, calcium and other metals. In this type of hardness, soluble salts of metal, bicarbonates are decomposed, yielding insoluble carbonates or hydroxides after heating.

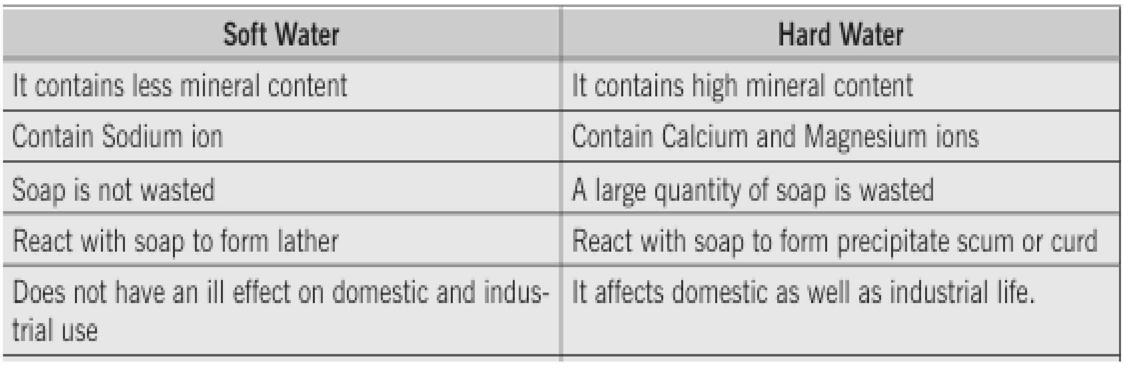
$$\underset{\text{Calcium Bicarbonates}}{Ca(HCO_3)_2} \xrightarrow{\Delta} \underset{\text{Calcium Carbonates}}{CaCO_3\downarrow} + H_2O + \underset{\text{Carbon Dioxide}}{CO_2\uparrow}$$

$$\underset{\text{Magnesium Bicarbonates}}{Mg(HCO_3)_2} \xrightarrow{\Delta} \underset{\text{Magnesium Hydroxide}}{Mg(OH)_2\downarrow} + \underset{\text{Carbon Dioxide}}{2\,CO_2\uparrow}$$

(B)Permanent hardness

A hardness that cannot be removed by mere boiling is known as permanent hardness. Such hardness is caused by chlorides, sulphides of magnesium, calcium and other heavy metals. In this type of hardness, dissolved chlorides, sulphates are not decomposed after boiling.

Difference between soft water and hard water



Soft Water	Hard Water
It contains less mineral content	It contains high mineral content
Contain Sodium ion	Contain Calcium and Magnesium ions
Soap is not wasted	A large quantity of soap is wasted
React with soap to form lather	React with soap to form precipitate scum or curd
Does not have an ill effect on domestic and industrial use	It affects domestic as well as industrial life.

Unit of hardness

Due to the calcium and magnesium salts, water becomes hard. The unit of hard water is expressed in terms of parts by weight of calcium carbonates. There are different systems to describe the hardness of the water.

a) Parts per million (ppm) b) French degree of hardness (^{0}Fr)
c) Degree clark (^{0}Cl) d) Milligrams per litre
e) Milliequivalent per litre

(a) Parts Per Million (ppm)

The number of parts by weight of calcium carbonate present per million parts by weight of water.

$$1 \text{ ppm} = \frac{1 \text{ part of } CaCO_3}{10^6 \text{ parts by weight of water}}$$

(b) French Degree of Hardness (^{0}Fr)

Number of parts by weight of $CaCO_3$ present in 100000 (or 10^5) parts by weight of water

$$1^0\text{French} = \frac{1 \text{ part of } CaCO_3}{10^5 \text{ parts by weight of water}}$$

(c) Degree Clark (^{0}Cl)

Number of parts by weight of calcium carbonate in 70000 parts by weight of water

$$1\,^0\text{Clark} = \frac{1 \text{ part of } CaCO_3}{70{,}000 \text{ parts by weight of water}}$$

(Or) The number of grains of $CaCO_3$ equivalent hardness per gallon of water.

$$1\,^0\text{Cl} = \frac{\text{No. of grains of } CaCO_3}{1 \text{ gallon of water}}$$

d) Milligrams Per Litre (mg/L)

Number of milligrams of $CaCO_3$ equivalent hardness present per litre of water.

1 mg/L = 1 mg of $CaCO_3$ equivalent of hardness of 1L of water

But 1L of water weighs = 1 kg
= 1000g
=1000 × 1000 mg
= 10^6 mg

1mg/L = 1mg of $CaCO_3$ equivalent per 10^6 mg of water
= 1ppm

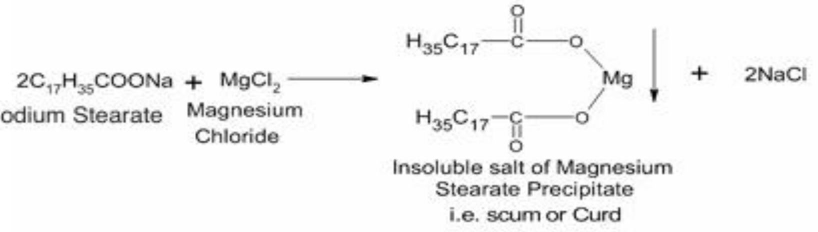
e) Milliequivalent Per Litre (meq/L)

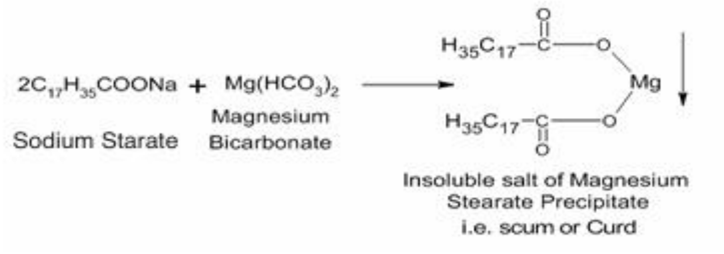
Number of milliequivalent of hardness is present per litre.
1meq/L= 1 meq of $CaCO_3$ per L of water
Calculation of meq/L for $CaCO_3$ molecule
Molecular weight of $CaCO_3$ = 100 g
Equivalent weight of $CaCO_3$ = 50 g = 50×10^{-3}g = 50 mg/L = 50 ppm

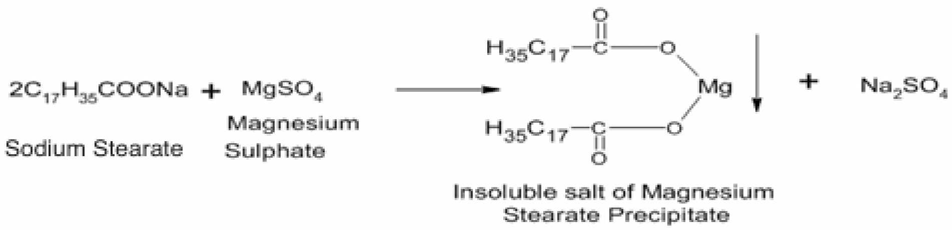
CAUSES OF HARD WATER

Causes of Poor Lathering of Soap in Hard Water Water is a universal solvent. Hence it is used in the domestic and industrial sector for cleaning purpose. When water combines with soap,it forms lather. Soap is a mixture of sodium or potassium salt of higher fatty acid. Some commonly used acids are palmitic acid, oleic acid and stearic acid. Soap is soluble in water forming two poles as the salty end and the fatty end. These poles react with the dirt and show cleaning property. Water containing dissolved salts like magnesium and calcium is mixed with soap, and insoluble salts of magnesium and calcium salts are obtained.

Reactions







When water contains calcium chloride, calcium bicarbonate and calcium sulphate, it shows a similar type of reactions as above The formed calcium and magnesium salts develop white precipitate called scum or curd, instead of lather. Hence dissolved salts present in water are responsible for the poor lathering of soap.

Problems caused by the Use of Hard Water in the Boiler

Water is helpful to a great extent in several industries. However, when hard water used for different processes, it gives other ill effects. Water containing dissolved salts of sulphates, carbonates, chlorides of calcium, magnesium and iron salts have an adhesive impact on steam boilers. The manufacturing industries need water for a different purpose, out of which steam generation is of the utmost importance. Hence, water for raising steam in boilers must be soft and must not contain dissolved matter to avoid sludge, scale, priming and foaming problems in the boiler.

Sludge: Due to the continuous boiling of water, the concentration of dissolved salt inside the boiler is increased. When the salt concentration reaches the saturation point, salts are thrown out of the water,precipitating on the inner wall of the boiler. [Fig.2.4] The loose and slimy precipitate deposited on inner wall of boiler is known as sludge. Excessive sludge formation disturbs the working of the boiler. It settles in the regions of poor water circulations such as pipe connection, plug opening, thereby causing even chocking of the pipes.

Properties of Sludge

Sludges are soft and less permeable precipitate Sludges are poor conductors of heat.

These are formed at comparatively cooler portions of the boiler.

Sludges are formed by substances that have greater solubility in hot water. e.g. $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$ etc.

Prevention of the Sludge Formation

We can decrease sludge formation by

Using well soften water.

Frequently blowdown operation by drawing off a portion of the concentrated water.

Mechanical means by scrapping off the sludge with a wire brush.

Giving thermal shocks.

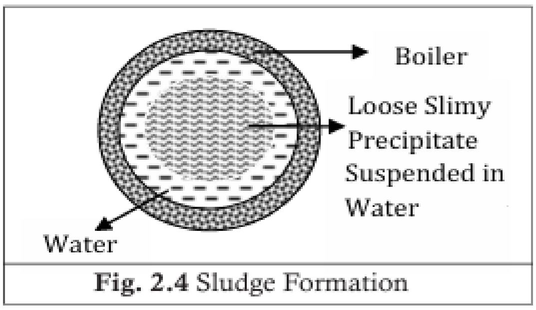


Fig. 2.4 Sludge Formation

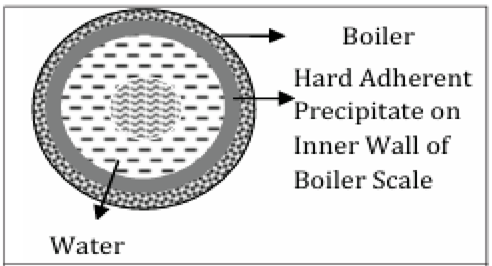


Fig. 2.5 Scale Formation

Scale

While continuously boiling the water inside the boiler, the salt concentration reaches the saturation point, the salts are thrown out of the water in the form of precipitates on the inner wall of the boiler. They are formed due to the presence of sulphate and silicates of calcium and magnesium [Fig. 2.5]. The hard adhering coating deposited on inner wall of boiler is known as scale.

Properties of Scale

Scale is very hard and firmly adhered to the boiler.

It is difficult to remove them, even with the hammer or chisel.

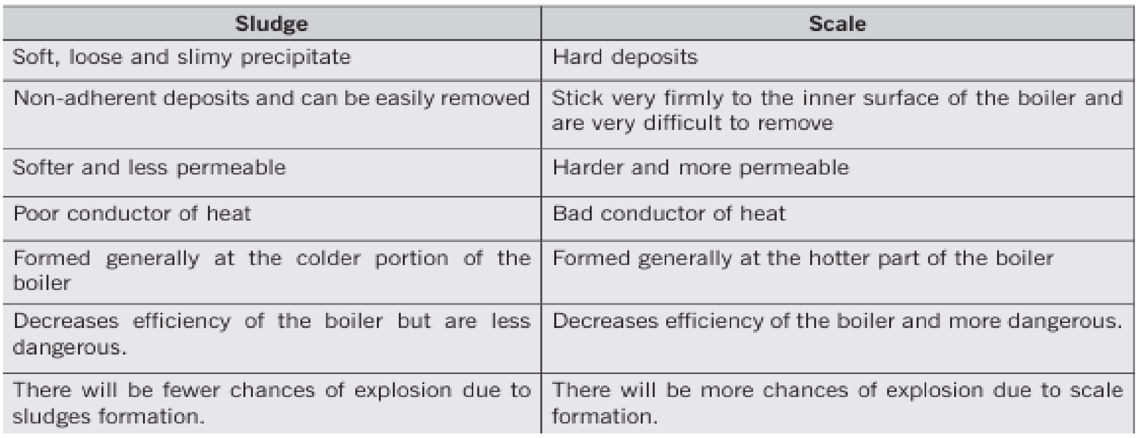
It is bad conductors of heat.

Prevention of the Scale Formation

The formed precipitate can be removed by thermal shocks with chisel hammer treatment.

Internal conditioning with different chemicals as phosphate, carbonate, calgon, tannin, agar gel, sodium aluminate, EDTA.

Difference between Sludge and Scale



Sludge	Scale
Soft, loose and slimy precipitate	Hard deposits
Non-adherent deposits and can be easily removed	Stick very firmly to the inner surface of the boiler and are very difficult to remove
Softer and less permeable	Harder and more permeable
Poor conductor of heat	Bad conductor of heat
Formed generally at the colder portion of the boiler	Formed generally at the hotter part of the boiler
Decreases efficiency of the boiler but are less dangerous.	Decreases efficiency of the boiler and more dangerous.
There will be fewer chances of explosion due to sludges formation.	There will be more chances of explosion due to scale formation.

Priming

When the boiler is being steamed rapidly, some liquid water particles are mixed with the steam. Priming is the conveyer of variable amounts of droplets of water in the steam.

Foaming

Foaming is the production of persistent foam and bubbles in boilers. Formed bubbles do not break easily. Foaming is generally due to the presence of substance like oils.

Causes of Priming and Foaming

Causes of priming and foaming are as follows

- Presence of a large amount of dissolved solid.
- High steam velocities.
- Sudden boiling.
- Improper boiler designs.
- The sudden increase in steam production rate.

Priming and Foaming can be Avoided by

- Fitting mechanical steam purifiers.
- Avoiding rapid change in steaming rate.
- Maintaining the low water level in boilers
- Efficient softening and filtration of the boiler feedwater. Adding antifoaming chemicals like castor oil.
- Rremoving oil from boiler water by adding compounds like sodium aluminate.

Problems due to priming and Foaming

Due to priming and foaming following problems are generated in the boiler

- Causes caustic embrittlement .
- Chocking of outlets .
- Do not allow steam to flow quickly due to the presence of foam.

Effect of Priming and Foaming

In boiler, water priming and foaming usually occur together because **.**

- The actual height of the water column cannot be adequately judged, thereby making the maintenance of the boiler pressure becomes difficult.
- Dissolved salts in water are carried by wet steam to different machinery parts, where salt gets deposited as water evaporates.
- Life of machinery decreases.

corrosion

Boiler corrosion is the decay or destruction of boiler material by a chemical or electrochemical environment. Corrosion of boiler takes place due to following reasons :

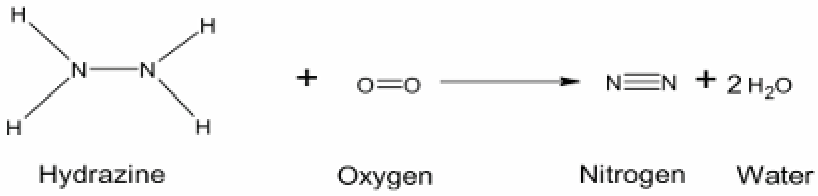
- Dissolved oxygen **.**
- Dissolved carbon dioxide **.**
- Dissolved salts causes of Boiler corrosion (i) Dissolved Oxygen Dissolved oxygen present in water interacts with boiler material at steaming temperature to form the ferrous hydroxide. Formed ferrous hydroxide further reacts with oxygen to form ferric oxide.

$$2Fe + 2H_2O + O_2 \longrightarrow 2Fe(OH)_2\downarrow$$

$$4Fe(OH)_2 + O_2 \longrightarrow 2[Fe_2O_3.2H_2O]\downarrow$$

(a)Removal of Oxygen by using Chemicals

There are different chemicals like hydrazine, sodium sulphate, tannin, which are used to remove dissolved oxygen. In the case of hydrazine reacts with dissolved oxygen to form nitrogen and water. Suppose we use a dissolved oxygen sensor and find that amount of dissolved oxygen in boiler water is increased; in that case, these chemicals react with dissolved oxygen and easily remove dissolved oxygen from boiler water.



Dissolved nitrogen is harmless, and there is no change in the percentage of dissolved solids after the addition of nitrogen.

(b) Removal of Dissolved Oxygen by Heating

Water is passed through the tower, which contains perforated plates, heating arrangement from the side and vacuum pump arrangement. High-temperature low pressure, and large exposed surface reduce the dissolved oxygen in water.[Fig. 2.6].

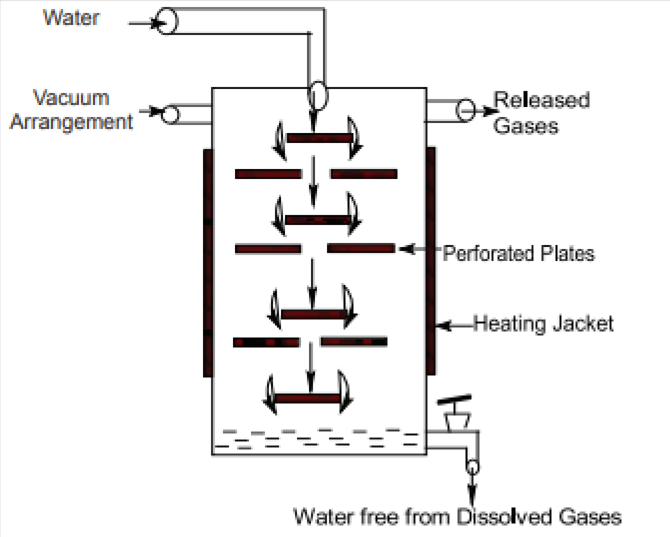


Fig. 2.6 Removal of Dissolved Oxygen by Heating

(ii) Dissolved CO2

Water associated with dissolved CO2 forms carbonic acid, which has a slow corrosive effect on boiler material. Water containing bicarbonates is also the source of CO2.

$$CO_2 + H_2O \longrightarrow \underset{\text{Carbonic Acid}}{H_2CO_3}$$

$$\underset{\text{Magnesium Bicarbonates}}{Mg(HCO_3)_2} \longrightarrow \underset{\text{Magnesium Carbonate}}{MgCO_3} + H_2O + CO_2\uparrow$$

Removal of CO2 by using ammonia

Carbon dioxide can be removed by adding calculated amount of ammonia.

$$H_2O + \underset{\text{Ammonia}}{NH_3} \longrightarrow \underset{\text{Ammonium Hydroxide}}{NH_4OH}$$

$$NH_4OH + CO_2 \longrightarrow \underset{\text{Ammonium Carbonate}}{(NH_4)_2CO_3} + H_2O$$

Removal of Carbon dioxide by Heating

Water associated with different types of gases is required to be removed by heating the water at high temperature. Low pressure reduces the dissolved CO2 [Fig.2.6]. If it is not removed they are responsible for corrosion of the boiler material.

(iii) Dissolved Salts

When Magnesium chloride combines with water, it forms magnesium hydroxide along with hydrochloric acid as a byproduct.

$$MgCl_2 + 2H_2O \longrightarrow \underset{\text{byproduct}}{Mg(OH)_2\downarrow} + 2HCl$$

The liberated acid reacts with the iron metal of the boiler in chain-like reactions producing HCl again and again. Hence the presence of a small amount of MgCl2 will cause corrosion of iron to a large extent.

$$Fe + 2HCl \longrightarrow \underset{\text{Ferrous Chloride}}{FeCl_2\downarrow} + H_2$$

$$\underset{\text{Ferrous chloride}}{FeCl_2 + 2H_2O} \longrightarrow \underset{\text{Ferrous hydroxide}}{Fe(OH)_2\downarrow} + 2HCl$$

During the water softening process, a small quantity of sodium carbonate is added. In high pressure boilers, sodium carbonate decomposes to give sodium hydroxide and carbon dioxide

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2\uparrow$$

Due to the formation of sodium hydroxide, water becomes alkaline. The number of minute cracks are observed on the inner wall of boiler. This alkaline water flows into such minute cracks by capillary action. Here due to water evaporation, dissolved caustic soda is left behind. The amount of caustic soda goes on increasing due to progressive evaporation. The alkaline action of caustic soda attacks the surrounding areas of cracks, thereby dissolving the iron material of the boiler.

Precautions to avoid Corrosion due to Salts

- Supply the water which is free from salts like MgCl2.
- By using sodium phosphate instead of sodium carbonate for water softening.
- By adding tannin or lignin as additives to the boiler water since these block the minute cracks.
- By adjusting the alkalinity of water to an optimum level (pH 7-8)

Quantitative Determination of Water Hardness by EDTA Method, Total Dissolved Solids (TDS) & Alkalinity Estimation

The practical performance /experiments under above title are mentioned at the end of this unit.

(a) Quantitative Determination of Water Hardness by EDTA Method

This method is used to determine the hardness of water using the EBT (Eriochrome Black T) indicator and EDTA (Ethylene Diamine Tetra Acetic acid). Eriochrome Black-T (EBT) indicator is an alcoholic solution of blue dye used for titration with pH of about 10. When Eriochrome Black T indicator is added to hard water buffered to about 10 pH, a wine red unstable complex is formed. Thus

$$\underset{\text{Blue}}{M^{2+} + EBT} \longrightarrow \underset{\text{Wine Red Colour Unstable complex}}{[M - EBT]}$$

During the titration, EDTA reacts with Ca-EBT or Mg-EBTunstable complex and forms a stable complex of Ca-EDTA or Mg-EDTA and releases EBT into the solution. However, when nearly all M2+ (Ca2+ or Mg2+) ions have formed [M-EDTA] complex, then the next drop of EDTA added displaces the EBT indicator from [M-EBT] complex and wine red colour changes to blue colour (due to EBT). Hence the endpoint of the titration is wine red to blue colour.

$$\underset{\substack{\text{Unstable}\\ \text{Wine Red}}}{[M\text{-}EBT]} + EDTA \longrightarrow \underset{\text{Stable complex}}{[M\text{-}EDTA]} + \underset{\text{Blue}}{EBT}$$

The structure of EDTA is present in disodium salt [Fig. 2.7] it yields the anion, which forms complex ions with Ca2+ and Mg2+ ions [Fig. 2.8]

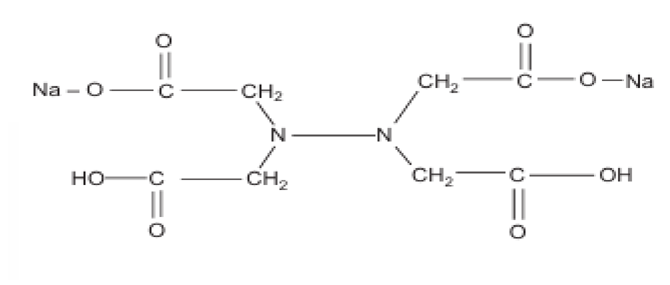


Fig. 2.7 Ethylene Diamine Tetra Acetic acid (EDTA)

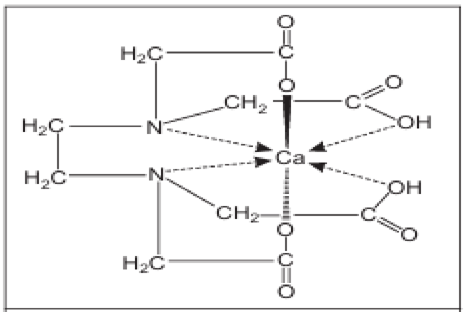


Fig. 2.8 Ca^{2+} EDTA Complex

Advantages of EDTA method This method is preferable to the other methods because of the (i)Greater accuracy (ii) Convenience (iii) More rapid procedure

(a)Quantitative Determination of Water Hardness and Total Dissolved Solids (TDS)

For determination of residue on evaporation or total dissolved solid, measure out volume of the filtered sample required for the main analysis and evaporate to dryness in porcelain dish. Dry the dish contents one and half hour at 1800C and weigh. The weight obtained is often reported as “total dissolved solid” .

(b) Quantitative Determination of Water Hardness by Alkalinity Estimation

Alkalinity is defined as the measure of the acid neutralising capacity of water. The alkalinity of water is attributed to the presence of the

- Caustic alkalinity (due to OH– and CO32– ions)
- Temporary hardness (due to HCO3– ions)

These can be estimated separately by titration against standard sulphuric acid, using phenolphthalein and methyl orange as indicators. The determination is based on the following reactions:

$$\left.\left.\begin{array}{l}\text{(i)}\ [OH^-] + [H^+] \longrightarrow H_2O\\ \text{(ii)}\ [CO_3^{2-}] + [H^+] \longrightarrow [HCO_3^-](M)\end{array}\right]\begin{array}{l}\text{Phenolphthalein}\\ \text{(P)pH=8.3}\\ \text{P-alkalinity}\end{array}\right]\begin{array}{l}\text{Methyl Orange}\\ \text{pH=4.5}\\ \text{Total alkalinity or}\\ \text{M-alkalinity}\end{array}$$

$$\text{(iii)}\ [HCO_3^-] + [H^+] \longrightarrow H_2O + CO_2$$

The titration of the water sample against a standard acid up to the phenolphthalein end-point marks the completion of the reaction (i) and (ii) only. This amount of acid used thus corresponds to hydroxide plus one half of the normal carbonate present. On the other hand, titration of the water sample against a standard acid to methyl orange end-point marks the completion of reaction i,ii and iii. Hence the amount of acid used after the phenolphthalein end-point corresponds to one half of normal carbonate plus all the bicarbonates, while the total amount of acid used represents the total alkalinity (due to hydroxide, bicarbonates and carbonate ions)

$$P = OH^- + \frac{1}{2}\,CO_3^{2-}$$

$$M = OH^- + CO_3^{2-} + HCO_3^-$$

The possible combinations of ions causing alkalinity in water are: (i) OH– only or (ii) CO32 only or (iii) HCO3– only or iv) OH– and CO32– together or CO32– and HCO3– together. The possibility of OH– and HCO3– ions together is ruled out, because they combine instantaneously to form CO32– ions.

$$OH + HCO_3^- \xrightarrow{\quad} CO_3^{2-} + H_2O$$

$$\text{e.g. } NaOH + NaHCO_3 \xrightarrow{\quad} Na_2CO_3 + H_2O$$

Thus OH– and HCO3– ions can not exist together in water. On the basis of same reasoning, all the three (OH–, CO32– and HCO3–) can not exist together.

Table 2.4 Calculation of Alkalinity of Water

Alkalinity Condition	Alkalinity due to the Presence of		
	OH^- (ppm)	CO_3^{2-} (ppm)	HCO_3^-(ppm)
P= 0	0	0	M
P = M	P = M	0	0
$P = \frac{1}{2}M$	0	2P	0
$P < \frac{1}{2}M$	0	2P	(M-2P)
$P > \frac{1}{2}M$	(2P-M)	2(M-P)	0

Interpretation of table 2.4 is as follows

(1) When P=0, both OH^- and CO_3^{2-} are absent and alkalinity, in that case, is due to HCO_3^- only.

(2) When P=M, only OH^- ions are present because neither CO_3^{2-} nor HCO_3^- ions are present. Thus, alkalinity due to OH^- =P=M

(3) When P= $\frac{1}{2}$M, only carbonate ions are present since, half of the carbonate neutralisation reaction $CO_3^{2-} + H \xrightarrow{\quad} HCO_3^-$ takes place with phenolphthalein while complete carbonate neutralisation reaction $CO_3^{2-} + H^+ \xrightarrow{\quad} HCO_3^-$;

$HCO_3^- + H^+ \xrightarrow{\quad} H_2O + CO_2$ occurs when the methyl orange indicator is used.

