STUDY MATERIAL

ON

APPLIED CHEMISTRY

for

2ND SEMESTER OF ALL ENGINEERING BRANCHES

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Course Objectives:

There are numerous materials used in fabricating and manufacturing devices for the comfort of life. The selection, characterization, and suitability assessment of natural raw materials essentially requires principles and concepts of Applied Chemistry for technicians. On successful completion of this course content will enable technicians to understand, ascertain and analyze and the properties of natural raw materials required for producing economic and eco-friendly finished products.

- Solve various engineering problems applying the basic knowledge of atomic structure and chemical bonding.
- Use relevant water treatment methods to solve domestic and industrial problems.
- Solve the engineering problems using knowledge of engineering materials and properties.
- Use relevant fuel and lubricants for domestic and industrial applications
- Solve the engineering problems using the concept of Electrochemistry and corrosion.

Course Content:

UNIT	CHAPTER	PAGES
1	Atomic Structure	
	Chemical Bonding	
	Acid – Base Theory	
	Solutions	
2	Water	
3	Engineering Materials	
4	Chemistry of Fuels	
	Lubricants	
5	Electrochemistry	

Syllabus
Applied Chemistry (Th-5)

(2nd Semester Common)

Theory: 4 Periods per Week
Total Periods: 60 Periods
Examination: 3 Hours

I.A: 30 Marks
Term End Exam: 70 Marks
TOTAL MARKS: 100 Marks

Unit 1: Atomic Structure, Chemical Bonding and Solutions

Rutherford model of atom, Bohr's theory (expression of energy and radius to be omitted), and hydrogen spectrum explanation based on Bohr's model of atom, Heisenberg uncertainty principle, Quantum numbers – orbital concept. Shapes of s, p and d orbitals, Pauli's exclusion principle, Hund's rule of maximum multiplicity, Aufbau rule, electronic configuration.

Concept of chemical bonding – cause of chemical bonding, types of bonds: ionic bonding (NaCl example), covalent bond (H_2, F_2, HF hybridization in $BeCl_2$, BF_3 , CH_4 , NH_3 , H_2O), coordination bond in NH^{4+}, and anomalous properties of NH_3 , H_2O due to hydrogen bonding, and metallic bonding.

Solution – idea of solute, solvent and solution, methods to express the concentration of solution- molarity (M = mole per liter), ppm, mass percentage, volume percentage and mole fraction.

Unit 2: Water

Graphical presentation of water distribution on Earth (pie or bar diagram). Classification of soft and hard water based on soap test, salts causing water hardness, unit of hardness and simple numerical on water hardness.

Cause of poor lathering of soap in hard water, problems caused by the use of hard water in boiler (scale and sludge, foaming and priming, corrosion etc.), and quantitative measurement of water hardness by ETDA method, total dissolved solids (TDS) alkalinity estimation.

i) Water softening techniques – soda lime process, zeolite process and ion exchange process.
ii) Municipal water treatment (in brief only) – sedimentation, coagulation, filtration, sterilization.

Water for human consumption for drinking and cooking purposes from any water sources and enlist Indian standard specification of drinking water (collect data and understand standards).

Unit 3: Engineering Materials

Natural occurrence of metals – minerals, ores of iron, aluminium and copper, gangue (matrix), flux, slag, metallurgy – brief account of general principles of metallurgy.

Extraction of - iron from haematite ore using blast furnace, aluminium from bauxite along with reactions. Alloys – definition, purposes of alloying, ferrous alloys and non-ferrous with suitable examples, properties and applications.

General chemical composition, composition-based applications (elementary idea only details omitted):

Port land cement and hardening, Glasses Refractory and Composite materials.

Polymers – monomer, homo and co polymers, degree of polymerization, simple reactions involved in preparation and their application of thermoplastics and thermosetting plastics (using PVC, PS, PTFE, nylon – 6, nylon-6,6 and Bakelite), rubber and vulcanization of rubber.

Unit 4: Chemistry of Fuels and Lubricants

Definition of fuel and combustion of fuel, classification of fuels, calorific values (HCV and LCV), calculation of HCV and LCV using Dulong's formula.

Proximate analysis of coal solid fuel petrol and diesel - fuel rating (octane and cetane numbers),

Chemical composition, calorific values and applications of LPG, CNG, water gas, coal gas, producer gas and biogas.

Lubrication – function and characteristic properties of good lubricant, classification with examples, lubrication mechanism – hydrodynamic and boundary lubrication, physical proper ties (viscosity and viscosity index, oiliness, flash and fire point, could and pour point only) and chemical properties (coke number, total acid number saponification value) of lubricants.

Unit 5: Electro Chemistry

Electronic concept of oxidation, reduction and redox reactions.

Definition of terms: electrolytes, non-electrolytes with suitable examples, Faradays laws of electrolysis and simple numerical problems.

Industrial Application of Electrolysis –

- Electrometallurgy
- Electroplating
- Electrolytic refining.

Application of redox reactions in electrochemical cells –

- Primary cells – dry cell,
- Secondary cell - commercially used lead storage battery, fuel and Solar cells.

Introduction to Corrosion of metals –

- definition, types of corrosion (chemical and electrochemical), H_2 liberation and O_2 absorption mechanism of electrochemical corrosion, factors affecting rate of corrosion.

Internal corrosion preventive measures –

- Purification, alloying and heat treatment and

External corrosion preventive measures: a) metal (anodic, cathodic) coatings, b) organic inhibitors.

Suggested Sessional work:

- Unit 1: Atomic Structure, Chemical Bonding and Solutions

  Assignments: Writing electronic configuration of elements up to atomic number 30 (Z= 30). Numerical on molarity, ppm, mass percentage, volume percentage and mole fraction of given solution.

  Seminar: 1. Quantum numbers,

  2. Discuss the metallic properties such as malleability, ductility, hardness, high melting point, conductance of heat and electricity, magnetic properties of metals.

  Projects: Model of molecules $BeCl_2$, BF_3 , CH_4 , NH_3 , H_2O.

- **Unit 2: Water**

  Assignments: Simple problems on hardness calculation.

  Seminar: 1. Quality and quantity requirement of water in house and industry.

  2. Quality of control measures of effluents (BOD & COD).

Projects: Collect water samples from different water sources and measure of hardness of water.

- **Unit 3: Engineering Materials**

Assignments: Preparation of table showing different ores of iron, copper and aluminium metals along with their chemical compositions and classify into oxide sulphide halide ores.

Seminar: Discuss the chemical reactions taking place in blast furnace in extraction of Fe, Cu and Al metals.

Projects: Make table showing place of availability of different ores in India and show places on India map.

Unit 4: Chemistry of Fuels and Lubricants

Assignments: Calculation of HCV and LCV of fuel using fuel composition in Dulong’s formula. Seminar: Chemical structure of fuel components influence on fuel rating.

Projects: Mapping of energy recourses in India. Collection of data of various lubricants available in the market.

Unit 5: Electro Chemistry

Assignments: Simple problems on Faradays laws of electrolysis.

Seminar: 1. Corrosion rate and units.
2. Corrosion preventions.

Projects: Mapping of area in India prone to corrosion. Collection of data of various electrochemical cells batteries used in equipment and devices and available in market. Visit to sites such as Railway station to watch corrosion area in railways and research establishment in and around the institution.

Learning Outcomes:

At the end of the course student will be able to

1. Understand the classification and general properties of engineering materials such as metal, alloys, glasses, cement, refractory and composite materials using knowledge of chemical bonding.

2. Understand and assess the suitability of water source for domestic and industrial application, effluents and minimize water pollution.

3. Qualitatively analyze the engineering materials and understand their properties and applications.

4. Choose fuel and lubricants suitable for economical industrial processing to obtain eco-friendly finished products.

5. a) Ascertain construction, mechanism efficiency of electrochemical cells, solar cell fuel cells

b) Understand corrosion and develop economical prevention techniques.

Syllabus Coverage up to I.A UNIT-1 & 2

References/Suggested Learning Resources:

(a) Books:

1) Textbook of Chemistry for Class XI& XII (Part-I, Part-II); N.C.E.R.T., Delhi, 2017-18.

2) Agarwal, & Shikha, Engineering Chemistry, Cambridge University Press; New Delhi, 2015.

3) C.N. R. Rao, Understanding Chemistry, Universities Press (India) Pvt. Ltd., 2011.

4) Dara, S. S. &Dr.S.S.Umare, Engineering Chemistry, S.Chand. Publication, New Delhi, New Del hi, 2015. 5) Jain & Jain, Engineering Chemistry, Dhanpat Rai and Sons; New Delhi, 2015.

6) Dr. Vairam, S., Engineering Chemistry, Wiley India Pvt. Ltd., New Delhi, 2013.

7) Dr. G. H. Hugar & Prof A. N. Pathak, Applied Chemistry Laboratory Practices, Vol. I and Vol. II, NITTTR, Chandigarh, Publications, 2013-14.

8) Agnihotri, Rajesh, Chemistry for Engineers, Wiley India Pvt. Ltd., 2014.

(b) Open-source software and website address:

1 www.chemguide.co.uk/atommenu.html (Atomic structure and chemical bonding)

2 www.visionlearning.com (Atomic structure and chemical bonding)

3 www.chem1.com (Atomic structure and chemical bonding)

4 https://www.wastewaterelearning.com/elearning/ (Water Treatment)

5 www.capital-refractories.com (Metals, Alloys, Cement, and Refractory Materials)

6 www.em-ea.org/guide%20books/book-2/2.1%20fuels%20and%20combustion.pdf (Fuel and Combustion)

7 www.chemcollective.org (Metals, Alloys) 8 www.wqa.org(Water Treatment)

UNIT - 1
Module -1: ATOMIC STRUCTURE

Introduction:

According to *Dalton's Atomic theory* "Every matter is composed of very small particles called 'atoms' (Greek, a = cannot be; tom = cut) which cannot be further subdivided". But modern research revealed that an atom is divisible and has a rather complex structure containing a large number of sub-atomic particles such as electrons, protons, neutrons, mesons, leptons, antiprotons, neutrinos, antineutrinos, positrons, quarks etc.

Fundamental Particles:

The sub-atomic particles 'electrons, protons and neutrons' are called fundamental particles of all matters.

Electron: Electron is a fundamental sub-atomic particle having negligible mass of 9.11×10^{-31}kg and carrying a charge of -1.602×10^{-19} Coulomb.

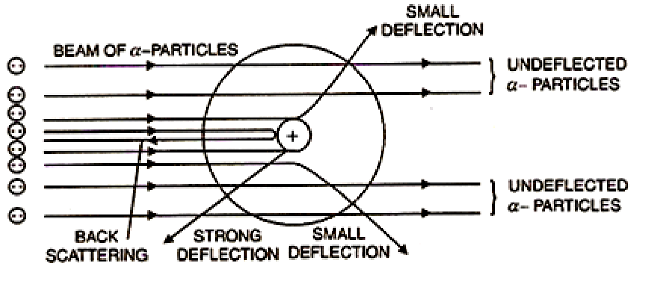
Proton: Proton is a fundamental sub-atomic particle having mass of 1.672×10^{-27}kg and carrying a charge of $+1.602 \times 10^{-19}$ Coulomb.

Neutron: Neutron is a fundamental sub-atomic particle having mass of 1.675×10^{-27} Kg and carrying no charge.

Fundamental Particle	Mass	Charge	Relative Charge
Electron	9.11×10^{-31}Kg	-1.602×10^{-19} Coulomb	– 1
Proton	1.672×10^{-27} Kg	$+1.602 \times 10^{-19}$ Coulomb	+1
Neutron	1.675×10^{-27} Kg	0	0

Rutherford's Gold-foil Experiment/Rutherford's α-scattering Experiment: (Discovery of Nucleus)

In 1911, **E. *Rutherford*** gave the first information about the almost-correct-picture of an atom. He bombarded a number of α-particles *(He^{2+} ions)* emitting from a radioactive material like Uranium on a very thin gold foil. A circular zinc sulphide **(ZnS)** screen was provided at the back side of the gold foil in order to register the impressions made by the α-particles.



(Rutherford's gold foil experiment)

Observations and Conclusions:

*From the **α-** scattering experiment, Rutherford observed that:*

1. Most of the α-particles went un-deflected, i.e. they passed straight through the gold foil without any deviation. This clearly indicates that most of the parts of an atom are empty.

2. A few α-particles were found to be deflected strongly from their normal paths. This indicates the presence of a heavy positively charged body inside the atom. This heavy positively charged body is called nucleus.
3. A very few (0.01%) α-particles were found to be retracted their original paths (deflected through almost 180^0). This indicates that the size of nucleus is very small. The size of atomic nuclei is of the order of 10^{-13} cm.

RUTHER FORD'S ATOMIC MODEL:

Based on the conclusions drawn from the α-scattering experiment, Rutherford proposed an atomic model, as follows:

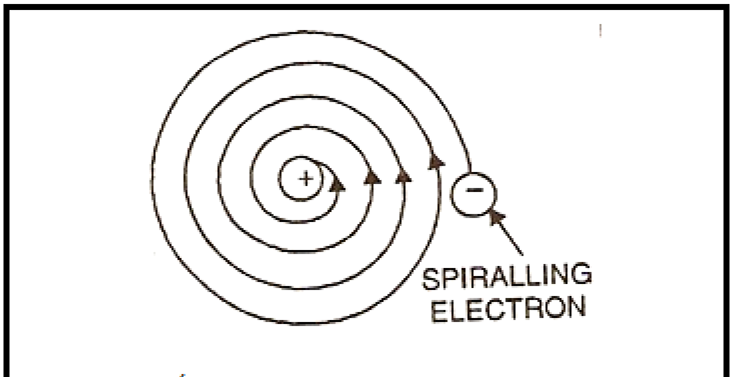
1. An atom consists of two parts; they are (i) Nucleus and (ii) extra nuclear part.
2. Every atom consists of a very small but heavy positively charged body, called nucleus.
3. The whole mass of an atom is concentrated at the nucleus.
3. Electrons revolve around the nucleus with tremendous speed, like planets revolve around the sun. Therefore, the electrons are also called as planetary electrons.
4. The electrostatic force of attraction (acting inward) between the nucleus and electrons is balanced by the centrifugal force (acting outward) arising due to the motion of electrons. That is why electrons do not fall into the nucleus.

DRAWBACKS OR FAILURES OF RUTHERFORD'S ATOMIC MODEL:

1. Stability of Atom:

The theory fails to explain the stability of atoms. According to the law of electrodynamics (by Clark Maxwell), whenever a charged particle revolves around another charged particle, the revolving charged particle emits (loses) energy continuously.

As the energy of the revolving electron decreases, it should be attracted towards the nucleus, and should follow a spiral path and ultimately fall into the nucleus. However, this never happens.



(Gradual decrease in the radius of orbit)

2. The model is silent about the definite energy and velocity possessed by the revolving electrons.

3. The theory fails to explain ***atomic spectra****.*

4. It fails to explain the cause of chemical combinations.

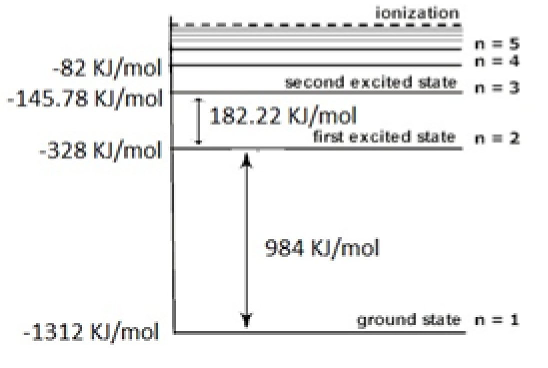
BOHR’S ATOMIC MODEL (THEORY)

An almost correct picture of atomic model was provided by a **Dutch physicist *Niels Bohr* in 1913**. The Bohr's Atomic model is based on ‘**Planck's Quantum Theory’** and **‘quantization of energy’**.

Postulates of Bohr’s atomic model:

1. Every atom consists of a heavy positively charged body at the center called ‘nucleus’ and electrons revolve around the nucleus in certain permitted definite circular paths called ‘shells’, ‘orbits’ or ‘stationary states’.

2. The stationary states or shells are designated as **K, L, M, N, O......etc.** for 1st, 2nd, 3rd, 4th.......shells respectively.
3. Each shell is associated with a certain definite quantity of energy. Hence the shells are also called '**Energy levels'**.



(Decreasing energy gap)

4. The energy content increases on moving from lower to higher shells and become zero for the shell which is present at an infinite distance from the nucleus.

5. The energy levels are not equally spaced.

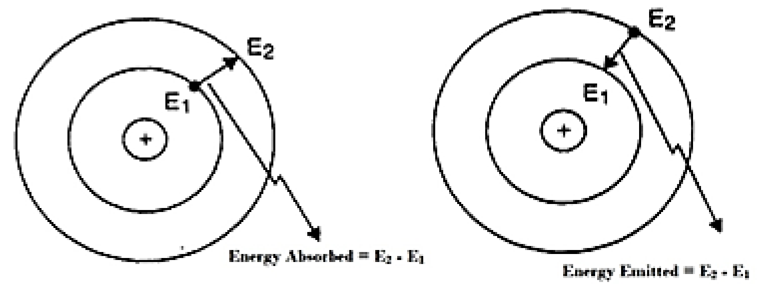
6. Through a large number of concentric circles are possible around the nucleus, only those circular paths are allowed for the electrons to revolve for which the **angular momentum** value (mvr) isa whole number multiple of $\frac{h}{2\pi}$, that is

$$mvr = n\frac{h}{2\pi}, \text{ where } n = 1, 2, 3,..........$$

Here, *m* = *mass of the electron,*
v = *tangential velocity of the revolving electron,*
r = *radius of the orbit.*
h = *Planck's constant,*

7. When the electrons in an atom are in their normal energy state (ground state), they keep on revolving in their respective orbits without losing energy.

8. When external source of energy is supplied to an atom, the electrons jump from lower ground states to the higher excited states by absorbing energy. Electrons in the excited states are unstable and jump back to the lower ground states by releasing energy. The energy thus released appears in the form of light which is the origin of spectral lines.



(Electronic Transition)

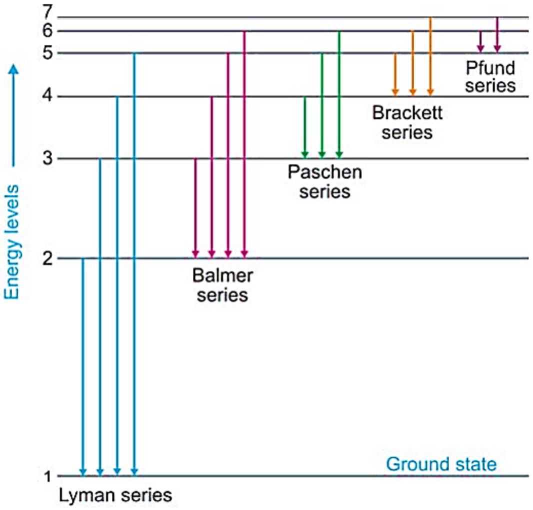
Failures of Bohr's Atomic Model:

1. According to Bohr's atomic model, the path followed by electrons is two-dimensional circular. But modern research (Heisenberg's Uncertainty Principle) revealed that electrons revolve in three-dimensional paths called orbitals.
2. It fails to explain the spectra of multi-electron species.
3. It fails to explain the relative intensities of spectral lines.
4. It fails to explain the splitting up of spectral lines when exposed to electric field (Stark Effect) and magnetic field (Zeeman Effect).
5. It fails to explain the cause of chemical combinations.

Explanation of Hydrogen Spectrum based Bohr's Theory

When electric discharge is passed through a sealed tube containing hydrogen gas and the radiation produced is analyzed with the help of a photo spectrometer or prism then six series of colours are obtained. These are Lyman, Balmer, Paschen, Brackett, P-fund, and Humphry series.

When electricity is passed through hydrogen gas, the hydrogen molecules get dissociated into hydrogen atoms. The hydrogen atoms absorb energy, and the electrons get excited to the higher energy levels. In the excited the electrons are unstable and jump back to the ground state either directly or in a stepwise manner by releasing light energy of different frequencies. When electrons jump from Higher energy levels to the 1st, 2nd, 3rd, 4th, 5th, and 6th levels, the series of lines are called Lyman, Balmer, Paschen, Brackett, P-fund, and Humphry series respectively.



Series	1st line		2nd line				Spectral Region
	n_1	n_2	n_1	n_2	n_1	n_2	
Lyman	1	2	1	3	1	4	Ultraviolet
Balmer	2	3	2	4	2	5	Visible
Paschen	3	4	3	5	3	6	Infrared
Brackett	4	5	4	6	4	7	Infrared
P-fund	5	6	5	7	5	8	Infrared
Humphrey	6	7	6	8	6	9	Far infrared

Heisenberg Uncertainty Principle

Heisenberg's uncertainty principle may be stated as "it is impossible to measure both the position and the momentum of a microscopic particle simultaneously with absolute accuracy". This principle is based on the wave-particle duality of matter. Since atoms and subatomic particles have very small masses, any increase in the accuracy of their positions will be accompanied by an increase in the uncertainty associated with their velocities.

Mathematically,

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

Where, Δx = Uncertainty in Position

Δp = Uncertainty in momentum

Accurate measurement of position or momentum automatically indicates larger uncertainty (error) in the measurement of the other quantity.

Heisenberg's principle applies to only dual-natured microscopic particles and not to macroscopic particles whose wave nature is minimal.

Since both position and momentum of an electron (microscopic particle) cannot be determined simultaneously, how we can say that electrons are moving in a specific fixed path. This is a direct clash with Bohr's atomic theory. This leads to the idea of atomic orbital.

Atomic Orbital:

The three-dimensional space or region around the nucleus where the probability of finding an electron is maximum is called an orbital. Generally, there are four types of orbitals, which are *s, p, d and f*.

Quantum Numbers:

The set of numbers used to describe the position and energy of the electron in an atom are called quantum numbers. There are four quantum numbers, namely, principal, azimuthal, magnetic and spin quantum numbers.

Principal Quantum Numbers (*n*)

1. It is denoted by the letter 'n'.
2. It represents the major energy level of the shell in which the electron is present.
3. Its values may be: 1, 2, 3, 4, …………∞.
4. For n = 1, 2, 3, 4, …., the shells are designated as K, L, M, N, …….respectively.
5. The maximum no. of electrons a shell can hold is given by $2n^2$.

Shell	n	Maximum no. of electrons ($2n^2$)
K	1	$2 \times 1^2 = 2$
L	2	$2 \times 2^2 = 8$
M	3	$2 \times 3^2 = 18$
N	4	$2 \times 4^2 = 32$ and so on…

6. With the value of 'n' we can calculate the energy content of a shell.
7. With the help of 'n' we can calculate the distance between the nucleus and the electron in a shell.
8. Larger the value of 'n' larger is the size of the electron cloud.

Azimuthal or angular momentum or subsidiary or secondary quantum number (l):

1. It is denoted by the letter 'l'.
2. It represents the number of sub-shells present in a given shell.
3. The values of 'l' may be l = 0, 1, 2, 3, ………., (n – 1).
4. For l = 0, 1, 2, 3, ….the corresponding sub-shells are called s, p, d, f, …...sub-shells respectively.

Shell	n	l	Sub-shells
K	1	0	1s
L	2	0, 1	2s, 2p
M	3	0, 1, 2	3s, 3p, 3d
N	4	0, 1, 2, 3	4s, 4p, 4d, 4f

5. A sub-shell can hold a maximum no. of ($4l$' + 2) electrons.

Sub-shell	l	No. of electrons ($4l$ + 2)
K	0	(4x0 + 2) = 2
L	1	(4x1 + 2) = 6
M	2	(4x2 + 2) = 10
N	3	(4x3 + 2) = 14

6. The angular momentum of an electron in an orbital is given by $\sqrt{l(l+1)}\frac{h}{2\pi}$

Magnetic Quantum Numbers (*m* or *m$_l$*)

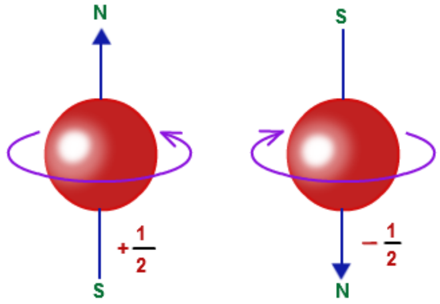
1. It is represented by *m* or *m$_l$*.
2. It represents the presence of sub-subshells or orbitals present in a sub-shell.
3. Its value may be, **$m = -l$ ....0...........+ l.**

Subshell	l	m	Orbitals
s	0	0	s
p	1	-1, 0, +1	p_x, p_y, p_z
d	2	-2, -1, 0, +1, +2	$d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}, d_{z^2}$
f	3	-3, -2, -1, 0, +1, +2, +3	-----------

Note: Orbitals having same or nearly same energy content are called degenerate orbitals.

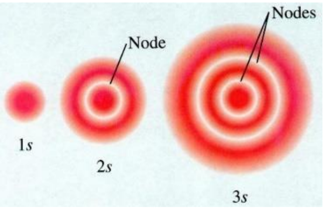
Spin Quantum Numbers: (s or m$_s$)

1. It represents the direction of spin of electrons around the nucleus along its own axis.
2. It has two values, s = + ½ and s = – ½ .

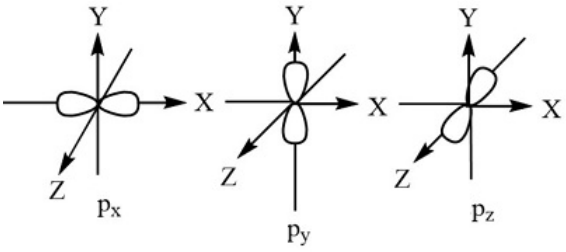


Shapes of Orbitals:

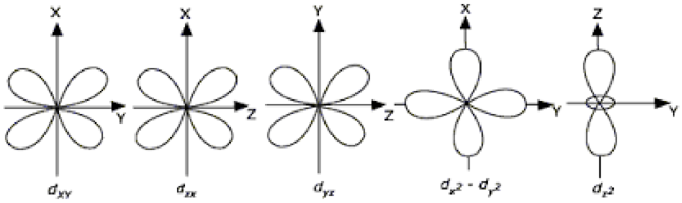
a. **Shapes of s- orbitals.**
   - S – orbitals are spherically symmetrical in nature.
   - The size and energy increase with the increase in the principal quantum numbers. Thus, the order of size and energy is 1s < 2s < 3s < ....
   - The region or the space in between two orbitals where the probability of finding an electron is zero is called 'nodal surface' or 'node'.



b. **Shapes of p – orbitals:**
   - p-orbitals are dumbbell in shapes.
   - A p-subshell has 3 related orbitals. They are p_x, p_y and p_z.
   - The plane passing through the nucleus on which the probability of finding an electron is zero is called nodal plane.



c. **Shapes of d – orbitals:**
   - The d – orbitals are double dumbbell in shape.
   - A d – subshell has 5 related orbitals namely, $d_{xy}, d_{yz}, d_{xz}, d_{x^2-y^2}$ and d_{z^2}.



Aufbau Principle:

The word *"Aufbau"*means **"building up".** This principle describes how the subs-hells are filled with electrons.

Aufbau principle may be stated as **"electrons are filled in different sub-shells in order of their increasing energy content"**.

The sub-shell with lowest energy is filled with electrons first and those with higher energies are filled with electrons later. The energy content of the various sub-shells can be compared by

(n+*l*′) rule.

The (n + *l*′) Rule:

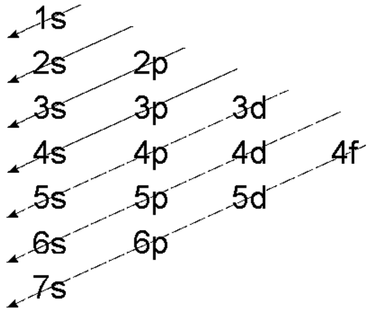
i. The sub-shell having lower (n+ *l*′) value possesses lower energy and is filled first.
ii. If the (n + *l*′) value for two given sub-shells are equal, then the one with lower value of 'n' possesses lower energy and is filled first.

Following the (n+ *l*′) rule, let us compare the energy possessed by various sub-shells.

Sub-shell→	**1s**	**2s**	**2p**	**3s**	**3p**	**3d**	**4s**	**4p**	**4d**	**4f**	**5s**	**5p**
(n+ *l*′)	1+0 =1	2+0 =2	2+1 =3	3+0 =3	3+1 =4	3+2 =5	4+0 =4	4+1 =5	4+2 =6	4+3 =7	5+0 =5	5+1 =6

Hence the increasing order of energy content of sub-shells is

1s < 2s < 2p < 3s < 3p <4s <3d < 4p < ...



ELECTRONIC CONFIGURATIONS: -

Electronic configuration is the arrangement of electrons of an atom in different sub-shells/orbitals in the increasing order of their energy content. The electronic configurations of some elements are given below:

Elements	**Electronic configurations**	**Elements**	**Electronic configurations**
$_1$H	$1s^1$	$_{16}$S	$1s^2\,2s^2 2p^6\,3s^2 3p^4$
$_2$He	$1s^2$	$_{17}$Cl	$1s^2\,2s^2 2p^6\,3s^2 3p^5$
$_3$Li	$1s^2\,2s^1$	$_{18}$Ar	$1s^2\,2s^2 2p^6\,3s^2 3p^6$
$_4$Be	$1s^2\,2s^2$	$_{19}$K	$1s^2\,2s^2 2p^6\,3s^2 3p^6 4s^1$
$_5$B	$1s^2\,2s^2 2p^1$	$_{20}$Ca	$1s^2\,2s^2 2p^6\,3s^2 3p^6 4s^2$
$_6$C	$1s^2\,2s^2 2p^2$	$_{21}$Sc	$1s^2\,2s^2 2p^6\,3s^2 3p^6 4s^2 3d^1$
$_7$N	$1s^2\,2s^2 2p^3$	$_{22}$Ti	$1s^2\,2s^2 2p^6\,3s^2 3p^6 4s^2 3d^2$

${}_{8}O$	$1s^2\,2s^2 2p^4$	${}_{23}V$	$1s^2\,2s^2 2p^6\,3s^2 3p^6 4s^2 3d^3$
${}_{9}F$	$1s^2\,2s^2 2p^5$	**${}_{24}Cr$**	**$1s^2\,2s^2 2p^6\,3s^2 3p^6 4s^1 3d^5$**
${}_{10}Ne$	$1s^2\,2s^2 2p^6$	${}_{25}Mn$	$1s^2\,2s^2 2p^6\,3s^2 3p^6 4s^2 3d^5$
${}_{11}Na$	$1s^2\,2s^2 2p^6\,3s^1$	${}_{26}Fe$	$1s^2\,2s^2 2p^6\,3s^2 3p^6 4s^2 3d^6$
${}_{12}Mg$	$1s^2\,2s^2 2p^6\,3s^2$	${}_{27}Co$	$1s^2\,2s^2 2p^6\,3s^2 3p^6 4s^2 3d^7$
${}_{13}Al$	$1s^2\,2s^2 2p^6\,3s^2 3p^1$	${}_{28}Ni$	$1s^2\,2s^2 2p^6\,3s^2 3p^6 4s^2 3d^8$
${}_{14}Si$	$1s^2\,2s^2 2p^6\,3s^2 3p^2$	**${}_{29}Cu$**	**$1s^2\,2s^2 2p^6\,3s^2 3p^6 4s^1 3d^{10}$**
${}_{15}P$	$1s^2\,2s^2 2p^6\,3s^2 3p^3$	${}_{30}Zn$	$1s^2\,2s^2 2p^6\,3s^2 3p^6 4s^2 3d^{10}$

Exceptional Electronic Configuration: Some elements like ‘Cr’ and ‘Cu’ show exceptional electronic configurations.

The electronic configurations of ‘Cr’ & ‘Cu’ should be:

${}_{24}Cr = [Ar]4s^2 3d^4$ & ${}_{29}Cu = [Ar]4s^2 3d^9$ respectively.

But the actual electronic configurations are

${}_{24}Cr = [Ar]4s^1 3d^5$ & ${}_{29}Cu = [Ar]4s^1 3d^{10}$

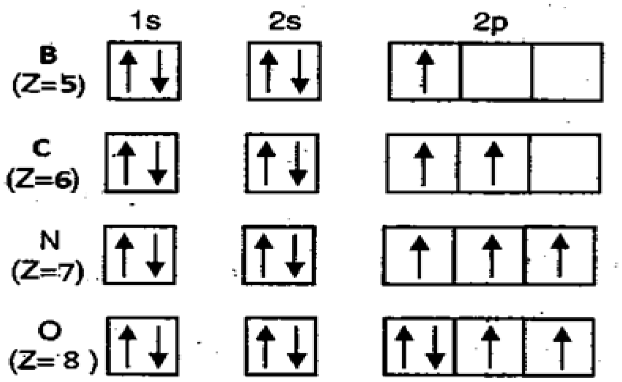
The exceptional electronic configuration is due to the fact that half-filled and ful-filled orbitals are more stable due to the orbital symmetry and exchange energy.
In case of Cr, one of the electrons of 4s sub-shell is transferred to the 3d sub-shell to become half-filled and stable.
On the other hand, in the case of Cu, one of the electrons of 4s sub-shell is transferred to the 3d sub-shell to become full-filled and stable.

Assignment:

Q 1. Write down the electronic configurations of the following: O^{2-}, Ca^{2+}, P^{3-}, Ti^{2+}, Cr^{3+}, Cu^{2+}.
Q 2. Arrange the following sub-shells in the increasing order of their energy content: 3d, 5p, 4s, 4p, 6s, 4d.
Q 3. What is (n+l) rule? Which out of 4s and 3d sub-shells has lower energy?
Q 4. What do you mean by $3d^2$?

Hund’s Rule: -

Hund’s rule may be stated as **“Pairing of electrons do not take place in the degenerate orbitals of *p, d,* and *f*-sub shells until each degenerate orbital in the given sub-shell contains one electron.”**



The above is due to the reason that electrons being identical in charge repel each other when present in the same orbital. This repulsion can, however, be minimized if two electrons move as far apart as possible by occupying different degenerate orbitals.

Let us consider the electronic configurations of the following elements.

Incase of boron the 5th electron is occupied by the $2p_x$orbital. In carbon the 6th electron will not be paired with the electron of the $2p_x$ orbital, rather it will be occupied by the $2p_y$ orbital. Similarly, in case of nitrogen all the

2*p* – electrons will remain unpaired. The rule is also called 'maximum multiplicity rule' because the total spin value of all the electrons of degenerate orbitals of a given sub-shell becomes maximum if they are arranged as per Hund's rule.

Assignment

Q 1. How many vacant orbitals are there in C, O, P and Ti?
Q 2. How many unpaired electrons are there in N, F, Fe and Na^+?
Q 3. What do you mean by $3d^5$?

Pauli's Exclusion Principle:

The principle may be stated as "No two electrons in an atom can have all the four quantum numbers alike".

Any two electrons in an atom can have the same three quantum numbers, but the fourth one must be different.

Let us consider two electrons e_1 and e_2 belong to the 1st shell or K – shell of an atom. The probable quantum numbers for the two electrons can be:

Electron	n	*l'*	m	s
e_1	1	0	0	+ ½
e_2	1	0	0	- ½

From the above tabulation we can see that three out of four quantum numbers are same, while the 4th quantum number, i.e. the spin quantum numbers, are different. The principle is called 'exclusion principle' as it excludes the possibility of more than two electrons in an orbital.

UNIT-1

Module -2: CHEMICAL BONDING

Chemical Bonding: Chemical bonding may be defined as “the force of attraction which holds together the constituent atoms in a molecule or ion”.

Cause of chemical bonding:

1. **Attainment of stability:** Every atom tries to attain stability.
2. **Noble gas configuration:** Every atom tries to attain the electronic configuration of the nearest noble gas.
3. **Electrostatic force:** Oppositely charged ions attract each other to form chemical bonds.
4. **Tendency to minimize energy:** When atoms approach each other the energy of the system decreases and the atoms attain stability.

Types of Chemical Bonding:

Depending upon the mode of bond formation (transfer or sharing of electrons), chemical bonding may be classified into the following types:

1. Ionic Bonding or Electrovalent bonding
2. Covalent bonding
3. Co-ordinate bonding or Dative Bonding
4. Hydrogen bonding
5. Metallic bonding

IONIC OR ELECTROVALENT BONDING:

"The chemical bond which is formed by the complete transfer of one or more valance electrons from one atom to another is called ionic or electrovalent bond and the compound formed is called ionic compound or electrovalent compound".

Features of Ionic bond: The formation of ionic bond involves:

- ☞ Formation of a positive ion by loss of electron/s from one kind of atom.
- ☞ Formation of a negative ion by gain of electron/s from another kind of atom.
- ☞ Electrostatic force of attraction between the oppositely charged ions.

Conditions for the formation of Ionic bond:

1. ***Nature of element:*** Atoms of different elements form ionic bonds. Atoms of the same element never form *ionic bond*.
2. ***Low Ionization potential:*** Ionization potential of an element is the quantity of energy required to remove one valence electron from an isolated, neutral, gaseous atom. One of the combining atoms should have low IP. The elements of **Gr 1 and Gr 2** of the modern periodic table have low ionization potential; and hence they can form *ionic bonds*.
3. ***High Electron Affinity:*** It is the amount of energy released when an extra electron is added to an isolated, neutral, gaseous atom. Another participating atom should have high electron affinity. The elements of **Gr 16** and **Gr 17** of the modern periodic table have high electron affinities; and hence they can form *ionic bonds*.

4. ***High Lattice Energy:*** The quantity of energy involved during the formation of or breaking of one mole of an ionic bond is called lattice energy. The higher the lattice energy greater is the stability of the ionic compound. Thus, the lattice energy of ionic compounds should be high.

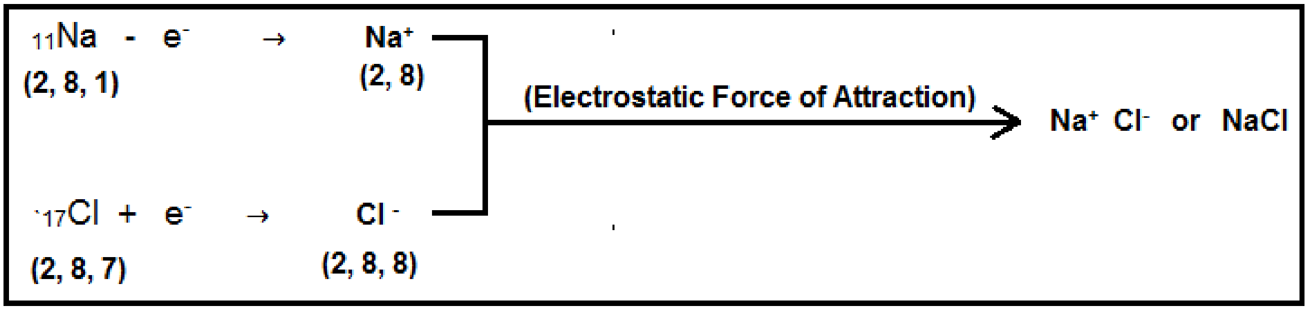
***Example: I*:** Formation of NaC*l.*

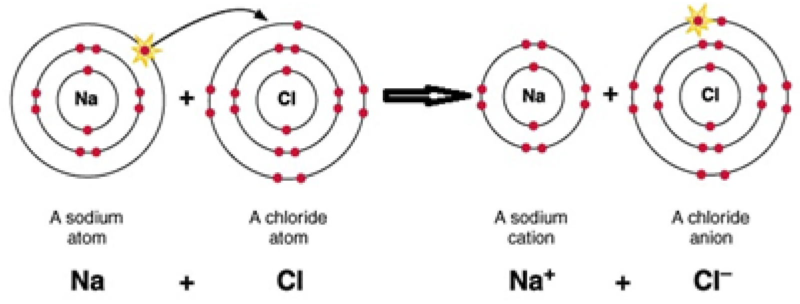
The electronic configurations of Na and Cl are given below:

$_{11}Na - 1s^2 2s^2 2p^6 3s^1$

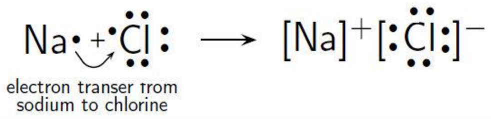
$_{17}Cl - 1s^2 2s^2 2p^6 3s^2 3p^5$

The electronic configurations indicate the presence of one and seven valence electrons in sodium and chlorine respectively. During the formation of NaC*l*, the sodium atom donates its valence electron completely to the chlorine atom (Fig. 2.1). Na becomes Na^+ with 8 electrons in valence shell and attains the nearest noble gas configuration of Ne; while C*l* atom becomes Cl^- ion with '8' electrons in valence shell and attains the nearest noble gas configuration of Ar.





(Figure: 2.1 Formation of NaCl)



Now the electrostatic force of attraction between the oppositely charged ions Na^+ and Cl^- results in the formation of **NaCl**.

Other examples of ionic compounds: *KCl, KBr, KI, CaF_2, $CaBr_2$, CaI_2, Na_2O, K_2O, CaO, MgO, Na_2S, K_2S etc.*

COVALENT BOND:

The chemical bond formed by the mutual (equal) sharing of valence electrons between two atoms is called covalent bond and the compound formed is called covalent compound.

The number of electrons shared by an atom during covalent bond formation is called **covalency**. A covalent may be formed between the atoms of similar or dissimilar elements. When two, four and six electrons are shared between two atoms, then a single, double and a triple bond are formed respectively.

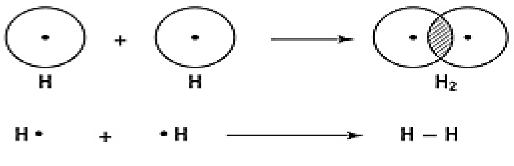


Figure: 2.3

Example: I: Formation of H_2 molecule.

The electronic configuration of 'H' is

$_{1}\mathrm{H}$ - $1s^{1}$

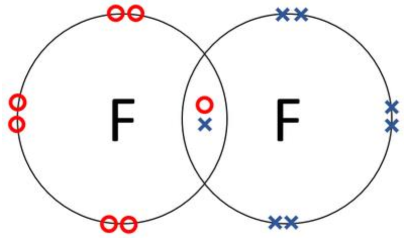
The electronic configuration indicates the presence of 1 valence electron in 'H' and requires one more electron to become duplet. Thus, each hydrogen atom shares its electron with each other to form a covalent bond (Fig. 2.3).

Example : 2 :Formation of F_2 molecule.

The electronic configuration of 'F' is

$_{9}\mathrm{F}$ - $1s^{2}2s^{2}2p^{5}$

The electronic configuration indicates the presence of 7 valence electrons in 'F' and requires one more electron to become an octet. Thus, each fluorine atom shares one of its valence electrons with each other to form a covalent bond.

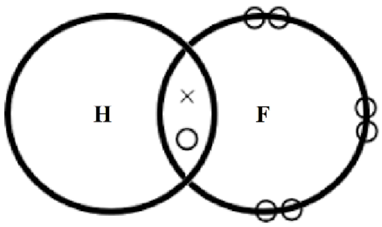


Example :3: Formation of HF molecule.

The electronic configuration of 'H' and 'F' are:

$_{1}\mathrm{H}$ - $1s^{1}$

$_{9}\mathrm{F}$ - $1s^{2}2s^{2}2p^{5}$



The electronic configurations indicate the presence of 1 and 7 valence electrons in 'H' and 'F' respectively. The hydrogen atom requires 1 more electron to become duplet, while the fluorine atom requires 1 more electron to become octet. Thus, the hydrogen and fluorine atoms share one of their valence electron each to form a covalent bond.

Other examples of covalent compounds: , Br_2, I_2, BF_3, $AlCl_3$, HCl, SiO_2,etc.

<u>Hybridization:</u>

The process of intermixing atomic orbitals having the same or nearly same energy content of an atom to give altogether different orbitals called hybrid orbitals having equivalent shape, size and energy is called ***hybridization***.

Steps involved in hybridization:

1. Promotion or Excitation: For some atoms excitation of electrons to the higher atomic orbitals is required.
2. Reorientation: The atomic orbitals then get intermixed with each other to form a new set of orbitals called hybrid orbitals.