Thus alkalinity due to CO_3^{2-} =2P

(4) When P<$\frac{1}{2}$M In this case, besides CO_3^{2-}, HCO_3^- ions are also present. Now alkalinity due to

CO_3^{2-} = 2P Therefore, alkalinity due to HCO_3^- = (M–2P)

(5) When P>$\frac{1}{2}$M In this case, besides CO_3^{2-}, OH^- ions are also present. Half of CO_3^{2-} (i.e.

$HCO_3^- + H^+ \xrightarrow{\quad} CO_2 + H_2O$ equal to (M–P)

So alkalinity due to complete CO_3^{2-} = 2(M–P)

Therefore, alkalinity due to OH^- = M-2(M–P) = (2P–M)

Water softening techniques

Water used for various industrial purposes e.g. steam generation should be pure and free from hardness producing salts before use. The process of removing hardness producing salts from water is known as softening of water. These salts can be removed from water by two types of treatment processes, as below

Treatment of Hard Water

External Treatment
- (i) SodaLime Process
- (ii) Zeolite Process
- (iii) Ion Exchange Process

Internal Treatment
- (i) Colloidal
- (ii) Phosphate
- (iii) Calogen

Soda Lime Process

In this process, lime (CaO) or hydrated lime [Ca(OH)2] and soda ash[Na2CO3] are used for the precipitation process of softening. The lime is required for the precipitation of compounds causing temporary or carbonate hardness. Soda ash is used for the precipitation of compound causing permanent hardness.

(i) For carbonate or temporary hardness

$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3\downarrow + H_2O$$
$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$
$$Mg(HCO_3)_2 + Ca(OH)_2 \longrightarrow MgCO_3\downarrow + CaCO_3\downarrow + 2H_2O$$

$MgCO_3$ formed further reacts in following manner

$$MgCO_3 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + CaCO_3\downarrow$$

(ii) For non carbonate or permanent hardness

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + Na_2SO_4\downarrow$$
$$MgSO_4 + Ca(OH)_2 + Na_2CO_3 \longrightarrow Mg(OH)_2\downarrow + CaCO_3\downarrow + Na_2SO_4$$
$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + CaCl_2$$
$$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2NaCl$$

(A)Cold Soda Lime Process

Lime and soda ash are added to hard water in chemical tank and are mixed thoroughly. The calcium carbonate formed during the reaction does not precipitate, but form supersaturated solution. To prevent super saturation, some previously formed sludge is mixed with treated water. Coagulants or flocculants such as aluminium sulphate, sodium aluminate are added to help the formation of coarse precipitate. Sodium aluminate helps in the removal of silica, if present in water.

$$\underset{\text{Sod. Aluminate}}{NaAlO_2} + 2H_2O \longrightarrow NaOH + Al(OH)_3\downarrow$$

$$\underset{\text{Coagulant}}{Al_2(SO_4)_3} + \underset{\text{Hardness in water}}{3Ca(HCO_3)_2} \longrightarrow 2Al(OH)_3\downarrow + 3CaSO_4 + 6CO_2\uparrow$$

Kinds of Softener –

Cold soda lime process uses two types of softeners

Intermittent Types Softener

In this method, lime and soda ash are mixed with raw water with continuous stirring [Fig. 2.9]. Small amount of precipitate from previous filtration is added to prevent super saturation. When the reaction is complete, precipitate is allowed to settle down and the sludge is taken out . Clear soft water is taken out in another tank through a pipe.

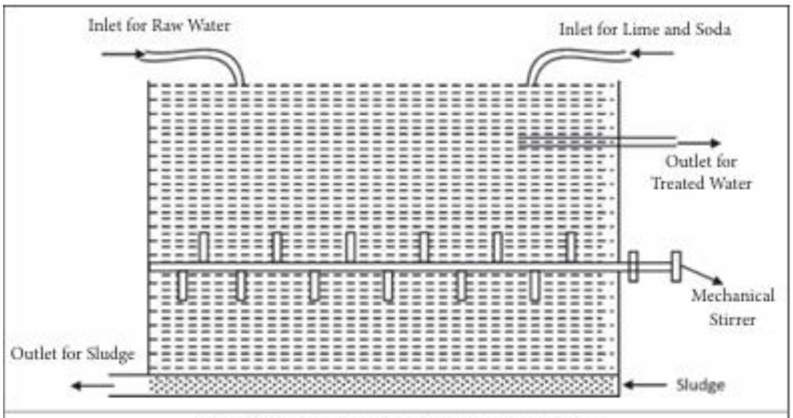


Fig 2.9 Intermittent Type Softener

Continuous Type Softener

It consists of big steel tank with inner and outer chambers. Raw material and required chemicals are put into the inner chamber with continuous stirring at room temperature as shown in [Fig. 2.10]. Softening of water occurs in inner chamber. Soft water moves upward in the outer chamber where all sludge is removed after complete filtration. Filtered water comes out through the water outlet and sludge is removed from the bottom. For softening the boiler feed water, cold soda lime method is not used because;

- Softened water does not have zero hardness.
- Residual hardness is harmful for water tubes in the boile.

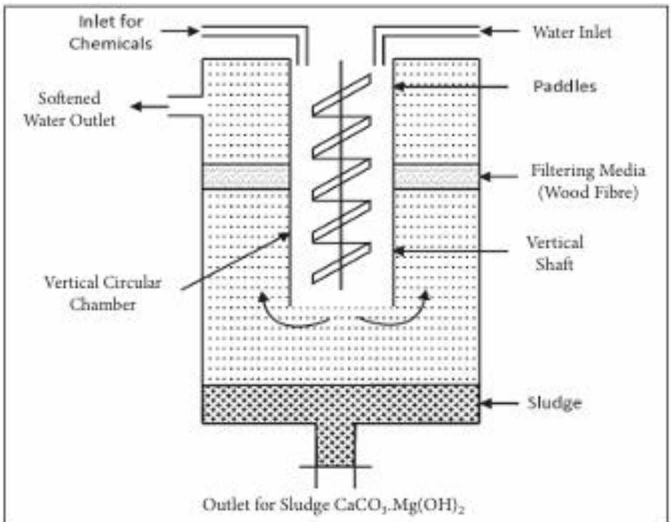


Fig 2.10 Continuous Type Softener

(B) Hot Soda Lime Process

It is similar to cold lime soda process except that mixture of raw water, softening chemicals, and small amount of sludge are heated at temperature of 800 to 1500 [Fig. 2.11]. By heating, the reaction is much faster and the precipitation is done in shorter time. Also the sludge formed is settled down quickly. No coagulants are required in this method. The softened water has hardness of 22 - 25 ppm.

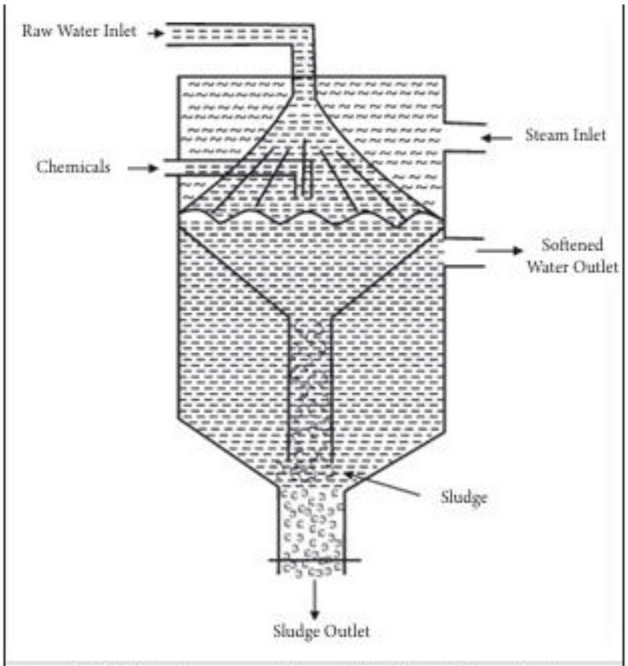


Fig 2.11 Continuous Type Hot Sodalime Softener

Advantages of Hot Soda Lime Process over Cold Soda Lime Process

- The reaction is faster and takes less time.
- By adding magnesium oxide and lime at 500C, silica also get precipitated.
- The quantity of chemical used is reduced.
- The precipitate formed is granular, more dense and can easily be removed.
- The temporary hardness, free carbon dioxide, dissolved oxygen, and other dissolved gases are removed by preheating.

Disadvantages of Soda Lime Process

- It is not suitable for turbid and acidic water.
- Huge amount of precipitate is formed which creates the disposal problem.
- The effluent cannot be reduced to zero hardness.
- Water with excessive hardness cannot be softened by this method.
- Not suitable for many industrial purposes as the water obtained is supersaturated with CaCO3.

Zeolite Process or Permutit Process

This process involves softening of water by natural or artificial zeolite. Zeolite is hydrated sodium aluminosilicate. Zeolites are substances that are insoluble in water and can act as base exchanger when placed in contact with water containing cations. Zeolites are commercially known as permutit and are of two main types i.e. natural and synthetic.

Natural Zeolites

They are non-porous, more durable and are derived from green sands by washing, heating and treating with sodium-hydroxide (NaOH).

Synthetic Zeolites

They are porous and possess a gel structure. They have higher exchange capacity per unit weight. They are prepared from solution of sodium silicate and aluminium hydroxide.They may also be prepared by heating together.

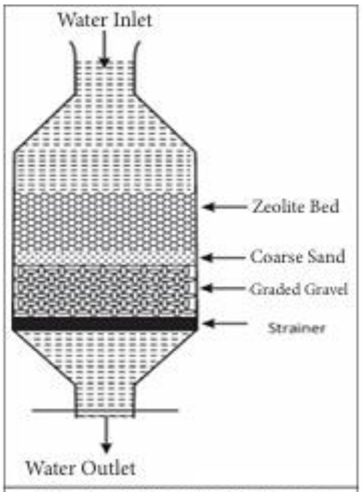


Fig 2.12 Zeolite Softener

Examples

Natural Zeolites	**Synthetic Zeolites**
Thomsonite $(Na_2O,CaO).Al_2O_3.2SiO_2.2\frac{1}{2}H_2O$,	ChinaClay, Feldspar, and Sodaash
Natrolite $Na_2O,Al_2O_3.3SiO_2.2H_2O$	Solution of sodium silicate & $Al_2(SO_4)_3$
Laumontite $CaO.Al_2O_3.4SiO_2.4H_2O$	Solution of sodium silicate and $NaAlO_2$

(A) Process

Zeolite softener consists of a steel tank with different layers as shown in [Fig. 2.12]. When water is poured from the top into the different layers,the following reaction takes place.

$$Na_2Z + Ca(HCO_3)_2 \longrightarrow CaZ + 2NaHCO_3$$
$$Na_2Z + Mg(HCO_3)_2 \longrightarrow MgZ + 2NaHCO_3$$

Sodium zeolite are used in water softening and is represented as Na2Z, where Z stands for insoluble zeolite radical framework. They can exchange basic radicals hence are also called as base exchanger.

Here $Z = Al_2Si_2O_8.xH_2O$

$$Na_2Z + CaCl_2 \longrightarrow CaZ + 2NaCl$$
$$Na_2Z + MgCl_2 \longrightarrow MgZ + 2NaCl$$
$$Na_2Z + CaSO_4 \longrightarrow CaZ + Na_2SO_4$$
$$Na_2Z + MgSO_4 \longrightarrow MgZ + Na_2SO_4$$
$$\underset{\text{Exhausted Zeolite}}{CaZ} + 2NaCl \longrightarrow \underset{\text{Regenerated Zeolite}}{Na_2Z} + CaCl_2$$
$$MgZ + 2NaCl \longrightarrow Na_2Z + MgCl_2$$

Regeneration

When we pass litres of water through zeolite tank, hardness causing Ca2+ and Mg2+are deposited over the zeolite while loosely bonded sodium ions goes along with water. After passing certain amount of water, all Na+ ions are replaced by Ca2+ and Mg2+ cations.In such case zeolite stops working i.e. after passing water through zeolite it is unable to remove hardness causing ions from water. In another words we can say that zeolite bed is exhausted i.e. saturated with Ca2+ ions and Mg2+ ions. It can be regenerated / recharged by using the NaCl solution (Brine solution).Sodium nitrate and sodium sulphate can also be used. Hence we can use regenerated zeolite for further removing the hardness. The regeneration steps comprises of back wasting, salting or brining and rinsing before reuse.

(B)Advantages

- The equipment occupies a small space and is easy to operate.
- Zero hardness water can be produced through this.
- No sludge formation occurs during the process.
- The method is cheap as the permutit can be regenerated.
- It automatically adjusts to the water of different hardness.
- The plant can be installed in the water supply line itself, avoiding double pumping.

(C)Limitations

- The feed water must be free from suspended particles; otherwise, the permutit will get clogged.
- Excess of acid or alkali present in the water must be neutralised to prevent the burning of zeolite. Thus pH of the water should be maintained to around 7.
- Regeneration of permutit is very hard when it is associated with Fe^{2+} and Mn^{2+} salts.
- Water treated by the zeolite process contains about 25% more dissolved solids than that treated by the soda-lime process.
- Treated water contains more sodium salts.
- All acidic ions such as HCO_3^- and CO_3^{2-} are left in softened water.
- Highly turbid water cannot be treated by this method.

Ion Exchange Process for Water Softening

In an ion exchanges process,a reversible exchange of ions take place between the stationary ion-exchange phase and the mobile external liquid phase. Certain synthetic organic compounds possess the property of exchanging ions (like zeolite). Such compounds are known as resins [Fig. 2.13]. Ion exchange resins are insoluble, cross linked, long chain organic polymers. Microporous structure and the functional groups attached to them are responsible for ion exchanging properties. The purely synthetic organic exchanges are made by Polycondensation and Polymerisations.

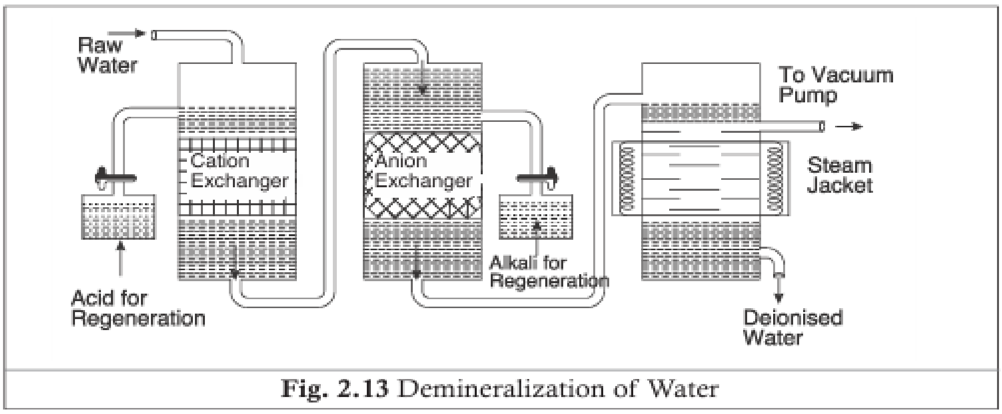


Fig. 2.13 Demineralization of Water

The functional groups are then introduced into the cross-linked resin network, either by subsequent treatment of the resin or by introducing the functional groups into the starting material itself. It is these functional groups which decide the nature of the exchanger (i.e., cationic or anionic).

Type of Ion-exchanger	Functional Groups
Strongly acidic cation exchangers	SO_3H
Moderately strong cation exchangers	$-PO(OH)_2$
Weakly acidic cation exchangers	$-COOH$ or $-OH$
Strongly basic anion exchanger	NR^{3+}; $=P+$ $-CH_3$; etc.
Weakly basic anion exchanger	NH_2; (C_2H_4) x (NH)y-

(A)Types of Ion Exchange Resins

Cation exchange resins: These resins are capable of exchanging cations by H+ ions. Cation exchanger resin can be represented as RH2

Anion exchange resins: These resins are capable of exchanging anions by OH– ions. Anion exchanger resin can be represented as R'(OH)2

(B)Properties of Ion Exchanger

1.For effective water treatment, ion exchangers should possess the following properties 1. Ion exchange resins should be non-toxic.

2. They should not decolourise the water being treated.
3. They should possess a high ion-exchange capacity. (It depends on the total number of ion active groups per unit weight to the exchanger and is expressed as milli equivalents per gram of the exchanger).
4. They should be physically durable, cheap and commonly available.
5. They should be resistant to chemical attack.
6. They must be capable of being regenerated and back-washed easily and economically.
7. They should have a large surface area since ion-exchange is a surface phenomenon.
8. Their resistance to flow must be compatible with hydraulic requirements.

(C) Process

It consist of two cylindrical towers, one cation exchanger and another anion exchanger. [Fig.2.13] Cation exchanger removes all the cations Ca2+, Mg2+,Na+, Fe2+ and releases H+ ions. Thus Cl–, SO42– bicarbonates are converted into corresponding acids HCl, H2SO4 and H2CO3. Thus water coming from the cation exchanger is free from all cations, but it is acidic. The hard water is passed through a cation exchange column, which removes all the cations like Ca2+, Mg2+, etc. from it, and the equivalent amount of H+ ions are released from this column to water as below.

$$RH_2 + CaCl_2 \longrightarrow RCa + 2HCl$$
$$RH_2 + MgSO_4 \longrightarrow RMg + 2HSO_4$$
$$RH_2 + Na_2CO_3 \longrightarrow RNa_2 + H_2CO_3$$

This acidic water is then passed through another tower containing an anion exchanger, where acids are converted into water.

In anion exchanger, following reactions take place.

$$R'(OH)_2 + 2HCl \longrightarrow R'Cl_2 + 2H_2O$$
$$R'(OH)_2 + H_2SO_4 \longrightarrow R'SO_4 + 2H_2O$$
$$R'(OH)_2 + H_2CO_3 \longrightarrow R'CO_3 + 2H_2O$$

Regeneration

When the cation exchanger gets exhausted,it is regenerated by passing the dilute acid (i.e. with HCl or H2SO4)solution.

$$RCa + 2HCl \longrightarrow RH_2 + CaCl_2$$
$$RMg + 2HCl \longrightarrow RH_2 + MgCl_2$$

Similarly exhausted anion exchanger is regenerated by passing a dilute solution of alkali through the second tower, i.e. with NaOH or KOH.

$$R'Cl_2 + 2NaOH \longrightarrow R'(OH)_2 + 2NaCl$$
$$R'SO_4 + 2NaOH \longrightarrow R'(OH)_2 + Na_2SO_4$$

(D)Advantages

(i) Highly acidic or alkaline water can be softened by this method.

(ii) As this method produces water of very low hardness ,it is used for treating water for use in high-pressure boilers .

(E) Disadvantages

(i) The equipment is costly and also more expensive chemicals are needed.

(ii) If water contains turbidity, then the output of the process is reduced. If it is more, it has to be removed first by coagulation and filtration.

MUNICIPAL WATER TREATMENT

Municipal Water Treatment- An Introduction

Safe water is essential for all domestic uses that include drinking, food preparation and personal hygiene. The World Health Organisation (2017) defines safe drinking water as water that does not have any risk to health when consumed over a period of time, including different sensitivities that may occur between life stages. River and wells are common sources of water which are used by municipalities. This water have several undesirable components that are harmful for human health. Water quality data shows that organic and bacterial contamination are becoming increasingly critical in water bodies leading to gradual degradation of water quality. Biological Oxygen Demand (BOD) for most of the rivers of India are increasing and exceeding the standards. Waterborne diseases are rampant in India due to high levels of biological contamination of water leading to cholera, acute diarrhoea, typhoid, hepatitis etc. Inorganic pollutants in water can be extremely harmful and lead to a range of chronic and fatal health problems ranging from poisoning to organ damage and cancers. For example, high levels of arsenic, lead, asbestos, cyanide, copper etc in water can be extremely harmful to health. Excessive levels of fluoride can lead to problems like dental and skeletal fluorosis, arsenicosis due to high levels of arsenic and endocrine disruptions and neurological damage due to presence of excessive amounts of mercury.Other organic and radiological contaminants can also lead to cancers, liver and kidney damage, reproductive and endocrine disorders, birth defects etc.

Screening

The raw water is allowed to pass through screens of appropriate size. Floating impurities like rags, paper, leaves, etc., are screened by the sieve and water is passed through the holes.

Sedimentation

Sedimentation is a process of removing suspended impurities. Suspended particles settle down due to the force of gravity. This process takes two to eight hours and removes 70%–75% of suspended impurities. It is done in large settlement tanks or reservoir.

Coagulation

Coagulation is the process by which the fine, suspended, and colloidal impurities are removed from the water by the addition of suitable chemicals as coagulants. The finely divided suspended inorganic matters do not settle down so easily, so these smaller particles are converted into larger ones, which have higher settling velocities. The commonly used coagulants are Al2SO4, Alum [K2SO4(Al2SO4)324H2O], Ferrous Sulphate (FeSO4.7H2O), Sodium Aluminate (NaAlO2). These coagulants react with water to form gelatinous precipitate in the form of hydroxides known as floc that absorbs the finely suspended and colloidal particles, which settle down rapidly. It is the most effective and economical means to remove impurities:

$$Al_2(SO_4)_3 + 6H_2O \longrightarrow 2Al(OH)_3 + 3H_2SO_4$$

$$NaAlO_3 + 2H_2O \longrightarrow NaOH + 2\,Al(OH)_3$$

Filteration

In this method, suspended impurities,all types of insoluble colloidal and bacterial impurities are removed by passing water through a bed of proper-sized material through filtration process. Two types of filters are commonly used for filteration.

(A)Gravity Sand filter

It consists of a large, rectangular tank made of concrete and a process medium, known as filter medium, which retains solid particles but allows the passage of water as shown in [Fig. 2.14]. It consists of three layers. The upper layer consists of fine sand (about 50 cm thick) and is a thick layer. The middle layer consists of coarse sand (about 20 cm thick), and the bottom layer consists of gravels (about 30 cm thick). It is provided with an inlet for sedimented water and an under drain channel at the bottom for the exit of filtered water. Sedimented water enters the sand filter from the top and is uniformly distributed over the fine sand layer. As the water percolates through the sand bed, finely suspended particles and most of the germs and bacteria are retained by the top layer. Clear and filtered water is collected and is drawnout. The rate of filteration becomes slow after some time due to clogging of pores of the top sand layer by the impurities. Therefore, the portion of the top fine sand layer is scrapped or replaced by a new sand layer. This filter is put to use again.

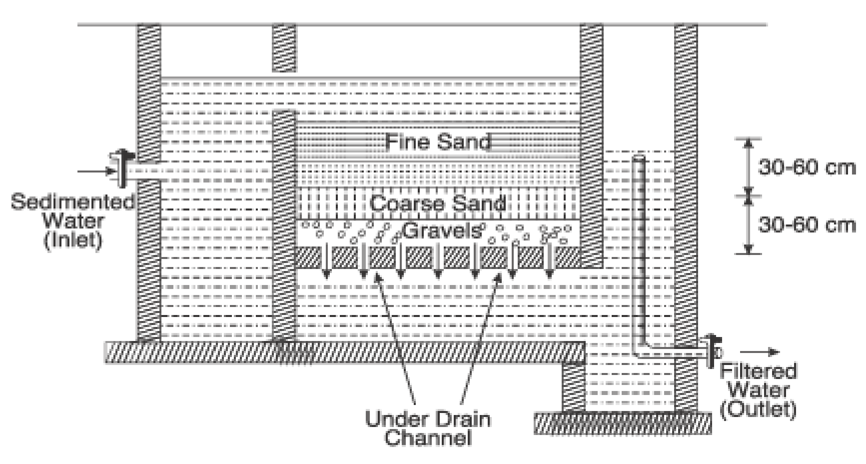


Fig. 2.14 Sand Filter

(B)Pressure filter

It consist of a cylindrical tank as shown in [Fig. 2.15]. Vertical steel tank is consisting of three layers of filtering media, one above the other. Pebbles layer (10–35 mm grain size) is placed at the bottom of the cylinder, coarse sand layer (5–7mm grain size) is placed at the middle and fine sand layer (1–2 mm grain size) is placed at the top of the cylinder tank. Impure, sedimented water is mixed with a small amount of alum solution, and then water is forced through filter bed under pressure. Alum forms the slimy layer on the filter bed, and this helps in the removal of colloidal and bacteriological impurities. The function of deflector plate, which is provided at the top, is to distribute the slimy layer of alum uniformly over the top of the filter bed. Filtered water, as it comes out from the bottom of filter, is under pressure and can be pumped directly. These filters are widely used for industrial purposes.

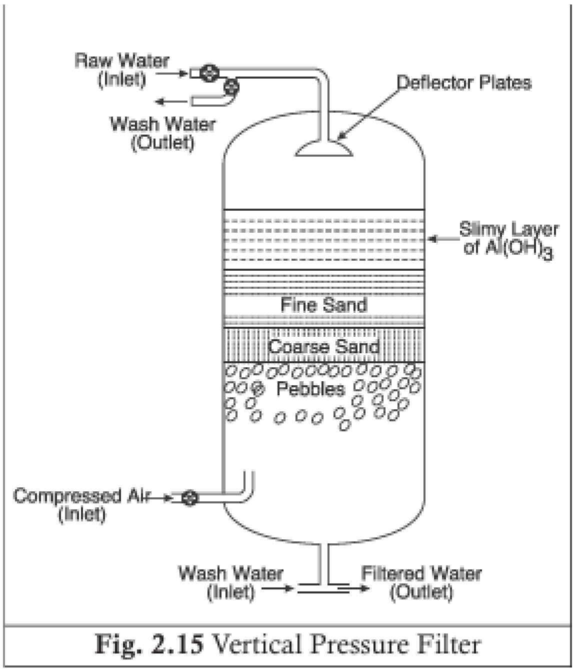
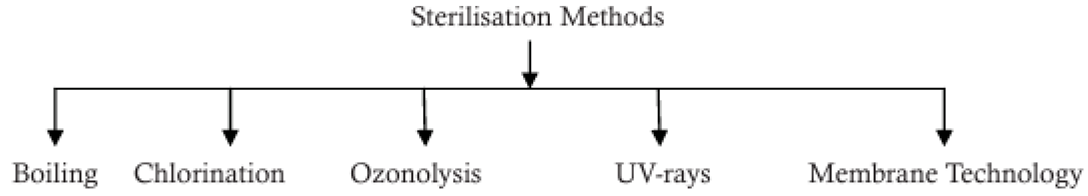


Fig. 2.15 Vertical Pressure Filter

Disinfection/Sterilization

Sterilisation of water means complete destruction of all living microorganisms such as bacteria, virus, etc. present in the water. We know that water after passing through different processes such as sedimentation, coagulation, and filteration processes still contains a small percentage of pathogenic bacteria. Therefore, it is necessary to remove these bacteria and microorganisms from water. The chemicals used for sterilisation are known as sterilisers or disinfectants.

Several methods have been adopted for sterilisation of water. Some of them are given below:



(A)Boiling Method

Water for domestic purposes may be sterilised by simple boiling method by boiling the water for about 20–30 min. This method kills the harmful disease-causing bacteria and germs. This process is very much expensive for municipal supply of water, and in addition, a large quantity of fuel is required to boil water on a large scale. It does not provide any protection for further contamination of water.

(B)Chlorination method

It is the most important method for sterilisation of water. Chlorination is done by using the following methods:

- Chlorine Gas or Concentrated Aqueous Solution
- Bleaching Powder
- Chloramine

(i)Chlorine gas or Concentrated Aqueous Solution

Chlorine is used directly as a gas or as chlorine water, is a powerful germicide and most commonly used disinfectant. It reacts with water to form hypochlorous acid and nascent oxygen, both of which are powerful germicides.

$$Cl_2 + H_2O \longrightarrow \underset{\text{Hypoclorous acid}}{HOCl} + HCl$$

$$HOCl \longrightarrow \underset{\substack{\text{Nascent}\\\text{Oxygen}}}{[O]} + HCl$$

Apparatus

The apparatus used for disinfection by chlorine is known as chlorinator [Fig.2.16]. It is a large tower containing number of baffle plates. From the top of the tower,proper dose of chlorine and water is introduced . They get thoroughly mixed during their passage through the tower,and treated water is taken out from the bottom.