Characteristics of Hybridization

Some of the following characteristics of Hybridization is give below-:

1. The orbitals of one and the same atom participate in hybridization.
2. The atomic orbitals having same or nearly same energy content can participate in hybridisation.
3. The number of hybrid orbitals equals the number of hybridising orbitals.
4. The hybrid orbitals formed are similar in shape, size and energy.
5. Only the atomic orbitals and not the electrons get hybridised.
6. The hybrid orbitals are so directed in space to have a stable arrangement and provide the molecule a proper shape.

Types of Hybridization: Depending on the number and the types of atomic orbitals get intermix, hybridization may be of the following types: sp, sp^2, sp^3, dsp^2, sp^3d^2, d^2sp^3, etc.

Hybridization in $BeCl_2$(Beryllium chloride):

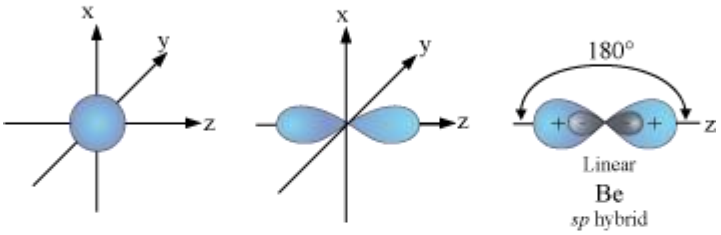
In $BeCl_2$, the central atom Beryllium uses sp hybridization. The electronic configuration of 'Be' in the ground state is:

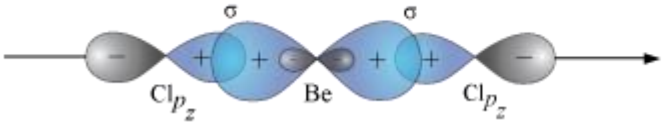
$_4Be : 1s^2 2s^2$

One of its 2s electrons is promoted to empty $2p_x$ orbital. Thus, in the excited state, the electronic configuration of 'Be' is

$_4Be^* : 1s^2 2s^1 2p_x^1 2p_y^0 2p_z^0$

The 2s and $2p_x$atomic orbitals of 'Be' get intermixed with each other to form two sp hybrid orbitals with equivalent shape size and energy.





These two half-filled orbitals form two σ bonds with chlorine. Therefore, $BeCl_2$ is linear and the bond angle between the two hybrid orbitals is 180°.

<u>Hybridization in BF_3 (Boron fluoride):</u>

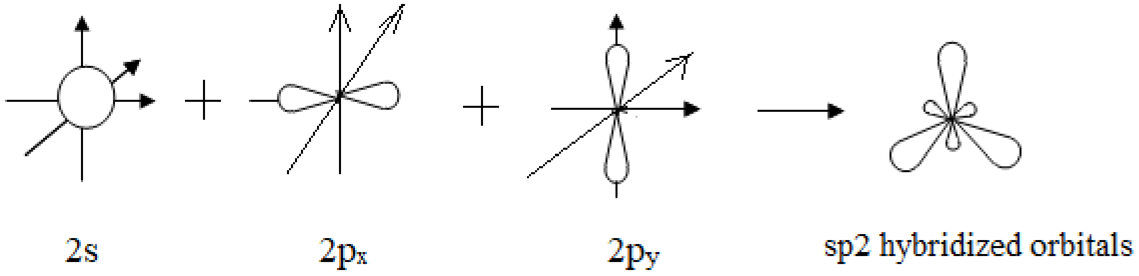
In BF_3, the central atom Boron uses sp^2 hybridization. The electronic configuration of 'B' in the ground state is:

$_5B : 1s^2 2s^2 2p_x^1 2p_y^0 2p_z^0$

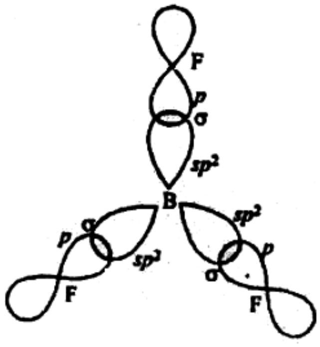
One of its 2s electrons is promoted to empty $2p_y$ orbital. Thus, in the excited state, the electronic configuration of 'B' is

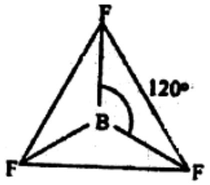
$_5B^* : 1s^2 2s^1 2p_x^1 2p_y^1 2p_z^0$

The 2s, $2p_x$ and $2p_y$ atomic orbitals of 'B' get intermixed with each other to form three sp^2 hybrid orbitals with equivalent shape size and energy.



Each sp^2 hybrid orbitals of boron overlap with the $2p_z$ orbital of fluorine to form three sigma bonds. The shape of BF_3 is trigonal planar with bond angle 120^0.





Hybridization in CH_4 (Methane):

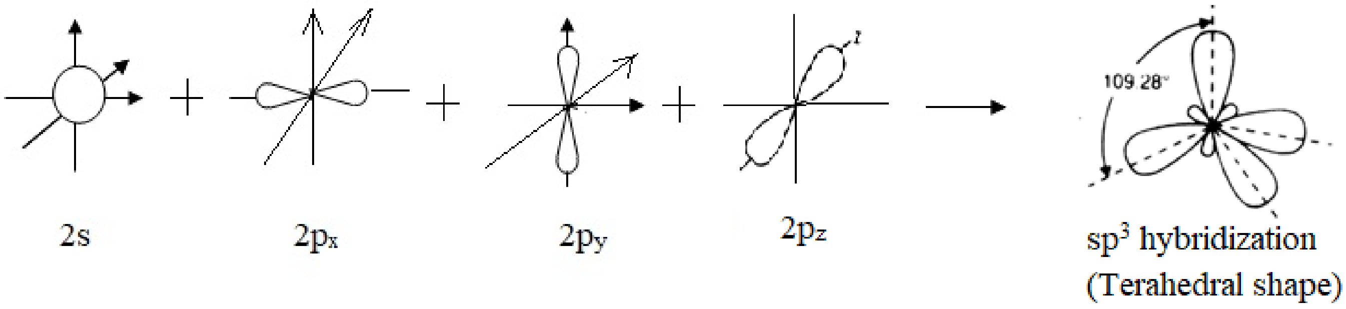
In CH_4 the central atom carbon uses sp^3 hybridization. The electronic configuration of 'C' in the ground state is:

$_6C - 1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$

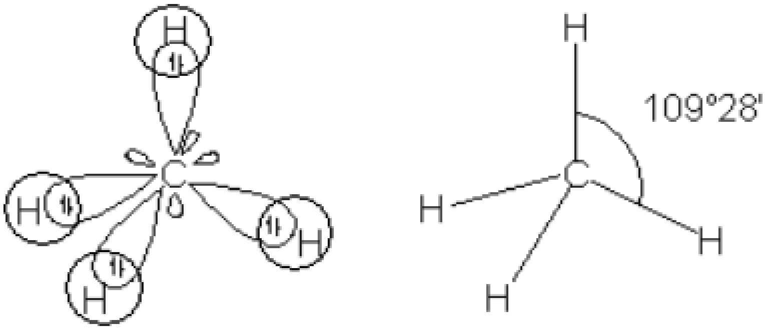
One of the electrons of 2s orbital gets excited to the $2p_z$ orbital. The electronic configuration of carbon in the excited state is:

$_6C^* - 1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$

The 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals of carbon atom get intermix with each other to form four sp^3 hybrid orbitals, all with equivalent shape size and energy.



Each sp^3 hybrid orbital of carbon overlaps with the 1s orbitals of hydrogen atoms to form four sigma bonds. The shape of CH_4 is tetrahedral with bond angle $109^0 28'$.



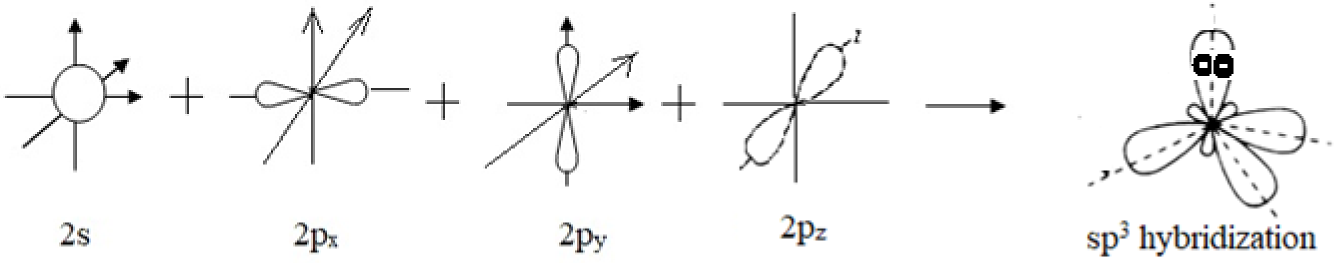
Tetrahedral structure of methane

Hybridization in NH_3 (Ammonia):

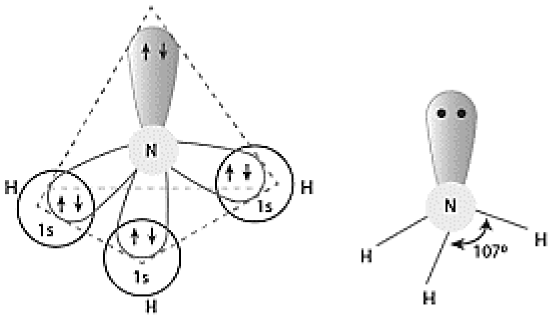
In NH_3 the central atom nitrogen uses sp^3 hybridization. The electronic configuration of 'N' in the ground state is:

$_{6}N - 1s^22s^22p_x^12p_y^12p_z^1$

The 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals of nitrogen atom get intermix with each other to form four sp^3 hybrid orbitals.



Out of the four hybrid orbitals, one is occupied by a lone pair of electrons. The remaining three sp^3 hybrid orbitals of 'N' overlap with the 1s orbitals of 'H' to form three sigma bonds. Due to the presence of a lone pair of electrons over nitrogen atom, the shape of NH_3 molecule is pyramidal with a reduced bond angle of 107^0.

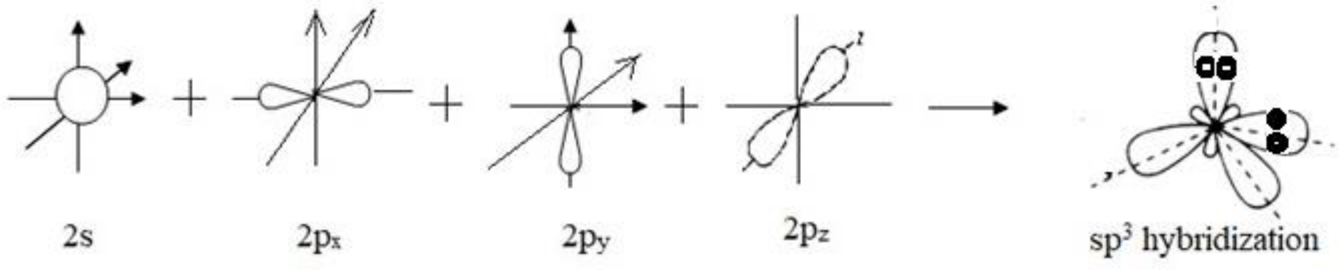


Hybridization in H_2O(Water):

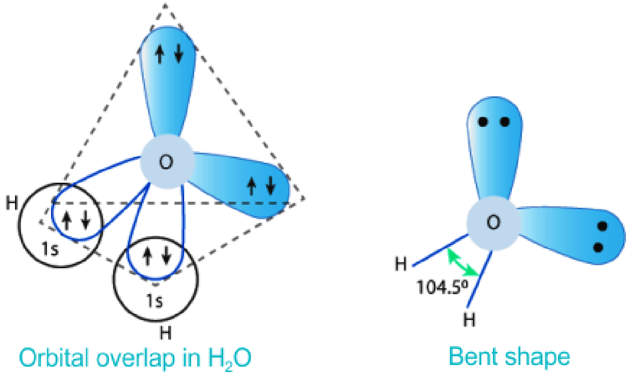
In H_2O, the central atom 'O' uses sp^3 hybridization. The electronic configuration of 'O' in the ground state is:

$_{8}O - 1s^22s^22p_x^22p_y^12p_z^1$

The 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals of oxygen atom get intermix with each other to form four sp^3 hybrid orbitals.



Out of the four hybrid orbitals, two are occupied by lone pair of electrons. The remaining two sp^3 hybrid orbitals of 'O' overlap with the 1s orbitals of 'H' to form two sigma bonds. Due to the presence of two lone pair of electrons over oxygen atom, the shape of H_2O molecule is 'bent' shape or 'V' shape with a reduced bond angle of 104.5^0.



Orbital overlap in H_2O

Bent shape

Hybridization of H_2O

CO-ORDINATE BOND:

The chemical bond formed by the partial donation and partial sharing of a lone pair of electrons between two atoms (or ions) is called a co-ordinate or dative bond.

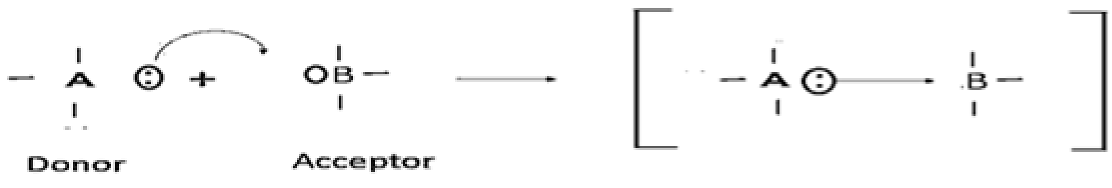
Conditions for the formation of co-ordinate or Dative bond:

i. *One of the participating atoms should have at least one lone or unshared pair of electrons.*

ii. *The other atom should be short of a pair of electrons than the nearest inert gas element.*

The lone pair of electrons present over one atom is partially shared by both the combining atoms. A co-ordinate bond is represented by an arrow (→) sign**,** the head of which points towards the acceptor atom, while the tail points towards the donor atom.

Since co-ordinate bonds have some polar character, it is also known as dative or semi-polar bond or co-ionic bond.



Formation of co-ordinate bond

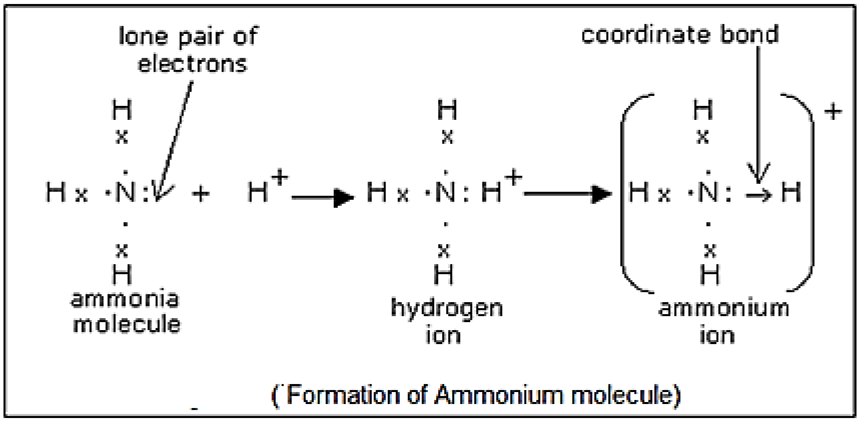
Example: 1: Formation of ammonium ion (NH_4^+).

Ammonium ion (NH_4^+) is formed by the combination of NH_3 and H^+ ion.

$NH_3 + H^+ \rightarrow NH_4^+$

Ammonia (NH_3) contains a lone pair of electrons over 'N' while 'H^+' ion contains no electron and requires two electrons to become duplet.

Thus, the unshared pair of electrons over nitrogen in NH_3 is partially shared with H^+ ion and a Co-ordinate bond is formed.



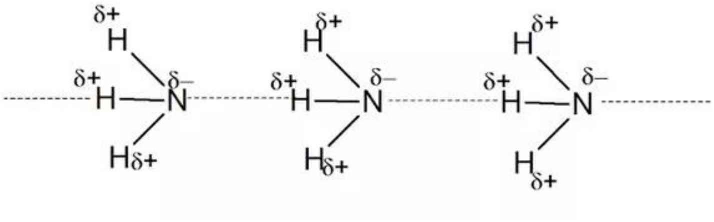
(Formation of Ammonium molecule)

Hydrogen Bonding:

The week force of intermolecular attraction between the hydrogen atom of a molecule and a most electronegative atom like F, O or N of the same or different molecules is called hydrogen bond.

Hydrogen bonding in NH_3:

In NH_3, nitrogen is more electronegative than hydrogen. Thus, the nitrogen atom drags the shared pair of electrons towards it in H – N bond and develops a partial negative charge over it. On the other hand, H' develops a partial positive charge on it. Now the weak force of attraction between the partially positively charged $H^{\delta+}$and the partially negatively charged $N^{\delta-}$forms hydrogen bonds.

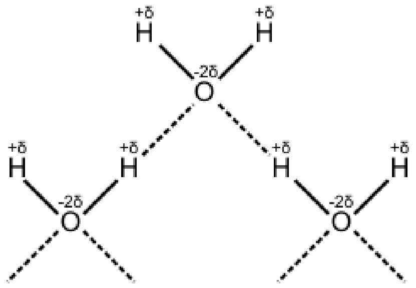


Anomalous Properties of NH_3 due to hydrogen bonding:

1. Because of strong intermolecular hydrogen bonding, NH_3 exists as an associated molecule.
2. Due to intermolecular hydrogen bonding NH_3 is highly soluble in water.
3. Ammonia has a higher boiling point than PH_3.

Hydrogen bonding in H_2O:

In H_2O, oxygen is more electronegative than hydrogen. Thus, the oxygen atom drags the shared pair of electrons towards it in H – O bond and develops a partial negative charge over it. On the other hand, 'H' develops a partial positive charge on it. Now the weak force of attraction between the partially positively charged $H^{\delta+}$ and the partially negatively charged $O^{\delta-}$forms hydrogen bonds.



Anomalous Properties of H_2O due to hydrogen bonding:

The following are the anomalous properties of water due to hydrogen bonding:

1. It exists as associated molecules.
2. It exists in liquid state while other hydrides of the group exist in gaseous state.
3. It has high surface tension.
4. It has high heat of vaporization.
5. It has decreased viscosity under pressure.
6. It has the properties of cohesion, adhesion and higher density than similar compounds which do not show hydrogen bonding.

Metallic Bonding:

The chemical bond which is formed between metal atoms is called a metallic bond.

It is a form of chemical bonding that arises from the electrostatic attractive force between conduction electrons and positively charged metal ions. It happens between similar atoms of metal in a free state. Valence electrons move freely among all metal atoms. Metallic bonding accounts for many physical properties of metals, such as lustre, malleability, resistivity, thermal conductivity and electrical conductivity, strengths and ductility. Such bonds are characterized by the following features.
Examples of substances having metallic bonding: Na, K, Fe, Cu, Al, etc.

UNIT - 1

Module -3: SOLUTION

Solute: Solutes are the substances that dissolve in solvents to form a solution. Solutes can be solids, liquids or gases. Solutes are present in lesser amount than solvents.

Solvent: Solvents are the substances that dissolve solutes. Liquids are the most common solvents, but gases and solids can also be used. Solvents are present in higher amount compared to solutes.

Solution: Solutions are mixtures of two or more substances. A solution can be in solid, liquid and gaseous state.

$$\boldsymbol{Solute + Solvent \rightarrow Solution}$$

Atomic weight/mass:

The atomic mass of an element may be defined as "the average relative mass of one atom of the element as compared to the mass of an atom of carbon (^{12}C) taken as 12".

Unit: amu (atomic mass unit) or simply '*u*'.

For example:

Element	**Atomic mass in amu**
H	*1.008 ≈ 1*
N	*14*
O	*16*

Atomic masses of some elements are given below:

Element	**Symbol**	**Atomic Weight in a.m.u**
Hydrogen	*H*	*1*
Helium	*He*	*4*
Lithium	*Li*	*7*
Berylium	*Be*	*9*
Boron	*B*	*11*
Carbon	*C*	*12*
Nitrogen	*N*	*14*
Oxygen	*O*	*16*
Fluorine	*F*	*19*
Neon	*Ne*	*20*
Sodium	*Na*	*23*
Magnesium	*Mg*	*24*
Aluminium	*Al*	*27*
Silicon	*Si*	*28*
Phosphorous	*P*	*31*
Sulphur	*S*	*32*
Chlorine	*Cl*	*35.5*
Argon	*Ar*	*40*
Potassium	*K*	*39*
Calcium	*Ca*	*40*
Chromium	*Cr*	*52*
Iron	*Fe*	*56*
Copper	*Cu*	*63.5*
Bromine	*Br*	*80*
Silver	*Ag*	*108*
Lead	*Pb*	*207*

Modes of Expression of Concentration of Solutions:

The following are the modes of expression of concentrations of solutions:

Molarity, Normality, Molality, Mass percentage, Volume percentage, mole fraction, ppm, ppb, etc.

1. Molarity (M):

Molarity of a solution may be defined as "the number of gram mole of the solute present per liter of solution".

Unit = gram mole/liter or M.

Mathematically,

$$M = \frac{w \times 1000}{M_S \times V_{ml}}$$; Where w = weight of the solute in gram

Ms = Molecular weight of the solute.

V_{ml} = Volume of solution in ml.

Molar solution:

The solution containing 1 gm mole of the solute per liter of solution is called a 'molar' solution.

For example: The solution containing 36.5 gm of HCl, 40 gm of NaOH, 58.5 gm of NaCl or 98 grams of H_2SO_4 per liter of solution is called molar solution.

NOTE: 1. Deci molar solution means (1/10) M solution, Semi-molar solution means (½) M solution, centi-molar solution means (1/100) M solution.

2. The solution whose strength is known is called *a standard solution.*

PROBLEMS FOR DISCUSSION:

QUESTION: 1. *0.4 gm of caustic soda (NaOH) is present in 200 ml of its solution. Find out the molarity of the solution.*

Solution **: Given Data**

weight of solute (w) = 0.4 gm

Volume of solution (V_{ml}) = 200 ml.