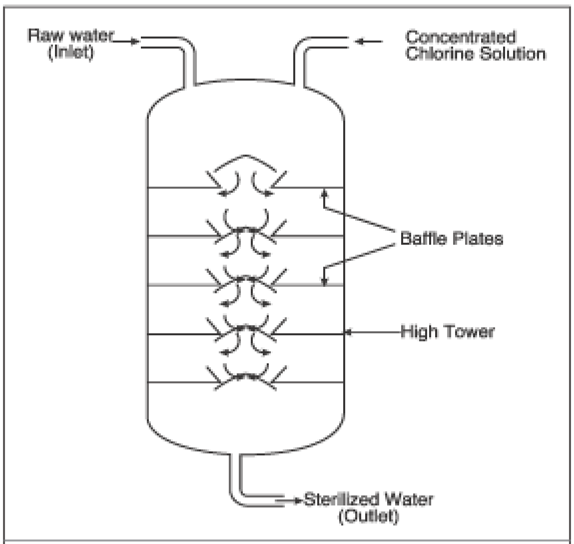


Fig. 2.16 Chlorinator

Advantages

- It is cheap, easily available disinfectant and effective at low concentration.
- It can be used at high and low temperatures.
- It is stable and does not deteriorate on keeping.
- Chlorine residue can be maintained in treated water, which provides additional safety for preventing regrowth of bacteria.

Disadvantages : Excess of chlorine produces an unpleasant taste and odour in water.

(ii)Bleaching Powder ($CaOCl_2$)

Bleaching powder is a strong oxidising agent and is having 30 percent available chlorine. When water is treated with bleaching powder, hypochlorous acid is formed. It releases nascent oxygen which deactivates the enzymes of micro-organisms and thus the metabolic activities will stop and the microorganisms will be killed.

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

About 1 kg of bleaching powder is sufficient for 1000 kilo litres of water.

Disadvantages

- Excess of bleaching powder creates bad taste and odour to water.
- It introduces calcium hardness in water due to the formation of Ca(OH)2
- It is unstable, hence its storage is difficult.

(iii)Chloramine (nH2Cl)

By mixing of chlorine and ammonia in 2 : 1 ratio, chloramines is formed. Whenever water is treated with chloramines, hypoclorous acid is formed which protect it from recontamination.

Advantages

Excess dose of NH2Cl does not create bad odour and taste in water.

Disadvantages

Excess of chlorine produces an unpleasant taste and odour in water.

(B)Ozonolysis Method

Ozone is used for this method. Ozone is a highly unstable and excellent disinfectant. It breaks down and gives nascent oxygen which is very powerful oxidising agent and kills all the bacteria and germs present in water.

Apparatus

The reaction of ozone and water is carried out in ozone steriliser as shown in [Fig. 2.17]. During the treatment of water, water is allowed to enter from top to bottom, and ozone is allowed to enter from bottom to top, when they come in contact with each other it kills the germs. Sterilized water is collected at the bottom of the tank. The contact time for ozone and water is about 10–15 minutes.

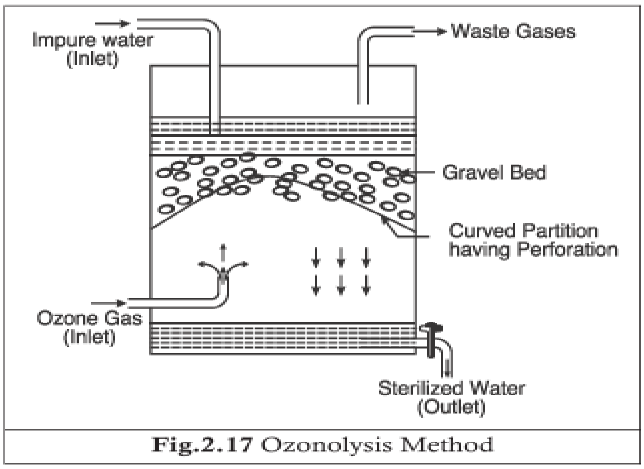


Fig.2.17 Ozonolysis Method

Advantages

- It removes colour and odour from water.
- It improves the taste of water.
- The excess dose of ozone is not harmful, because it releases oxygen on decomposition.

(D)UV-Rays Method

When water is exposed to UV-rays from electric mercury lamp that is immersed in water, most of the pathogenic bacteria are destroyed. This method is widely used for the disinfection of swimming pool water.

Advantages

- It does not require any chemicals.
- It does not produce any odour in water.

Disadvantages: It is very expensive, so it is not widely used on a large scale.

(E)Membrane Technology Method

Membrane filtration is a technique for testing water samples. In this procedure, water is drawn through a special porous membrane designed to trap microorganisms larger than 0.45 µm. Water is forced through membranes made of synthetic materials cellulose acetate, cellulose nitrate (collodion), polyamide (nylon), polycarbonate, polypropylene, and polytetrafluoroethylene (Teflon by the application of high pressure (in the range of 10 to 50 atm. pressure). Membrane processes are widely used for removal of bacteria, microorganisms, particulates, and natural organic material, which can impart colour, tastes, and odours to water and react with disinfectants to form disinfection by products. The four types of membrane filtration are known as reverse osmosis, nanofiltration, ultrafiltration and microfiltration, in order of increasing pore size.

Indian Standard Specification of Drinking water

Introduction

Most of the human being cannot survive more than 3-4 days without water. Water is the primary necessity. Yet, it is a horrific fact that there are billions of people around the world who do not have access to clean drinking water. Safe and clean drinking water is important for public health. In 2010, the UN General Assembly explicitly recognised the human right to water and sanitation. Everyone has the right to sufficient, continuous, safe, acceptable, physically accessible, and affordable water for personal and domestic use. The Indian Standard Drinking Water Specification (Second revision IS 10500:2012), was adopted by Bureau of Indian Standard (BIS) after the draft finalised by drinking water sectional committee had been approved by Food and Agriculture Division Council. Though spectrum of parameters are given by IS Specifications, but here the most important and widely tested parameters are mentioned.

WATER FOR HUMAN CONSUMPTION FOR DRINKING AND COOKING PURPOSES FROM ANY WATER SOURCES

Water covers two thirds of the earth's surface, most of it is salty and not suitable for drinking purpose. Only 3% of the available water on earth is freshwater and only 1 percent of the available freshwater can be accessed for use from rivers, lakes and groundwater. About 97% of the water on the earth's surface is covered with sea water. The details of the distribution of water had already been explained in previous section. The three main sources of water are:

- Groundwater – This includes water bodies like borewells, tubewells, dugwells, handpumps and springs.
- Surface water – This includes different water bodies like sea, oceans, reservoirs, rivers, streams, ponds, lakes and tanks.
- Rainwater.

India's total annual utilisable water resources is 1123 billion cubic metres (690 bcm surface water + 433bcm ground water). Drinking water in India is mostly derived from groundwater. Rivers and wells are also major sources of water which are used by municipalities. The data shows that groundwater is the most reliable source of drinking water for nearly 43 percent of the rural Population in the country (National Sample Survey Office's (NSSO) data).

Groundwater is an important source for domestic usage. It is also a major source of drinking water in urban and rural India. 80% of domestic water comes from ground water reserve. The main source of ground water is the recharge from monsoon precipitation.

Other sources of recharge viz. seepage from canals, tanks, ponds and other water structures and irrigation account for about 32%. Although India receives plenty of water as rainfall during monsoon but due to lack of storage, only a small percentage of that water is actually added to the reserve. There is significant mismatch of spatial distribution of available water with the population, the situation becomes alarming; ironically less water is available where more people live.

CHAPTER-3

Engineering Materials

Introduction to natural occurrence of metals

Earth crust is a great source of metals. These metals are found to occur in nature in two states, either in the free state (native state) or in the combined state, in the form of their compounds (with other elements).

(i)Native State or Free State

A metal is said to occur in a free state when it is found in the crust of the earth in the elementary or uncombined form. These are unreactive and have no tendency to react with oxygen and are not attacked by moisture, carbon dioxide of air or other non-metals. Only a few less reactive metals like copper, silver, gold and platinum are found in the free state as metals because of their low chemical reactivity. It is important to note that copper and silver metals occur in free state as well in the combined state.

(ii) Combined State

Most metals are found to occur in a combined state in the form of its compounds. This is due to the reaction of metals with moisture, air and other substance present in the earth surface under high temperature and pressure. These compounds are called minerals and ores.

Minerals and Ores

Minerals

The naturally occurring chemical substances in which metals or their compounds occur either in native state or combined state are called minerals. The place where these minerals are found is called mine. Some minerals may contain large percentage of metal whereas others may contain small percentage of metal. Some minerals may not contain any objectionable impurities whereas others may contain objectionable impurities which hamper the extraction. Thus all the minerals cannot be used to extract metals. Example : Aluminium occurs in the earth crust in the form of two minerals, bauxite and clay ($Al_2O_3.2H_2O$) ($Al_2O_3.2SiO_2.2H_2O$). Out of these two, aluminium can be conveniently and economically extracted from bauxite so bauxite is an ore of aluminium.

Table 3.1 Difference between Minerals and Ore

Minerals	Ores
All the naturally occurring substances that are present in the earth's crust are known as Minerals.	Ores are usually used to extract metals economically. A large number of metals are present
All minerals are not ores	All ores are minerals.
Minerals are native forms in which metals exist	Ores are mineral deposits

Ores

Those minerals from which the metals are extracted easily and economically are called ores. An ore contains a good percentage of metal and there are no objectionable impurities. Thus, all the ores are minerals, but all the minerals are not ores. The ores generally contain unwanted impurities such as sand, stone, earthy particles, limestone, mica. These are called gangue or matrix.

Types of Ores

The most common ores of metals are oxides, sulphides, carbonates, halides etc. (a) Metals which are only slightly reactive occur as sulphides (CuS, PbS etc.) (b) Reactive metals occur as oxides

($MnO2$, $Al2O3$ etc.) (c) Most reactive metals occur as salts as carbonates, sulphates, halides etc. (Ca, Mg, K etc.)

(a) Ores of iron, aluminium and copper Ores of iron, aluminium and copper are given below in table 3.2

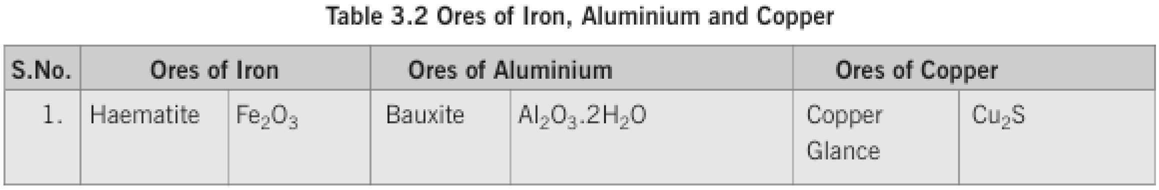
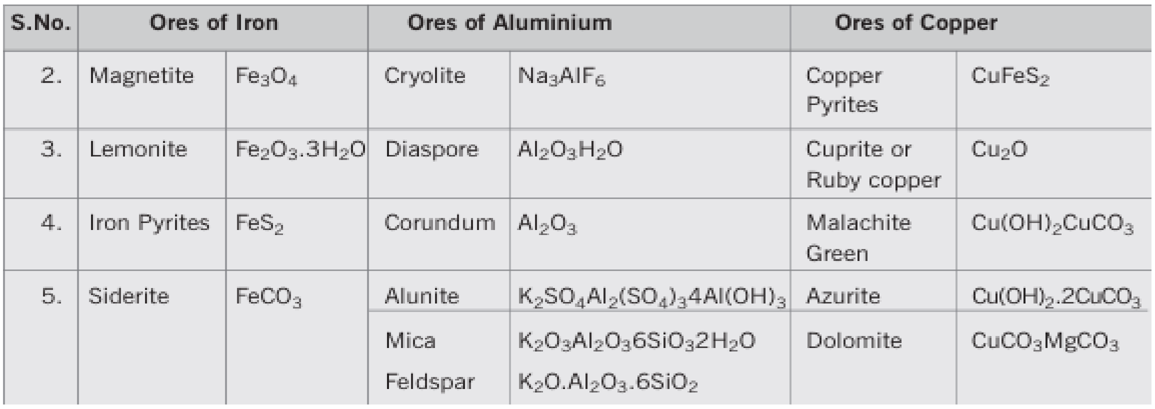


Table 3.2 Ores of Iron, Aluminium and Copper

S.No.	Ores of Iron		Ores of Aluminium		Ores of Copper	
1.	Haematite	Fe_2O_3	Bauxite	$Al_2O_3.2H_2O$	Copper Glance	Cu_2S



S.No.	Ores of Iron		Ores of Aluminium		Ores of Copper	
2.	Magnetite	Fe_3O_4	Cryolite	Na_3AlF_6	Copper Pyrites	$CuFeS_2$
3.	Lemonite	$Fe_2O_3.3H_2O$	Diaspore	$Al_2O_3H_2O$	Cuprite or Ruby copper	Cu_2O
4.	Iron Pyrites	FeS_2	Corundum	Al_2O_3	Malachite Green	$Cu(OH)_2CuCO_3$
5.	Siderite	$FeCO_3$	Alunite	$K_2SO_4Al_2(SO_4)_34Al(OH)_3$	Azurite	$Cu(OH)_2.2CuCO_3$
			Mica Feldspar	$K_2O_3Al_2O_36SiO_32H_2O$ $K_2O.Al_2O_3.6SiO_2$	Dolomite	$CuCO_3MgCO_3$

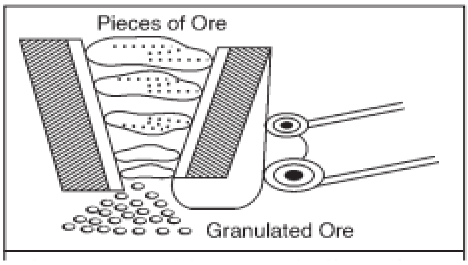
General Principles of metallurgy

After mining the ore from the ground, it needs to be converted into pure metal. To obtain a metal from its ore is called extraction of metal. The process of extracting metals from their ores and then refining them for use is called metallurgy. The process of metallurgy depends upon the nature of metal and type of impurities present. There is not a single method for the extraction of all metals. However, most of the metals can be extracted by a general principles and procedure which involves the following steps. Various steps involved in metallurgical processes are :

- Crushing and grinding of the ore
- Concentration of the ore or enrichment of the ore
- Extraction of metal from the concentrated ore
- Refining or purification of the impure metal

(A)crushing and Grinding of Ore:

Most of the ore occur as big rock in nature. After digging out the ore from mines, it is crushed into small pieces with the help of jaw crusher . These pieces are then reduced to fine powder with the help of ball mill or stamp mill.



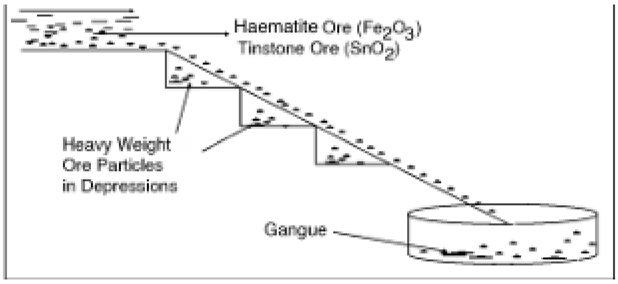
(FIG.CRUSHING AND GRINDING OF ORE)

(C)concentration of the Ore

The process of removal of unwanted impurities (or gangue) from the ore is called ore concentration. The methods used for removing gangue from ore depend on differences in the some of the physical properties or chemical properties of the ore and gangue. After removing gangue, we get a concentrated ore containing much higher percentage of the metal. Concentration of Ores is carried out by physical concentration and Chemical Concentration method Physical Concentration methods are a) Gravity Separation b) Magnetic Separation c) Froth flotation. Chemical Concentration methods are a) Calcination b) Roasting Following are some common methods of concentration of ores.

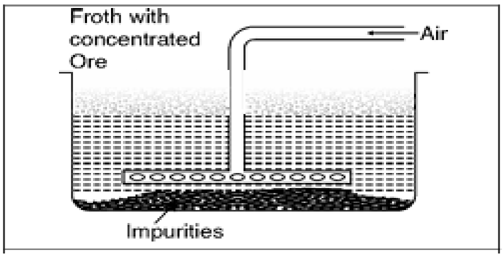
(i)Gravity Separation or Hydraulic Washing

This method is based on difference in the densities of the ore particles and the impurities (gangue). The crushed ore is washed with a running stream of water or agitated with water. The heavy ore particles settle down rapidly and lighter gangue particles are washed away. Haematite (Fe2O3) and tinstone (SnO2) ores are concentrated with this method.



(fig. gravity separation method)

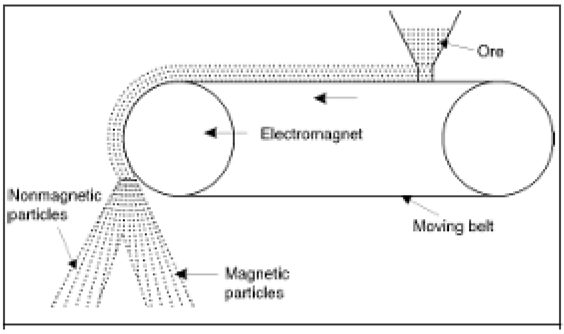
(ii)Froth Flotation Process : This method is based on the principle of difference in the wetting properties of the ore and gangue particles with oil and water respectively. This method is used for concentration of sulphide ores. Crushed ore is taken in big iron tank containing water. Some pine oil is also added in the tank. The ore particles acquire an oily layer on their surface while the gangue particles get wetted with water and settle down under gravity. Froth Flotation Process Now a current of air is bubbled into the tank. The oily ore particles come on the surface with the froth and the gangue particles settle down in the tank. The froth is removed from time to time and purified ore is obtained . Ores like zinc blende (ZnS), galena (PbS), cinnabar (HgS), nickel sulphide(NiS), copper pyrite (CuFeS2) can be concentrated with this method.



(fig.froth flotation method)

(iii)magnetic Separation

This method depends upon the difference in the magnetic properties of the ores and gangue. The crushed ore is spread over a moving belt in a strong magnetic field. When the ore falls down, the magnetic substances are attracted by the magnet and collected on one side. The nonmagnetic substances collect on the other side. This method is used for the concentration of haematite, an ore of the iron. Non magnetic ore like tinstone (SnO_2) can be concentrated from magnetic impurities like tungstates of iron and manganese.



(fig. magnetic separation method)

Flux

The metal ores sometimes contains non-fusible impurities. They are fused easily with suitable substances called flux. The impurities react with flux forming a fusible product called slag which can be removed. Thus flux is a substance that chemically combines with gangue (earthy impurities), which may still be present in the roasted or calcined ore to form an easily fusible material called slag.

Flux + Gangue = Slag

The flux are of two types

(a) Acidic Flux: If non-fusible impurities are basic, then the acidic flux is used. Example In the extraction of Copper, iron impurities are removed by SiO_2.

$$\underset{\text{Acidic flux}}{SiO_2} + \underset{\text{Basic impurity}}{FeO} \longrightarrow \underset{\text{Fusible slag}}{FeSiO_3}$$

(b) Basic Flux CaO, MgO, FeO are the basic fluxes which are used when the non-fusible impurities are acidic.

$$\underset{\text{Basic flux}}{MgCO_3} + \underset{\text{Acidic impurities}}{SiO_2} \longrightarrow MgSiO_3 + CO_2\uparrow$$

$$\underset{\text{Basic flux}}{CaO} + \underset{\text{Acidic impurity}}{SiO_2} \longrightarrow \underset{\text{Fusible slag}}{CaSiO_3}$$

(B)Extraction of Metal from the Concentrated Ore

Metal is extracted from the concentrated ore by the following steps

(i) Conversion of the Concentrated Ore into its Metal Oxide

The production of metal from the concentrated ore mainly involves reduction process. This can be usually done by two processes known as calcination and roasting depending upon the nature of the o(a) Calcination It is the process of heating the concentrated ore in the absence of air. It is used for hydrated and carbonate ores. The calcinations process is carried out to

- convert carbonate ores into metal oxide.
- remove water from the hydrated ores.
- remove volatile impurities from the ore.

For example

$$\underset{\text{Calamine}}{ZnCO_3(s)} \xrightarrow{\text{Calcination}} \underset{\text{Zinc oxide}}{ZnO(s)} + \underset{\text{Carbon dioxide}}{CO_2(g)}$$

$$\underset{\text{Siderite}}{FeCO_3(s)} \xrightarrow{\text{Calcination}} \underset{\text{Iron(II) oxide}}{FeO(s)} + \underset{\text{Carbon dioxide}}{CO_2(g)}$$

$$\underset{\text{Haematite}}{Fe_2O_3.3H_2O} \xrightarrow{-H_2O} \underset{\text{Moisture}}{Fe_2O_3} + 3H_2O$$

$$\underset{\substack{\text{Malachite}\\\text{(Hydroxide)}}}{CuCO_3.Cu(OH)_2} \longrightarrow \underset{\text{(Oxide)}}{2CuO} + CO_2 + H_2O$$

(c) Roasting

It is the process of heating the concentrated ore strongly in the presence of excess air, below melting point of ore. This method is used for extraction of sulphide ores. This process is used for converting sulphide ores to metal oxide. In this process, the following changes takes place:

- the sulphide ores undergo oxidation to their oxides.
- the sulphide ores undergo oxidation to their sulphate.
- moisture is removed.
- volatile impurities are removed

For example

$$\underset{\substack{\text{Zinc sulphide}\\\text{(Zinc blende)}}}{2ZnS(s)} + \underset{\text{Oxygen}}{3O_2(g)} \xrightarrow[\text{(from air)}]{\text{Roasting}} \underset{\text{Zinc oxide}}{2ZnO(s)} + \underset{\text{Sulphur dioxide}}{2SO_2(g)}$$

$$\underset{\text{Zinc sulphide}}{ZnS} + 2O_2 \longrightarrow \underset{\text{Zinc sulphate}}{ZnSO_4}$$

$$\underset{\text{Iron pyrites}}{4FeS_2(s)} + \underset{\text{Oxygen}}{11O_2(g)} \xrightarrow{\text{Roasting}} \underset{\text{Ferric oxide}}{2Fe_2O_3(s)} + \underset{\text{Sulphur dioxide}}{8SO_2(g)}$$

(iii)Conversion of Metal Oxide into Metal : The metal oxide formed after calcination or roasting is converted into metal by reduction. The method used for reduction of metal oxide depends upon the nature and chemical reactivity of metal. The metals can be grouped into the following three categories on the basis of their reactivity:

Metals of low reactivity. Metals of medium reactivity. Metals of high reactivity.

These different categories of metals are extracted by different techniques. The different steps involved in separation are as follows.

(a)Reduction by Heating

Metals placed low in the reactivity series are very less reactive. They can be obtained from their oxides by simply heating in air.

$$\underset{\text{Mercuric sulphide}}{2HgS(s)} + \underset{\text{Oxygen}}{3O_2(g)} \xrightarrow{\text{Roasting}} \underset{\text{Mercuric oxide}}{2HgO(s)} + \underset{\text{Sulphur dioxide}}{2SO_2(g)}$$

$$\underset{\text{Mercuric oxide}}{2HgO(s)} \xrightarrow{\text{Heat}} \underset{\text{Mercury metal}}{2Hg(l)} + \underset{\text{Oxygen}}{O_2(g)}$$

(b) Chemical Reduction

The metals in the middle of the reactivity series, such as iron, zinc, lead, copper etc. are moderately reactive. These are usually present as sulphides or carbonates. Therefore, before reduction, the metal sulphides and carbonates must be converted to oxides. This is done by roasting and calcinations. The oxides of these metals cannot be reduced by heating alone. Therefore, these metal oxides are reduced to the free metal by using reducing agents like carbon, aluminium, sodium or calcium.

Reduction with Carbon

The oxides of moderately reactive metals (occurring in the middle of reactivity series) like zinc, copper, nickel, tin, lead etc. can be reduced by using carbon as reducing agent. Coke is very commonly used as a reducing agent because it is cheap.

$$\underset{\substack{\text{Zinc oxide} \\ \text{(Reducing agent)}}}{ZnO(s)} + \underset{\substack{\text{Carbon} \\ \text{metal}}}{C(s)} \xrightarrow{\text{Heat}} \underset{\text{Zinc}}{Zn(s)} + \underset{\text{Carbon monoxide}}{CO(g)}$$

Reduction with Aluminium

Alumino-Thermic Process This method is used to reduce such metallic oxides (eg. Cr2O3, MnO2) which cannot be reduced by carbon. Here metal oxide is mixed with aluminium powder and the mixture is taken in a crucible. This mixture is ignited by means of magnesium ribbon, inserted into aluminium and barium peroxide mixture inside the crucible. The reaction is exothermic and produce a very high temperature of about 30000C. The oxide is reduced into metal and Al2O3 is formed.

$$Cr_2O_3 + 2Al \longrightarrow Al_2O_3 + 2Cr + \text{Heat}$$

$$3MnO_2 + 4Al \longrightarrow 2Al_2O_3 + 3Mn + \text{Heat}$$

(c)Reduction by Electrolysis or Electrolytic Reduction

The oxides of active metals (which are high up in the activity series) are very stable and cannot be reduced by carbon or aluminium. These metals are commonly extracted by the electrolysis of their fused salts using suitable electrodes. This is also called electrolytic reduction i.e. reduction by electrolysis. The process of extraction of metals by electrolysis process is called electrometallurgy. Example Aluminium oxide is very stable and aluminium cannot be prepared by reduction with carbon. It is prepared by the electrolysis of molten alumina (Al_2O_3).

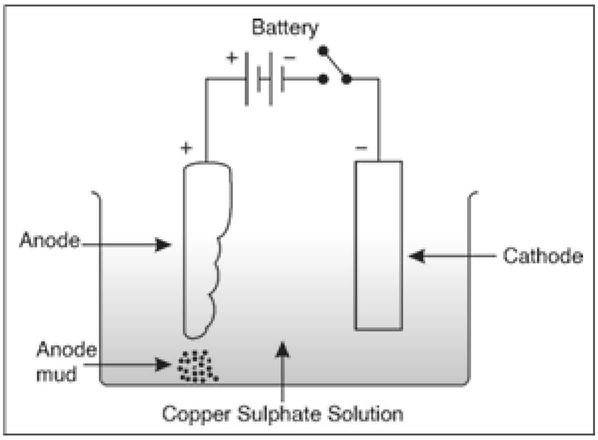
(D)Purification of Metals

The metals obtained by any of the above methods are usually impure and is known as crude metal. The process of purifying the crude metal is called refining.

(i)Liquation: This is based on the principle that the metal to be refined is easily fusible but the impurities do not fuse easily. The impure metal is placed on the sloping hearth of a furnace and gently heated. The metal melts and flows down leaving behind the impurities on the hearth. This method is used for refining the metals having low melting points, such as tin, lead, bismuth etc.

(ii) Distillation :This method is used for the purification of volatile metals. Impure metal is heated and its vapours are separately condensed in a receiver. The non-volatile impurities are left behind. This is used for mercury, cadmium and zinc.

(iii)Electrolytic Refining; This is most widely used method for the refining of impure metals. In this method impure metal is made anode while pure metal is made cathode. Many metals such as copper, zinc, tin, nickel, silver, gold etc. are refined electrolytically. It is based upon the phenomenon of electrolysis. In this method, the crude metal is casted into thick rods and is made as anode. An aqueous solution of salt of the same metal is used as an electrolyte .On passing current through the electrolyte, the pure metal from the anode dissolves into the electrolyte. An equivalent amount of pure metal from the electrolyte is deposited on the cathode. The soluble impurities go into the solution whereas the insoluble impurities settle down at the bottom of the anode and are known as anode mud. In this way, the pure metal from anode goes into electrolyte and from electrolyte it goes to the cathode.



Extraction of Iron from Haematite

Iron is extracted in three forms; Cast Iron, Wrought Iron and Steel. Iron is usually extracted from the oxide ore, i.e. haematite. It involves the following steps:

(A) Concentration: The ore is crushed in jaw crushers and the crushed ore is concentrated by gravity separation process in which the crushed ore is washed in a stream of water when lighter sand and clay particles are washed away while the heavier ore particles settle down. In case of sulphide ore i.e. iron pyrites concentration is carried out by froth floatation process.

(B) Calcination ;The concentrated ore is then calcined i.e., heated strongly in the presence of a limited supply of air in a reverberatory furnace [Fig. 3.9]. During calcination, the following changes occur.

(i) Moisture is removed.

(ii) Impurities of sulphur, phosphorus & arsenic escape as their volatile oxides.

$$S_8 + 8\,O_2 \longrightarrow 8\,SO_2$$

$$P_4 + 5\,O_2 \longrightarrow P_4O_{10}$$

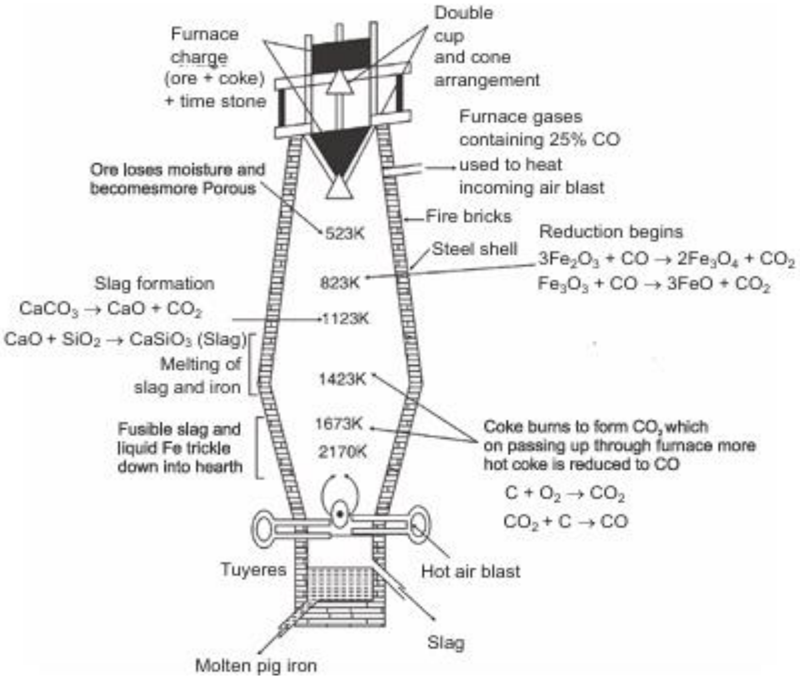
$$4As + 5\,O_2 \longrightarrow 2As_2O_5$$

(iii) Ferrous oxide is oxidised to ferric oxide thereby preventing the loss of iron as slag during smelting.

(iv) The ore becomes porous and hence is more suitable for reduction to the metallic state. In case of carbonate ore i.e. siderite, during calcination, it is converted into ferric oxide.

(c)Smelting

The calcined ore is reduced with carbon, i.e., smelted in a blast furnace . It is a tall cylindrical furnace made of steel and lined inside with refractory material. It is slightly narrow at the top and again at the bottom. This facilitates the proper flow of materials. The furnace is provided with a double cup and cone arrangement which helps to feed the charge from the top without letting any gases from inside to escape. Near the top, furnace is also provided with an outlet for waste gases. At the base, the furnace is provided with (i) small pipes called tuyeres through which a blast of hot air is flown inside. (ii) a tapping hole for with drawing molten iron. (iii) a slag hole for withdrawing slag. The charge consisting of calcined ore (8 parts), coke (4 parts) and limestone (1 part) is introduced into the furnace from the top through cup and cone arrangement. At the same time, a blast of hot air pre-heated to about 1000 K is blown into the furnace through tuyeres. The added coke serves both as a fuel as well as a reducing agent while added limestone acts as the basic flux.



(D)Reduction of Iron oxide in the Blast Furnace

In the blast furnace, reduction of iron oxides takes place in different temperature ranges as summarised below.

At 500-800 K (lower temperature range in the blast furnace)

$$3\,Fe_2O_3 + CO \longrightarrow 2Fe_3O_4 + CO_2$$

$$Fe_3O_4 + 4CO \longrightarrow 3Fe + 4CO_2$$

$$Fe_2O_3 + CO \longrightarrow 2FeO + CO_2$$

At 900-1500 K (higher temperature range in the blast furnace)

$$C + CO_2 \longrightarrow 2CO$$

$$FeO + CO \longrightarrow Fe + CO_2$$

(E)Reactions in the Blast Furnace

The following reactions occur in the blast furnace.

(i) Zone of Combustion Near the tuyeres, coke burns to form carbon dioxide.

(ii) Zone of Heat Absorption This is lower part of the furnace and the temperature here is between 1423-1673 K. As CO2 formed near tuyeres moves up, it meets the descending charge. The coke present in the charge reduces CO2 to CO.

(i) Zone of Slag Formation It is the middle part of the furnace. The temperature here is around 1123 K. In this region, limestone decomposes to form CaO and CO2. The CaO thus formed acts as a flux and combines with silica (present as an impurity) to form fusible calcium silicate slag.

(ii) Zone of Reduction This is the upper part of the furnace. The temperature here is around 823 K. Here, the ores are reduced to FeO by CO.

Extraction of Aluminium from Bauxite

(A) Introduction

Bauxite is the main ore of aluminium from which the metal is extracted. Extraction of aluminium is done by the reduction of bauxite ore. Electrode Potential of aluminium is high and hence aluminium oxide can not be reduced by chemical reducing agents. The extraction of metal is done by electrolytic reduction method. The process is carried out in three steps.

(B)Purification of Bauxit

The ore contains about 55% Al2O3 along with impurities of Fe2O3, SiO2, TiO2 etc. If the metal is extracted from crude alumina, it is contaminated with these impurities which make it brittle. Hence it is necessary to purify the ore. It is done by the following methods.

(i)Hall's process : In this process bauxite ore is powdered and fused with sodium carbonate. Alumina reacts with Na2CO3 producing sodium aluminate while Fe2O3 and SiO2 are not affected. This mixture is agitated with water to dissolve the aluminate. The insoluble impurities are removed by filtration.

$Al_2O_32H_2O + Na_2CO_3 \longrightarrow 2NaAlO_2 + CO_2 + 2H_2O$

The solution thus obtained is heated to 50-60^oC and carbon dioxide is passed.
The aluminate is hydrolysed to aluminium hydroxide which is precipitated.

$2NaAlO_2 + CO_2 + 3H_2O \longrightarrow 2Al(OH)_3\downarrow + Na_2CO_3$

This precipitate is filtered and heated to 1500^0C to get pure Alumina.

$2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$

(ii) Bayer's process When the bauxite ore contains high percentage of Fe2O3 impurity, Bayer's process is employed. The crushed ore is roasted to convert FeO, if present, into Fe2O3. The roasted ore is treated with a strong solution of caustic soda at 150C and 80 atmospheric pressure for several hours in an autoclave. Aluminium oxide reacts with alkali forming soluble sodium aluminate complex salt. The impurities remain in the form of precipitate which is filtered.

Seeding

In the solution of sodium aluminate, a small quantity of freshly precipitated aluminium hydroxide is added and the mixture is agitated for several hours. Sodium aluminate gets hydrolysed into aluminium hydroxide. The ppt of Al(OH)3 is filtered and dried. It is then heated to 7500C to get pure Al2O3.

$NaAlO_2 + 2H_2O \longrightarrow NaOH + Al(OH)_3$

$2Al(OH)_3 \longrightarrow Al_2O_3 + 3H_2O$

(iv)Serpek's process

This process is used to purify bauxite having much silica (SiO2) as impurity. The ore is first powdered. It is then mixed with carbon and the mixture is heated to 18000C in a current of nitrogen. Aluminium is converted into aluminium nitride. The Silica of bauxite is reduced to silicon which, being volatile, escapes as vapour.The product obtained is allowed to react with hot water when it forms a precipitate of aluminium hydroxide. The precipitate is filtered, dried and heated to 15000C to get pure Al2O3.

$Al_2O_3 + 3C + N_2 \xrightarrow{1800^0C} \underset{\text{Aluminium nitride}}{2AlN} + 3CO$

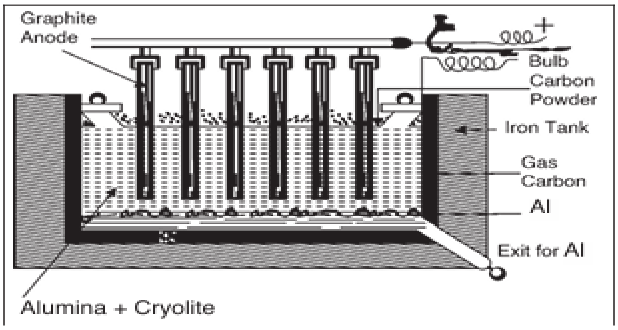
$AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$

$SiO_2 + 2C \longrightarrow 2CO + Si$

$2Al(OH)_3 \xrightarrow{1500^0C} Al_2O_3 + 3H_2O$

(B)Electrolysis of Bauxite

The purified bauxite is mixed with fused mixture of cryolite and fluorspar and is taken in an iron tank. The purpose of taking cryolite is to reduce the melting point of alumina from 20500C to only 9000C. Moreover, cryolite is used as an electrolyte also. The iron tank has a thick inner lining of carbon which serves as cathode . The anode is made of graphite rods which are suspended in the fused mixture. An electric bulb is connected in parallel with the electrolytic cell. Some powdered charcoal is spread over the surface to check the glow produced by the vigorous action of oxygen at the anodes. A current of 6-7 volts and 100 amperes is passed through the cell. The high current brings about the following changes and also it maintains a temperature of about 900°C which keeps the mass in molten form. Cryolite is a mixed fluoride of Sodium and aluminium which decomposes into sodium fluoride.



$$Na_3AlF_6 \longrightarrow 4NaF + AlF_3$$

AlF_3 undergoes electrolysis as follows :

$$AlF_3 \longrightarrow Al^{3+} + 3F^-$$

$$Al^{3+} + 3e^- \longrightarrow Al \quad \text{at cathode.}$$

$$3F^- \longrightarrow 3F + 3e^- \quad \text{at anode.}$$

Aluminium is deposited at cathode and is collected from the bottom of the tank. Fluorine is liberated at anode which reacts with alumina producing aluminium fluoride & oxygen.

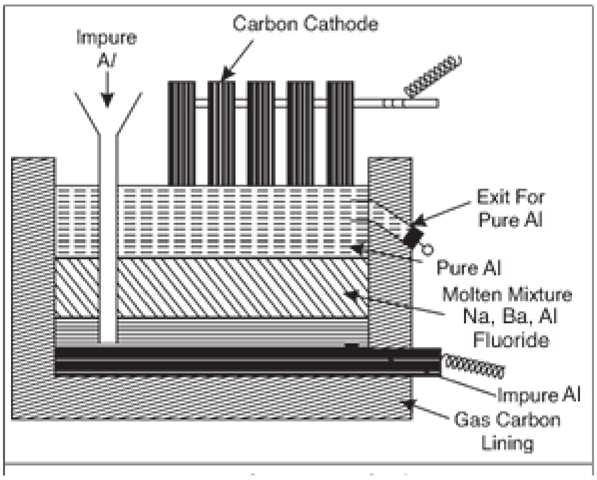
$$2Al_2O_3 + 12F \longrightarrow 4AlF_3 + 3O_2$$

In this way alumina is decomposed and Al metal is obtained. The oxygen liberated at anode reacts with the carbon of anode forming CO and CO2. Thus the anode gets smaller and smaller. This is checked by the charcoal powder spread over the surface. As more and more Al2O3 is decomposed, the resistance of the cell increases. It is indicated by the glowing of electric bulb connected with the cell. More alumina is added to continue the process. Aluminium obtained by this process is about 99%.

(C)Purification of Aluminium

The metal obtained from the above process contained the impurities of iron and silicon. The method is called Hoope's method.Purification is done in an iron tank having a lining of carbon at its bottom which acts as anode. The electrolytic cell contains three liquids layers of different densities. The lowermost layer is of molten impure aluminium which is in contact with carbon anode. The middle layer is a fused mixture of sodium, aluminium and barium fluorides and the top layer is of molten pure aluminium in which carbon rods are dipped which act as cathode.

When current is passed, Al3+ ions come in the middle layer migrate towards the top layer of pure aluminium cathode and are discharged. More Al3+ ions come in the middle layer from the impure aluminium anode. In this way pure aluminium collects at the top and is removed from time to time. The metal thus obtained is 99.94% pure.



Alloys

An alloy is a homogenous mixture of two or more metals or a metal and a non-metal. For example, iron is the most widely used metal. But it is never used in the pure form. This is because iron is very soft and stretches easily when hot. But when it is mixed with a small amount of carbon (about 0.5 to 1.5%), it becomes hard and strong. The other form of iron is called steel.

Classification of Alloys

Alloys are classified as follows

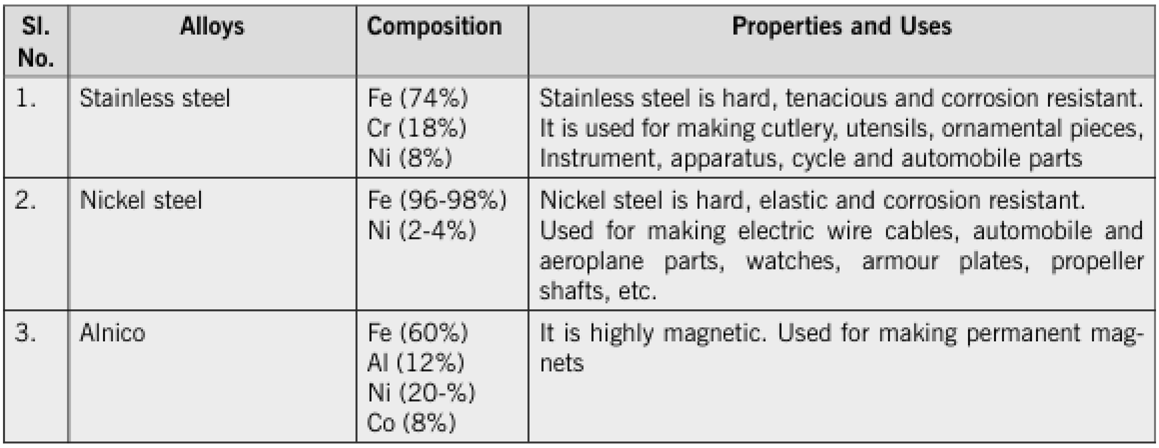
Ferrous Alloy : Alloys which contain iron as one of the main component known as ferrous alloys. e.g. In stainless steel alloy, Fe is present as one of the main component with Cr and Ni.

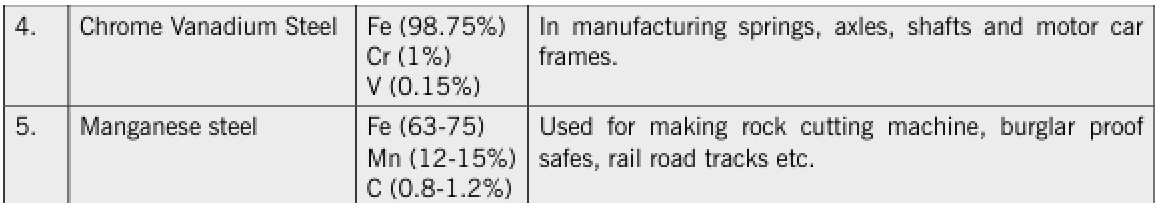
Non-ferrous Alloys : Alloys which do not contain iron as one of the main component known as non-ferrous alloys. e.g. Brass consist of Cu and Zn, it does not contains iron hence it is non-ferrous alloy.

Composition, Properties and Uses of Some Alloys of Copper

Sl. No.	Alloys	Composition	Properties and Uses
1.	Brass	Cu (60-80%) Zn (20-40%)	Brass is used for decoration purposes, for making many scientific instruments, telescopes, microscopes, barometers etc.
2.	Bronze	Cu (75-90%) Sn (10-25%)	It is used for making statues, cooking utensils and coins.
3.	German Silver	Cu (30-60%) Zn (25-35%) Ni(15-35%)	It is silvery white. Malleable and ductile. It is used as imitation silver, in making ornaments and utensils and also for decoration.
4.	Gun metal	Cu (88%) Sn (10%) Zn (2%)	It is used for making gears, bearing and gun barrels.
5.	Bell metal	Cu (80%) Sn (20%)	It is used for casting bells.
6.	Aluminium Bronze	Cu 90% Al 10%	Golden yellow, used for cheap jewellery, coins, paints etc.

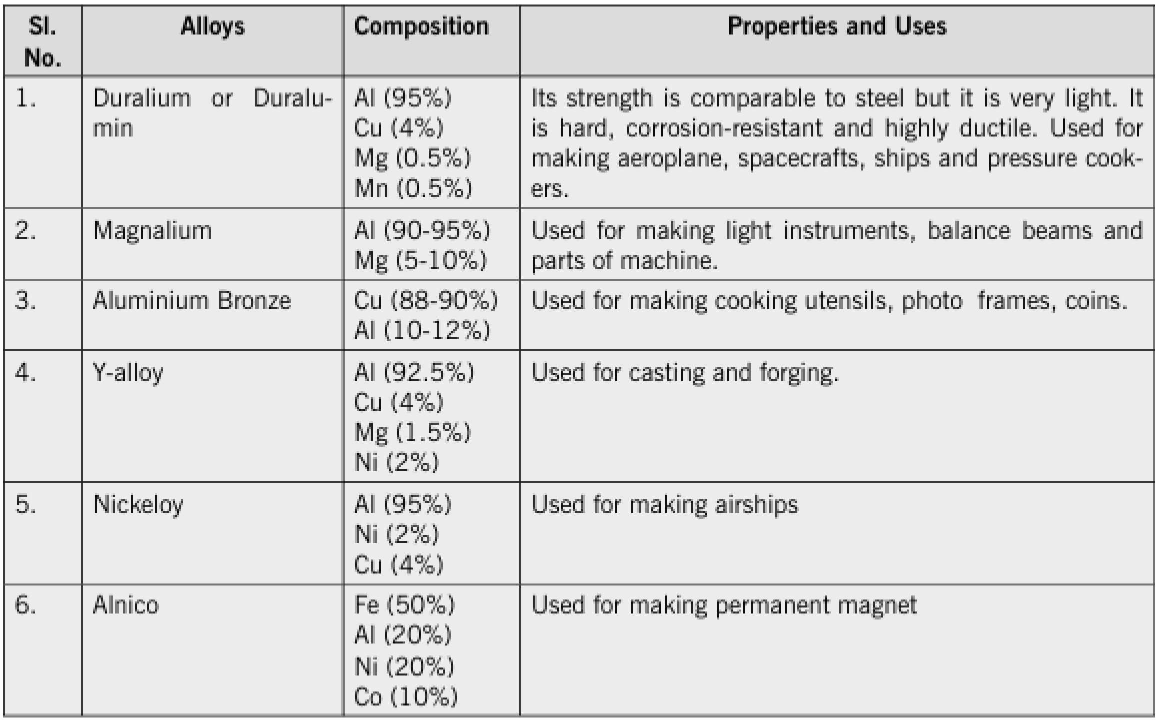
Composition, Properties and Uses of Some Alloys of Iron





Sl. No.	Alloys	Composition	Properties and Uses
1.	Stainless steel	Fe (74%) Cr (18%) Ni (8%)	Stainless steel is hard, tenacious and corrosion resistant. It is used for making cutlery, utensils, ornamental pieces, Instrument, apparatus, cycle and automobile parts
2.	Nickel steel	Fe (96-98%) Ni (2-4%)	Nickel steel is hard, elastic and corrosion resistant. Used for making electric wire cables, automobile and aeroplane parts, watches, armour plates, propeller shafts, etc.
3.	Alnico	Fe (60%) Al (12%) Ni (20-%) Co (8%)	It is highly magnetic. Used for making permanent magnets
4.	Chrome Vanadium Steel	Fe (98.75%) Cr (1%) V (0.15%)	In manufacturing springs, axles, shafts and motor car frames.
5.	Manganese steel	Fe (63-75) Mn (12-15%) C (0.8-1.2%)	Used for making rock cutting machine, burglar proof safes, rail road tracks etc.

Composition, Properties and Uses of Some Alloys of Aluminium



Sl. No.	Alloys	Composition	Properties and Uses
1.	Duralium or Duralumin	Al (95%) Cu (4%) Mg (0.5%) Mn (0.5%)	Its strength is comparable to steel but it is very light. It is hard, corrosion-resistant and highly ductile. Used for making aeroplane, spacecrafts, ships and pressure cookers.
2.	Magnalium	Al (90-95%) Mg (5-10%)	Used for making light instruments, balance beams and parts of machine.
3.	Aluminium Bronze	Cu (88-90%) Al (10-12%)	Used for making cooking utensils, photo frames, coins.
4.	Y-alloy	Al (92.5%) Cu (4%) Mg (1.5%) Ni (2%)	Used for casting and forging.
5.	Nickeloy	Al (95%) Ni (2%) Cu (4%)	Used for making airships
6.	Alnico	Fe (50%) Al (20%) Ni (20%) Co (10%)	Used for making permanent magnet

GENERAL CHEMICAL COMPOSITION, COMPOSITION BASED APPLICATIONS OF ENGINEERING MATERIALS

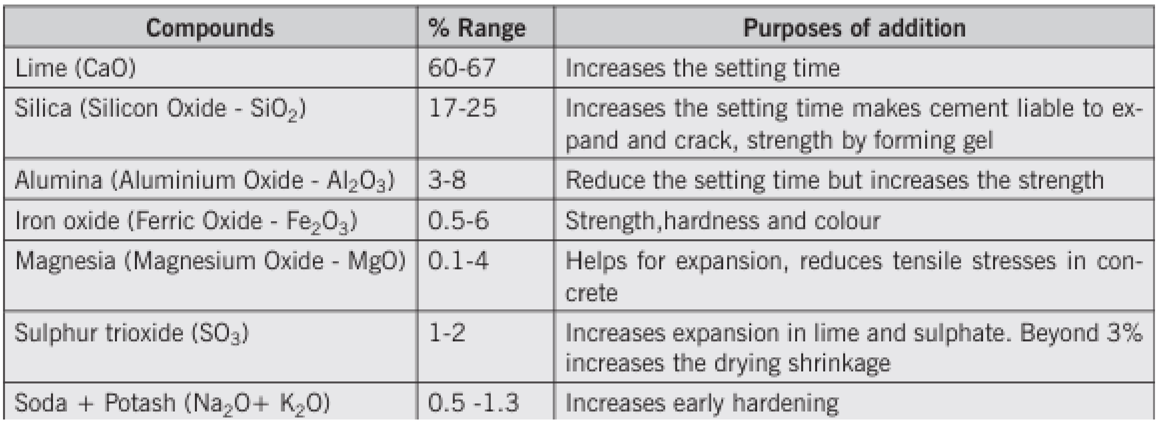
Materials used in manufacturing and construction of buildings, where particular requirements are needed, are called engineering materials. These include cement, glasses, refractories, and composite materials.

Cement

Cement may be broadly described as a finely ground mixture of various metals and non-metal oxides of different compositions with adhesive and cohesive properties. It helps in bonding of materials like stones, bricks, and other building blocks. The cement has the peculiar property of setting and hardening in contact with water hence is called hydraulic cement. Different types of cement are used for construction purposes. They differ in their composition and are manufactured for various uses. Some different types of cement are portland cement or ordinary portland cement (OPC), quick setting cement (QSC), low heat cement (LHC), sulphate-resisting cement (SRC), blast furnace slag cement (BFSC), white cement (WC), coloured cement (CC), pozzolanic cement (PzC), rapid hardening cement (RHC) ,air entraining cement (AEC), hydrophobic cement (HpC), expanding cement (EC), natural cement (NC), high alumina cement (HAC)

(A)Portland Cement

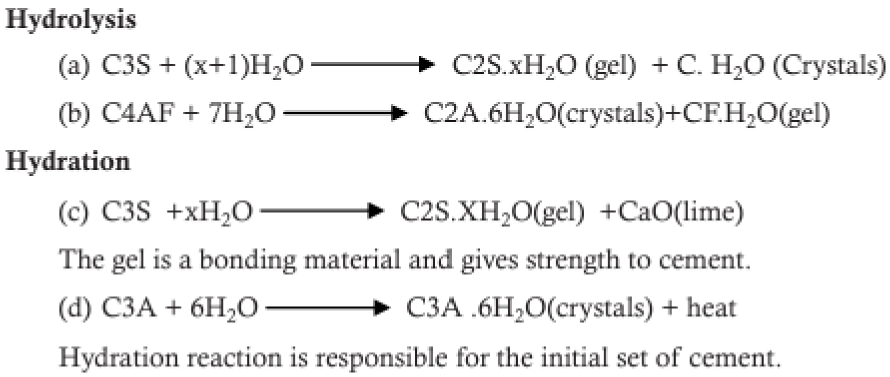
Portland cement is a mixture of metal and non-metal oxides along with gypsum. When cement is mixed with an adequate quantity of water, it forms a paste with the property of setting in a short time also becomes rigid and durable on standing. Cement manufactured from chalk and clay which hardens in contact with water and on hardening, resembles Portland stone in colour hence called Portland cement. Analysis of portland cement gives information about silica, alumina, iron, magnesia, etc., in various proportions, as shown in table 3.6. Although the analysis of cement gives an idea about the constituent present, it does not indicate how these constituents are combined in it. During the manufacturing of cement, the ingredients of raw materials merged to form the compound. It is clear from the table that lime is the main ingredient forming about 2/3 rd of the cement.



Compounds	% Range	Purposes of addition
Lime (CaO)	60-67	Increases the setting time
Silica (Silicon Oxide - SiO_2)	17-25	Increases the setting time makes cement liable to expand and crack, strength by forming gel
Alumina (Aluminium Oxide - Al_2O_3)	3-8	Reduce the setting time but increases the strength
Iron oxide (Ferric Oxide - Fe_2O_3)	0.5-6	Strength,hardness and colour
Magnesia (Magnesium Oxide - MgO)	0.1-4	Helps for expansion, reduces tensile stresses in concrete
Sulphur trioxide (SO_3)	1-2	Increases expansion in lime and sulphate. Beyond 3% increases the drying shrinkage
Soda + Potash (Na_2O+ K_2O)	0.5 -1.3	Increases early hardening

(B)Hardening of Portland Cement

When cement is mixed with water, a plastic mass called cement paste becomes rigid when a short time is known as the initial set or flash state. The setting and hardening of cement are mainly due to hydration and hydrolysis reactions taking place. Hydration is not the absorption of water or surface condensation but is taking up the water elements into the compound’s crystal structure. Anhydrous compounds react with water and undergo hydration resulting in the formation of insoluble gels and crystalline products. The process of setting and hardening of cement is believed to be partly chemical change and somewhat physical. Hydrolysis and hydration and of cement are mentioned below.