Mol.wt. of solute (NaOH), M_S = 23.+16+1 = 40 amu.

Thus, Molarity (M) $= \frac{w \times 1000}{M_S \times V_{ml}} = \frac{0.4 \times 100}{40 \times 200}$ = 0.05 M

Hence, the molarity of the solution is 0.05M.

QUESTION:2. *How many grams of caustic potash (KOH) are required to prepare 1.5 lit. of a decimolar solution?*

Solution **: Given Data**

Weight of solute(w) = ?

Volume of the solution (V_{ml}) = 1.5 lit = 1500 ml.
Molecular weight of solute, Ms for KOH =39+16+1 =56 amu
Molarity of the solution = 1/10 M = 0.1M

Thus, $M = \frac{w\times1000}{M_s\times V_{ml}} \Rightarrow w = \frac{M\times M_s\times V_{ml}}{1000} = \frac{0.1\times56\times1500}{1000} =$ = 8.4 gram.

Thus, 8.4 gm *of caustic potash is required to prepare 1.5 lit. of deci-molar solution.*

2. Mole Fraction (X)

The mole fraction of a component is the number of moles of that component in the solution divided by the total number of moles in the given solution.

$$\textbf{Mole fraction of Solute} = \frac{\boldsymbol{No.of\ moles\ of\ Solute}}{\boldsymbol{No.of\ moles\ of\ Solute + No.of\ moles\ of\ Solvent}}$$

$$\textbf{Mole fraction of Solvent} = \frac{\boldsymbol{No.of\ moles\ of\ Solvent}}{\boldsymbol{No.of\ moles\ of\ Solute + No.of\ moles\ of\ Solvent}}$$

Note: Mole fraction of solute + mole fraction of solvent = 1

Q. 1. A mixture of gases contains 4 moles of H_2, 8 moles of N_2 and 2 moles of O_2. Find the mole fractions of each component.

Solution:

$$\text{Mole fraction of } H_2 = \frac{n_{H_2}}{n_{H_2} + n_{N_2} + n_{O_2}} = \frac{4}{4+8+2} = \frac{4}{14} = 0.28$$

$$\text{Mole fraction of } N_2 = \frac{n_{N_2}}{n_{H_2} + n_{N_2} + n_{O_2}} = \frac{8}{4+8+2} = \frac{8}{14} = 0.57$$

$$\text{Mole fraction of } O_2 = \frac{n_{O_2}}{n_{H_2} + n_{N_2} + n_{O_2}} = \frac{2}{4+8+2} = \frac{2}{14} = 0.14$$

Q. 2. A mixture of gases contains 4 gm of H_2, 14 gm of N_2 and 8 gm of O_2. Find the mole fractions of each component.

Solution:

$$\text{No. of moles of } H_2 = \frac{Mass\ of\ H_2}{Molecular\ mass\ of\ H_2} = \frac{4}{2} = 2$$

$$\text{No. of moles of } N_2 = \frac{Mass\ of\ N_2}{Molecular\ mass\ of\ N_2} = \frac{14}{28} = 0.5$$

$$\text{No. of moles of } O_2 = \frac{Mass\ of\ O_2}{Molecular\ mass\ of\ O_2} = \frac{8}{32} = 0.25$$

$$\text{Mole fraction of } H_2 = \frac{n_{H_2}}{n_{H_2} + n_{N_2} + n_{O_2}} = \frac{2}{2 + 0.5 + 0.25} = \frac{2}{2.75} = 0.72$$

$$\text{Mole fraction of } N_2 = \frac{n_{N_2}}{n_{H_2} + n_{N_2} + n_{O_2}} = \frac{0.5}{2 + 0.5 + 0.25} = \frac{0.5}{2.75} = 0.18$$

$$\text{Mole fraction of } O_2 = \frac{n_{O_2}}{n_{H_2} + n_{N_2} + n_{O_2}} = \frac{0.025}{2 + 0.5 + 0.25} = \frac{0.025}{2.75} = 0.009$$

3. Parts per million (PPM)

Parts per million may be defined as "the ratio between the no. of parts of solute dissolved to a million parts of the total volume.

$$ppm = \frac{No.\,of\ parts\ of\ the\ component}{Total\ no.\,of\ parts\ of\ all\ components} \times 10^6$$

$$ppm = \frac{weight\ of\ solute}{Volume\ of\ solution} \times 10^6$$

Q 1. What is the concentration, in ppm, if 0.025 g of KCl is dissolved in 100 grams of water?

Solution:

Given Data:

Weight of solute = 0.025 gm

Weight of solution = 0.025 + 100 = 100.025 gm.

$$ppm = \frac{weight\ of\ solute}{weight\ of\ solution} \times 10^6 = \frac{0.025}{100.025} \times 10^6 = 249.94\ ppm.$$

Q 2. 500 cc of an aqueous solution contains 10 gm of NaOH. Calculate its concentration in ppm.

Solution:

Given Data:

Weight of solute = 10 gm

Weight of solution = 500 cc.

$$ppm = \frac{weight\ of\ solute}{Volume\ of\ solution} \times 10^6 = \frac{10}{500} \times 10^6 = 20,000\ ppm.$$

4. **Mass Percentage (w/w):**The mass percentage of a solute may be defined as " the mass of solute in grams present in 100 gm of the solution".

$$Mass\ \%\ of\ solute = \frac{mass\ of\ solute}{Total\ mass\ of\ solution} \times 100$$

Q 1. What is the concentration in terms of mass percent of a solution in which 40 g of salt is dissolved in 200 mL of water?

Solution:

1 ml of water has a mass of 1 g.

So, mass of 200 ml of water = 200g

Mass of the solution = mass of the solute + mass of the solvent = 200 + 40 = 240 g

$$Mass\ \%\ of\ solute = \frac{mass\ of\ solute}{Total\ mass\ of\ solution} \times 100 = \frac{40}{240} \times 100 = 16.66\%$$

5. **Volume Percentage (v/v):** The volume percentage of a solute may be defined as "the volume (in cc) of solute i present per 100 cc of the solution".

$$\boldsymbol{Volume\ \%\ of\ solute = \frac{Volume\ of\ solute}{Total\ volume\ of\ solution} \times 100}$$

Q 1. 10 cc of HCl is present in 200 cc of its solution. Calculate the volume percentage of HCl in the solution.

Volume of solute (HCl) = 10 cc.

Volume of solution = 200 cc.

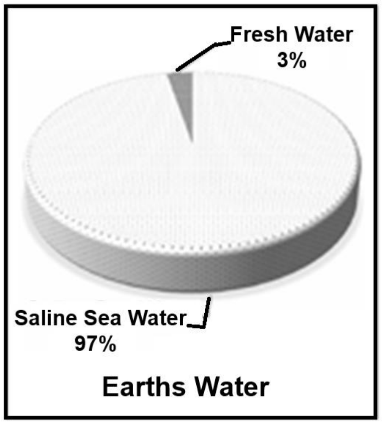
$$Volume\ \%\ of\ solute = \frac{Volume\ of\ solute}{Total\ volume\ of\ solution} \times 100 = \frac{10}{200} \times 100 = 5\%$$

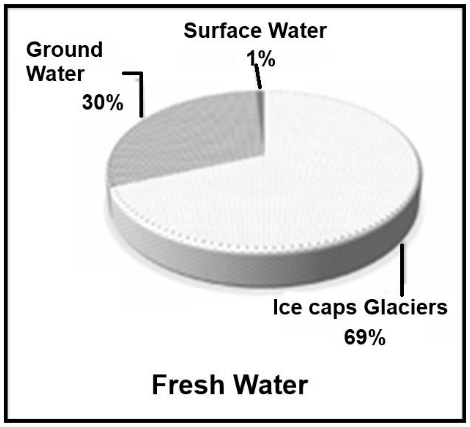
UNIT - 2

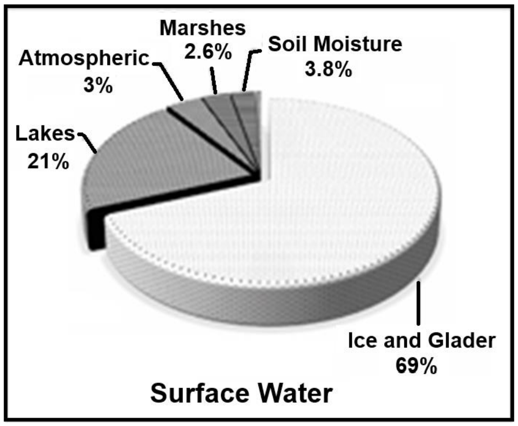
WATER

Graphical representation of water distribution on Earth:

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. Out of total existing water, only 3% of water is freshwater, while the remaining 97% of water is saline or seawater. 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.







Classification of water based on soap test:

1. Soft water: - Water which lathers or produces enough foam with soap solution is called soft water.

Ex: - Rainwater, de-mineralized water, distilled water etc.

1. **Hard water: -** Water which does not lather or does not produce enough foam with soap solution is called hard water. Instead, it forms a curdy white precipitate.

Ex: - Sea water, river water, Pond water etc.

Hardness of water:

It is the characteristic of water which prevents the lathering of soap due to the presence of bicarbonate, sulphate and chloride of calcium and magnesium in it.

Distinction between soft water and hard water

SN	Soft Water	Hard Water
1	It has low mineral content.	It has high mineral content.
2	It does not contain Ca and Mg ions.	It contains Ca and Mg ions.
3	Soap is not wasted.	A large quantity of soap is wasted.
4	React with soap to form lather.	React with soap to form precipitates.
5	It does not have ill effects on domestic and industrial use.	It has ill effects on domestic and industrial use.

6	It is suitable for drinking.	It is not suitable for drinking.

Types of hardness:

Hardness of water is of two types:

A. Temporary or Carbonate hardness

B. Permanent or Non-carbonate hardness

A. **Temporary hardness:** The temporary hardness of water arises due to the presence of bicarbonates of **Ca and Mg, [$Ca(HCO_3)_2$, $Mg(HCO_3)_2$]**.

It is named temporary hardness because the soluble bicarbonates decompose into insoluble carbonates simply on heating. Thus, water becomes soft. It is also called carbonate hardness.

B. **Permanent hardness: The** permanent hardness of water arises due to the presence of chlorides of Ca, Mg ($CaCl_2$, $MgCl_2$).It is named permanent hardness because such a hardness cannot be removed by simply boiling the water.

Unit of hardness

(1) PPM – Parts per million.

(2) mg/L – Milligrams per Litre.

Causes of poor lathering of soap in hard water:

Hard water contains calcium and magnesium ions. When soap comes in contact with hard water, these ions form calcium and magnesium salts of fatty acids which are insoluble in water. These calcium or magnesium salts precipitate out in the form of scum.

Soap reacts with hard water as

$$2C_{17}H_{35}COONa + MgSO_4 \rightarrow (C_{17}H_{35}COO)_2Mg + Na_2SO_4$$

(Sodium stearate) (Impurity in hard water) (Magnesium stearate)

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.

(A) 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.

The loose and slimy precipitate deposited on the inner wall of boiler is known as sludge.

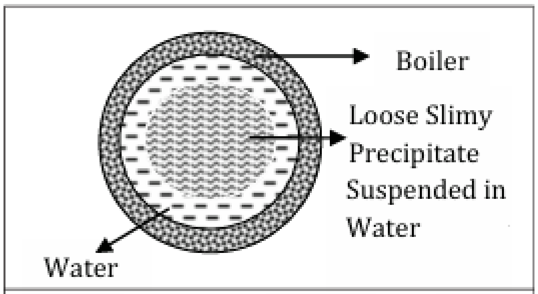
Excessive sludge formation disturbs the working of the boiler. It settles in the regions of poor water circulation such as pipe connection, plug opening, thereby causing even choking of the pipes.

Properties of Sludge

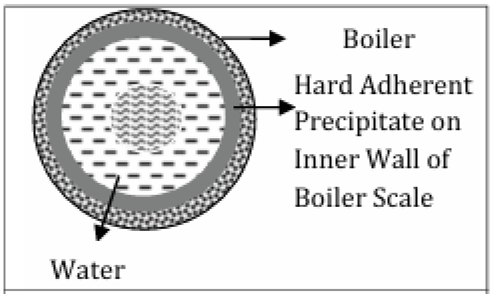
- Sludges are soft and less permeable precipitate.
- Sludges are poor conductors of heat.
- These are formed at comparatively cooler portions of the boiler.
- Sludges are formed by substances that have greater solubility in hot water. e.g. $MgCO_3$, $MgCl_2$, $CaCl_2$, $MgSO_4$ etc.

Prevention of 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.



Sludge Formation



Scale Formation

(B) 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.

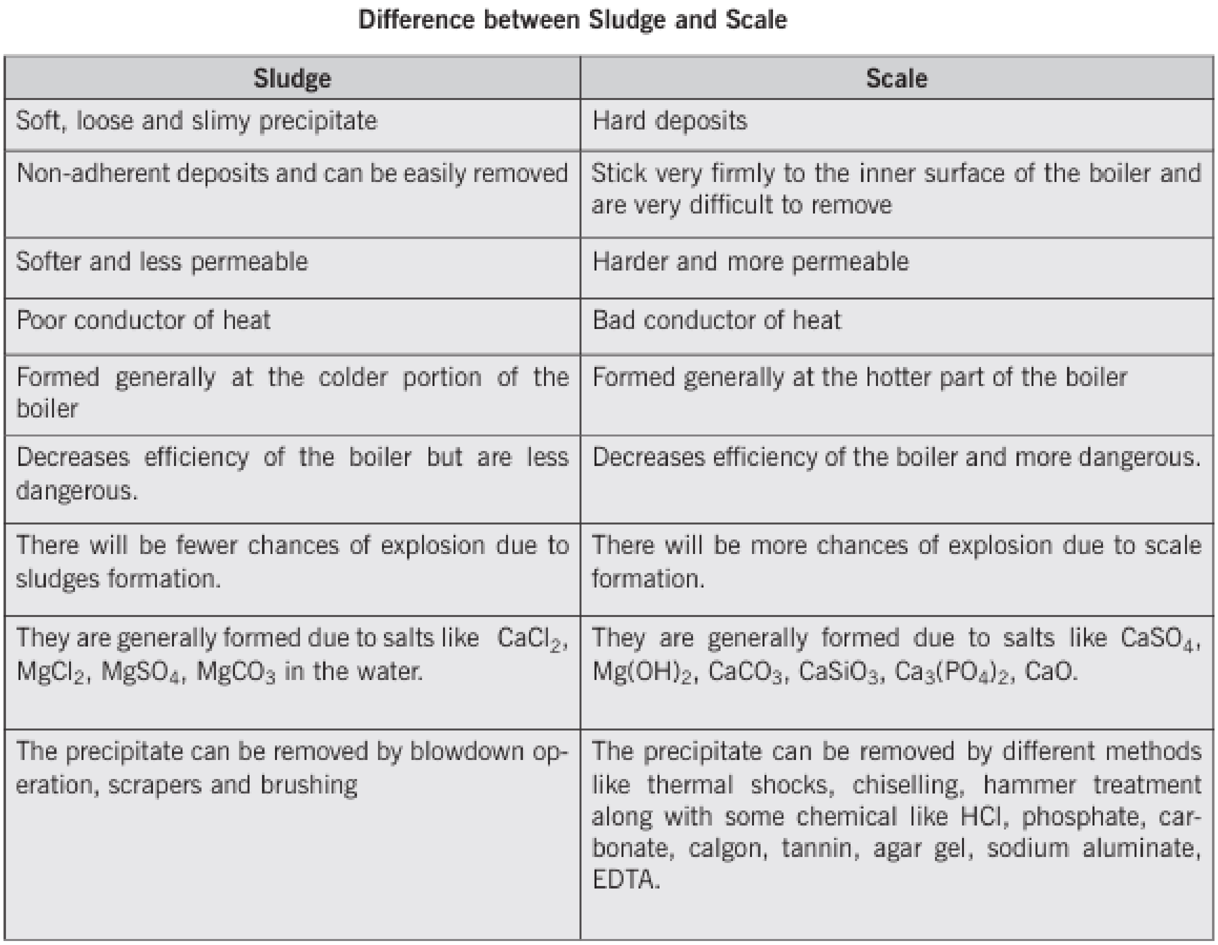
The hard adhering coating deposited on the inner wall of boiler is known as scale.

Properties of Scale

- The scale is very hard and firmly adhered to the boiler.
- It is difficult to remove them, even with the hammer or chisel.
- It is a bad conductor 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.
They are generally formed due to salts like $CaCl_2$, $MgCl_2$, $MgSO_4$, $MgCO_3$ in the water.	They are generally formed due to salts like $CaSO_4$, $Mg(OH)_2$, $CaCO_3$, $CaSiO_3$, $Ca_3(PO_4)_2$, CaO.
The precipitate can be removed by blowdown operation, scrapers and brushing	The precipitate can be removed by different methods like thermal shocks, chiselling, hammer treatment along with some chemical like HCl, phosphate, carbonate, calgon, tannin, agar gel, sodium aluminate, EDTA.

(C) 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.

(D) 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 substances like oils.

Causes of Priming and Foaming

The causes of priming and foaming are as follows:

- Presence of a large amount of dissolved solids.
- 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 low water level in boilers.
- Efficient softening and filtration of the boiler feed water. Adding antifoaming chemicals like castor oil.
- Removing 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.

(E) 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:

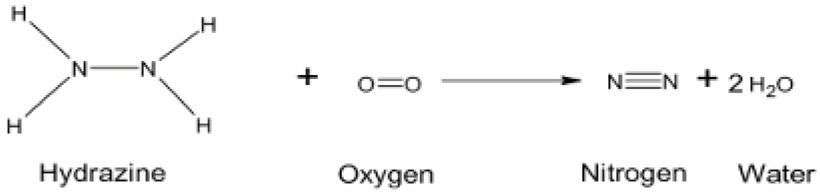
(i) Dissolved Oxygen

Dissolved oxygen present in water interacts with boiler material at steaming temperature to form ferrous hydroxide. Formed ferrous hydroxide further reacts with oxygen to form ferric oxide.

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

(a) Removal of Oxygen by using Chemicals

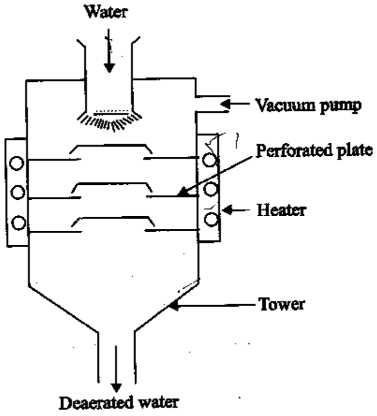
There are different chemicals like hydrazine, sodium sulphite, tannin, which are used to remove dissolved oxygen. In the case of hydrazine reacts with dissolved oxygen to form nitrogen and water. Suppose we use a dissolved oxygen sensor and find that amount of dissolved oxygen in boiler water is increased;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



(ii) Dissolved CO2

Water associated with dissolved CO_2 forms carbonic acid, which has a slow corrosive effect on boiler material. Water containing bicarbonates is also the source of CO_2.

$CO_2 + H_2O \rightarrow H_2CO_3$(Carbonic acid)

$Mg(HCO_3)_2 \rightarrow MgCO_3 + H_2O + CO_2^{\uparrow}$

Removal of CO$_2$ by using ammonia

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

$H_2O + NH_3 \rightarrow NH_4OH$

$NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O$

Removal of Carbon dioxide by Heating

The solubility of gases in water reduces with the rise in temperature. Thus, water is heated to a high temperature to remove dissolved carbon dioxide. If it is not removed, they are responsible for corrosion of the boiler material.

(iii) Dissolved Salts

The presence of some salts like magnesium chloride in water can corrode boilers. When MgCl$_2$ combines with water, it forms magnesium hydroxide along with hydrochloric acid as a byproduct.

$$MgCl_2 + 2H_2O \rightarrow 2Mg(OH)_{2\downarrow} + 2HCl$$

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 MgCl$_2$ will cause corrosion of iron to a large extent.

$Fe + HCl \rightarrow FeCl_2 + H_2$

$FeCl_2 + 2H_2O \rightarrow Fe(OH)_2 + 2HCl$

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.

$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2$

Due to the formation of sodium hydroxide, water becomes alkaline. The numbers 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 water which is free from salts like MgCl$_2$.
- ☞ By using sodium phosphate instead of sodium carbonate for water softening.
- ☞ By adding tannin or lignin as additives to the boiler water since these blocks the minute cracks.
- ☞ By adjusting the alkalinity of water to an optimum level (pH 7-8)

Quantitative measurement of water hardness by EDTA method:

The estimation of hardness of water is of great importance for the chemical industry in general. There are various methods available for estimating the hardness of water.

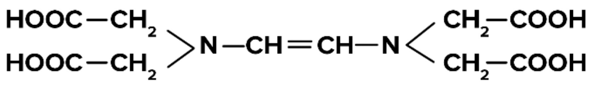
Some of them are:

1. Soap titration method
2. Alkali titration method

3. EDTA method

Estimation of hardness of water by **EDTA method:**

EDTA is Ethylene Di-amine Tetra Acetic acid. The structure of EDTA is



(EDTA)

In this method the water sample is titrated against EDTA solution using Eriochrome-Black-T indicator (EBT) at a pH of 8-10. Ammonia buffer solution (NH_4Cl & NH_4OH mixture) is used to maintain the required P^H.

When the EBT indicator is added to the water sample, it forms wine red coloured weak complex with Ca^{2+} and Mg^{2+} ions.

$$[Ca^{2+} Mg^{2+}] \ + \ EBT \xrightarrow{P^H=8-10} [Ca\, Mg - EBT] Complex$$

When this solution is titrated against EDTA, it replaces the indicator from the weak complex form stable EDTA complex. When all the hardness causing ions are complexed by EDTA, the indicator is set free. The color of the free indicator is steel blue. Thus, the end point is the change of color from wine red to steel blue.

$$[Ca\, Mg - EBT] Complex + EDTA \xrightarrow{P^H=8-10} [Ca\, Mg - EDTA] + EBT$$

Wine red coloured weak complex Stable complex Steel blue

Preparation of solutions

EDTA Solution

It is prepared by dissolving 4 gms of EDTA in 1000 ml of distilled water.