Hydrolysis

(a) $C3S + (x+1)H_2O \longrightarrow C2S.xH_2O$ (gel) + $C. H_2O$ (Crystals)

(b) $C4AF + 7H_2O \longrightarrow C2A.6H_2O$(crystals)+$CF.H_2O$(gel)

Hydration

(c) $C3S + xH_2O \longrightarrow C2S.XH_2O$(gel) +CaO(lime)

The gel is a bonding material and gives strength to cement.

(d) $C3A + 6H_2O \longrightarrow C3A .6H_2O$(crystals) + heat

Hydration reaction is responsible for the initial set of cement.

The hydrated tricalcium aluminate (C3A) generally exist as Cubic - C3A.6H2O, Hexagonal C3A.12H2O, Orthorhombic-C3A.18H2O. The setting and hardening of cement are due to interlocking crystals reinforced by the rigid gels. Finally, they bind the inert particles of aggregates like sand and crushed stones into a compact rock-like material. This solid mass on setting and hardening has excellent mechanical strength and forms a valuable building material.

(B)Applications of Portland Cement

Portland cement is used in wide variety of applications as follows

- Production of concrete and mortar for masonry work.
- Laying floors, roofs, constructing lintels, beams, weather sheds, stairs, pillars, etc.
- Construction of essential engineering structures such as bridges, culverts, dams, tunnels, storage reservoirs, lighthouses, docks etc.
- Construction of water tanks, tennis courts, septic tanks, lamp posts, roads, telephone cabins, etc.
- Making of joints for drains, pipes etc.

GlASS

Glass is an amorphous, hard, brittle transparent or translucent or super cooled liquid of infinite viscosity having no definite melting point. It is obtained by fusing a mixture of several metallic silicates or borates of sodium, potassium, calcium and lead.

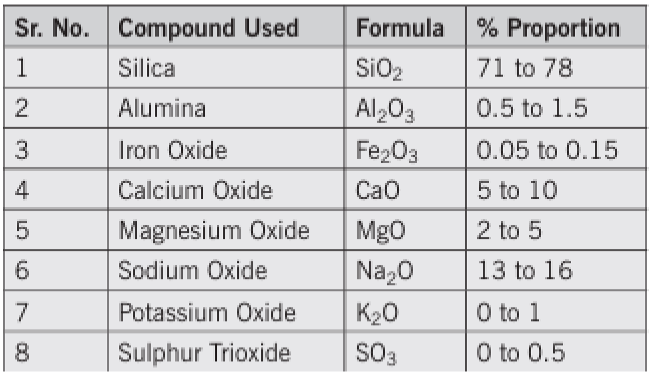
(A)Composition of Glass

Glass is made from the materials shown in below table

Properties of Glass

Hardness and Brittleness- It is a hard material as it has great impact resistance against applied load. However, at the same time, it is a brittle material as its breaks immediately when subjected to load. **Weather Resistance**- It is weather resistant as it can withstand the backlash of rain, sun and wind. It can absorb, reflect and

Fire Resistant- Glass protect heat from 2000C to 8000C.



Sr. No.	Compound Used	Formula	% Proportion
1	Silica	SiO_2	71 to 78
2	Alumina	Al_2O_3	0.5 to 1.5
3	Iron Oxide	Fe_2O_3	0.05 to 0.15
4	Calcium Oxide	CaO	5 to 10
5	Magnesium Oxide	MgO	2 to 5
6	Sodium Oxide	Na_2O	13 to 16
7	Potassium Oxide	K_2O	0 to 1
8	Sulphur Trioxide	SO_3	0 to 0.5

Refractory

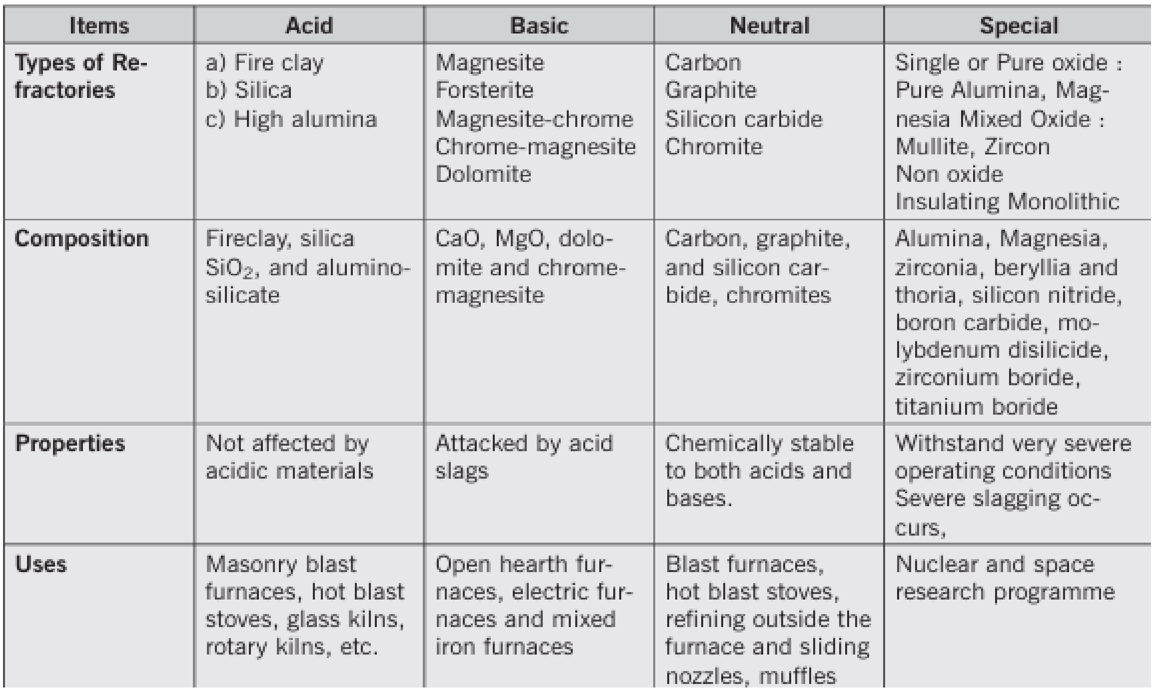
Refractory are inorganic, non-metallic materials which can withstand at high temperature without undergoing physicochemical changes i.e. deformation in shape,while remaining in contact with molten slag, metal and gases.

(A) **Composition of Refractories**

Refractories are classified based on their chemical composition and physical shape such as acid refractory, basic refractory, neutral refractory and special refractory.

(B) **Applications of Refractories**

Depending upon the constituents, refractories are used composition, properties and uses of refractories, as shown in below table.



Items	Acid	Basic	Neutral	Special
Types of Refractories	a) Fire clay b) Silica c) High alumina	Magnesite Forsterite Magnesite-chrome Chrome-magnesite Dolomite	Carbon Graphite Silicon carbide Chromite	Single or Pure oxide : Pure Alumina, Magnesia Mixed Oxide : Mullite, Zircon Non oxide Insulating Monolithic
Composition	Fireclay, silica SiO_2, and alumino-silicate	CaO, MgO, dolomite and chrome-magnesite	Carbon, graphite, and silicon carbide, chromites	Alumina, Magnesia, zirconia, beryllia and thoria, silicon nitride, boron carbide, molybdenum disilicide, zirconium boride, titanium boride
Properties	Not affected by acidic materials	Attacked by acid slags	Chemically stable to both acids and bases.	Withstand very severe operating conditions Severe slagging occurs,
Uses	Masonry blast furnaces, hot blast stoves, glass kilns, rotary kilns, etc.	Open hearth furnaces, electric furnaces and mixed iron furnaces	Blast furnaces, hot blast stoves, refining outside the furnace and sliding nozzles, muffles	Nuclear and space research programme

Composite Materials

A composite material is a mixture of two or more micro constituents, which combine to give properties superior to those of the individual constituents. Composite materials are excellent multiphase materials that find applications where very stringent and specific requirements are needed. Each class of basic engineering materials, e.g. metal, high polymers and ceramics, has its own outstanding and distinct and specific requirements are required.

(A)Constituents of Composites

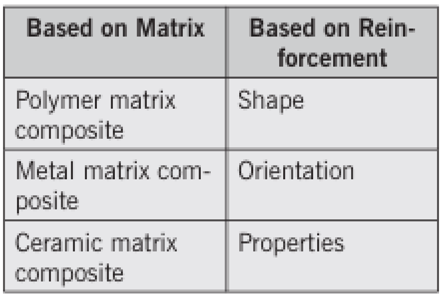
Reinforced Cement Concrete (RCC) structure contain concrete, metallic rods and mixture of different materials. Concrete is good in compression but poor in tension, while metallic rods are good in tension but poor in compression. Concrete acts as matrix and reinforcement is provided by metallic rods.

(B)Classification of Composite

Composites are broadly classified as Natural composite and Synthetic composite.

Natural composite: Wood is composite of cellulose fibers and lignin as cementing materials. Human or animal bone is a composite of soft and strong protein collagen and brittle and hard material apatite.

Synthetic Composite: Based on types of matrix and reinforcement, they can be further classified as shown in table.



Based on Matrix	Based on Reinforcement
Polymer matrix composite	Shape
Metal matrix composite	Orientation
Ceramic matrix composite	Properties

(C) **Applications of Composites**

- As composite materials are light in weight with high strength, they are used in the aerospace industry to prepare aircraft.
- These materials are also used in the preparation of automobile parts.
- Composite materials are used for medical assistance devices.
- They are used for the preparation of long tennis and hockey sticks.

Polymers

Polymer: The polymer is a combination of two Greek words obtained by combining poly means many and mer means unit. The polymer may have a molecular weight in the range of 1000-10000000 μ (mu). For understanding the process of polymerisation, some of the basic terms are given below.

Monomer: Single (identical or different) units that undergo repeated addition forming polymer.

e.g. (1) Vinyl chlrode in PVC (2) Hexamehyelenediamine and adipic acid in Nylon 6:6.

Homomers : Polymers that are derived from single monomers are known as homomers. e.g.PVC.

Co-polymer: Polymers that are derived from two different monomers are known as co polymers.

e.g. Nylon 6:6.

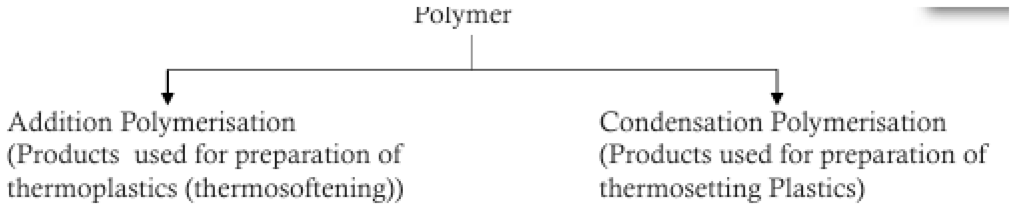
Polymerisation: It is the process of uniting or linking together monomer molecules to form a large polymer molecule under specific conditions of temperature, pressure, and catalyst known as polymerisation.

Degree of polymerisation: It is the ratio of the average molecular weight of polymer to the weight of monomer.

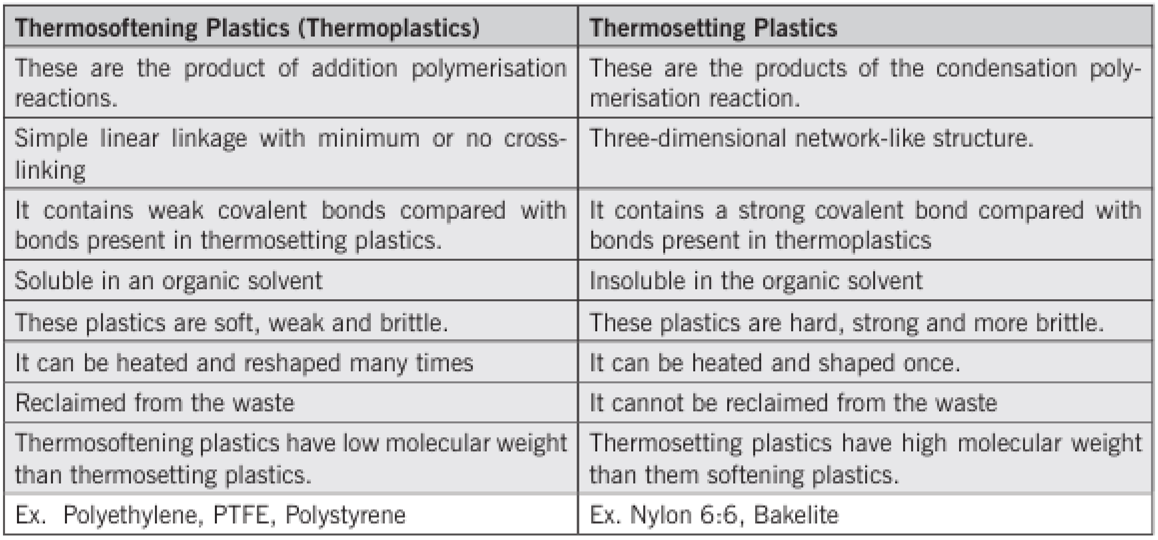
$$\textbf{Degree of polymerisation} = \frac{\text{Average weight of polymer}}{\text{Weight of monomer}}$$

Classification of Polymers

Polymers are divided as follows :



Difference between Thermoplastics and Thermosetting Plastics



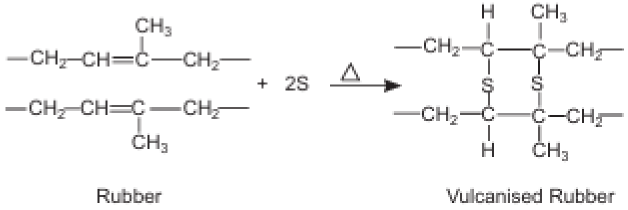
Thermosoftening Plastics (Thermoplastics)	Thermosetting Plastics
These are the product of addition polymerisation reactions.	These are the products of the condensation polymerisation reaction.
Simple linear linkage with minimum or no cross-linking	Three-dimensional network-like structure.
It contains weak covalent bonds compared with bonds present in thermosetting plastics.	It contains a strong covalent bond compared with bonds present in thermoplastics
Soluble in an organic solvent	Insoluble in the organic solvent
These plastics are soft, weak and brittle.	These plastics are hard, strong and more brittle.
It can be heated and reshaped many times	It can be heated and shaped once.
Reclaimed from the waste	It cannot be reclaimed from the waste
Thermosoftening plastics have low molecular weight than thermosetting plastics.	Thermosetting plastics have high molecular weight than them softening plastics.
Ex. Polyethylene, PTFE, Polystyrene	Ex. Nylon 6:6, Bakelite

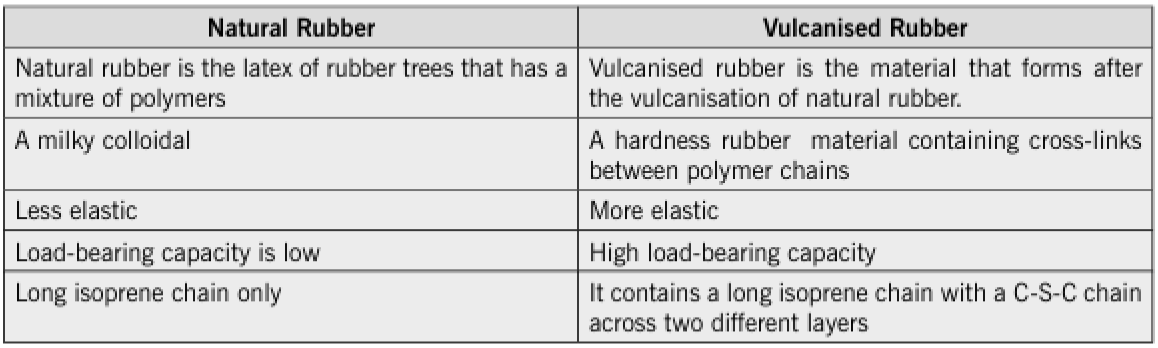
Rubber

It is a substance that can be extracted naturally from trees or synthesised in laboratories which can be stretched in length after applying the force and regain its original shape and dimensions after removal of the force. This property of rubber is called elasticity A rubber molecule is having a spring or coil-like nature. When force is applied, it gets converted into straight nature, and after removal of the force, it acquires its original spring-like nature.

Vulcanisation of Rubber

Natural rubber is soft in summer and hard in winter. Natural rubber absorbs water, soluble in organic solvents and undergoes oxidation. In the vulcanisation process, crude rubber is mixed with sulphur(S) or hydrogen sulphide H2S or benzoyl chloride or zinc oxide or stearic acid under high pressure at high temperatures up to 1500C. The added sulphur reacts chemically at the double bond in rubber molecules of different rubber springs and preventing intermolecular movement or sliding. It also protects rubber from future deformation, vulcanised rubber won't deform as easily as conventional, non-vulcanised rubber. Rubber also becomes harder when vulcanised, which subsequently increases its tensile strength and reduces the risk of physical damage.





Natural Rubber	Vulcanised Rubber
Natural rubber is the latex of rubber trees that has a mixture of polymers	Vulcanised rubber is the material that forms after the vulcanisation of natural rubber.
A milky colloidal	A hardness rubber material containing cross-links between polymer chains
Less elastic	More elastic
Load-bearing capacity is low	High load-bearing capacity
Long isoprene chain only	It contains a long isoprene chain with a C-S-C chain across two different layers

Applications of Rubber

- Due to elasticity, strength and toughness, it is used for making rubber bands, tubes for bicycles, automobiles.
- Due to excellent abrasion resistance, used for making conveyor belts, shock absorbers mounting heavy machinery.
- Due to electrical resistance, rubbers are used for the insulation of wires, cables, electrical power transmission, plugs, sockets, battery cases.
- Due to chemical resistance, it is also used to make lined metal tank vessels used in the chemical industry.
- Due to chemical resistance to petrol, mineral oil and some solvents, rubber hose pipes are used for their transmission.

CHAPTER-4

Chemistry of Fuels and Lubricants

FUELS AND COMBUSTION OF FUELS –

INTRODUCTION

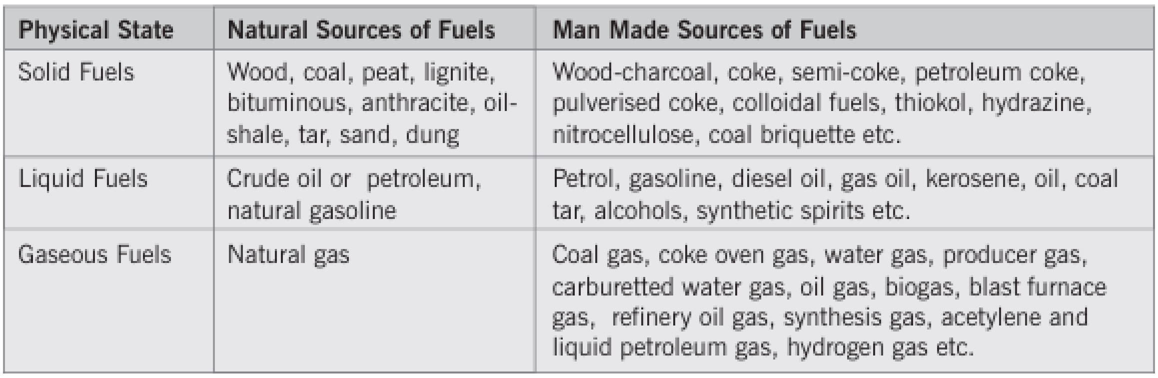
Industries require power for their routine operations. Heat energy is the primary source of power. These are combustible substances, & the heat produced by burning of fuels can be utilised economically, both for industrial and domestic purposes and to meet these expanding requirements, we should look for various kinds of fuels. The present unit is focused on the study of fuels and lubricants.

Fuels and its combustion

Fuel is a combustible substance, containing carbon as main constituent, which on proper burning gives large amount of heat and can be used economically for domestic and industrial purpose. E.g. Wood, coal, kerosene oil, gasoline, liquefied petroleum gas (LPG), petrol, diesel, hydrogen gas, ethanol etc. During the process of combustion of fuel, the atoms of carbon, hydrogen etc. combine with oxygen with the simultaneous liberation of heat at rapid rate. This energy is liberated due to the rearrangement of valence electrons in these atoms, resulting in the formation of new compounds.

Combustion of fuel : It is a temperature rising exothermic reaction between a fuel and oxygen.

classification of Fuels



Physical State	Natural Sources of Fuels	Man Made Sources of Fuels
Solid Fuels	Wood, coal, peat, lignite, bituminous, anthracite, oil-shale, tar, sand, dung	Wood-charcoal, coke, semi-coke, petroleum coke, pulverised coke, colloidal fuels, thiokol, hydrazine, nitrocellulose, coal briquette etc.
Liquid Fuels	Crude oil or petroleum, natural gasoline	Petrol, gasoline, diesel oil, gas oil, kerosene, oil, coal tar, alcohols, synthetic spirits etc.
Gaseous Fuels	Natural gas	Coal gas, coke oven gas, water gas, producer gas, carburetted water gas, oil gas, biogas, blast furnace gas, refinery oil gas, synthesis gas, acetylene and liquid petroleum gas, hydrogen gas etc.

calorific Values

The calorific value of fuel is its essential property, which supplies heat. The amount of heat supplied by a definite quantity of fuel varies from fuel to fuel. Calorific value helps to assess the efficiency of the fuel. The calorific value of fuel is the amount of heat obtained by complete combustion of unit mass of fuel.

(a)Higher calorific Value (HcV) or Gross calorific Value

Usually, all fuel contains some hydrogen and when the calorific value of hydrogen- containing fuel is determined experimentally, the hydrogen is converted into steam. If the products of combustion are condensed to room temperature, the latent heat of condensation of steam also get included in the measured heat, which is called higher or gross calorific value. So the gross or higher calorific value is HCV It is the total heat generated when a unit quantity of fuel is completely burnt and the products of combustion are cooled down to 150C.

(b)Lower calorific Value (LcV) or net calorific Value

In actual use of any fuel, the water vapour and moisture, etc., are not condensed and escape as such along- with hot combustion gases. Hence a lesser amount of heat is available. So net or lower calorific value is LCV It is the net heat produced when a unit quantity of fuel is completely burnt and the products of combustion are allowed to escape.

ANALYSIS OF COAL

Proximate analysis of coal (Solid Fuel)

The composition of coal varies with mines, hence, it is necessary to analyse the quality of coal, which helps commercial classification, price fixation, and industrial utilisation. Proximate analysis of coal involves the determination of moisture, volatile matter, ash and fixed carbon. The proximate analysis gives information about the practical utility of coal.

1. Determination of Moisture : Weigh about 1 g of finely powdered air-dried coal sample in a silica crucible with a lid. The crucible is placed inside the electric hot-air oven, maintained between 1050-1100 C. The crucible is allowed to remain in the oven for about an hour, and then taken out with the help of pair of tongs, cooled in a desiccator and weighed. By knowing the loss in weight of coal, the percentage of moisture can be calculated as.

   $$\% \text{ of Moisture} = \frac{\text{Loss in weight of coal}}{\text{Weight of coal taken}} \times 100$$

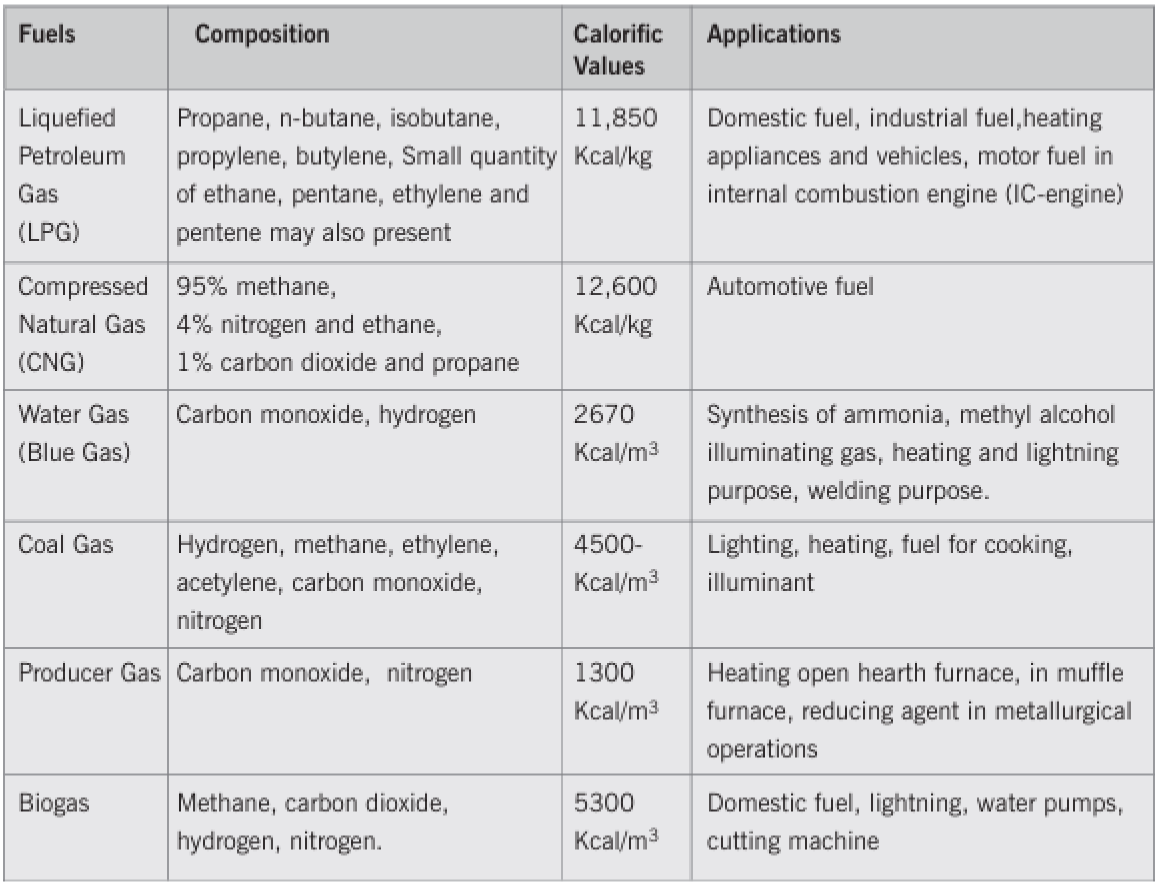
2. Determination of Volatile Matter: The dried sample of coal left in the crucible (in stage 1, i.e. determination of moisture) is then covered with a lid and placed in an electric muffle furnace maintained at 9250C. The heating is carried out for 7 minutes. The hot crucible is then taken out and cooled first in the air, then inside a desiccator and weighed again. Loss in weight is reported as volatile matter on percentage basis. By knowing the weight of volatile matter removed from coal, its percentage can be calculated as

   $$\% \text{ of Volatile Matter } = \frac{\text{Loss in weight due to removal of volatile matter}}{\text{Weight of coal taken}} \times 100$$

3. Determination of Ash : The residual coal in the crucible (in stage 2 i.e. determination of volatile matter) is then heated in an open crucible (without lid i.e. in the presence of oxygen of air) at 7500C for half hour in a muffle furnace. Here the coal is converted into ash by burning in the air. The crucible is taken out, cooled first in the air, then in desiccator and weighed. Heating, cooling and weighing is repeated till constant weight is obtained.

$$\% \text{ Ash} = \frac{\text{Weight of ash left}}{\text{Weight of dry coal taken}} \times 100$$

Chemical composition, calorific Values and applications of Fuels



Fuels	Composition	Calorific Values	Applications
Liquefied Petroleum Gas (LPG)	Propane, n-butane, isobutane, propylene, butylene, Small quantity of ethane, pentane, ethylene and pentene may also present	11,850 Kcal/kg	Domestic fuel, industrial fuel,heating appliances and vehicles, motor fuel in internal combustion engine (IC-engine)
Compressed Natural Gas (CNG)	95% methane, 4% nitrogen and ethane, 1% carbon dioxide and propane	12,600 Kcal/kg	Automotive fuel
Water Gas (Blue Gas)	Carbon monoxide, hydrogen	2670 Kcal/m^3	Synthesis of ammonia, methyl alcohol illuminating gas, heating and lightning purpose, welding purpose.
Coal Gas	Hydrogen, methane, ethylene, acetylene, carbon monoxide, nitrogen	4500-Kcal/m^3	Lighting, heating, fuel for cooking, illuminant
Producer Gas	Carbon monoxide, nitrogen	1300 Kcal/m^3	Heating open hearth furnace, in muffle furnace, reducing agent in metallurgical operations
Biogas	Methane, carbon dioxide, hydrogen, nitrogen.	5300 Kcal/m^3	Domestic fuel, lightning, water pumps, cutting machine

LUBRICATION

Introduction

In all types of machines, the surfaces of moving metals or sliding or rolling parts rub against each other. Due to the mutual rubbing of one part against another, a resistance is offered to their movement. Any substance introduced between the two moving/sliding surfaces with a view to reduce the friction or frictional resistance between them, is known as lubricant. This resistance is known as friction. It causes a lot of wear & tear of surfaces of moving parts. Due to friction, large amount of energy is liberated in the form of heat which reduces the efficiency of machine.The main purpose of a lubricant is to keep the moving/sliding surfaces apart, so that friction and consequent destruction of material is minimised The process of reducing friction between moving/sliding surfaces, by the introduction of lubricants in between them, is called lubrication. Either oil or grease is used for rolling bearings to prevent noise, wear, tear and heat from being generated from their rolling and sliding movements. In some special cases, solid lubricants are used. The amount and kinds of lubricants for rolling bearings are determined depending on operation speed, temperature, surrounding condition etc. Lubricants have to be periodically replaced or oiled.