Standard hard water

1 gm of pure $CaCO_3$ is dissolved in minimum quantity of HCl and then made up to 1000 ml using distilled water.

∴ 1 ml of standard hard water ≡ 1 mg of $CaCO_3$ equivalent hardness.

EBT indicator

0.5 gms of EBT is dissolved in 100 ml of alcohol.

Buffer solution

67.5 gms of NH4Cl and 570 ml of NH_3 are dissolved and the solution is made up to 1000 ml using distilled water.

Standardization of EDTA

50 ml of standard hard water is taken in a clean conical flask. 10 ml of buffer solution and 4-5 drops of EBT indicator are added in to the conical flask and titrate it against EDTA solution taken in the burette. The end point is the change of colour from wine red to steel blue.

Let the volume of EDTA consumed be V_1 ml

Estimation of total hardness of water sample

50 ml of the given hard water sample is taken in clean conical flask and is titrated against EDTA as before.

Let the volume of EDTA consumed be V_2 ml

Estimation of permanent hardness of water sample

100 ml of the same hard water sample is taken in a 250 ml beaker. It is boiled for 15 minutes. During boiling temporary hardness gets removed. It is then cooled and filtered, and the volume is made up to 100 ml in a standard flask by adding distilled water.
50 ml of the made-up solution is pipetted out into a clean conical flask and is titrated against EDTA as before.
Let the volume of EDTA consumed be V_3 ml.

Calculations
Standardization of EDTA
1 ml of Std. hard water = 1 mg of $CaCO_3$
50 ml of Std. hard water = 50 mgs of $CaCO_3$
50 ml of Std. hard water consumes = V_1 ml of EDTA
$\therefore V_1$ ml of EDTA ≡ 50 mgs of $CaCO_3$ equivalent hardness.

Or,1 ml of EDTA ≡ 50 V1 mgs of $CaCO_3$ equivalent hardness.

Estimation of total hardness of water sample
50 ml of the given hard water sample consumes = V_2 ml of EDTA
= $V_2 \times 50/V_1$ mgs of $CaCO_3$ equivalent hardness
[$\therefore$ 1 ml of EDTA = 50 V_1 mgs of $CaCO_3$]
$\therefore$ 1000 ml of the given hard water sample = $V_2 \times 50 / V_1 \times 1000 / 50$
= $1000 \times V_2 / V_1$mgs of $CaCO_3$ equivalent hardness
$\therefore$ Total hardness = $1000 \times V_2/V_1$ ppm

Estimation of permanent hardness of water sample
50 ml of the same hard water sample after boiling, filtering, etc., consumes = V_3 ml of EDTA
= $V_3 \times 50/V_1$ mgs of $CaCO_3$ equivalent hardness
$\therefore$ 1000 ml of the given hard water sample = $V_3 \times 50/V_1 \times 1000/50$
= $1000 \times V_3/V_1$ mgs of $CaCO_3$ equivalent hardness
$\therefore$ Permanent hardness = $1000 \times V_3/V_1$ ppm

Temporary hardness
Temporary hardness = Total hardness − Permanent hardness
= $[1000 \times V_2 /V_1] - [1000 \times V_3/V_1]$
$\therefore$ Temporary hardness = $1000/V_1(V_2 - V_3)$ ppm.

Q 1. 100 ml of a water sample requires 20 ml of EDTA solution for titration. 1 ml of EDTA solution is equivalent to 1.1 mgs of $CaCO_3$. Calculate hardness in ppm.

Solution

Given 1 ml of EDTA solution = 1.1 mgs of $CaCO_3$

$\therefore$ 20 ml of EDTA solution = 20×1.1 mgs of $CaCO_3$

= 22 mgs of $CaCO_3$

100 ml of water sample requires = 20 ml of EDTA Solution

= 22 mgs of $CaCO_3$

∴ 1000 ml of water sample = $\frac{22}{100} \times 1000 = 220$ mgs/lit or ppm

Q 2.100 ml of a sample of water requires 18 ml of an EDTA solution for titration. 22 ml of the same EDTA solution was required for the titration of 100 ml of standard hard water containing 1 gm $CaCO_3$ per litre. Calculate hardness of water sample in ppm.

Solution

Given 1 litre of std. hard water contains 1 gm of $CaCO_3$

i.e. 1000 ml of std. hard water contains 1000 mgs of $CaCO_3$

∴ 1 ml of std. hard water = 1 mg of $CaCO_3$

22 ml of EDTA = 100 ml of std. hard water

= 100 × 1 mg of $CaCO_3$

∴ 1 ml of EDTA = 100/22mgs of $CaCO_3$

100 ml of sample of water = 18 ml of EDTA

$= \frac{100}{22} \times 18 = 81.818$ mg of $CaCO_3$

∴for 1000 ml of sample water = 81.818 X 10 mg of $CaCO_3$

Hardness = 818.18 mgs/lit or ppm.

Q 3. 0.28 gm of $CaCO_3$ was dissolved in HCl and the solution was made up to one litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution on titration. 100 ml of hard water sample required 33 ml of same EDTA solution on titration. 100 ml of this water, after boiling cooling and filtering required 10 ml of EDTA solution on titration. Calculate the temporary and permanent harness of water.

Solution

Given 1000 ml of std. hard water contains = 0.28 gm of $CaCO_3$

i.e., 1000 ml of std. hard water contains = 0.28 × 1000 mgs of $CaCO_3$

= 280 mgs of $CaCO_3$

∴ 1 ml of std. hard water = 0.28 mg of $CaCO_3$

28 ml of EDTA = 100 ml of the std. hard water

= 100 × 0.28 mgs of $CaCO_3$

= 100 × 0.28 = 28 mg of $CaCO_3$

∴1 ml of EDTA = 1 mg of $CaCO_3$.

Total hardness

100 ml of hard water = 33 ml of EDTA

= 33 × 1 mgs of $CaCO_3$

= 33 mgs of $CaCO_3$

∴ 1000 ml of hard water = $\frac{33}{100} \times 1000 = 330$ mgs/lit or ppm.

Total Dissolved Solids (TDS)

Total dissolved solids (TDS) is the total amount of dissolved salts like calcium, magnesium, potassium, sodium, bicarbonates, chlorides, and sulphates and some small amounts of organic matter that are dissolved in water.

Sources of dissolved solids in water:

TDS in drinking-water comes from natural sources, sewage, urban run-off, industrial wastewater, and chemicals used in the water treatment process, and the nature of the piping or hardware used to convey the water, i.e., the plumbing.

The total dissolved solids test provides a qualitative measure of the amount of dissolved ions but does not tell us the nature or ion relationships. In addition, the test does not provide us insight into the specific water quality issues such as hardness, salty taste, staining, odour, corrosiveness, or the presence of trace metals and microbiological contaminants. Therefore, the total dissolved solids test is used as an indicator test to determine the general quality of the water. The following table can be used as a generalization of the relationship of TDS to water quality problems:

Cations combined with:	Negative impact
Carbonate	Scale formation, bitter taste
Chlorides/Sulphates	Salty, brackish taste, corrosion, odours

How Does Total Dissolved Solids become a problem?

- If the total dissolved solids are too low, it is possible that the water may be corrosive to metal piping and fixtures and therefore have a bitter or off-taste because of corrosion byproducts. This may also mean the water could have elevated levels of trace metals either leached from the piping in the home or from the aquifer.

☞ If the total dissolved solids are extremely high, the water would have a salty taste, greatly corrode the metal piping, and cause the premature failure of appliances.

An elevated TDS indicates the following:

- The concentration of the dissolved ions may cause the water to be corrosive with a salty taste as well as result in scale formation, decreasing the efficiency of hot water heaters.
- It would also suggest that there are many ions that are above the Primary or Secondary Drinking Water Standards, such as an elevated level of nitrate, arsenic, aluminium, copper, lead, etc.

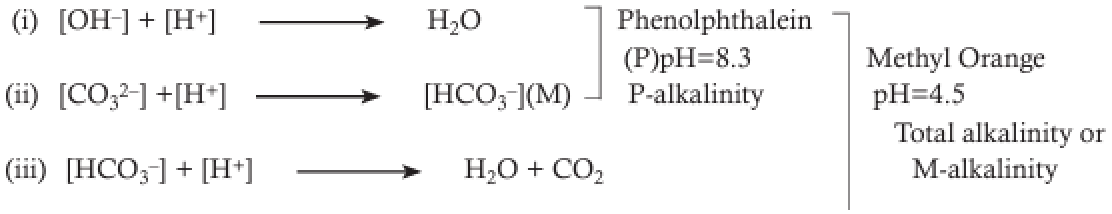
Classification Total Dissolved Solids	
Freshwater	0 to 1000 mg/L
Slightly Saline	1000 to 3000 mg/L
Moderately Saline	3000 to 10,000 mg/L
Very Saline	10,000 to 35,000 mg/L
Briny	> 35,000 mg/L

Quantitative Determination of Water Hardness by Alkalinity Estimation

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

- Caustic alkalinity (due to OH^- and CO_3^{2-} ions)
- Temporary hardness (due to HCO_3^- 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:



The sample water is first titrated against a standard H_2SO_4 solution using phenolphthalein indicator. The end-point indicates the completion of the reaction (i) and (ii) only. Then the sample water is titrated against the same acid using methyl orange indicator. The end-point indicates the completion of reactions i, ii and iii.

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

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

The possible combinations of ions causing alkalinity in water are: (i) OH^- only or (ii) CO_3^{2-} only or (iii) HCO_3^- only or iv) OH^- and CO_3^{2-} together or CO_3^{2-} and HCO_3^- together.

The possibility of OH^- and HCO_3^- ions together is ruled out, because they combine instantaneously to form CO_3^{2-} ions.

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

Thus OH^- and HCO_3^- ions can not exist together in water. On the basis of same reasoning, all the three (OH^-, CO_3^{2-} and HCO_3^-) can not exist together.

$$Alkalinity = \frac{(Volume\ of\ Acid) \times (Strength\ of\ Acid) \times 50 \times 1000}{Volume\ of\ water\ sample} ppm\ or\ mg/L$$

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 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 $CO_3^{2-} + H \longrightarrow HCO_3^-$ takes place with phenolphthalein while complete carbonate neutralisation reaction $CO_3^{2-} + H^+ \longrightarrow HCO_3^-$;

$HCO_3^- + H^+ \longrightarrow H_2O + CO_2$ 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.

$HCO_3^- + H^+ \longrightarrow CO_2 + H_2O$ equal to (M–P)

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

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

Units of Alkalinity: $CaCO_3$ equivalent, ppm, mg/L

Water Softening Techniques:

A. **Lime Soda Process:** In this process hard water is treated with a calculated quantity of lime and soda. Lime and soda convert the soluble hardness causing chemicals present in hard water into insoluble substances called sludges. The precipitate or sludge formed is then removed by filtration to get soft water.

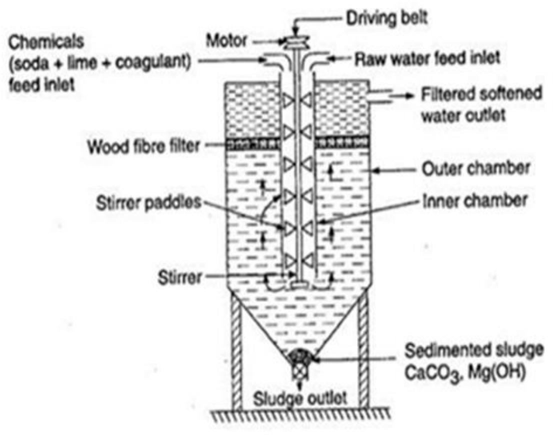
$$\underset{\text{(soluble)}}{CaCl_2} + \underset{\text{soda}}{Na_2CO_3} \rightarrow \underset{\text{(insoluble)}}{CaCO_3\downarrow} + 2NaCl$$

$$\underset{\text{(soluble)}}{MgCl_2} + \underset{\text{soda}}{Ca(OH)_2} \rightarrow \underset{\text{(Insoluble)}}{Mg(OH)_2\downarrow} + CaCl_2$$

Lime-Soda process is of two types.
(a) Cold Lime soda process (b) Hot lime soda process

(a) Cold Lime Soda Process:

Principle: When hard water is treated with calculated amount of lime [$Ca(OH)_2$] and soda (Na_2CO_3) at room temperature 25ºC, the soluble Ca and Mg salt present in hard water are chemically converted into ppt. of calcium carbonate ($CaCO_3$) and magnesium hydroxide [$Mg(OH)_2$]. These ppts are removed by filtration. Thus, soft water is obtained.



Cold Lime-Soda Process)

$$\underset{\textbf{hard water}}{CaCl_2} + \underset{\textbf{soda}}{Na_2CO_3} \rightarrow \underset{\textbf{ppt}}{CaCO_3\downarrow} + 2NaCl$$

$$\underset{\textbf{hard water}}{MgCl_2} + \underset{\textbf{lime}}{Ca(OH)_2} \rightarrow \underset{\textbf{ppt}}{Mg(OH)_2\downarrow} + CaCl_2$$

Process:

The apparatus consists of a conical shaped steel tank. Raw water, lime, soda and coagulants are added from the top inner vertical circular chamber which is fitted with rotating shaft carrying many paddles. The dissolved salts of Ca and Mg combine with lime soda and coagulants and form an insoluble precipitate as sludge. Softened water rises upwards, and the heavy sludge settles down. Then the softened water passes through wood fibre filter and the filtered soft water is collected through the outlet. The sludge setting down at the bottom is removed. The residual hardness left in this process is about 50 - 60 ppm.

Dis-advantages:

- It is a slow process because reactions during water softening take place in very dilute solutions and room temp.
- It requires coagulant for setting particles of ppt. formed during reaction of water softening.
- Softening capacity of this process is less.
- Soft water obtained by this process consists of dissolved gases.

(b) Hot Lime Soda process:

Principle: This process involves treatment of hard water with lime and soda at a temp. of 80-150^{0}C.

Process: In the hot lime soda process, the reactions take place at higher temperature near the boiling point of water. The chemical mixing process is the same as the cold lime soda process, but steam is applied in mixture tank. As a result, precipitation becomes almost complete very quickly.

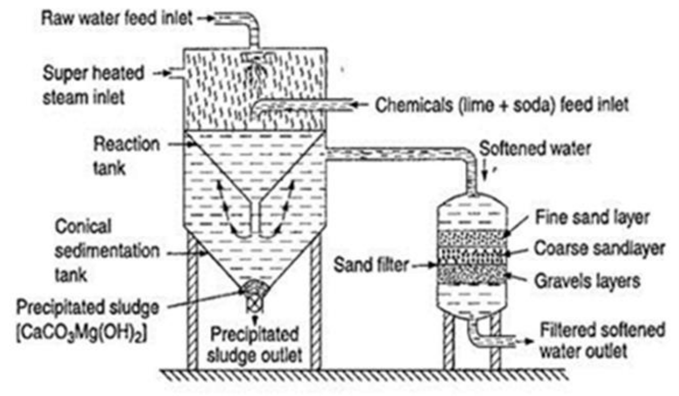
Apparatus:

The apparatus consists of 3 main parts.

(a) Reaction tank – in which hard water, lime & soda are mixed thoroughly.

(b)Conical sedimentation vessel – in which sludges settle down.

(c)Sand filter – where sludge is completely removed.



Hot Lime-soda Process)

Advantages:

1. It is much more economical.
2. The reaction is completed within a short period.
3. The reaction proceeds faster. Hence the softening capacity is increased.
4. No coagulant is required, as the sludge settles down easily.
5. Dissolved gases like CO_2, air etc. are removed.
6. Under hot conditions, the viscosity of water is lowered. Thus, filtration becomes easier.

7. Pathogenic bacteria are destroyed.
8. The residual hardness left in this process is much lower (15-30 ppm) as compared to that in the cold L-S process (50-60 ppm).

Disadvantages:

d economical softening careful operation and skilled supervision is required.
e amounts of sludge creates problems.
e hardness only up to 15 ppm, which is not suitable for high pressure boilers.

Difference between cold lime soda process & hot lime soda process

Cold Lime soda process	Hot lime soda process
1. This process is conducted at room temp. (25^{0}C)	This process is conducted at 80^0 to 150^0 C.
2. It is costlier.	It is much more economical.
3. The process takes longer time to complete.	It takes comparatively less time for completion.
4. The reaction is slower.	The reaction proceeds faster. Hence the softening capacity is increased.
5. Coagulant like alum is required.	No coagulant is required, as the sludge settles down easily.
6. Dissolved gases do not escape.	Dissolved gasses like CO_2, air etc. are removed.
7. Filtration is comparatively slower.	Under hot condition the viscosity of water is lowered. Thus, filtration becomes easier.
8. Pathogenic bacteria are not destroyed.	Pathogenic bacteria, if any, are destroyed.
9. The residual hardness left is more, i.e., 50 – 60 ppm.	The residual hardness left in this process is much lower (15-30 ppm) as compared to that in the cold L-S process (50-60 ppm).

Zeolite Process:

Zeolite Softening Process is the process of removing permanent as well as temporary hardness of the water. Zeolite Softening occurs when magnesium (Mg) and calcium (Ca) zeolites (insoluble) in water get precipitated. In this zeolite softening process, zeolite works as a catalyst which helps in exchanging ions from Ca^{2+} or Mg^{2+} with sodium ions.

Certain complex inorganic salts possess the property of exchanging calcium and magnesium ions present in hard water for Na^+ ions. An important salt of this type is sodium aluminium orthosilicate or sodium zeolite ($Na_2Al_2Si_2O_8.xH_2O$), commonly known as permutit (artificially synthesized zeolite).

Zeolite Softening Process of Water

When hard water containing magnesium and calcium ions passes through a zeolite bed of sodium, then sodium (Na^+) ions get displaced or replaced by the ions of Mg^{2+} and Ca^{2+} and when the replacement is complete i.e. all the sodium ions get replaced by Mg^{2+} and Ca^{2+} ions then the zeolite get inactivated. This zeolite then gets regenerated by passing brine solution through the inactive zeolite bed. This process of softening water is mainly used in laundry.

Reactions involved:

$Ca^{2+} + Na_2Al_2Si_2O_8.xH_2O \rightarrow CaAl_2Si_2O_8.xH_2O + 2Na^+$

$Mg^{2+} + Na_2Al_2Si_2O_8.xH_2O \rightarrow MgAl_2Si_2O_8.xH_2O + 2Na^+$

Advantages

- Clean and easy process.
- The equipment occupies less space as well as it is compact.
- Time effective i.e. it does not require much time for water softening.
- Easy to maintain.
- No precipitation of impurities occurs.

Limitations

- Turbidity in water may cause clogging in the zeolite bed.
- The presence of large quantities of Mn^{2+} or Fe^{2+} coloured ions must be removed from water as they may produce their own zeolites.
- Mineral acids present in water must be neutralised with soda as they may destroy the bed of zeolites.

Ion – Exchange Process [Deionization or De-mineralization process]:

In this method, the ions responsible for hardness are exchanged with other ions which don't make water hard. In this method ion exchange resin are used.

Organic ion-exchangers (Ion-exchange resins): -

These are organic polymers having:

(i) high molecular weight.

(ii) Open and permeable molecular structure.

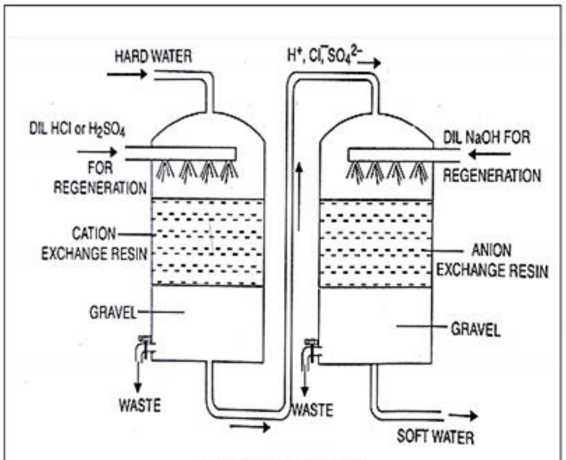
(iii) acidic (-COOH, $-SO_3H$) or basic groups ($-OH^-$, $-NH_2$) attached with them.

Ion-exchange resins are of two types:

(a) Cation-exchange resin(R-H^+): If the active ion in ion-exchanger is a cation, generally acidic functional groups, the resin is called cation-exchange resin, Ex – (Resin-H^+)

(b) Anion-exchange resin (R-H^-): If the active ion in ion-exchanger is an anion, generally basic functional groups, the resin is called anion-exchange resin Ex – (Resin-OH^-)

Process: The hard water is passed through a column of cation exchange resin called zero-carb. All the cations present in hard water get exchanged with H^+ ions of the resin.



Organic Ion-Exchanger

$2RH \quad + \quad Ca^{2+} \quad \rightarrow \quad R_2Ca \quad + \quad 2H^+$

(Cation-Exchange Resin) hard water Exhausted Resin

$2RH \quad + \quad Mg^{2+} \quad \rightarrow \quad R_2Mg \quad + \quad 2H^+$

(Cation-Exchange Resin) hard water Exhausted Resin

Then the hard water is passed through the column of anion exchange resin. All the anions present in water get exchanged with OH- ions of the resin.

$ROH \quad + \quad Cl^- \quad \rightarrow \quad RCl \quad + \quad OH^-$

(Anion-Exchange Resin) hard water Exhausted Resin

H^+ and OH^- ions released from the cation and anion exchange columns respectively get combined to produce water molecules.

$H^+ + OH^- \rightarrow H_2O$

Thus, the water coming out from the exchanger is free from cations as well as anion. Such water is known as deionized or demineralized water.

Regeneration of resins:

When all the H^+ and OH^- ions of the resins are exchanged by the cations and anions present in hard water, then the resins are said to be exhausted, and regeneration can be done.

The cation-exchange resin can be regenerated by the treatment with diluted acids like dil. HCl or dil.H_2SO_4.

$R_2Ca \quad + \quad 2HCl \quad \rightarrow \quad 2RH \quad + \quad CaCl_2$

(Exhausted resin) (Regenerated resin)

Similarly, the anion-exchange resin can be regenerated by the treatment with dilute alkali like, dil NaOH solution.