FUNCTIONS OF LUBRICANTS

The main functions of lubricants are as follows

- prevent overheating of bearings and to prevent lubricants, deterioration by radiating the generated heat to outside.
- prevent foreign material penetration, rust, and corrosion.
- reduce wear and tear of the surfaces by avoiding direct metal to metal contact between the rubbing surfaces, i.e. by introducing lubricants between the two surfaces.
- reduce expansion of metal due to frictional heat and destruction of material. as coolant of metal due to heat transfer media.
- avoid unsmooth relative motion.
- reduce maintenance cost. reduce power loss in internal combustion engine.
- reduce the friction between two moving surface.
- rust and corrosion inhibitors.

application of Lubricants

Lubricants are used in

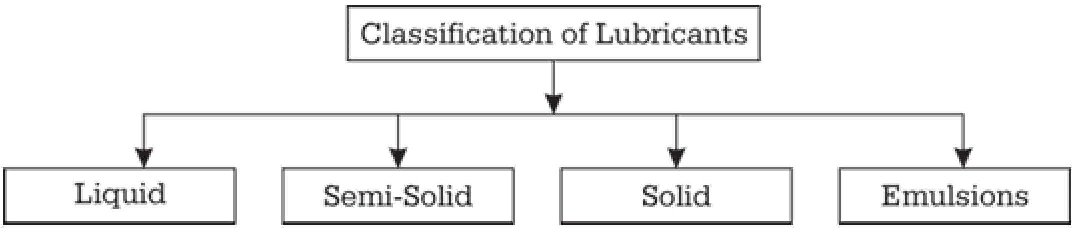
- the soap and paint industries.
- medicines.
- cutting fluid in cutting, grinding, drilling of metals.
- anti-wear, antioxidants, and antifoaming agents.

CHARACTERISTICS PROPERTIES OF GOOd LUBRICANTS

Good lubricants should have

- high boiling point
- low freezing point
- adequate viscosity for proper functioning
- high resistance to oxidation and heat
- non-corrosive properties
- stability to decomposition at the operating temperatures
- high viscosity index
- higher flash and fire points than the operating temperature of the machine
- high oiliness
- lower cloud and pour points than the operating temperature of the machine
- low volatility.
- deposit least amount of carbon during use
- higher aniline point.
- higher resistance towards oxidation.
- good detergent quality.

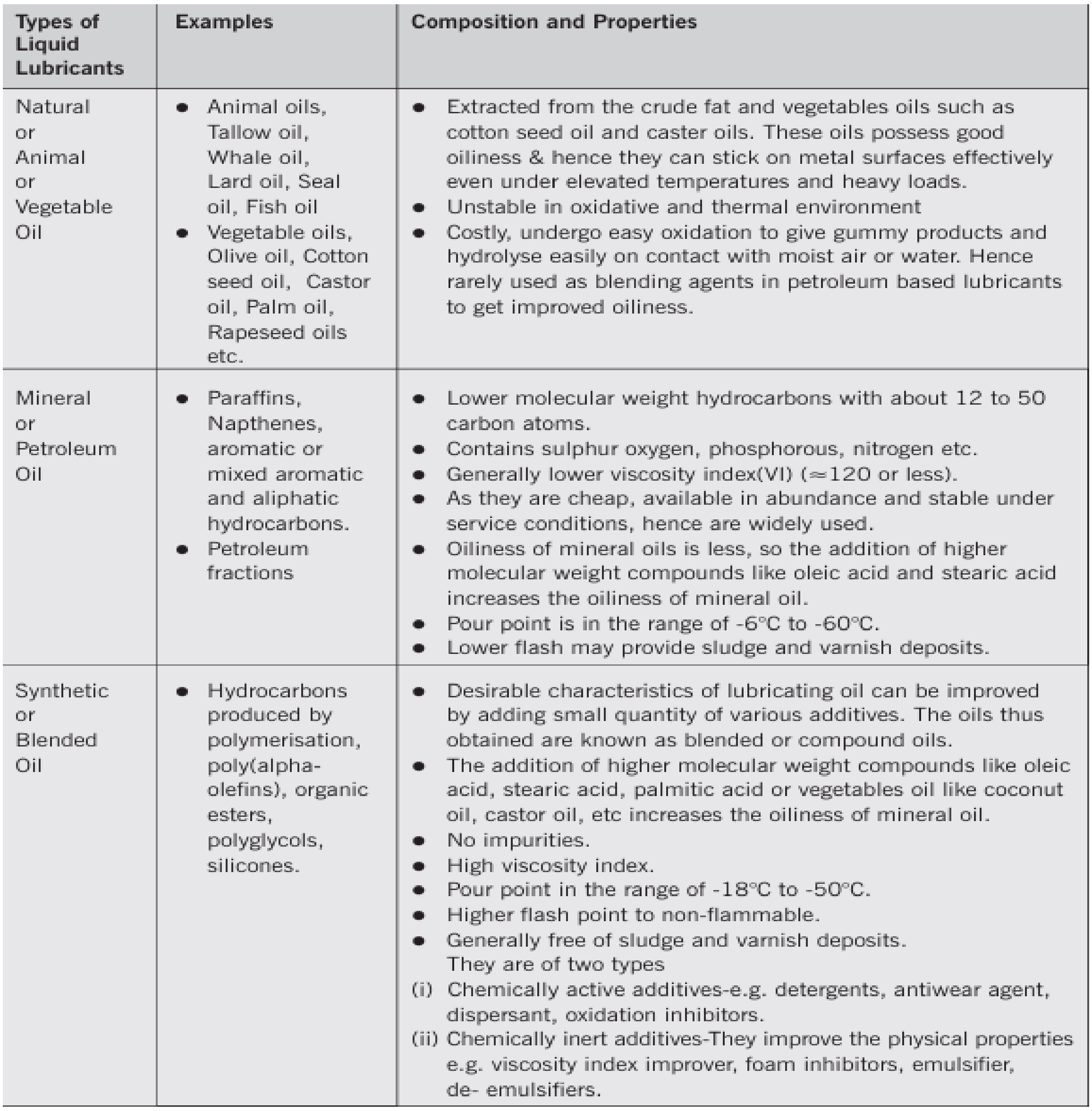
CLASSIFICATION BOF LUBRICANTS



Liquid Lubricants, classification and Properties

Liquid lubricants are classified into three category i.e.

(1) Natural or animal or Vegetable oil (2) Mineral or Petroleum oil (3) Synthetic or Blended oil.

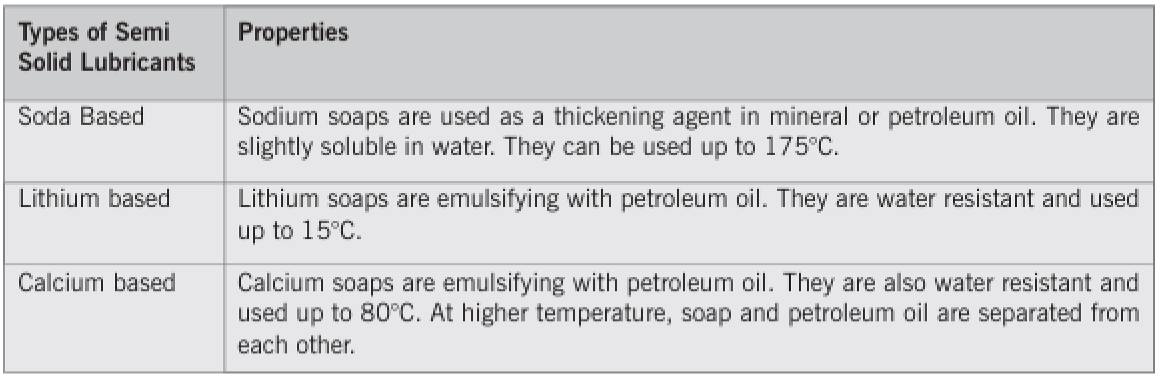


Types of Liquid Lubricants	Examples	Composition and Properties
Natural or Animal or Vegetable Oil	• Animal oils, Tallow oil, Whale oil, Lard oil, Seal oil, Fish oil • Vegetable oils, Olive oil, Cotton seed oil, Castor oil, Palm oil, Rapeseed oils etc.	• Extracted from the crude fat and vegetables oils such as cotton seed oil and caster oils. These oils possess good oiliness & hence they can stick on metal surfaces effectively even under elevated temperatures and heavy loads. • Unstable in oxidative and thermal environment • Costly, undergo easy oxidation to give gummy products and hydrolyse easily on contact with moist air or water. Hence rarely used as blending agents in petroleum based lubricants to get improved oiliness.
Mineral or Petroleum Oil	• Paraffins, Napthenes, aromatic or mixed aromatic and aliphatic hydrocarbons. • Petroleum fractions	• Lower molecular weight hydrocarbons with about 12 to 50 carbon atoms. • Contains sulphur oxygen, phosphorous, nitrogen etc. • Generally lower viscosity index(VI) (≈120 or less). • As they are cheap, available in abundance and stable under service conditions, hence are widely used. • Oiliness of mineral oils is less, so the addition of higher molecular weight compounds like oleic acid and stearic acid increases the oiliness of mineral oil. • Pour point is in the range of -6°C to -60°C. • Lower flash may provide sludge and varnish deposits.
Synthetic or Blended Oil	• Hydrocarbons produced by polymerisation, poly(alpha-olefins), organic esters, polyglycols, silicones.	• Desirable characteristics of lubricating oil can be improved by adding small quantity of various additives. The oils thus obtained are known as blended or compound oils. • The addition of higher molecular weight compounds like oleic acid, stearic acid, palmitic acid or vegetables oil like coconut oil, castor oil, etc increases the oiliness of mineral oil. • No impurities. • High viscosity index. • Pour point in the range of -18°C to -50°C. • Higher flash point to non-flammable. • Generally free of sludge and varnish deposits. They are of two types (i) Chemically active additives-e.g. detergents, antiwear agent, dispersant, oxidation inhibitors. (ii) Chemically inert additives-They improve the physical properties e.g. viscosity index improver, foam inhibitors, emulsifier, de- emulsifiers.

Semi-Solid Lubricants, classification and their Properties

Semi-solid lubricants are obtained by combining lubricating oil with thickening agents such as grease. Lubricating oils may be petroleum oil or synthetic hydrocarbon of low to high viscosity. The thickeners may be special soaps of Li, Na, Ca, Ba, Al etc. Non soap thickeners include carbon black, silica gel, polyureas and other synthetic polymers, clays, etc. Grease can support much heavier load at lower speed. Internal resistance of grease is much higher than that of lubricating oils, therefore it is better to use oil instead of grease. Grease cannot effectively dissipate heat from the bearings, so work at relatively lower temperature. The most important semi-solid lubricants are greases and vaselines.

(a) classification and Properties of Semi-Solid Lubricants



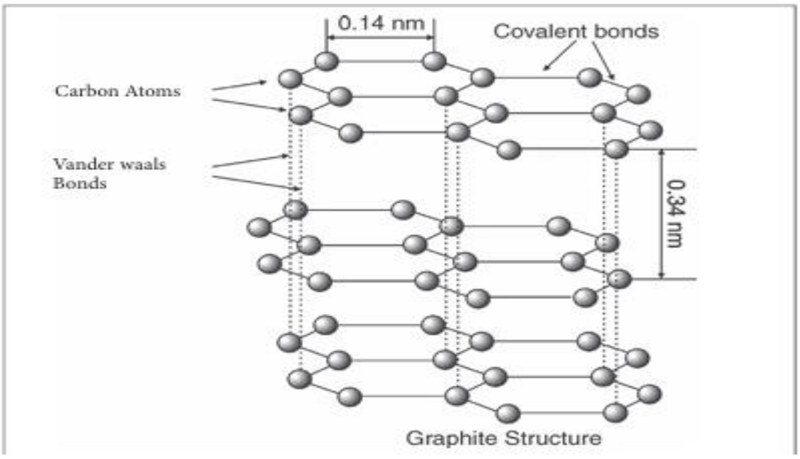
Types of Semi Solid Lubricants	Properties
Soda Based	Sodium soaps are used as a thickening agent in mineral or petroleum oil. They are slightly soluble in water. They can be used up to 175°C.
Lithium based	Lithium soaps are emulsifying with petroleum oil. They are water resistant and used up to 15°C.
Calcium based	Calcium soaps are emulsifying with petroleum oil. They are also water resistant and used up to 80°C. At higher temperature, soap and petroleum oil are separated from each other.

Solid Lubricants, classifications and Properties

A solid lubricant is a material that separates two moving surfaces under boundary conditions and decrease the amount of wear. Graphite, molybdenum disulphide (MoS2), boron nitride (BN)x are mostly used as a solid lubricant. They are used under high temperature and high pressure.

Graphite

It is most widely used as a solid lubricant. Graphite has layered structure. Layers are held together with the help of weak vander waals' forces which facilitate the easy sliding of one layer over the other layer. It is very soapy to touch, non-inflammable.It is used at higher temperature (around 450°C) condition.



(a)classification of Solid Lubricants

The various types of solid lubricants are as under :

(i)Structural Lubricants: Structural lubricants are those whose lubricating properties are due to their layer lattice structure. Example graphite, molybdenum disulphide, talc, mica, vermiculite etc. These function by cleaving within themselves and fixing themselves on or into bearing surface.

(ii) Mechanical Lubricants: They form a continuous adherent film on the rubbing surfaces and reduce the wear. Example Metals and plastics are characterised by their sacrificial wear.

(**iii)Soaps:** Soap function by in situ formation of compounds in the metal surface by the interaction of fatty acids and the metal.

(**iv) Chemically Active Lubricants**: These include extreme pressure additives and other chemicals which interact with the metal surface to produce a lubricating layer. Examples are phosphates, chlorides and oxidising agents.

(v) Refractories, Ceramics and Glass: These are used in defence programmes and rocketry. Combinations of refractory materials work satisfactorily as lubricants for short periods at high temperatures. Glass functions by softening at the operating temperature and assists in hydrodynamic lubrication.

Emulsions

In machining operations such as milling, threading, turning and boring, the tools gets heated to a very high temperature, particularly at the cutting edge. In a cutting process, the pressure at the knife-edge may sometimes reach as high as 100,000 psi and a lot of heat is generated, which lead to oxidation and rusting of the metal. To prevent overheating and injury to the tool, efficient cooling and lubrication have to be provided. This is usually done by employing emulsions of oil droplets in water, which are called cutting oils or cutting fluids or cutting emulsions. Oil has a poor specific heat but it has good lubricating properties, whereas water is a poor lubricant but it is an excellent cooling medium because of its high specific heat and high heat of vaporisation. Hence the combination of the two in the form of an emulsion can provide both lubrication and cooling effects. The corrosive action of water on the tools, the machines and the work piece are objectionable and is therefore checked by the addition of soaps or other inhibitive alkaline substances. A good cutting oil increases the accuracy of the cuts and reduces the cost of the work by-

(a) making possible to achieve higher cutting speeds

(b) prolonging the life of the cutting tool,

(c) reducing the power demand and the number of rejects.

The two types of emulsions are used for lubricating jobs, as below

Oil-in-Water Type Emulsions or Cutting Emulsions. These are prepared by mixing together an oil containing about 3 to 20% of a water soluble emulsifying agent (e.g., water soluble soap, alkyl or aryl sulfonate, alkyl sulphates) and suitable quantity of water. Chemicals like glycols, glycerols and triethanol amine are also added sometimes. Oil-in water type emulsions are used as coolant cum lubricant for cutting tools and in diesel motor pistons and large internal combustion engines.

Water-in-Oil Type Emulsions or Cooling Liquids. These are prepared by mixing together water and an oil containing 1 to 10% of water insoluble emulsifiers (e.g., alkaline earth metal soaps).

MECHANISM OF LUBREICATION

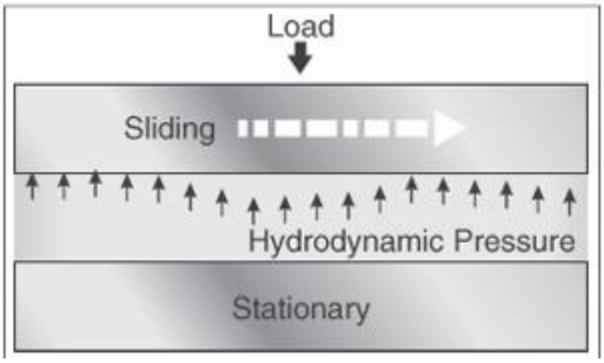
At microscopic or atomic level, all the surfaces in nature are rough. When two rough surfaces slide against each other, the rough surfaces come close to each other and interlock, adhere and generate friction. The purpose of lubrication is to separate the rubbing surfaces by a lubricant layer, which prevents or minimises direct contact of the bodies. By choosing appropriate lubricant, the friction and wear of the materials can be controlled. The phenomenon of lubrication can be explained with the help of the following mechanism

(a) Thick-Film lubrication or Fluid-Film or Hydrodynamic lubrication

(b) Thin Film lubrication or Boundary lubrication.

Thick Film or Fluid Film or Hydrodynamic Lubrication

Hydrodynamic is derived from the two words, hydro and dynamic. Hydro meaning liquid and dynamic meaning relative motion. In this mechanism, two moving and sliding surfaces are separated by thick film of lubricant fluid of about 1000A0, applied to prevent direct surface to surface contact and consequently reduce wear and tear of metals [Fig. 4.2]. The lubricant film covers/fills the irregularities of moving/sliding surfaces and forms a thick layer between them, so that there is no direct contact between the material surfaces. This consequently reduces the friction. The lubricant chosen should have the minimum viscosity (to reduce the internal resistance between the particles of the lubricant) and should remain in place and separate the surfaces. Hydrocarbon oils (mineral oils which are lower molecular weight hydrocarbons with about 12 to 50 carbon atoms) are considered to be satisfactory lubricants for thick-film lubrication. In order to maintain the viscosity of the oil in all seasons of year, ordinary hydrocarbon lubricants are blended with selected long chain polymers. In this case fluid is formed by mixing of hydrocarbon oils and anti-oxidants with long chain polymer so as to maintain viscosity. Fluid film lubrication is useful in delicate and light machines like watches, clocks, guns, scientific equipment.

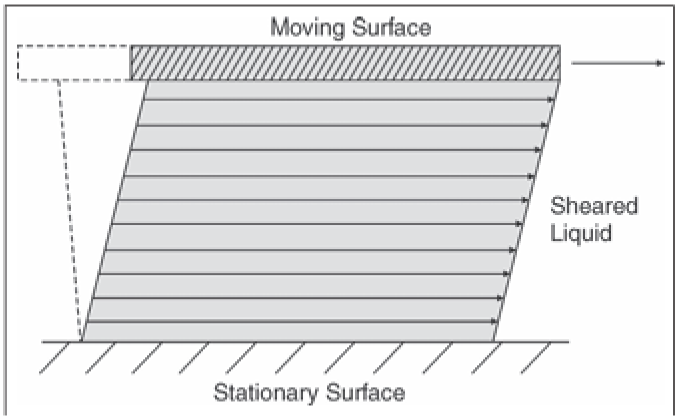


Thin Film or boundary Lubrication

Boundary lubrication is a condition in which the lubricant film becomes too thin to provide total separation. Thin film lubrication is operating at relatively low speed and heavy loading or pressure. This type of lubrication is preferred where a continuous film of lubricant cannot persist when lubricant with lower viscosity is used. In such cases, the clearance space between the moving/sliding surfaces is lubricated by such a material which can get adsorbed on both the metallic surfaces by either physical or chemical forces or weak vander waals forces. This adsorbed film helps to keep the metal surfaces away from each other at least up to the height of the peaks present on the surface. Vegetable and animal oils and their soaps can be used in this type of lubrication because they can get either physically adsorbed or chemically react to the metal surface to form a thin film of metallic soap which can act as lubricant. Although these oils have good oiliness, but they will break down at high temperatures. On the other hand, mineral oils are thermally stable and by the addition of vegetable or animal oils to mineral oils, their oiliness can also be brought up. Graphite and molybdenum disulphide are also suitable for thin film lubrication.

PHYSICAL PROPERTIES OF LUBRICANTS

Some of the physical properties of lubricants are viscosity, viscosity index, oiliness, flash and fire p Viscosity Viscosity is the important physical property of a lubricant and is a measure of the intermolecular interactions of the oil and hence of the resistance to flow. Viscosity is the property of a fluid that determines its own resistance to flow. This resistance to flow of liquid is known as viscosity. Or scientifically a force in dynes required to move 1cm square of the liquid over another surface with a velocity of 1 cm per sec. oint, cloud and pour point. We will learn these one by one. The unit of viscosity is poise. If the viscosity of the oil is too low, a liquid oil film cannot be maintained between two moving/sliding surfaces. On the other hand, if the viscosity of the oil is too high, excessive friction will result. It is an indicator of flow ability of lubricating oil. The lower the viscosity, greater will be the flow ability. If temperature increases, viscosity of the lubricating oil decreases. If the pressure increases, viscosity of lubricating oil increases. Thus a good lubricating oil is that whose viscosity does not change with temperature.



Higher viscosity lubricants are thick and don’t flow, while lower viscosity lubricants have a closer consistency to water and do flow. Example The ball sinks faster in the thinner, low viscosity oil while it sinks slower in the higher viscosity blends as oil heats up. We will be learning about the determination of viscosity of lubricating oil using Redwood viscometer in detail through practical performance in lab mentioned at the end of this unit.

Viscosity Index

The variation of viscosity of a liquid with temperature is called viscosity index. Viscosity of liquids decreases with increasing temperature and, consequently, the lubricating oil becomes thinner as the operating temperature increases. Hence, viscosity of good lubricating oil should not change much with change in temperature, so that it can be used continuously, under varying conditions of temperature. The rate at which the viscosity of lubricating oil changes with temperature is measured by an arbitrary scale, known as viscosity index (V. I). If the viscosity of lubricating oil falls rapidly as the temperature is raised, it has a low viscosity index. On the other hand, if the viscosity of lubricating oil is only slightly affected on raising the temperature, its viscosity index is high.

Oiliness

Oilness of a lubricant is the measure of its capacity to stick on to the surface of machine parts under condition of pressure or load. When a lubricating oil of poor oiliness is applied under high pressure, it gets squeezed out from the surface and lubrication stops. If the oil has good oiliness, it can remain in place and can give lubrication even under pressure. It is an important property of a lubricant under boundary or thin film lubrication conditions. Mineral oils have very poor oiliness whereas animal and vegetable oils have good oiliness. Hence, oiliness of mineral oils is generally improved by adding small quantities of high molecular weight fatty acids like oleic acid, stearic acid, chlorinated esters of these acids, etc. There is no perfect method for the determination of absolute oiliness of on oil,only relative oiliness is considered while selecting a lubricating oil for a particular job.

Flash Point and Fire Point Flash Point

The flash point of a volatile material is the lowest temperature at which vapours of the material will ignite for a moment when an ignition source brought near to it. The temperature at which a lubricant will ignite when heated and mixed with air, but a flame is not sustained.

Fire point

The fire point of a fuel is the lowest temperature at which the vapour of that fuel will continue to burn for at least 5 seconds when an ignition source brought near to it. In most cases, the fire points are 50°C to 40°C higher than the flash points. The flash and fire do not have any bearing with lubricating property of the oil, but these are important when oil is exposed to high temperature service. A good lubricant should have flash point at least above the temperature at which it is to be used. This safeguards against risk of fire, during the use of lubricant. We will be learning about the determination of flash point and fire point of lubricating oil using Able’s flash point apparatus in detail through practical performance in the lab mentioned at the end of this unit.

Cloud Point and Pour Point

Cloud Point : When the lubricant oil is cooled slowly, the temperature at which lubricating oil becomes cloudy in appearance is called cloud point.

Pour Point : The lowest temperature at which the lubricant oil become semi-solid and ceases to flow is called pour point.

CHEMICAL PROPERTIES OF LUBRICANTS

Some of the chemical properties of lubricants are coke number or carbon residue, total acid number (TAN) and saponification value.

coke number or carbon Residue

Carbon residue of lubricant is an indication of the coke-forming tendency of an oil or in other words it is the tendency to form carbon deposits under high-temperature conditions in an inert atmosphere.

Total acid number (TAN)

Total Acid Number (TAN) is a measure of acid concentration present in a lubricant. The acid concentration of a lubricant depends on the presence of additives, acidic contamination, and oxidation by-products. The depletion of an additive package may cause an initial decrease in TAN of fresh oil. TAN is a measurement of acidity that is determined by the amount of potassium hydroxide in milligrams that is needed to neutralise the acids in one gram of oil. It is an important quality measurement of crude oil. TAN value itself can not be used to predict the corrosive nature of an oil, as the test only measures the amount of acid in a sample, not the specific quantities of different acidic compounds in the sample. Two sample might have same TAN value but one have high level of corrosive acids while the other may have low level of the same. Corrosive acids, an increase in viscosity and the formation of gums and refines are the negative effects attributed to increased TAN value. TAN values specify the quantity of acidic compounds present in the petrochemical sample. TAN is an analytical test to determine the deterioration of lubricants. The more acidic is the lubricant, the more degradation occurs. As fluid degrades, the level of corrosive acid increases along with danger of component failure.

Importance of TAN

- It is an important quality measurement of crude oil and used as a guide in the quality control of lubricating oil formulations.
- It is also sometimes used as a measure of lubricant degradation in service. Testing for TAN is essential to maintain and protect equipment, preventing damage in advance.
- TAN testing is a measure of both the weak organic acids and strong inorganic acids present within oil.

Saponification Value(SV) or Saponification number (Sn)

Saponification is the process by which the fatty acids in the triglycerides or fat are hydrolysed by an alkali to give glycerol and potassium salts of fatty acids. A known quantity of fat or oil is refluxed with an excess amount of alcoholic KOH.