$RCl \quad + \quad NaOH \quad \rightarrow \quad ROH \quad + \quad NaCl$

(Exhausted resin) (Regenerated resin)

The regenerated resins may be used again.

Advantages of Ion – Exchange Process –

i. This process can be used to soften highly acidic or alkaline water.
ii. It produces water of very low hardness (up to 2 ppm). So, it is good for treating water for use in high pressure boilers.

Dis-advantages of Ion – Exchange Process:

- The equipment is costly and more expensive chemicals are needed.
- If water contains turbidity, then output of the process is reduced.

Municipal Water Treatment:

Depending upon the type of impurities, different methods are employed for purification of water for potable use. The following sequential steps are taken for municipal water treatment.

1. *Screening:* Removes the floating materials like leaves.
2. *Coagulation:* Removes finely divided suspended particles.
3. *Sedimentation:* Removes suspended impurities likes and clay etc.
4. *Filtration:* Removes colloidal impurities and large organisms.
5. *Disinfection:* Kills the bacteria.

1. 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.

2. 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 commonly used coagulants are Al_2SO_4, Alum $[K_2SO_4(Al_2SO_4)_3 24H_2O]$, Ferrous Sulphate ($FeSO_4.7H_2O$), Sodium Aluminate ($NaAlO_2$). These coagulants react with water to form gelatinous precipitates 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:

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

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

The efficiency of the coagulation process can be increased by using coagulant aids such as lime, fullers earth, bentonite clay and polyelectrolyte. Coagulants are generally added in the solution form to the water with the help of mechanical flocculators provided with stationary or rotating baffles.

3. Sedimentation:

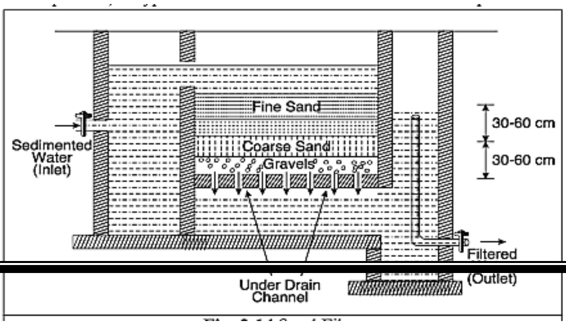
Sedimentation is a process of removing suspended impurities. Suspended particles settle down due to the force of gravity. This process takes two to eight hours and removes 70%–75% of suspended impurities. It is done in large settlement tanks or reservoirs.

4. Filtration:

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 filtration. Types of filtrations:

(A) Gravity Sand filter:

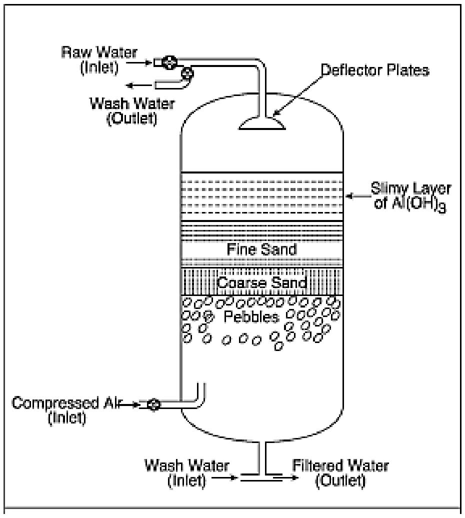
It consists of a large, rectangular tank made of concrete and a process medium, known as filter medium, which retains solid particles but allows the passage of water. It consists of three layers. The upper layer consists of fine sand. The middle layer



consists of coarse sand and the bottom layer consists of gravel. 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 drawn out. The rate of filtration 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.

(B) Pressure filter

It consists of a cylindrical vertical steel tank. The tank consists of three layers of filtering media, one above the other. The bottom layer consists of Pebbles, the middle layer consists of coarse sand and the top layer consists of fine sand. The 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 the 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 comes out from the bottom of the cylinder. These filters are widely used for industrial purposes.



5. Sterilization or Disinfection:

Sterilization, also known as disinfection, is the process of killing or inactivating microorganisms, such as bacteria, viruses, and protozoa, to prevent waterborne diseases.

Some common methods used in water sterilization are:

1. **Boiling**
2. **Chlorination**
3. **Ozonolysis**
4. **UV-Rays Treatment**
5. **Membrane Technology**

a) **Boiling:** Water for domestic purposes may be sterilized by simple boiling method by boiling the water for about 20–30 min. This method kills harmful disease-causing bacteria and germs. This process is very 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:** It is the most important method for sterilization 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/tablet or as chlorine water. It 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.

$Cl_2 + H_2O \rightarrow HOCl + HCl$
$HOCl \rightarrow [O] + HCl$

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 oxidizing agent. 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.

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

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 (NH_2Cl)

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

Advantages: Excess dose of NH_2Cl does not create bad odour and taste in water.

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

c) Ozonolysis Method:

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

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 lamps 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 purifying 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. Membrane processes are widely used for removal of bacteria, microorganisms, particulates, and natural organic material, which can impart colour, tastes, and odour to water and react with disinfectants to form disinfections 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:

The following various parameters of drinking water quality have been set for public health protection in India.

1. **P^H:** The P^H of drinking water should be between 6.5 and 8.5.
2. **Turbidity:** The maximum turbidity for drinking water is 10 NTU (Nephelometric Turbidity Unit).
3. **Total hardness:** The maximum total hardness for drinking water is 300 ppm as $CaCO_3$.
4. **Calcium:** The maximum calcium content for drinking water is 75 ppm as Ca.
5. **Other parameters:** The maximum levels for other parameters include iron (0.3 ppm), copper (0.05 mg/l), manganese (0.1 ppm), sulfate (250 ppm), fluoride (0.6 to 1.2 ppm) and chloride (250 ppm) .

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.

The three main sources of water are:

- **Groundwater –** This includes water bodies like borewells, tubewells, dug wells, handpumps and springs.
- **Surface water –** This includes different water bodies like sea, oceans, reservoirs, rivers, streams, ponds, lakes and tanks.
- **Rainwater –** Rain is water droplets that have condensed from atmospheric water vapor and then fall under gravity.
  - India's total annual utilisable water resources is 1123 billion cubic metres.
  - 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.
  - 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.
  - 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.
  - Surface water sources such as rivers and wells are the major source of water, used by municipalities for public use. Studies by the Central Water Commission (2015) also show that surface drinking water source rivers in India are loaded with heavy metals such as *lead, arsenic, copper, cadmium, mercury and nickel* that are highly toxic and carcinogenic. Ensuring safe water supply and sanitation is a state responsibility under the Indian Constitution.

UNIT –3

ENGINEERING MATERIALS

Metallurgy

Natural Occurrence of Metals:

Mostly, the metals occur in nature in a combined state but sometimes they can also occur in the free state.

Native metals: The metals which occur in nature in their pure form or uncombined form are called native metals. Such metals have very low reactivity. Examples of native metals are gold (Au), silver (Ag), and platinum (Pt).

Mineral: - The natural material in which the metal or their compounds occur in the earth's crust is known as mineral.

Example: Bauxite ($Al_2O_3.2H_2O$) and Kaolin ($Al_2O_3.2SiO_2.2H_2O$) are the minerals of Aluminium.

Ores: - Ores are the minerals from which the metals concerned can be extracted conveniently and profitably.

Example: Both Bauxite and Kaolin are the minerals of 'Al'. However, 'Al' can be extracted easily and profitably from Bauxite. Thus, Bauxite is an ore of 'Al'. On the other hand, it is difficult and non-profitable to extract 'Al' from Kaolin, thus Kaolin is only a mineral of 'Al'.

All ores are minerals, but all minerals are not ores.

Minerals and Ores of Iron, Aluminium and Copper

Metals	Minerals	Formula
Fe	Haematite Magnetite Limonite	Fe_2O_3 Fe_3O_4 $Fe_2O_3.3H_2O$
Al	Bauxite Cryolite	$Al_2O_3.2H_2O$ Na_3AlF_6
Cu	Copper pyrite Copper glance Cuprite	$CuFeS_2$ Cu_2S Cu_2O

Gangue: The earthly impurities such as sand, mud, clay, etc. contaminated with ores are called gangue or, matrix.

Brief account of General principle of metallurgy:

The process of extraction of metals from ores conveniently and profitably is called metallurgy or metallurgical operation. The following steps are followed during the process of metallurgical operation.

1. ***Crushing and grinding.***
2. ***Concentration or Ore dressing.***
3. ***Oxidation.***
4. ***Reduction.***
5. ***Refining.***

1. **CRUSHING AND GRINDING**:- The ores obtained from mines are in the form of solid rocks. These are first crushed into small pieces with the help of jaw crusher and then grinded into their powder form with the help of stamp mill or ball mill. The powdered form of ore is called pulverized ore.
2. **CONCENTRATION OR ORE DRESSING**: - The process of removal of maximum impurities (gangue or matrix) from the powdered ore is called ore concentration. The method of concentration to be followed depends upon the nature of the impurities present. The following are the different methods of concentration:

   (i) Gravity Separation Method: - This method of concentration is adopted only when there is a gravity difference between the ore and impurities. Normally, Carbonate and oxide ores are heavier than the impurities associated with them and hence they are concentrated by this method. In this method the powdered ores are kept in some containers over a specially designed table called Wilfley table.

The table contains a number of horizontal grooves. The table is kept slightly in an inclined position and is provided with a rocking motion. When water is spread over the ore, lighter impurities are washed away while heavier ore particles get deposited in the grooves, which are finally carried out into the main canal.

(ii) Froth Floatation Method: -

This method is generally used for the concentration of sulphide ores. In this method, two interconnected tanks are used. In one of the tanks, a mixture of oil (pine oil), water and a little quantity of mineral acid is agitated strongly by blowing air through it. Due to the preferential wetting of the sulphide ores by oil than by water, a layer of oil gets covered over the surface of sulphide ores. These sulphide ores become lighter and float over the surface of the mixture, which are carried out into the second container along with the foam formed due to agitation.

(iii) Magnetic Separation method: -

This method of concentration is suitable only when there is a difference in magnetic behavior between the ores and the impurities. Normally, the magnetic ores containing non-magnetic impurities are concentrated by this method. In this method, a belt is tied over two rollers of which one is made of a magnet. Powdered ore is added over the belt through a hopper. The magnetic part of the ore is attracted by the magnetic roller and forms a heap near it. Whereas the non-magnetic part of the ore forms a separate heap a little away from magnetic part.

(iv) Leaching: -

This is a chemical method in which the impure ore is treated with a suitable solvent which dissolves the ore leaving behind the impurities. The solution is filtered, impurities are removed, and the mother liquor is treated with another suitable chemical reagent to get the pure ore.

For example: Impure bauxite ore is treated with dil NaOH solution which dissolves Bauxite to form soluble sodium meta-aluminate.

$$Al_2O_3.2H_2O + 2NaOH \rightarrow 2NaAlO_2 + 3H_2O$$

The solution is filtered to remove the impurities. The solution obtained is diluted with plenty of distilled water when a precipitate of $Al(OH)_3$ is formed.

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

The precipitate obtained is dried and heated strongly to get pure alumina from which aluminium is extracted.

$$2Al(OH)_3 \overset{\Delta}{\rightarrow} Al_2O_3 + 3H_2O$$

3. OXIDATION: - In this step of metallurgical operation, the concentrated ores are converted into their respective metal oxides. This is achieved by the following two methods:

(i) 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,

$$ZnCO_3 \xrightarrow{Calcination} ZnO_{(s)} + CO_{2(g)}$$
$$FeCO_3 \xrightarrow{Calcination} FeO_{(s)} + CO_{2(g)}$$
$$Fe_2O_3.3H_2O \xrightarrow{Calcination} Fe_2O_{3_{(s)}} + 3H_2O$$
$$CuCO_3.Cu(OH)_2 \xrightarrow{Calcination} 2CuO_{(s)} + CO_{2(g)} + H_2O$$

(ii) 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,

$$2ZnS_{(s)} + 3O_{2(g)} \xrightarrow{Roasting} 2ZnO_{(s)} + 2SO_{2(g)}$$
$$4FeS_{2(s)} + 11O_{2(g)} \xrightarrow{Roasting} 2Fe_2O_{3(s)} + 8SO_{2(g)}$$

4. REDUCTION: - In this step of metallurgical operation, the roasted ores are reduced to convert the metal oxides into the respective metals. 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.

$$2HgS_{(s)} + 3O_{2(g)} \xrightarrow{Heat} 2HgO_{(s)} + 2SO_{2(g)}$$

$$2HgO_{(s)} \xrightarrow{Heat} 2Hg_{(l)} + O_{2(g)}$$

(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.

$$ZnO_{(s)} + C_{(s)} \xrightarrow{Heat} Zn_{(s)} + CO_{(g)}$$

$$PbO_{(s)} + C_{(s)} \xrightarrow{Heat} Pb_{(s)} + CO_{(g)}$$

$$Fe_2O_{3(s)} + 3C_{(s)} \xrightarrow{Heat} 2Fe_{(s)} + 3CO_{(g)}$$

Disadvantage of using carbon as reducing agent is that small traces of carbon are added to metal as impurity, which contaminates the metals.

Note:

Flux and Slag:

The metal ores sometimes contain non-fusible impurities. 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.

Solid impurities + Flux → Fusible Slag

Flux is of two types, acidic flux and basic flux.

(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.

$$\underset{Acidic\ Flux}{SiO_2} + \underset{Basic\ impurity}{FeO} \rightarrow \underset{Fusible\ Slag}{FeSiO_3}$$

(b) Basic Flux

If non-fusible impurities are acidic, then basic flux is used.

Example:

$$\underset{Basic\ Flux}{MgCO_3} + \underset{Acidic\ impurity}{SiO_2} \rightarrow \underset{Fusible\ Slag}{MgSiO_3} + CO_2$$

$$\underset{Basic\ Flux}{CaO} + \underset{Acidic\ impurity}{SiO_2} \rightarrow \underset{Fusible\ Slag}{CaSiO_3}$$

Reduction with Carbon Monoxide

Certain metals can be obtained from oxides by reduction with carbon monoxide in the furnace.

$$Fe_2O_{3(s)} + 3CO_{(g)} \xrightarrow{Heat} 2Fe_{(s)} + 3CO_{2(g)}$$

$$CuO_{(s)} + CO \xrightarrow{Heat} Cu + CO_{2(g)}$$
$$PbO_{(s)} + CO \xrightarrow{Heat} Pb + CO_{2(g)}$$

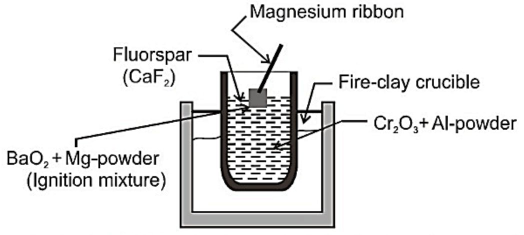
Reduction with Aluminium

Alumino-Thermic Process: This method is used to reduce such metallic oxides (eg. Cr_2O_3, MnO_2) which cannot be reduced by carbon. Here metal oxide is mixed with aluminium powder taken in a crucible and ignited 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 3000 ^{0}C. The oxide is reduced into metal and Al_2O_3 is formed.

$$CrO_3 + 2Al \rightarrow Al_2O_3 + 2Cr + Heat$$

$$3MnO_2 + 4Al \rightarrow 2Al_2O_3 + 3Mn + Heat$$

The impurities are removed as slag by heating the metal with suitable flux.



Reduction of Cr_2O_3 by Al-powder (Aluminothermic process).

(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).

$$\underset{\text{(From molten Alumina)}}{Al^{3+}} \quad + \quad \underset{\text{(From Cathode)}}{3e^-} \quad \xrightarrow{Heat} \quad \underset{\text{(At cathode)}}{Al}$$

Thus, aluminium metal is collected at the cathode.

5. **REFINING:** The metals obtained after reduction still contain some impurities. The process of removal of impurities from crude metal is called refining. The method of refining to be followed depends upon the nature of the metal and the impurity contaminated with it. The following are the methods of refining:
   - **(i)** **Distillation Method**: - This method of refining is suitable for volatile metals like Hg, Zn, Cd contaminated with non-volatile impurities. The impure metal is heated in a distillation flask attached with a water condenser. During heating the volatile metal gets evaporated and condensed which is collected in a separate container while the non-volatile impurities are left at the bottom of the distillation flask.
   - **(ii)** **Electro refining**: - This method is employed to refine the less electropositive metals such as Zn, Pb, Cu, Al, Ag, Au, etc. The impure metal bar is used as anode while a pure metal (same metal) bar is taken as cathode. Both the electrodes are dipped in a suitable aqueous salt solution of the concerned metal.

During the process of electrolysis, the impure metal dissolves in its aqueous salt solution providing metal ions which get discharged and deposited at the cathode.

(iii) **Liquation**: This method is applicable for metals with low melting points such as tin, lead, bismuth, etc. In this method the impure metal is heated and then it flows on a sloped surface. The pure metal will collect at the bottom of the slope while the impurities will remain behind.

(iv) **Poling:** Poling is a method used for metals that have oxidized impurities to purify them. Poling is mainly used to purify metals that are in the impure form like copper or tin of copper oxide or tin oxide. In the poling method a log of wood is taken that is still green and then used to stir the liquid metal. The hydrocarbons of the green wood reduce the metal, and the oxygen leaves as CO_2 gas.

(v) **Vapour-Phase Refining:** In vapour-phase refining, for releasing a metal from impurities, it is first converted into a suitable volatile compound by heating it. And the heating requirements are:

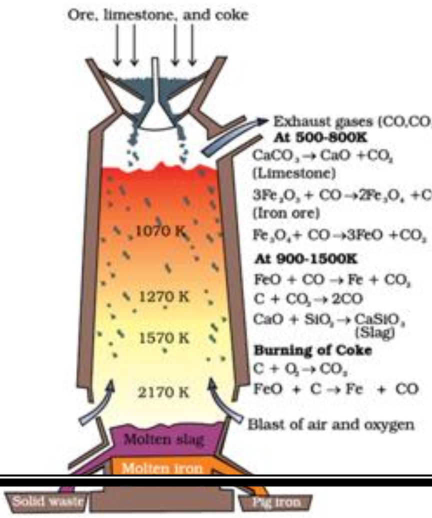
- The metal used for this process should form a volatile compound with a suitable reagent.
- The volatile compound that is to be used should be easily decomposable so that the recovery is easy. $Ni + 4CO \rightarrow Ni(CO)_4 \xrightarrow{Heat} Ni + 4CO$.

(vi) **Zone refining:** It is a special method used to purify metals. In this method, metals are purified to a very high degree. Impure metal rod is placed in a container filled with inert gas. Then a circular heater is placed around the rod at the top for heating the impure metal. And when the heater shifts to the next zone, the pure metal cools and crystallizes. The impurities that are melted will move along with the movement of the heater and shift to the next zone. All these impurities are then collected to the last zone and then it can be separated.

(vii) **Cupellation:** This method is used to purify silver containing lead as impurity. In this method the impure silver is heated in a current of air. The impurity, i.e. lead present in the metal gets oxidized into volatile lead oxide, which leaves the heating apparatus called cupel leaving behind pure silver.

Extraction of iron from haematite ore using blast furnace:

- Iron is extracted from haematite (Fe_2O_3) in a blast furnace.
- Haematite is first crushed, grinded and concentrated to get pure pulverized ore.
- Then, the ore is roasted with coke in a free supply of air.
- The roasted ore along with coke and limestone is then fed into a Blast furnace.
- Blast furnaces have three major zones.



The details of the reactions which take place in various zones are described below:

(1) Base of the furnace *(Zone of Combustion), (1200 – 1500^{0}C):*

Here coke burns with oxygen to form carbon dioxide. The reaction is exothermic, and the temperature rises to about 1500^{0}C.

$$C + \mathrm{O_2} \rightarrow \mathrm{CO_2} + \mathrm{Heat}$$

Carbon dioxide formed reacts with coke to form carbon monoxide and the reaction is endothermic which lowers the temperature to about 1200 – 1300^{0}C.

$$\mathrm{CO_2} + C \rightarrow \mathrm{2CO} - \mathrm{Heat}$$

Fe_2O_3 present undergoes reduction by hot coke to form iron.

$$\mathrm{Fe_2O_3 + 3C \rightarrow 2Fe + 3CO}$$

(2) Middle of the Furnace *(Zone of Slag formation), (800 – 1000^{0}C):*

In this zone of the Blast furnace limestone decomposes to form lime and CO_2. This CaO reacts with impurities (SiO_2) to form fusible slag.

$$CaC\mathrm{O_3} \rightarrow \mathrm{CaO + CO_2}$$
$$CaO + SiO_2 \rightarrow \mathrm{CaSiO_3}(slag)$$

(3) Top of Furnace (Zone of reduction), (400 – 600^{0}C):

In this zone the upcoming CO reduces iron oxide to form spongy iron.

$$\mathrm{3Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2}$$

$$\mathrm{Fe_3O_4 + 4CO(g) \rightarrow 3FeO + 4CO_2}$$

$$\mathrm{FeO + CO \rightarrow Fe + CO_2}$$

The molten iron being heavier collected at the bottom of the Blast furnace while the slag formed being lighter is collected above the molten iron. The iron obtained from the blast furnace contains 4% carbon and many impurities in small amount. This iron is called pig iron.

Extraction of Aluminium for Bauxite ore:

Bauxite is the main ore of aluminium. The extraction of metal is done by electrolytic reduction method. The process is carried out in three steps.

A. Purification of Bauxite
B. Electrolysis of Bauxite
C. Purification of Aluminium

(A) Purification of Bauxite

Bauxite contains about 55% Al_2O_3 along with impurities like Fe_2O_3, SiO_2, TiO_2 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.

a) Hall's process

In this process bauxite ore is powdered and fused with sodium carbonate. Alumina reacts with Na_2CO_3 producing sodium aluminate while Fe_2O_3 and SiO_2 are not affected. This mixture is agitated with water to dissolve the aluminate. The insoluble impurities are removed by filtration.

$$\mathrm{Al_2O_3}.2H_2\mathrm{O} + \mathrm{Na_2}CO_3 \rightarrow 2NaAlO_2 + \mathrm{CO_2} + 2H_2O$$

The solution thus obtained is heated to 50-60 ^{0}C and carbon dioxide is passed. The aluminate is hydrolysed to aluminium hydroxide which is precipitated.

$$NaAl\mathrm{O_2} + C\mathrm{O_2} + 3H_2\mathrm{O} \rightarrow 2Al(OH)_3 + Na_2CO_3$$

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

$$Al(OH)_3 \xrightarrow{1500^0C} \mathrm{Al_2O_3} + \ 3H_2\mathrm{O}$$

b) Bayer's process

When the bauxite ore contains high percentage of Fe_2O_3 impurity, Bayer's process is employed. The crushed ore is roasted to convert FeO, if present, into Fe_2O_3. The roasted ore is treated with a strong solution of caustic soda at 150 ^{0}C and 80 atmospheric pressure for several hours in a closed vessel. Aluminium oxide reacts with alkali forming soluble sodium aluminate complex salt. The impurities remain in the form of precipitate which is filtered.

$$\mathrm{Al_2O_3}.2H_2\mathrm{O} + 2\mathrm{NaOH} \rightarrow 2NaAlO_2 + 3H_2O$$

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 strongly to get pure alumina.

$$NaAl\mathrm{O_2} + 2H_2\mathrm{O} \rightarrow 2Al(OH)_3 + \mathrm{NaOH}$$

$$Al(OH)_3 \xrightarrow{Heat} \mathrm{Al_2O_3} + \ 3H_2\mathrm{O}$$

c) Serpek's process

This process is used to purify bauxite containing high quantity of silica (SiO_2) as impurity. The ore is first powdered. It is then mixed with carbon and the mixture is heated to 1800^{0}C 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 1500^0C to get pure alumina.

$$Al_2O_3 + 3C + N_2 \xrightarrow{1800^0C} 2AlN \;\; + 3CO$$

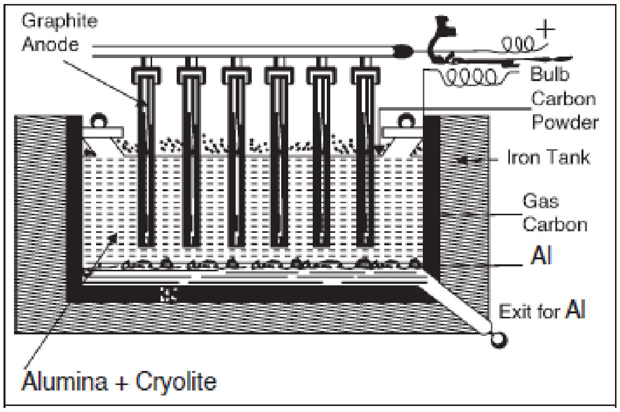
$$AlN + 3H_2O \rightarrow \; Al(OH)_3 + NH_3$$

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

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

(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 2050^0C to only 900^0C. 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 burning of the anodes. When electricity is passed through the electrolytic cell, the following changes take place at different electrodes.



$$Na_3AlF_6 \rightarrow 4NaF + AlF_3$$

AlF_3 undergoes electrolysis as follows:

$$AlF_3 \xrightarrow{Electrolysis} Al^{3+} + 3F^-$$

$$At\ Anode: 6F^- - 6e^- \rightarrow 3F_2$$

$$At\ Cathode: 2Al^{3+} + 6e^- \rightarrow 2Al$$

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.

$$2Al_2O_3 + 14F \rightarrow \; 4AlF_3 + 3O_2$$

The oxygen liberated at anode reacts with the carbon of anode forming CO and CO_2. Thus, the anode gets smaller and smaller. This is checked by the charcoal powder spread over the surface. As more and more Al_2O_3 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%.

Alloys: An alloy is a homogeneous material obtained by mixing metals or metals with non-metals or metals with metalloids.

Types of alloys:

1. **Ferro Alloys:** The alloy containing iron is called a ferro alloy.
   Example: Stainless Steel, Manganese Steel etc.
2. **Non-Ferro Alloy:** The alloy which does not contain iron is called a non-ferro alloy.
   Example: Brass, Bronze, Gun metal etc.
3. **Amalgam:** Alloys containing mercury as one of the constituents is called amalgam.
   Example: Silver Amalgam, Sodium amalgam, Copper amalgam is used for filling dental cavities; Tin amalgam is used for silvering cheap mirrors.

Purpose of alloying:

Alloys are made to:

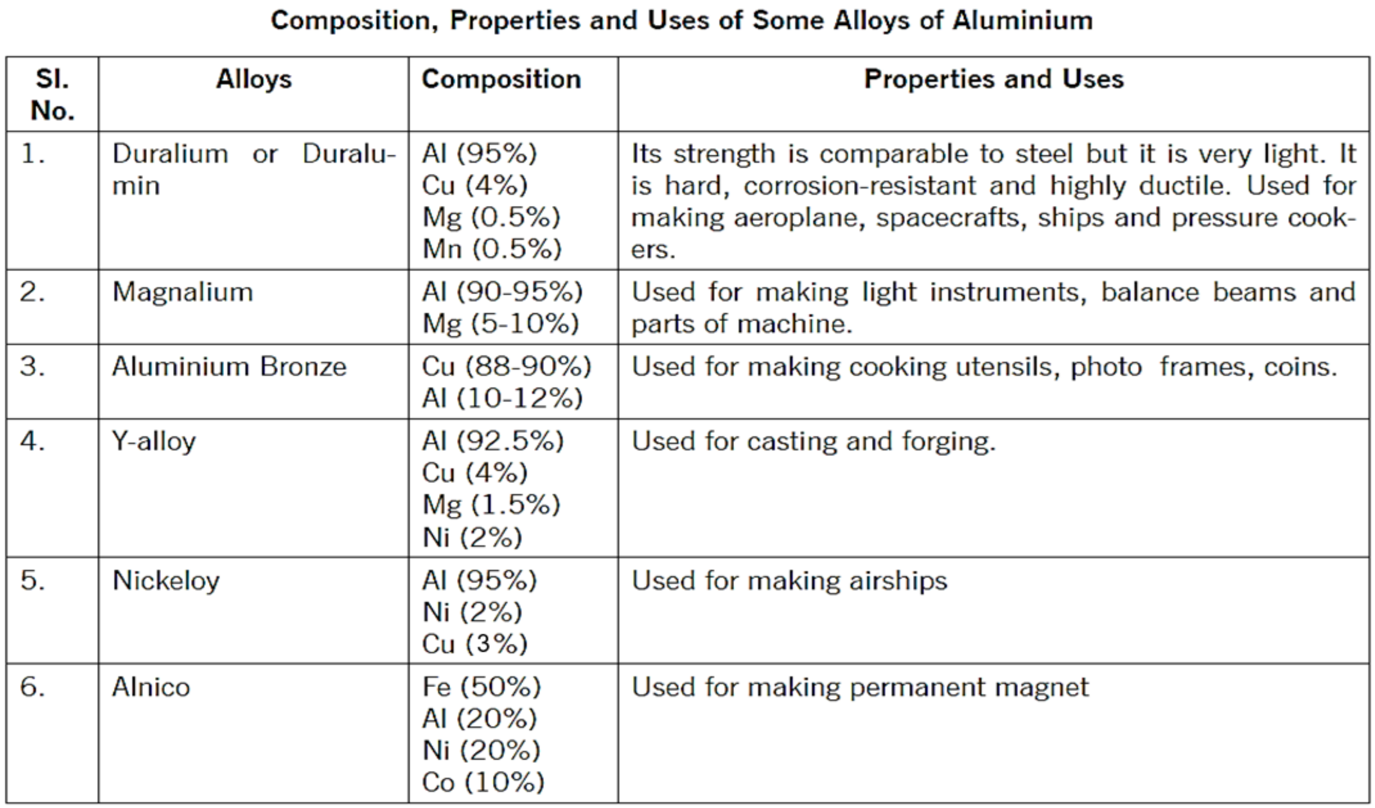
- ☞ **Enhance the hardness of a metal:** An alloy is harder than its components. Pure metals are generally soft. The hardness of a metal can be enhanced by alloying it with another metal or nonmetal.
- ☞ **Lower the melting point:** Pure metals have a high melting point. The melting point lowers when pure metals are alloyed with other metals or nonmetals. This makes the metals easily fusible. This property is utilized to make useful alloys called solders.
- ☞ **Enhance tensile strength:** Alloy formation increases the tensile strength of the parent metal.
- ☞ **Enhance corrosion resistance:** Alloys are more resistant to corrosion than pure metals. Metals in pure form are chemically reactive and can be easily corroded by the surrounding atmospheric gases and moisture. Alloying a metal increases the inertness of the metal, which, in turn, increases corrosion resistance.
- ☞ **Modify colour:** The color of pure metal can be modified by alloying it with other metals or nonmetals containing suitable color pigments.
- ☞ **Provide better cast ability:** One of the most essential requirements of getting good castings is the expansion of the metal on solidification. Pure molten metals undergo contraction on solidification. Metals need to be alloyed to obtain good castings because alloys expand.

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.
7.	Monel metal	Cu 30% Ni 67% Fe+Mn 3%	Pumps and containers for acids, caustic alkali industry
8.	Manganin	Cu 84.2% Ni 12.1% Mn 3.7%	Electrical apparatus
9.	Muntzmetal	Cu 60% Zn 40%	Covering of wooden ships

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 (50%) Al (20%) Ni (20%) Co (10%)	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.
6.	Tungsten steel	Fe (83-78%) W (14%) Cr (3-8%)	For high speed tools.



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 (3%)	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:

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.

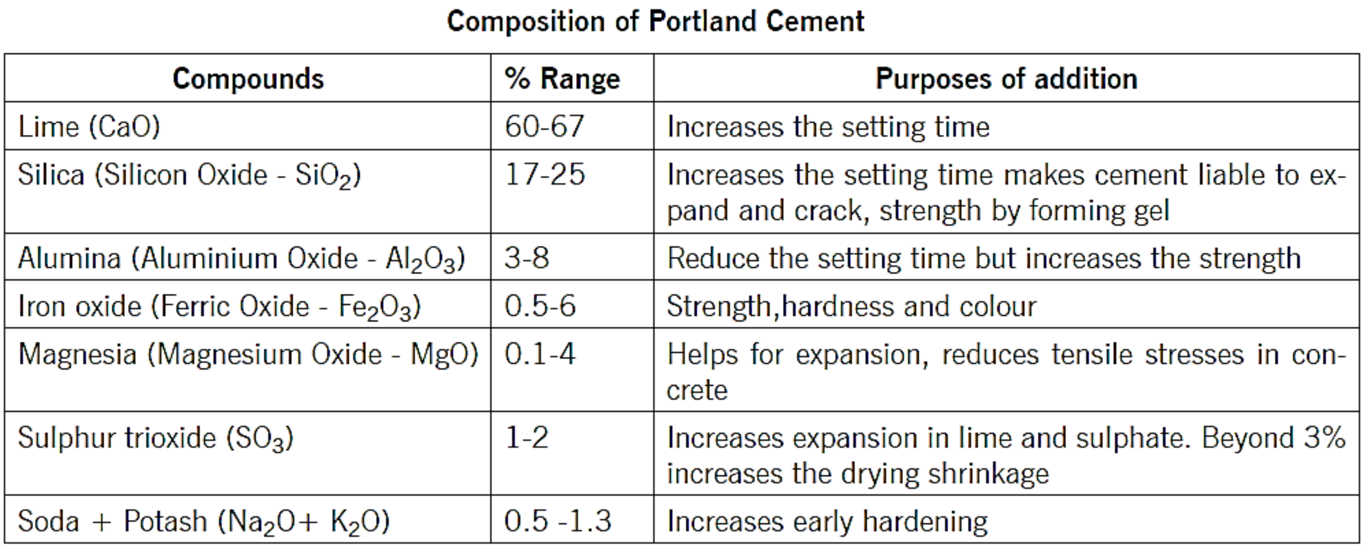
Different types of cement are used for construction purposes. They differ in their composition and are manufactured for various uses. Some different types of cement are portland cement or ordinary portland cement (OPC), quick setting cement (QSC), low heat cement (LHC), sulphate-resisting cement (SRC), 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.

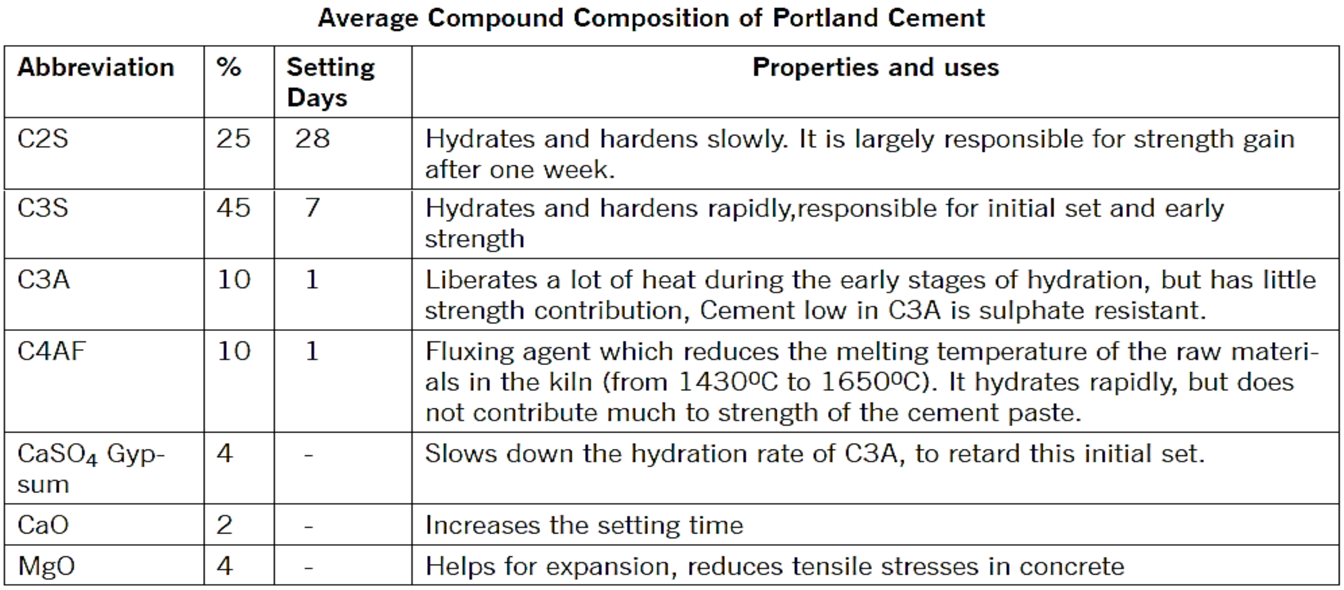
Cement manufactured from chalk and clay which hardens in contact with water and on hardening, resembles Portland stone in colour hence called Portland cement.

Analysis of portland cement gives information about silica, alumina, iron, magnesia, etc., in various proportion.



Composition of Portland 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



Average Compound Composition of Portland Cement

Abbreviation	%	Setting Days	Properties and uses
C2S	25	28	Hydrates and hardens slowly. It is largely responsible for strength gain after one week.
C3S	45	7	Hydrates and hardens rapidly,responsible for initial set and early strength
C3A	10	1	Liberates a lot of heat during the early stages of hydration, but has little strength contribution, Cement low in C3A is sulphate resistant.
C4AF	10	1	Fluxing agent which reduces the melting temperature of the raw materials in the kiln (from 1430ºC to 1650ºC). It hydrates rapidly, but does not contribute much to strength of the cement paste.
$CaSO_4$ Gypsum	4	-	Slows down the hydration rate of C3A, to retard this initial set.
CaO	2	-	Increases the setting time
MgO	4	-	Helps for expansion, reduces tensile stresses in concrete

Legend: C - Calcium oxide (CaO), A- Aluminium oxide (Al2O3), F - Fe2O3, S - SiO2., C2S - Dicalcium silicate, C3S - Tricalcium silicate, C3A - Tricalcium aluminate, C4AF – Tetracalcium alumino ferrite, CaSO4 - Calcium sulphate (Gypsum), MgO - Magnesium oxide.

(B) Hardening of Portland Cement

Setting and hardening of cement is due to the formation of interlocking crystals reinforced by the rigid gel formation by the hydration and hydrolysis of the constitutional compounds.

When cement is mixed with water, it gets rigid within a short period of time. It is called initial set or flash set.

The component responsible for early setting and hardening (initial set) is C3A. The rigidness of the cement paste is due to the hydration of tricalcium aluminate (C3A) and the gel formation of tetra calcium alumino ferrite. The process of setting and hardening of cement is believed to be partly chemical change and somewhat physical. The initial setting time of cement is usually between 30 and 60 minutes. Hydration reaction is responsible for the initial set of cement.

Hydration

(a) $C3S + XH_2O \rightarrow C2S.XH_2O$(gel) +$CaO$(lime)
(b) $C3A + 6H_2O \rightarrow C3A.6H_2O$ (crystals) + heat

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

Role of Gypsum in Cement:
Gypsum plays an important role in cement manufacturing. To prevent flash setting or to increase the initial set time 2 – 3 % gypsum ($CaSO_4.2H_2O$) is added during pulverisation of cement clinker.

$3C3A + xH_2O + y\,CaSO_4.2H_2O \rightarrow 3C3A.yCaSO_4.zH_2O$
(Gypsum) (Tricalcium sulpho aluminate)
(Here, $y = 1 – 3$ and $z = 10 – 33$)

The process of solidification comprises setting and hardening. The setting is defined as stiffening of the original plastic mass due to initial gel formation. Hardening is the development of strength due to crystallisation. After setting, hardening starts due to the gradual process of crystallisation into the interior of the mass. The strength developed by cement paste at any time depends upon the amount of gel formed and the extent of crystallisation.

(C) 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.
- Manufacture of precast pipes, garden seats, artistically designed urns, flowerpots, dustbins, fencing posts, etc.
- Preparation of foundations, watertight floors, footpaths, etc.
- Creating fire-proof structures in the form of concrete, making acid-resistance and waterproof structures.
- Structuring the tunnel or geological walls to strengthen the structure.
- Coloured cement can be used for decorating or colouring the structures.

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. The general formula of glass is $xR_2O.\ yMO.\ 6SiO_2$. Where R = monovalent alkali metals like Na, K and M = bivalent metal atoms like Mg, Ca, Pb, Zn)

(A) Composition of Glass

Glass is made from different materials like Silica, Alumina, Oxides of Iron, Calcium, Magnesium, Sodium, Potassium and sulphur.

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

(B) 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 refract.
- ***Fire Resistant***- Glass protect heat from 200^0C to 800^0C.
- ***Insulation***- It is an excellent insulator against heat, electricity and electromagnetic radiation because of its good insulating response against visible light transmission.
- ***Chemical Resistance***- It can withstand the effect of the chemical reaction under different environment conditions or acidic effects.
- ***Colour and Shape Varieties***- It can be blown, drawn and pressed to any colour, shape, and variety and is available in the market depending upon their use, dimensional requirements, and safety requirement.
- ***Transparency***- The transparency is one such property of glass which creates a visual connect with the outside world. With the advent of technology, clear glass can also be altered, making it opaque.
- ***Property Modification***- It is also possible to modify some of its properties to suit different purposes.

(C) Applications of Different types of Glasses

Types of Glasses	Uses
Soda-lime glass or soft glass	Window glass, electric bulbs, plate glass, bottles, jars, test tubes, and reagent bottles
Potash lime glass	Chemical apparatus, combustion tubes, and glassware used for heating operations
Lead glass	High-quality tableware, optical lenses, neon sign tubing, cathode ray tubes, electrical insulation windows, and shields for protection against X-rays, gamma rays, medical and atomic energy fields
Borosilicate glass	Corrosive liquids, superior chemistry laboratory apparatus, kitchen wares, chemical plants, television tubes, electrical insulation
Alumino-silicate glass	High-pressure mercury discharge tubes, chemical combustion tubes and domestic equipment
Silica glass	Chemical plants, laboratory crucibles, induction furnace lining and electrical insulators
Alkali-free glass	Thermal insulating material e.g. Glass wool, filtration of corrosive chemicals and sound insulation.

Refractory

Refractories are materials that can withstand very high temperatures (above 1000°F or 538°C) and retain their structural integrity and strength. These do not fuse or undergo deformation in shape, while remaining in contact with molten slag, metal and gases. Refractories serve two purposes thermal insulation and conduction.

(A) Composition of Refractories

Refractories are produced from natural and synthetic materials, usually non-metallic such as alumina, fireclays, bauxite, chromite, dolomite, magnesite, silicon carbide, and zirconia.

(B) Classification of refractories:

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

1. **Acid refractories:** These are silica, fireclay, alumina and aluminium silica. These are acid resistant.
2. **Basic refractories:** These are magnesia, bauxite and Dolomite. These are alkali resistant.
3. **Neutral refractories:** These are Chrome, chrome-magnesite and forsterite. These can resist both acids and alkalis.

(C) Properties of good refractories: A good refractory should have the following properties.

- It should be able to withstand sudden alternating heating and cooling, thermal shocks.
- It should be able to withstand high temperatures generated in the furnace.
- It should have good heat insulating properties.
- If used in electric furnaces, it must have low electrical conductivity
- It should be able to withstand abrasion and rough usage.

- ➢ It should be chemically inactive at elevated temperatures.

(D) Applications of Refractories

- ☞ furnaces,
- ☞ nuclear reactors,
- ☞ jet engine, boilers,
- ☞ electrolytic cell for aluminium production etc.

Composite Materials

Composite materials are the materials obtained from two or more constituent materials with significantly different physical or chemical properties. When combined, these materials produce a material with characteristics different from the individual components.

A composite material is made up of two components, one is matrix and the other is reinforcement of fibre.

Types of Composite Materials:

1. Fiber-reinforced polymers (FRP): Combine fibres (e.g., carbon, glass) with a polymer matrix.
2. Ceramic matrix composites (CMC): Combine ceramic fibres or particles with a ceramic matrix.
3. Metal matrix composites (MMC): Combine metal fibres or particles with a metal matrix.
4. Hybrid composites: Combine different types of fibres or matrices.