Saponification Value or Saponification number (SV or Sn)

Saponification value of lubricating oil is the number of milligrams of potassium hydroxide (KOH) required to saponify one gram of fatty oil. It is a measure of the average molecular weight (or chain length) of all the fatty acids present in the sample as triglycerides. Saponification number is an indication of the amount of fatty saponifiable material in a compounded oil. Caution must be used in interpreting test results if certain substances such as sulfur compounds or halogens are present in the oil, since these also react with KOH, thereby increasing the apparent saponification number.

Difference between acid value and Saponification value

The key difference between acid value and saponification value is that acid value gives the mass of potassium hydroxide that is required to neutralise one gram of a chemical substance whereas saponification value gives the mass of potassium hydroxide required to saponify one gram of fat. Saponification literally means “soap making”. The long chain fatty acids found in fats have low saponification value because they have a relatively fewer number of carboxylic functional groups per unit mass of the fat and therefore high molecular weight.

CHAPTER-5

Electrochemistry

ELECTROCHEMISTRY

INTROdUCTION

Electrochemistry is the branch of chemistry that deals with the inter conversion of electrical energy into chemical energy. Electric current flows from higher electric potential to lower electric potential. Electric current is the flow of electrons through a wire or solution. In solid state, the electrons are passed from one positively charged metallic atom to the next atom, while in a solution or a fused state, the electrons are carried by the ions present in the solution. Hence free electrons in metals are responsible for the conduction of electricity, while ions are responsible for the conduction of electricity in a fused state or solution.

Electronic concept of Oxidation-Reduction

We come across many processes like burning of fuels, rusting of metals, extraction of metal, and protection of metal, electroplating etc. All are based upon the redox reactions. These redox reactions are the basis of electrochemistry. Let us understand certain terms oxidation, reduction and redox reactions.

Oxidation : It is the process that involves the loss of electrons by an atom, ion or molecule. The loss of electrons involves an increase in positive charge or decrease in negative charge of species undergoing oxidation.

$2Na \longrightarrow 2Na^+ + 2e^-$ (1)

2,8,1 2,8

Sodium loses one electron, oxidation reaction takes place at sodium.

$Cu \longrightarrow Cu^{2+} + 2e^-$ (2)

In the case of copper metal, it loses two electrons, oxidation reaction takes place at copper.

$Pb^{2+} \longrightarrow Pb^{4+} + 2e^-$ (3)

(II) (IV)

Reduction: It is the process that involves the gain of an electron by atom ion or molecule. The gain of electrons results in the decrease of positive charge or increase of negative charge of the species.

$Cl_2 + 2e^- \longrightarrow 2Cl^-$ (4)

Chlorine Chloride

$O + 2e^- \longrightarrow O^{2-}$ (5)

Oxygen Oxygen ion

$Pb^{4+} + 2e^- \longrightarrow Pb^{2+}$ (6)

(IV) (II)

Redox or Net Reactions : These are interdependent reactions in which one species is reduced and other is oxidized. Consider the formation of sodium chloride. Reaction no (1) and (4) is called half cell reaction, showing the involvement of electrons. The Sum of the half-reactions gives the overall reactions called Redox or Net reaction.

$2Na \longrightarrow 2Na^+ + 2e^-$ Oxidation

$Cl_2 + 2e^- \longrightarrow 2Cl^-$ Reduction

$2Na + Cl_2 \longrightarrow 2Na^+ + 2Cl^- \longrightarrow 2NaCl$ Redox/ Net Reaction

ELECTROLYTES AND NON ELECTROLYTES

A solid substance that allows electric current to pass through it is called a conductor e.g. all metals, graphite. When a substance is present in solution, the conduction of electricity can be expressed in the following way.

Electrolytes

Electrolyte : Substance in fused state or in solution generates ions and allow electricity to pass through is known as electrolyte or electrolytic conductor Example Fused NaCl, NaCl solution, CuSO4 solution, HCl, H2SO4,KOH, NaOH, NH4OH, CH3COOH. NaCl salt in a fused state gives two ions, positively charged Na+ cation and negatively charged Cl– anion. When electricity is passed through a fused state,cations and anions present in the solution are responsible for the conduction of electricity. Hence fused NaCl is an electrolyte.

Electrolytes are of two types

(A) Strong Electrolyte B) Weak Electrolyte

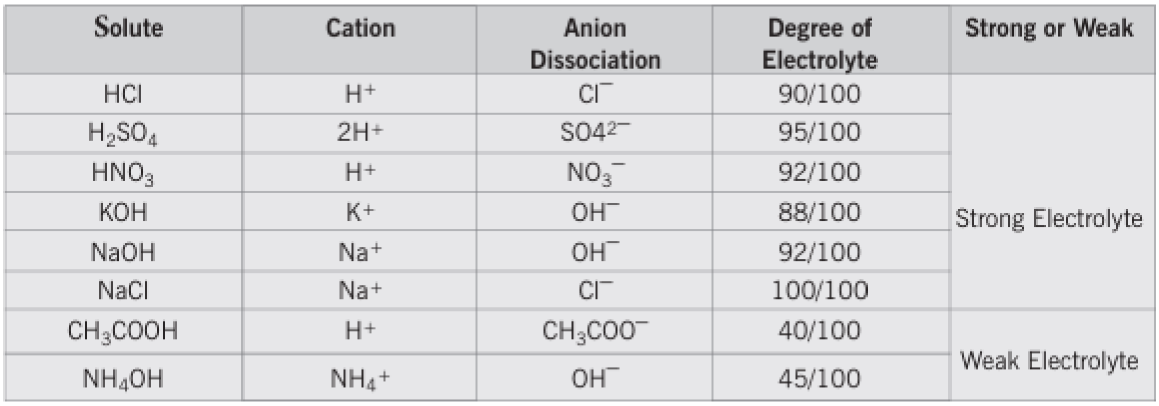
(**A) Strong Electrolyte** Solutes are strongly or highly dissociated or ionised into cation and anion, when dissolved in a solvent.Solutes like HCl, H2SO4, KOH, NaOH, and NaCl are highly separated into cations and anions, called strong electrolytes or strong solutes.

(i) Dissociation Separation of already existing ions is called dissociation. e.g. When ionic compounds like NaCl dissolve in the solvent, it gets separated into Na+ and Cl– and the process is called dissociation.

(ii) Ionisation Generation and separation of ions called ionisation. e.g. When a covalent compound like HCl dissolves in solvent, generates ions H+ and Cl– and the process is called ionisation.

(C) **Weak Electrolyte** Solutes are weakly or feebly ionised into cations and anions, when dissolved into a solvent. Solutes like NH4OH, CH3COOH are weakly dissociated hence called weak electrolytes Fraction of total number of solute molecules that are dissociated or ionised known as degree of dissociation as shown in table 5.1 (Values are only for concept clarity)

STRONG ELECTROLYTES AND WEAK ELECTROLYTES



Solute	Cation	Anion Dissociation	Degree of Electrolyte	Strong or Weak
HCl	H^+	Cl^-	90/100	Strong Electrolyte
H_2SO_4	$2H^+$	$SO4^{2-}$	95/100	
HNO_3	H^+	NO_3^-	92/100	
KOH	K^+	OH^-	88/100	
NaOH	Na^+	OH^-	92/100	
NaCl	Na^+	Cl^-	100/100	
CH_3COOH	H^+	CH_3COO^-	40/100	Weak Electrolyte
NH_4OH	NH_4^+	OH^-	45/100	

Non Electrolyte

Substances in fused state or in solution does not generates ions and does not allow electricity to pass through it is known as non-electrolyte. When electricity is passed through non-polar solutions like benzene or CCl4 or CS2 or sugar solution, methane, ethane, there is an absence of ions, hence these solutions are examples of non electrolytes.

Faraday's Law of Electrolysis

(A) Faraday's First law of Electrolysis

The weight of substance deposited or liberated at an electrode is directly proportional to the quantity of electricity passed through the electrolytes.

Mathematically,

$$W \propto Q$$
$$W \propto It \quad \therefore Q = I\,t$$
$$W = ZIt$$

Where W - Weight of substance deposited or liberated at an electrode(in grams)

Q - Quantity of electricity passed through electrolyte (in coulombs) Proportionality constant is electrochemical equivalent (E.C.E.)and represented by 'Z' (in g/coulomb)

I - Current in ampere

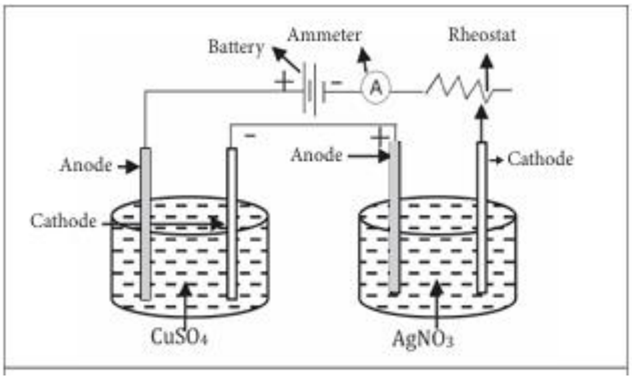
t - Time in seconds

When t=1 sec, and I= 1 ampere then $W = Z \times 1 \times 1$

$$\boxed{W = Z}$$

(B)Faraday's Second Law of Electrolysis

When the same quantity (amount) of electricity is passed through different electrolytes arranged in series, then the weights of the different substances deposited or liberated at the respective electrodes are directly proportional to their chemical equivalent (equivalent weights of the substances).



Let the same amount of electricity is passed through two cells connected in series and containing the solution of say copper sulphate & silver nitrate respectively, [Fig. 5.1], then according to Faraday's second law of electrolysis, weight of silver and copper deposited will be proportional to their equivalent weight also known as chemical equivalent.

$$\text{Weight of copper deposited}(W_1) \propto \text{Equivalent weight of copper } (E_1) \qquad (1)$$
$$\text{Weight of silver deposited}(W_2) \propto \text{Equivalent weight of silver}(E_2) \qquad (2)$$

Dividing equation 1 by 2 we get,

$$\frac{\text{Weight of copper deposited } (W_1)}{\text{Weight of silver deposited } (W_2)} = \frac{\text{Equivalent weight of copper}(E_1)}{\text{Equivalent weight of silver } (E_2)}$$

Thus, by knowing the three terms, we can calculate the fourth very easily.

$$\frac{W1}{W2} = \frac{E1}{E2}$$

Relation between Faraday and coulomb

From Faraday's second law,the quantity of electricity which liberates one gram equivalent of copper is 31.75 g of copper, or one gram equivalent of silver, i.e.107.88g of silver. Electrochemical equivalent of silver i.e. 0.001118 g. will be deposited by 1 coulomb of electricity For deposition of 0.001118 g of silver it requires 1 Coulomb of electricity hence for the deposition of 107.88 g silver, the quantity of electricity would be

$$\text{For silver} = \frac{107.88}{0.001118} = 96496 \text{ coulombs}$$

Electrochemical equivalent of copper i.e. 0.000329 g. will be deposited by 1 coulomb of electricity For deposition of 0.000329 g of copper it requires 1 Coulomb of electricity Hence to liberate 31.75 g equivalent of copper, the quantity of electricity would be

$$\text{For copper} = \frac{31.75}{0.000329} = 96504 \text{ coulombs}$$

Faraday experimentally determined that the average quantity of electricity required to liberate or deposit one gram equivalent of any substance from its solution hence this quantity is known as one Faraday (F).

1 Faraday = 96500 coulombs

Relation between Equivalent Weight (C.E.) and Electrochemical Equivalent (E.C.E)

96500 coulomb ≡ 1 gram equivalent of substance or Chemical equivalent of substance
1 Coulomb ≡ 1 gram electrochemical equivalent of substance (E.C.E. of substance)
∴ 1 g chemical equivalent of substance =96500 x electrochemical equivalent of substance
C. E . = 96500 x E. C. E.
Thus the equivalent weight of the substance is 96500 times the electrochemical equivalent

INDUSTRIAL APPLICATIONS OF ELECTROYSIS

In the electrolysis process,by using electrical energy,chemical changes are taking place. Hence in these cells, non-spontaneous chemical reactions are taking place. Such types of cells are also known as electrolytic cells.

The significant industrial applications of electrolysis are as follows

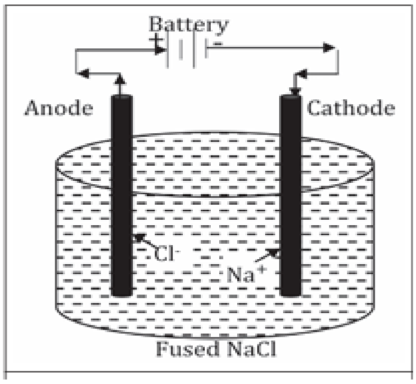
1. Electrometallurgy
2. Electroplating
3. Electrolytic Refining

1.Electrometallurgy

It is the extraction of metal from its ore by electrolysis .Some active metals like sodium, magnesium, potassium and calcium are extracted by the electrolysis of their corresponding fused metal salts, while other metals are obtained from its aqueous solution.

Extraction of Sodium from Fused Sodium chloride

In this electricity is passed through fused sodium chloride, using graphite electrode, In this process, graphite electrode does not actively participate in the chemical reactions taking place in the cell but only used for conduction of electrons (acting as inert electrode).Hence Sodium cations are migrated towards cathode and chloride anion migrated towards anode. These shows following chemical reactions.



Reaction at Anode

Chloride ions loses electrons and converted into chlorine atom in the primary stage (first step) Then two neutral chlorine combines with each other thus there is liberation of chlorine gas.

$Cl^- \longrightarrow Cl + e^-$ Oxidation Reaction (Primary stage)

$Cl^- \longrightarrow Cl + e^-$ Oxidation Reaction

$Cl + Cl \longrightarrow Cl_2\uparrow$ Secondary reaction

Reaction at cathode

$Na^+ + e^- \longrightarrow Na$ Reduction reaction

In this way more active metal can be easily extracted from the fused salt

Electroplating

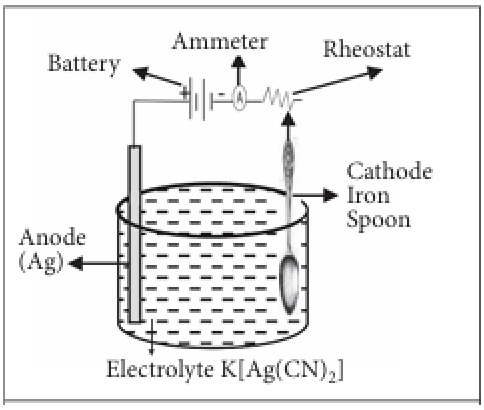
The process of metallic coating of more resistant metal (or superior metal or less active metals like silver gold, nickel, chromium,copper etc.) on the surface of the base metal (or inferior metal or more active metal) with the help of electric current is called electroplating. The purpose of electroplating is a) to protect the metal from corrosion, b) to decorate the ornaments and cutlery to increase the market price, and c) to repair the cracks and cavities developed in the damaged machinery part. In this process, the article to be electroplated is cleaned thoroughly by the hot solution of alkali or soap to remove the grease or grit or dirt. Then it is treated with dilute acid to remove the oxide layer or other impurities that stickup to the article. The treatment with dilute acids is called acid pickling. Further, it is washed with water and then carefully polished by polishing paper. The cleaned article is then suspended into the electrolytic cell and mount as a cathode. An anode is a pure metal plate or rod whose coating is desired on the article and suspended in the cell.

Reaction at Anode (Active Electrode)

$Ag \longrightarrow Ag^+ + 1e^-$ (Oxidation)
Silver anode

Reaction at Cathode (Inert Electrode)

$Ag^+ + e^- \longrightarrow Ag$ (Reduction)
Silver ion electrolyte → Silver metal



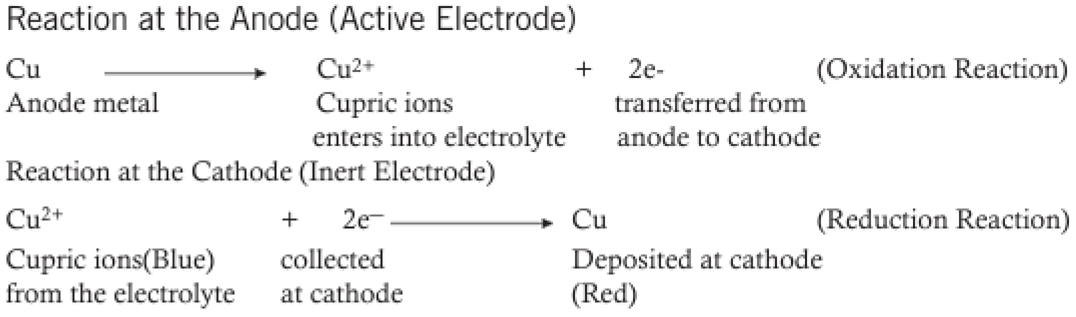
Instead of discharging of the anion with lower discharge potential, anode metal is immersed into its own salt solution, therefore having a tendency to dissolve into solution.

As silver metal rod/electrode has actively participated in the chemical reactions taking place in the solution, it is known as an active electrode. Size of anode –metal decreases. Electron loss by Ag metal is transferred from anode to cathode.

Electrolytic Refining

Electrolytic refining is the process of extraction of metals from the impure metallic rod. In this electrolysis process, pure metal is obtained from an impure metal rod by passing an electric current. Impure metal in the form of a thick rod or plate is made as an anode, and a thin sheet of the same metal is made the cathode.

The electrolyte is the solution of a salt of the metal to be refined. Using the required voltage, the anode of the impure metallic rod goes into solution in the form of metal ions. The electrolyte also breaks up into positively charged metal and negatively charged anions. Positively charged metal atoms get discharged at the cathode and deposited. Anode dissolves, and impurities get settled down below the anode, called anode mud. The cathode is refined metal, and it is washed, dried and put to use. The electrolysis process refines the metals like Zn, Cu, Sn, Ag, Al, etc. Impure copper obtained by the extraction process may contain about 3% to 5% impurities like S, As, Zn, Fe, Ni, Ag, Pt etc. Such impure copper is not fit to be used as an electrical conductor. The conductivity is appreciably lowered due to the traces of impurities present in it. Copper with 100% purity is required for electrical conductivity. Hence, crude copper is refined by the process called electro-refining. The electro-refining of copper is carried out in a large lead tank. Impure copper is cast into large plates suspended into the tank acts as anodes. Cathodes are thin plates of pure copper, and each is suspended between two plates of the anode. The electrolyte is a mixture of 15% copper sulphate solution, and 10% dilute sulphuric acid.



Reaction at the Anode (Active Electrode)

$Cu \longrightarrow$	Cu^{2+}	+ $2e-$	(Oxidation Reaction)
Anode metal	Cupric ions enters into electrolyte	transferred from anode to cathode	

Reaction at the Cathode (Inert Electrode)

Cu^{2+}	+ $2e^- \longrightarrow$	Cu	(Reduction Reaction)
Cupric ions(Blue) from the electrolyte	collected at cathode	Deposited at cathode (Red)	

APPLICATIONS OF REDOX REACTIONS IN ELECTROCHEMICAL CELL

Redox reactions are characterised by the actual transfer of electrons from one electrode to another electrode. The electrode at which metal or ions loses electrons has been oxidised, while the electrode at which metal or ions accepts electrons has been reduced. The chemicals present in the cell reacts spontaneously with each other and produces electrical energy. Such types of cell are known as an electrochemical cell. Oxidation and reduction reactions are taking place in the cell. Some of the examples of electrochemical cells are as follows

1. Primary cell

2. Secondary cell

1. Primary cell or dry cell: Primary cells are non-rechargeable and disposable. The electrochemical reactions in these batteries are non-reversible. The primary cell is also known as dry cell or pencil cell. It is not dry inside but it is pasty. Construction of primary cell and redox reactions taking place in the cells are given below.

construction : The dry cell consists of a graphite rod at the centre surrounded by a paste of manganese dioxide (MnO2), ground carbon and water. This whole arrangement is placed in muslin cloth, which allows some ions to pass through it. At the top of the graphite rod steel cap is present, which represent the positive terminal. Around the muslin cloth, an electrolyte is present in the paste form. Zinc chloride and ammonium chloride paste are placed around the muslin cloth and covered with a metallic zinc container that acts as an anode representing a negative terminal.

Reaction at Anode (At Zn Electrode)

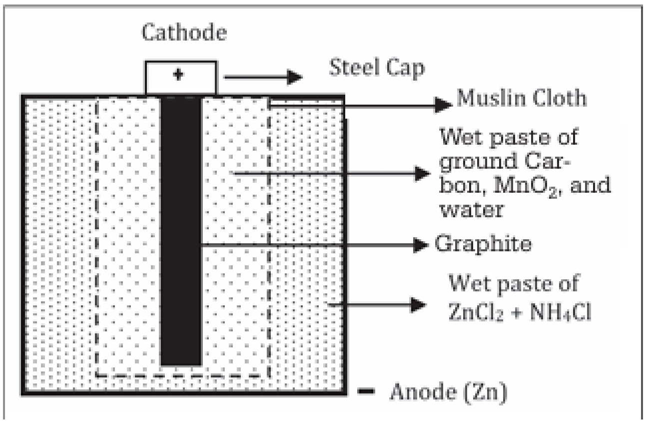
$Zn \longrightarrow Zn^{2+} + 2e^-$ (Oxidation Reaction)

$Zn + 4NH_3 \longrightarrow [Zn(NH_3)_4]^{2+}$

Reaction at Cathode

$2MnO_2 + 2NH_4^+ + 2e^- \longrightarrow Mn_2O_3 + 2NH_3 + 2H_2O$ (Reduction Reaction)

Oxidation and reduction reactions are taking place in the cell. As there is a transfer of electrons from anode to cathode,it represents the generation of electricity. Hence primary cell develops 1.5 V of electricity. As the cell generates electricity after the primary action of the chemicals hence known as the primary cell.



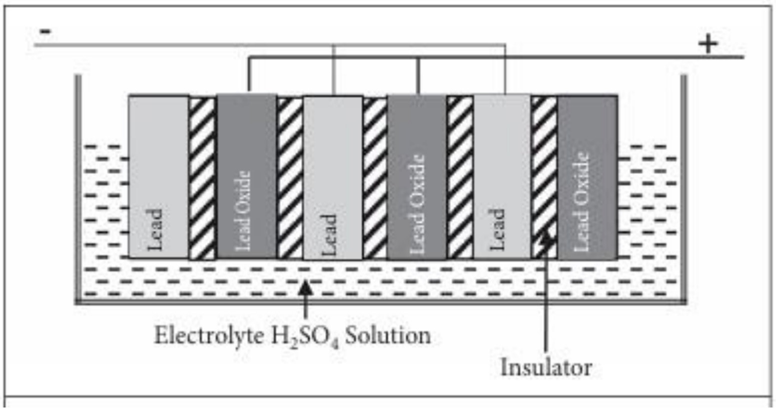
As chemicals are responsible for electricity generation, this cell is known as an electrochemical cell, and hence spontaneous chemical reactions are taking place. Zn is connected with zinc chloride dissolved in electrolyte paste, acting as an active electrode and graphite acting as an inert electrode. The dry cell does not have a long life, as acidic ammonium chloride corrodes the zinc container, even when it is not in use.

2. Secondary cell

Electricity cannot be generated on a large scale by primary cells because it needs the replacement of exhausted electrodes by the new one. There are reversible cells in which chemical energy is transformed into electrical energy, and reverse transformation of electrical energy into chemical energy can be carried out. The spent electrodes can be regenerated by passing an electric current through the cell in the reverse direction. Such cells which allow electric energy to be stored and expanded are called storage cells or secondary cells or accumulators. The process of storing electrical energy in an accumulator is called charging, while the reverse process of providing electrical energy is known as discharging. Several storage cells are connected in series to make up a storage battery. These storage cells are of different types like alkaline type, lead-acid storage cells, lithium-ion batteries.

(A)Lead- Acid Storage cell or Lead Accumulator

Storage cells are operated in both ways as a voltaic cell and as an electric cell. When operating as a voltaic cell,it supplies electrical energy and is finally discharged. Then it must be recharged. When being recharged, the cell operates as an electrolytic cell. The advantage of the storage cell is its ability to work both ways, to receive electrical energy and supply it. In a lead-acid storage cell, one of its electrodes is made of lead (Pb), and the other electrode is made of lead oxide (PbO2,also known as lead dioxide).



The number of lead plates (-ve values) are connected in parallel, and a number of lead oxide plates (+ve values) are also connected in parallel. Lead plates are placed in between the two lead oxide plates. These plates are separated from adjacent ones by insulators such as a strip of glass or rubber, or wood. These are then immersed in 20% dilute H2SO4 (with specific gravity 1.15 at 25°C).

Discharging

When the cell is operating as the voltaic cell, i.e. it supplies electrical energy, then it is said to be discharging. The lead electrode enters into solution with the formation of lead ions. Therefore, oxidation takes place at the lead electrode.

Reactions at Lead (Pb) Electrode

$Pb \longrightarrow Pb^{++} + 2e^-$ (Oxidation Reaction)

Active electrode Pb enters into the electrolyte in the form of ions by the loss of electrons. Formed lead ions react with sulphate ions to form lead sulphate precipitate.

$$Pb^{++} + SO_4^{--} \xrightarrow{\hspace{3em}} \underset{\text{Lead Sulphate Precipitate}}{PbSO_4\downarrow}$$

Reactions at Lead oxide (PbO2) Electrode

Lead oxide electrode also enters into the electrolyte in ionic form by accepting electrons from the external circuit. Hence reduction reaction occurs at the lead oxide electrode. Hence oxidation state of Pb changes from +4 to +2.

$$\underset{(4+)}{PbO_2} + 2e^- + 4H^+ \xrightarrow{\hspace{3em}} \underset{(2+)}{Pb^{++}} + 2H_2O \qquad \text{(Reduction Reaction)}$$

Lead ions formed react with sulphate ions from the electrolyte to form lead sulphate precipitate

$$Pb_2^+ + SO_4^{2-} \xrightarrow{\hspace{3em}} \underset{\text{Lead Sulphate}}{PbSO_4}$$

So redox reaction in lead storage cell is

$$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \xrightarrow{\hspace{3em}} 2PbSO_4 + 2H_2O + \text{Energy}$$

During discharging, lead and lead oxide electrodes slowly dissolve in the electrolyte, releasing Pb2+. The amount of lead sulphate precipitate and amount of water increases in the electrolytes during discharging while the percentage of H2SO4 decreases during discharging. A pair of Pb and PbO2 gives 2 Volt of electricity.

charging

When both electrodes are covered with lead sulphate, the cell stops functioning as a voltaic cell(electrochemical cell). Then it is necessary to recharge it. So the reactions taking place during discharging are reversed by passing external electromotive force (e.m.f.)greater than 2 volts from an external supply, hence the cell is called an electrolytic cell. Non-spontaneous chemical reactions will take place.

Reactions at Pb (Lead) Electrode

Pb^{2+} ions are present in the electrolyte as $PbSO_4$.

$$Pb^{2+} + 2e^- \xrightarrow{\hspace{3em}} \underset{\text{Regeneration of electrode}}{Pb} \qquad \text{(Reduction Reaction)}$$

Reactions at PbO2 (Lead oxide) Electrode

$$\underset{(2+)}{Pb^{2+}} + 2H_2O \xrightarrow{\hspace{3em}} \underset{(4+)}{PbO_2} + 2e^- + 4H^+ \qquad \text{(Oxidation Reaction)}$$

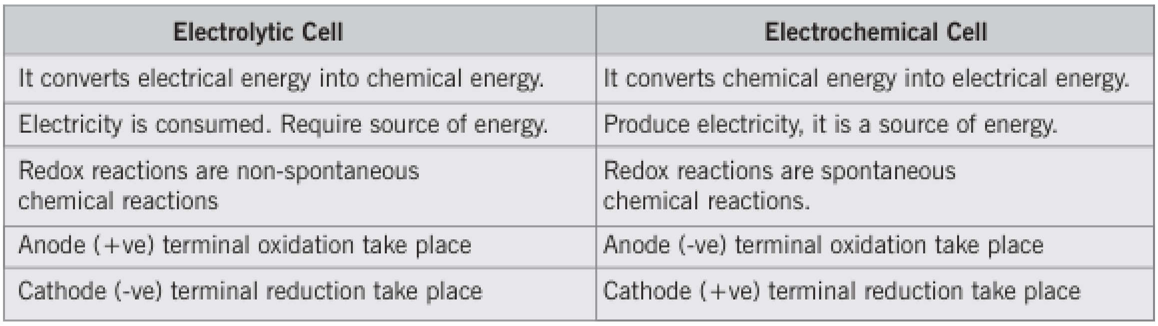
Regeneration of PbO_2 electrode

Hence net reaction during charging is

$$2PbSO_4 + 2H_2O + \text{Energy} \xrightarrow{\hspace{3em}} Pb + PbO_2 + 4H^+ + 2SO_4^{2-}$$

The redox cell reaction during discharging and charging can be shown as

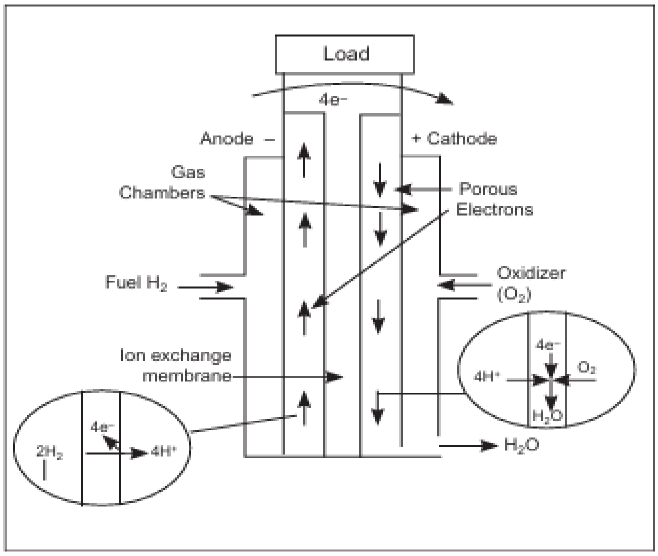
$$PbO_2 + Pb + 2H_2SO_4 \underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftharpoons}} 2PbSO_4 + 2H_2O$$



Electrolytic Cell	Electrochemical Cell
It converts electrical energy into chemical energy.	It converts chemical energy into electrical energy.
Electricity is consumed. Require source of energy.	Produce electricity, it is a source of energy.
Redox reactions are non-spontaneous chemical reactions	Redox reactions are spontaneous chemical reactions.
Anode (+ve) terminal oxidation take place	Anode (-ve) terminal oxidation take place
Cathode (-ve) terminal reduction take place	Cathode (+ve) terminal reduction take place

(B)Fuel cell

Fuel cell is an electrochemical cell that can convert the chemical energy contained in a readily available fuel oxidant system into electrical energy by an electrochemical process, in which fuel is oxidised at the anode. Similar to any other electrochemical cell, the fuel cell consists of an electrolyte and two electrodes. However, the fuel and the oxidising agent are continuously and separately supplied to the cell's electrodes at which they undergo reactions. These primary cells are capable of supplying current as long as the reactants are supplied. We know that voltaic cells involve an oxidation reduction reaction. Fuel cells work at high efficiency & the resulting emission levels are far below the permissible limits.



The basic arrangement in the fuel cell can be represented as follows

Fuel | Electrode | Electrolyte | Electrode |oxidant

The essential process in the fuel cell is

$$\text{Fuel + Oxygen} \longrightarrow \text{Oxidation products +Electricity}$$

One of the simplest and most successful fuel is the hydrogen-oxygen fuel cell. It consists essentially of an electrolytic solution such as 25%KOH solution and two inert porous electrodes. Hydrogen and oxygen gases are bubbled through the anode and cathode compartment, respectively, where the following reactions take place.

At Anode $2H_2 \longrightarrow 4H^+ + 4e^-$

$4H^+ + 4OH^- \longrightarrow 4H_2O$

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

Redox $2H_2 + O_2 \longrightarrow 2H_2O$

The standard emf of the cell, $E^\circ = E^\circ ox + E^\circ red = 0.83V + 0.40\ V = 1.23\ V$

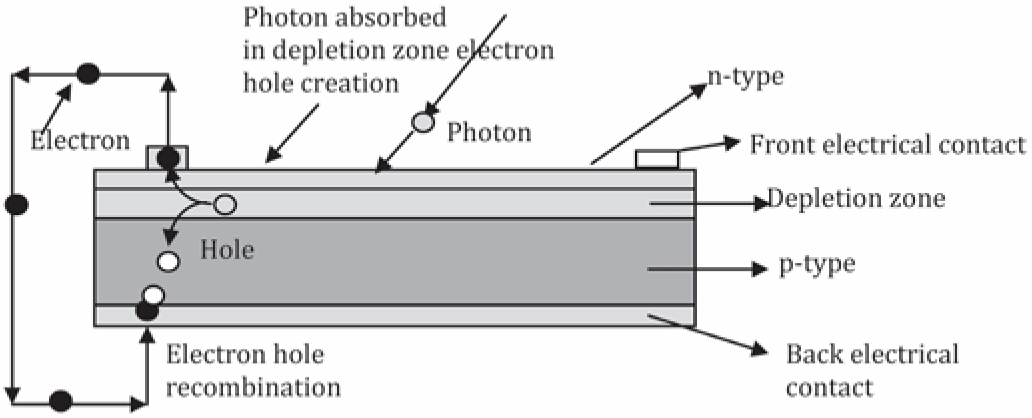
In actual practice, the emf of the cell is 0.8 to 1.0 V. Usually, large number of these cells are stacked together in series to make a battery called fuel cell battery or fuel battery. Hydrogen gas reacts with electrolytes and solid conducting structures to produce 2H+ ions. Two protons react with hydroxyl ions of the electrolyte to form water, which dilutes the KOH electrolyte. Two electrons are made available to the external circuit. The hydroxyl ions which are thus used up are replenished from the cathode reaction, in which O2 reacts with two water to produce 4OH– ions, taking up the four electrons from the outer circuit. These facts are reflected in the cell reactions given above.

Applications

Hydrogen oxygen fuel cells are used as an auxiliary energy source in space vehicles, submarines or other military vehicles. In H2-O2 fuel cells, the product water proved to be a valuable source of freshwater by the astronauts.

(**b)Solar cell**

Solar energy is obtained from the sun by conversion to electrical energy directly using a photovoltaic cell.[Fig 5.8] shows a photovoltaic cell in which a p-type semiconductor (such as Si doped with B) is in contact with an n-type semiconductor (such as Si doped with P). The sun light travels in packets of energy called quanta or photons. The electric current is generated inside the depletion zone of the p-n junction diode. When a photon of light is incident and absorbed by one of these atoms in the n-type silicon material, it will dislodge an electron, creating a free electron and a hole. The free electron and hole have sufficient energy to jump out of the depletion zone. The electron is attracted to the positive charge of the p-type material and travels through the external circuit, creating a flow of electric current. The hole created by the dislodged electron is attracted to the negative charge of n-type material and migrates to the back electrical contact. Electrons move from n-type material and enters into p-type material from back electrical contact where it combines with the hole which restores electrical neutrality.

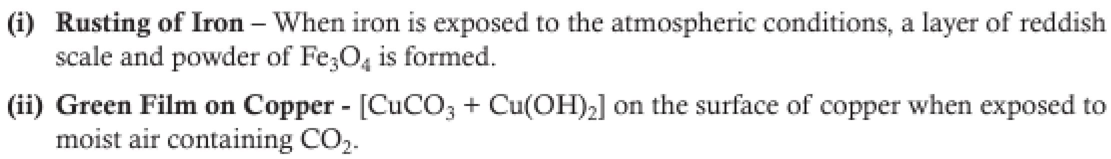


Generally a solar panel is made up of 32, 36, 48, 60, 72 and 96 photovoltaic cells. The solar array is a system made up of a group of solar panels connected together. A solar panel comprising 32 cells typically can produce 14.72 volts output (each cell producing about 0.46 volt of electricity).

corrosion – An Introduction

Surface of many metals is easily attacked when exposed to atmosphere. They react with air or water present in the environment and form undesirable compounds on their surfaces. These undesirable compounds are generally oxides. Thus the process of deterioration or destruction and consequent loss of a solid metallic material through an unwanted chemical, electrochemical and biochemical attack by its environment at its surface is called corrosion. Thus corrosion is a reverse process of extraction of metals. Metals and alloys are used as fabrication or construction materials in engineering. If the metals or alloy structures are not properly maintained, they deteriorate slowly by the action of atmospheric gases, moisture and other chemicals. This phenomenon of destruction of metals and alloys is known as corrosion.

Examples :



(i) **Rusting of Iron** – When iron is exposed to the atmospheric conditions, a layer of reddish scale and powder of Fe_3O_4 is formed.

(ii) **Green Film on Copper -** [$CuCO_3$ + $Cu(OH)_2$] on the surface of copper when exposed to moist air containing CO_2.

consequences of corrosion

The process of corrosion is slow and occurs only at surface of metals but the losses incurred are enormous. Destruction of machines, equipment, building materials and different types of metallic products, structures etc. Thus the losses incurred are very huge and it is estimated that the losses due to corrosion are approximately 2 to 2.5 billion dollars per annum all over the world. There are many social and economic consequences of corrosion. The economic and social consequences of corrosion include the following

- Due to formation of corrosion product over the machinery, the efficiency of the machine is reduced or reach to the stage of failure which leads to plant shut down.
- Corrosion releases the toxic products which affect the health of mankind.

Causes of corrosion

Metallic corrosion

The metals are extracted from their ores. During the extraction, ores are reduced to their metallic states by applying energy in the form of various processes. In the pure metallic state, the metals are unstable as they are considered in excited state (higher energy state). Therefore, as soon as the metals are extracted from their ores, the reverse process begins and form metallic compounds, which are thermodynamically stable (lower energy state). Hence, when metals are used in various forms, they are exposed to environment, these exposed metal surface begin to decay or convert into more stable compounds. This is the basic reason for metallic corrosion.

$$\text{Metal} \xrightleftharpoons[\text{Metallurgy-Reduction}]{\text{Corrosion-Oxidation}} \text{Metallic Compound + Energy}$$

Types of corrosion

The primary factors which initiate corrosion of metals are atmospheric air and water Based on the environment, corrosion is classified into

(i)Dry or Chemical Corrosion (ii) Wet or Electrochemical Corrosion

(i)Dry or chemical corrosion

It occurs in the absence of moisture or conducting electrolyte medium. This type of corrosion is due to the direct chemical attack of metal surfaces by the atmospheric gases such as oxygen, halogen, hydrogen sulphide, sulphur dioxide, nitrogen, anhydrous inorganic liquid etc. The chemical corrosion is defined as the direct chemical attack of metals by the atmospheric gases present in the environment. This causes to form an oxide layer over the surface of metals and alloys.

Example : (i) Silver materials undergo chemical corrosion by atmospheric H2S gas.

(ii) Iron metal undergo chemical corrosion by HCl gas.

Wet or Electrochemical corrosion

Electrochemical corrosion involves:

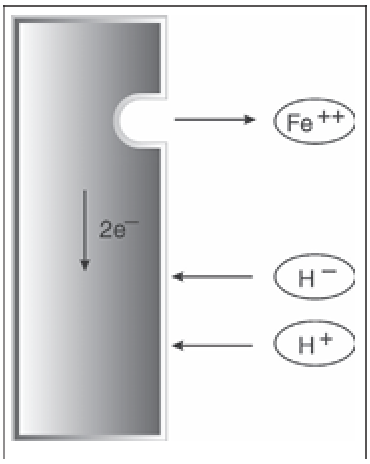
(i)The formation of anodic and cathodic areas or parts in contact with each other

(ii) Presence of a conducting medium

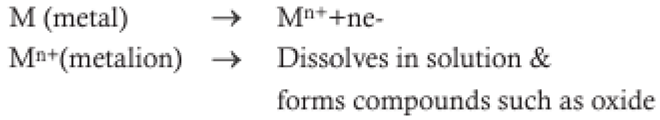
(iii)Corrosion of anodic areas only and

(iv)Formation of corrosion product somewhere between anodic and cathodic areas.

This involves flow of electron-current between the anodic and cathodic areas. At anodic area oxidation reaction takes place (liberation of free electron). Hence anodic metal is destroyed by either dissolving or assuming combined state (such as oxide, etc.). Hence corrosion always occurs at anodic areas.



Wet or Electrochemical Corrosion



M (metal) → M^{n+}+ne-

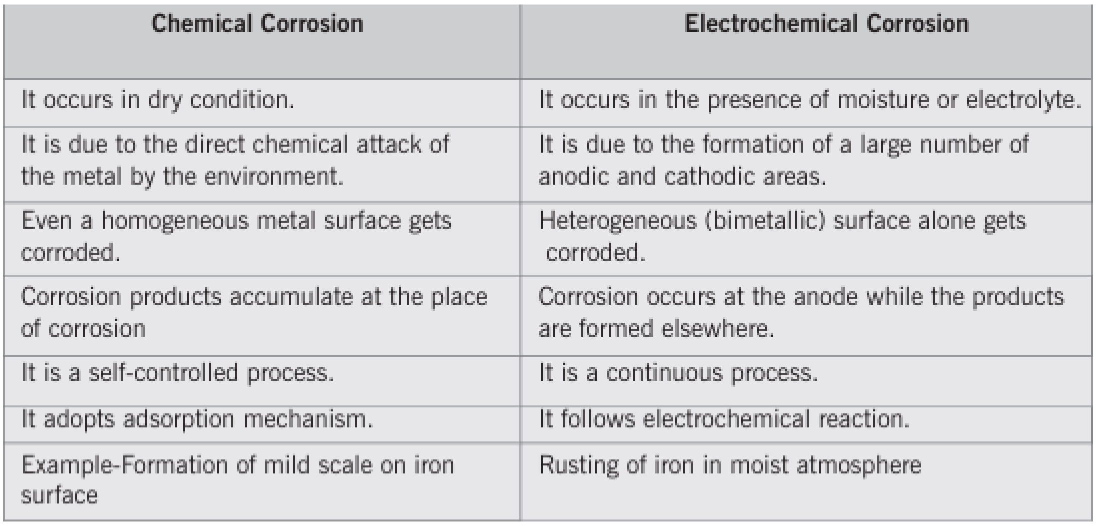
M^{n+}(metalion) → Dissolves in solution &
forms compounds such as oxide

At cathodic area, reduction reaction takes place (gain of electrons). Cathodic reactions do not affect the cathode, since most metals cannot be further reduced. So at cathodic part, dissolved constituents in the conducting medium accepts the electrons to form some ions like OH– and O2-.

Depending on the nature of the corrosive environment, cathodic reaction consumes electrons with either by (a) Evolution/Liberation of Hydrogen (b) Absorption of Oxygen

difference between dry/chemical and Electrochemical corrosion

The difference between chemical and electrochemical corrosion is mentioned in table:



Chemical Corrosion	Electrochemical Corrosion
It occurs in dry condition.	It occurs in the presence of moisture or electrolyte.
It is due to the direct chemical attack of the metal by the environment.	It is due to the formation of a large number of anodic and cathodic areas.
Even a homogeneous metal surface gets corroded.	Heterogeneous (bimetallic) surface alone gets corroded.
Corrosion products accumulate at the place of corrosion	Corrosion occurs at the anode while the products are formed elsewhere.
It is a self-controlled process.	It is a continuous process.
It adopts adsorption mechanism.	It follows electrochemical reaction.
Example-Formation of mild scale on iron surface	Rusting of iron in moist atmosphere

FACTORS INFLUENCING RATE OF CORROSION

Following factors influence the rate of corrosion

1.Nature of metals 2 .Nature of the corroding environment

1.Nature of metals

Many factors related to nature of metals contribute to the rate of corrosion. Some of them are

(i)Position in Galvanic Series The metal higher in series is more active and suffer corrosion. The rate and extent of corrosion is directly proportional to electrode potential difference between them.

(ii) Over Voltage The over voltage of a metal in a corrosive environment is inversely proportional to corrosion rate. For example, the over voltage of hydrogen is 0.7 v. When zinc metal is placed in 1 M sulphuric acid, the rate of corrosion is low. When we add small amount of copper sulphate to dilute sulphuric acid, the hydrogen over voltage is reduced to 0.33V. This results in the increased rate of corrosion of zinc metal.

(iii)Purity of Metal Impurity of a metal generally causes heterogeneity and form minute electrochemical cells and the anodic part gets corroded. For e.g. Zn metal containing impurity such as Pb or Fe undergoes corrosion. The rate and extent of corrosion increases with extent of impurities.

(iv)Nature of the Surface Film When metals are exposed to atmosphere, practically all metals get covered with a thin surface film of metal oxide. The ratio of the volume of metal oxide to the metal is known as specific volume ratio.

2. Nature of the corroding Environment

(i) Temperature With increase of temperature, the corrosion rate also increases because the reaction as well as diffusion rate of ions in the corrosion medium increases.

(ii) Humidity of Air The rate of corrosion will be more when the relative humidity of the environment is high. The moisture acts as a solvent for oxygen, carbon dioxide, sulphur dioxide etc. in the air to produce the electrolyte which is required for setting up a corrosion cell.

(iii) Effect of pH Rate of corrosion increases with decrease in pH. If $pH>10$, the rate of corrosion ceases due to the formation of protective coating of hydrous oxides on the metal. If pH is between 3-10, the rate of corrosion depends upon the presence of oxygen on the cathodic area for reduction. Higher the concentration of O_2, higher the rate of corrosion.

INTERNAL CORROSION PREVENTIVE MEASURES

Some of the internal corrosion preventive measures such as purification of metals, alloying and heat treatment are given below:

Purification of metal

The impurities present in metal decreases their corrosion resistance. Hence purification of metals may be carried out by appropriate methods of purification. Based on the properties and composition of different metals to be purified, different methods of purification of metals are employed as mentioned below :

- Distillation
- Liquation
- Poling
- Electrolysis
- Zone Refining
- Vapour Phase Refining
- Chromatographic Methods

Alloying

Use of corrosion resistant alloys should be used for prevention of corrosion. Several corrosion resistant alloys have been developed for specific purposes and environment

For example,

(a) Stainless steel containing chromium produce an exceptionally coherent oxide film which protects the steel from further attack.

(b) Cupro -nickel (70% Cu + 30% Ni) alloys are now used for condenser tubes and for bubble trays used in fractionating column in oil refineries.

(c) Highly stressed Nimonic alloys (Ni -Cr-Mo alloys) used in gas turbines are very resistant to hot gases.

Heat Treatment

Heat treatment is found to effect the corrosion rates. Both ferrous as well as non-ferrous metals undergo heat treatment before putting them to use. Heat treatments can be used to homogenize cast metal alloys to improve their hot workability, to soften metals prior to, and during hot and cold processing operations, or to alter their microstructure in such a way as to achieve the desired mechanical properties. Over the course of this process, the metal's properties such as electrical resistance, magnetism, hardness, toughness, ductility, brittleness and corrosion resistance will change. Thermal treatment of metallic alloys are also used to alter the surface chemistry of a material. This is achieved by diffusing carbon, nitrogen and other gaseous or solid material on to the surface of the component. These processes are used to give defined surface hardness and to improve wear, corrosion and fatigue resistance. Heat treatment is the process of heating and cooling metals, using different methods to obtain desired properties. The physical properties of steel change on heating and cooling. Following are some heat treatment methods by which steel of different properties are obtained.

(i)Annealing It is the process of heating steel to a bright red heat and then cooling it slowly. By this, steel becomes soft and pliable.

(ii) Hardening or Quenching It is the process of heating steel to bright redness and then cooling suddenly by putting in oil or water. By doing so, steel becomes very hard and brittle.

(iii)Tempering It is the process of heating the hardest steel to a temperature much below redness and cooling it slowly. The steel thus obtained is neither too hard nor too soft. It is also not so brittle.

EXTERNAL CORROSION PREVENTIVE MEASURES

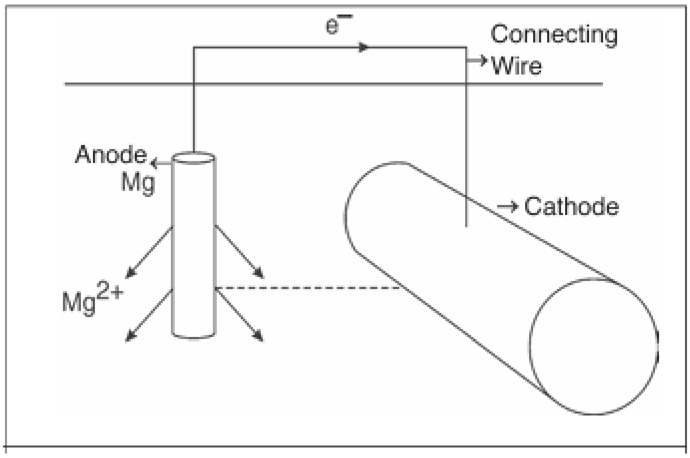
Corrosion process is very harmful and losses incurred are tremendous. Since the types of corrosion are numerous and the conditions under which corrosion occurs are so different, diverse methods are used to control corrosion. As the corrosion is a reaction between the metal or alloy and the environment, any method or corrosion control must be aimed at either modifying the alloy/metal or the environment.

Cathodic Protection

The metal to be protected is made as cathode thereby corrosion doesn't occur. There are two types of cathodic protection .

(A)Sacrificial Anodic Protection method

In this method the metallic structure to be protected is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal . The more active metal itself gets corroded slowly, while the parent structure which is cathodic is protected. The more active metal so employed is called "sacrificial anode". Whenever the corroded sacrificial anode is consumed completely, it is replaced by a fresh one. Metals commonly employed as sacrificial anodes are Mg, Zn, Al and their alloys.



Applications

Some of the applications are

(i)Protection of buried pipelines, underground cables from soil corrosion.

(ii)Protection from marine corrosion of cables, ship hulls, piers etc.

(iii)Insertion of magnesium sheets into the domestic water boilers to prevent the formation of rust.

(iv) Calcium metal is employed to minimize engine corrosion.

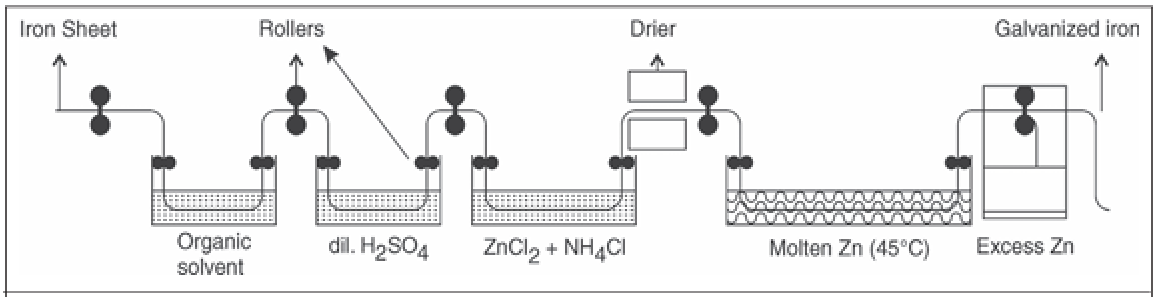
(B)Impressed current cathodic

Protection In this method an impressed current is applied in opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode. Usually the impressed current is derived from a direct current source (like battery or rectifier on AC line) with an inert anode, like graphite, high silica iron, scrap iron, stainless steel or platinum. Usually a sufficient DC is applied to an inert anode, buried in the soil (or immersed in the corroding medium) and connected to the metallic structure to be protected. The anode is composed of coke breeze or gypsum which enhance the electrical contact with the surrounding soil. Impressed current cathodic protection has been applied to open water box coolers, water tanks, buried oil or water pipes, condensers, transmission line towers, laid up ships etc. This protection technique is useful for large structures for long term operations.

Anodic Protection

Galvanizing is commonly used for anodic protection.

(A) galvanizing (Zinc coating on Iron) The process of coating a layer of zinc on iron by hot dipping is called as galvanizing.



Galvanizing process involves the following steps

(i)Iron sheet is passed through organic solvent to remove oil or grease present on it.

(ii)Then it is washed with dil. H_2SO_4 (pickling) to remove any rust (oxide layer) present on the surface

(iii)Then it is treated with a mixture of aqueous solution of zinc chloride ($ZnCl_2$) and ammonium chloride (NH_4Cl) which acts as flux and then dried.

(iv)The treated sheet is dried and dipped in molten zinc at 430-470°C.

(v) Excess zinc present on iron sheet is removed by rolling, wiping or passing blast of air.

Uses : Galvanization is used for roofing sheets, buckets, bolts, nuts, nails, pipes etc. Galvanizing and tinning by hot dipping is more economical than electroplating. Hot dipping is limited to the coating of low melting point metals like Zn, Sn and Al over iron. But galvanized utensils cannot be used for preparing and storing food stuffs, especially acidic ones since zinc gets dissolved in all acids forming highly toxic compounds.

Organic Inhibitors: Inhibitors are organic or inorganic substances which decrease the rate of corrosion. Usually the inhibitors are added in small quantities to the corrosive medium. Inhibitors are classified as follows **:**

- Anodic inhibitors (chemical passivators)
- Cathodic inhibitors (adsorption inhibitors)
- Vapour phase inhibitors (volatile corrosion inhibitors)

(A)Anodic Inhibitors: Inhibitors which retard the corrosion of metals by forming a sparingly soluble compound with a newly produced metal cations. This compound will then adsorb on the corroding metal surface forming a passive film or barrier.

Anodic inhibitors are used to repair

(i)the crack of the oxide film over the metal surface (ii) the pitting corrosion

(iii) the porous oxide film formed on the metal surface.

Examples: Chromate, phosphate, tungstate, nitrate, molybdate etc.

(B) cathodic Inhibitors :Depending on the nature of the cathodic reaction in an electrochemical corrosion, cathodic inhibitors are classified into

(a) In an acidic solution : The main cathodic reaction is the liberation of hydrogen gas, the corrosion can be controlled by slowing down the diffusion of H+ ions through the cathode. e.g., Amines, Mercaptans, Thiourea etc.

$$2\,H^+ + 2e^- \longrightarrow H_2$$

(b)In a neutral solution : In a neutral solution, the cathodic reaction is the adsorption of oxygen or formation of hydroxyl ions. The corrosion is therefore controlled either by eliminating oxygen from the corroding medium or by retarding its diffusion to the cathodic area. The dissolved oxygen can be eliminated by adding reducing agents like Na2SO3. The diffusion of oxygen can be controlled by adding inhibitors like Mg, Zn or Ni salts. e.g. Na2SO3, N2H4, Salts of Mg, Zn or Ni.

$$\tfrac{1}{2}\,O_2 + H_2O + 2e^- \longrightarrow 2OH^-$$

(c) vapour Phase Inhibitors

These are organic inhibitors which are readily vapourised and form a protective layer on the metal surface. These are conveniently used to prevent corrosion in closed spaces, storage containers, packing materials, sophisticated equipments etc. Examples are Dicyclohexyl ammonium nitrate, dicyclohexyl ammonium chromate, benzotriazole, phenylthiourea etc.