Properties of Composite Materials:

1. High strength-to-weight ratio
2. Improved stiffness and toughness
3. Enhanced thermal and electrical properties
4. Resistance to corrosion and fatigue
5. Tailorable properties through design and material selection

Examples of Composite Materials:

Fiberglass*:* A composite of glass fibres woven into a cloth and bonded with a plastic or resin. Fiberglass is used in many applications, including bathtubs, doors, decking, and window frames.

Concrete*:* A composite of cement and aggregate.

Mud bricks*:* A composite of mud and straw. The ancient Egyptians used mud bricks, and developing countries still use them today.

Wood*:* A composite of long cellulose fibres held together by lignin. Engineered wood, like plywood, is made by cutting weaker woods into thin pieces and gluing them together.

High Density Polyethylene (HDPE)*:* A durable and strong composite material made from recycled milk jugs and laundry detergent bottles. HDPE is resistant to moisture, insects, and rot.

Bakelite*:* It is a condensation co-polymer of phenol and formaldehyde. It is used in making electric al insulating parts like switches, plugs, etc. also it is used in making telephone parts.

Machine tool cutting tips*:* Made from a cermet, a combination of ceramic and metal.

Benefits of Composite Materials:

1. Weight reduction
2. Increased performance
3. Improved safety
4. Reduced maintenance

5. Extended lifespan

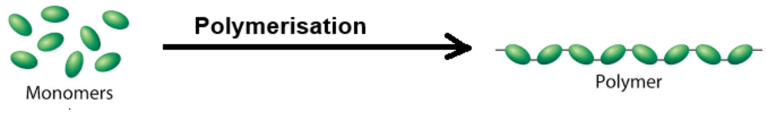
Applications of Composites

As composite materials are light in weight with high strength, they are used

- In the aerospace industry to prepare aircraft.
- in the preparation of automobile parts.
- for medical assistance devices.
- for the preparation of long tennis and hockey sticks.

Polymers

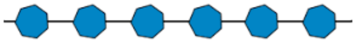
Polymerisation: The chemical process in which a large no of smaller molecular units is joined together to get a bigger unit of high molecular weight is called polymerisation.



Monomers: The single units that undergo repeated addition forming a polymer are called monomers.
Examples: Ethene is the monomer of polythene, vinyl chloride is the monomer of PVC.

Polymer: The bigger unit of high molecular weight obtained due to the polymerisation of monomer units is called a polymer.
Examples: Polythene, PVC, Teflon, Polystyrene, Terylene, Nylon, Bakelite, etc.

Homopolymer: The polymer containing monomer units of the same chemical composition is called a homopolymer.
Examples: Polythene, PVC, Teflon, Polystyrene, etc.



Homopolymers

Copolymer: The polymer containing monomer units of different chemical compositions is called a Copolymer.
Examples: Bakelite, Terylene, Nylon, Buna-S, Buna-N, etc.

Copolymers

Degree of polymerisation: The total no of monomer units present in a polymer is called degree of polymerisation or it is the ratio of the average molecular weight of polymer to the weight of monomer.

$$Degree\ of\ Polymerisation\ (DP) = \frac{Average\ molecular\ weight\ of\ polymer}{molecular\ weight\ of\ monomer}$$

Classification of Polymers:

Polymers may be classified as thermoplastic and thermosetting plastics.

Thermoplastics: These are the polymers obtained by addition polymerisation. In this type of polymerisation, the monomer units are simply get added with each other without elimination of any simple molecules. Examples: Polythene, Polystyrene, Teflon, etc.

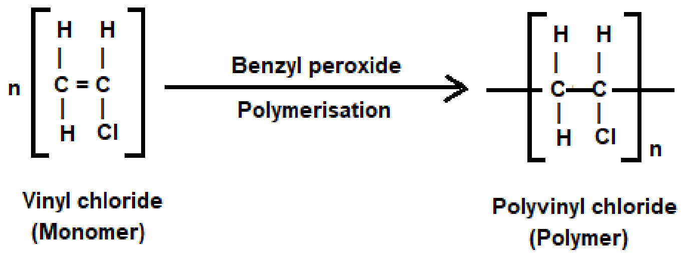
Thermosetting plastics: These are the polymers obtained by condensation polymerisation. In this type of polymerisation, the monomer units are added with each other with the elimination of simple molecules such as HCl, H_2O, NH_3, etc. Examples: Terylene, Nylon, Bakelite, etc.

Distinction between Thermoplastics & Thermosetting.

	Thermoplastics	Thermosetting
1	These are formed by addition polymerization.	These are formed by condensation polymerization.
2	These are generally linear polymers.	These are three dimensional cross-linked polymers.
3	These are soft.	These are hard and rigid.
4	These are soluble in some solvents.	These are insoluble in any solvent.
5	These become soft on heating and become hard on cooling.	These burn to char on prolong heating.
6	These can be remoulded, reshaped and recycled.	These cannot be remoulded, reshaped and cannot be recycled.
7	Examples: Polythene, PVC, Nylon, etc.	Examples: Bakelite, Urea-formaldehyde resin, Terylene, etc.

Preparation and uses of Thermoplastics:

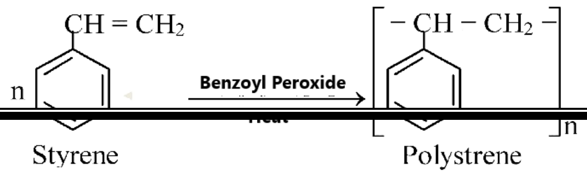
1. **Polyvinyl chloride (PVC):** PVC is obtained by the polymerization of Vinyl chloride in presence of benzyl peroxide under pressure.



Uses: It is used for making:

- Sheets for tank lining
- Safely helmets.
- Credit cards
- Refrigerator components
- Tyres, cycle and motorcycle mudguards
- Raincoat
- Tablecloths
- Electrical insulators
- Chemical containers, etc.

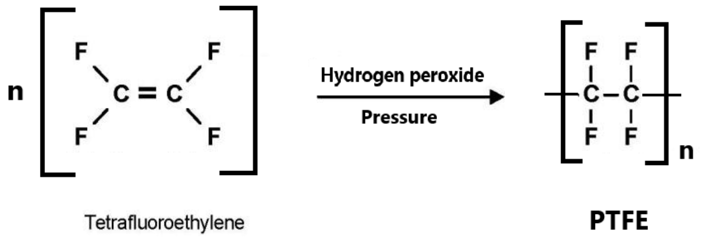
2. **Polystyrene (PS):** Polystyrene is obtained by the polymerization of styrene in the presence of benzoyl peroxide.



Uses: It is used for making:

- Food packaging, household appliances,
- consumer electronics products,
- building and construction,
- insulation foam, panels,
- bath and shower units,
- lighting, and plumbing fixtures.
- Medical items include tissue culture trays, test tubes, petri dishes, diagnostic components, etc.

3. **Teflon (Polytetrafluoroethylene or PTFE):** Teflon is obtained by the polymerization of styrene in presence of hydrogen peroxide under high pressure.

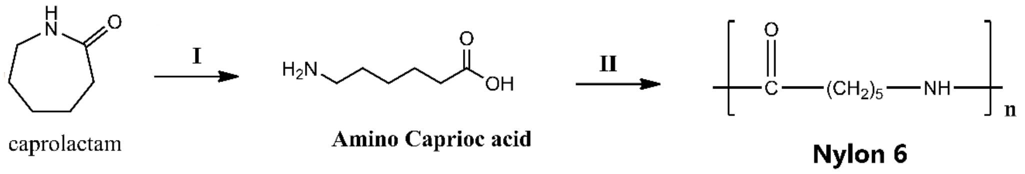


Uses: It is used for making:

- Non-stick cookware,
- Chemical containers and pipes
- High frequency electrical insulators like switch, plug, etc.
- dental industry for filling, etc.

Preparation and uses of Thermosetting plastics:

1. **Nylon-6:** Nylon 6 is synthesized by ring-opening polymerization of caprolactam. When caprolactam is heated at about 533 K in an inert atmosphere of nitrogen for about 4–5 hours, the ring breaks and undergoes polymerization.

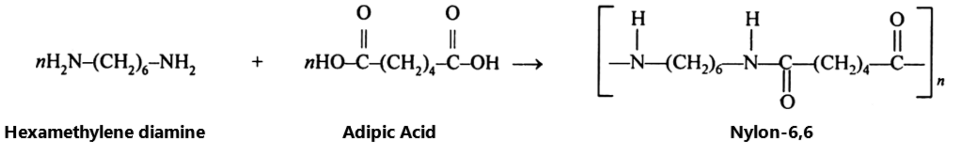


Uses: It is used for making:

- Bristles of toothbrushes,
- Surgical sutures,

- threads, rope,
- nets,
- knitted garments, etc.

2. **Nylon - 6,6:** Nylon-6,6 is prepared by condensation polymerization of hexamethylene diamine with adipic acid at high temperature and pressure.

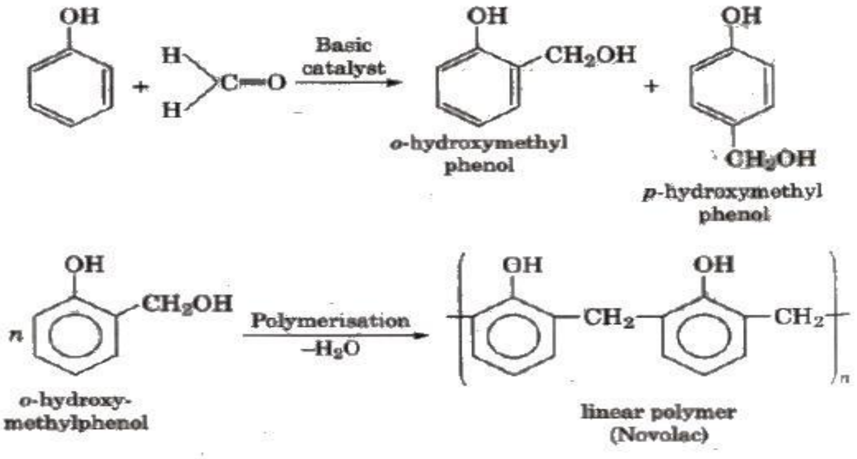


$$n\,H_2N\text{–}(CH_2)_6\text{–}NH_2 + n\,HO\text{–}\overset{O}{\overset{\|}{C}}\text{–}(CH_2)_4\text{–}\overset{O}{\overset{\|}{C}}\text{–}OH \longrightarrow \left[\text{–}\overset{H}{\overset{|}{N}}\text{–}(CH_2)_6\text{–}\overset{H}{\overset{|}{N}}\text{–}\underset{O}{\underset{\|}{C}}\text{–}(CH_2)_4\text{–}\overset{O}{\overset{\|}{C}}\text{–}\right]_n$$

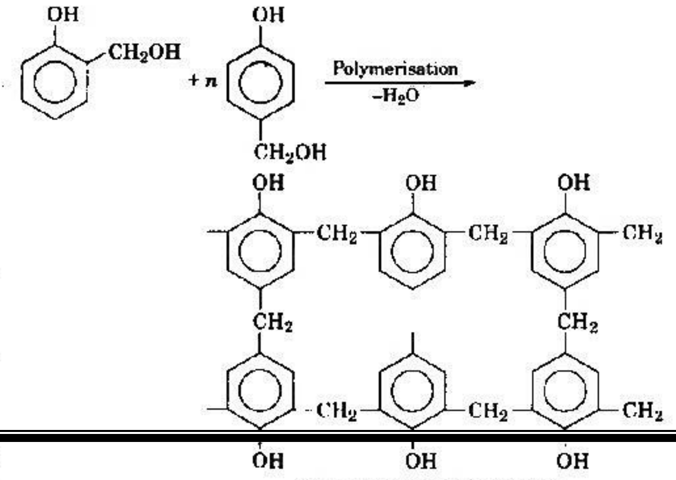
Uses: It is used for making:

- Airbags,
- tyres,
- ropes,
- conveyor belts,
- parachutes,
- swimwear, etc.

3. **Bakelite (Phenol-Formaldehyde Resin):** It is obtained by the polymerization of *phenol and formaldehyde*. When phenol and formaldehyde are reacted together two isomeric compounds *O-hydroxy methylphenol and P-hydroxy methylphenol are obtained.*



The orthohydroxymethylphenol thus formed undergoes polymerization with phenol to form a linear polymer compound called **"NOVOLAC"**. During the process of polymerization, a little quantity of hexamethylene tetraamine *[$(CH_2)_6N_4$]* is added which converts 'novolac' into a hard resinous mass ***called Bakelite.***



cross linked polymer (bakelite)

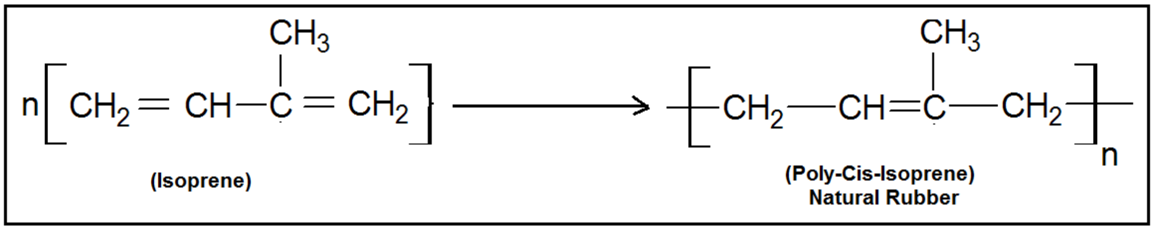
Uses: *It is used in the manufacture of:*

1. *Electrical insulators like plug, switch etc.*
2. *Cabinets for Radio and TV*
3. *Telephone parts*
4. *Paints, varnishes*
5. *Hydrogen exchange resin for softening of hard water.*

Rubber:

Rubber is a substance 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.

Natural rubber consists of "***isoprene***" as the monomer units, which is in the form of the polymer poly cis-isoprene. Thus, natural rubber is nothing but the polymer ***poly cis isoprene*.**



$$n\left[CH_2=CH-\overset{CH_3}{\overset{|}{C}}=CH_2\right] \longrightarrow \left[CH_2-CH=\overset{CH_3}{\overset{|}{C}}-CH_2\right]_n$$

Draw backs of natural rubber:

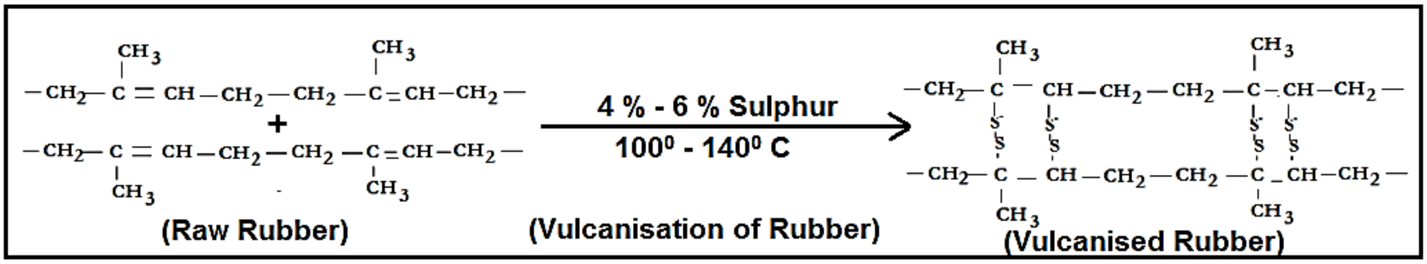
Natural rubber or raw rubber has the following drawbacks:

1. *It has very low thermal stability*
2. *It has very low tensile strength*
3. *It has high water absorption capacity.*
4. *It is attacked by atmospheric oxygen and ozone.*
5. *It is attacked by acids and alkalis.*
6. *It has the property of tackiness.*

Vulcanization of rubber:

Natural rubber is a thermoplastic. There are no cross links between the polymer chains. It becomes soft and sticky when heated. It is not hard and tough. The properties of natural rubber can be modified and improved by the process of vulcanization. To improve the properties of natural rubber, it is heated with sulphur or sulphur containing compounds at a temperature of *100^0 -140^0C.*

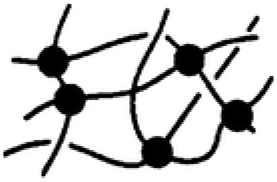
The chemical process in which natural rubber is heated with 4% to 6% sulphur or sulphur containing compounds at 100^0 – 140^0C with a view to overcome the drawbacks of natural rubber is called vulcanization.



During vulcanizationsulphur cross-links are formed in between the layers of polyisoprene at the carbon atoms containing double bond.

The formation of cross links makes *rubber hard, tough with greater tensile strength*. Although natural rubber is thermoplastic substance, yet on vulcanization, it is set into a given shape which is retained.

Raw Rubber



Vulcanized Rubber

Advantages of Vulcanization:

After vulcanization, almost all the drawbacks of raw rubber are eliminated. Vulcanized rubber:

i. has higher thermal stability
ii. has comparatively lower tensile strength
iii. has low water absorption capacity.
iv. is not attacked by atmospheric oxygen and ozone.
v. is resistant to acids and alkalis.

UNIT - 4

CHEMISTRY OF FUELS AND LUBRICANTS

Fuel: Fuel is a combustible substance, containing carbon as the 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, petrol, diesel, kerosene, liquefied petroleum gas (LPG), Compressed natural gas (CNG), 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.

$$Fuel + Oxygen \rightarrow Product/s \ + \ Heat$$

$$C + O_2 \rightarrow CO_2 \ + 94.1 \ Kcal/mol$$

These new compounds have less energy and, therefore the energy released during the combustion process is the difference in the energy of reactants and that of the product formed.

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

Classification of fuel:

A. On the basis of their occurrence, fuels may be classified into two categories: -

1. **Natural Fuels:** Such fuels are found in nature. Ex-Wood, coal, petroleum, natural gas etc.
2. **Artificial Fuels:** Such fuels are prepared from natural fuels. Ex-Coke, kerosene, petrol, water gas, producer gas etc.

B. Based on their physical state, fuels may be classified into three categories:

1. **Solid Fuels**: Fuels which are found in their solid state at room temperature are generally referred to as Solid Fuels. *Ex-Wood, coal, charcoal, straw etc.*
2. **Liquid Fuels:** Most liquid fuels are derived from the fossilized remains of dead plants and animals by exposure to heat and pressure in the Earth's crust. *Ex-Petroleum, Kerosene, Petrol, Diesel, alcohol etc.*
3. **Gaseous Fuels:** Most gaseous fuels are composed of hydrocarbons, carbon monoxide, hydrogen, or a mixture of them all. *Ex- Natural gas, Coal gas, Producer Gas, Water Gas, Hydrogen etc.*

Calorific value of fuel:

Calorific value may be defined as "the amount of heat energy produced by the complete combustion of a unit mass or unit volume of fuel in air or oxygen."

Units of Calorific value are: Cal/gm, Kcal/Kg, KJ/Kg, B.Th.U/lb (British Thermal Unit/pound) etc.

(A) Higher Calorific Value (HCV) or Gross Calorific Value

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 15^0C.

(B) Lower Calorific Value (LCV) or Net Calorific Value

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.

$$LCV = HCV - Latent\ heat\ of\ vapourisation\ of\ water$$

Calculation of HCV and LCV using Dulong's formula.

The calorific value of fuel can be approximately computed by noting the amounts of the fuel constituents. The higher calorific values of some of the chief combustible constituents of fuel are given below.

Constituents	Hydrogen	Carbon	Sulphur
HCV (Kcal/Kg)	34500	8080	2240

The oxygen is present in the fuel and is assumed to be present in a combined form with hydrogen, i.e., fixed hydrogen [H_2O].
So, the amount of H available for combustion = Total mass of H in fuel – fixed H
Since 8 part of oxygen combines with one part of hydrogen to form H_2O
Hence, the amount of H available for combustion = Total mass of hydrogen in fuel $-\frac{1}{8}$ mass of oxygen in the fuel.
Dulong's formula for higher calorific values (HCV) from the chemical composition of fuel is:

$$\boldsymbol{HCV = \frac{1}{100}\left[8080C + 34500\left(H - \frac{O}{8}\right) + 2240S\right] Kcal/Kg}$$

Where C, H, O and S are the percentage of carbon, hydrogen, oxygen and sulphur in the fuel, respectively. In this formula, oxygen is assumed to be present in combustion with hydrogen as water, this is based on the fact that one part of H by mass gives nine parts of H_2O.

LCV = HCV – Latent heat of condensation of the water vapour produced
= HCV (Mass of H per unit weight of the fuel burnt × 9 × latent heat of vaporisation of water)
The Latent heat of steam is 587 Kcal/kg.
Dulong's formula for lower calorific values (LCV) from the chemical composition of fuel is:

$$\boldsymbol{LCV = \left[HCV - \frac{H}{100} 9 \times 587\right] Kcal/Kg}$$

$$\boldsymbol{LCV = [HCV - 0.09H \times 587] Kcal/Kg}$$

Where H = % of hydrogen in the fuel.
In actual practical use of fuel, it is rarely feasible to cool the combustion products to room temperature to allow the combustion of water vapour formed and utilise that latent heat. Hence the water vapour created also is allowed to escape along with the hot combustion gases.

Q 1. A sample of coal has the following composition by mass: C = 85% H = 6% O=8%, S = 0.5% and Ash=0.5%. Calculate HCV and LCV using Dulong's Formula. Give Atomic weights: (C = 12 H = 1 S = 32 O = 16) .
Ans:

Dulong's formula for higher calorific values (HCV) from the chemical composition of fuel is:

$$HCV = \frac{1}{100}\left[8080C + 34500\left(H - \frac{O}{8}\right) + 2240S\right] Kcal/Kg$$

$$= \frac{1}{100}\left[8080 \times 85 + 34500\left(6 - \frac{8}{8}\right) + 2240 \times 0.5\right] Kcal/Kg$$

$$= \frac{1}{100}[686800 + 207000 + 1120] Kcal/Kg$$

$$= 8949.2 Kcal/Kg$$

Proximate Analysis of Coal (Solid Fuel)

The composition of coal depends upon the mines from which it is extracted. 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:** About 1 g of finely powdered air-dried coal sample is taken in a silica crucible with a lid. The crucible is placed inside the electric hot-air oven, maintained between 105^0C - 110^0C. 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:

$$\%\ of\ Moisture = \frac{loss\ in\ weight\ of\ coal}{weight\ of\ coal\ taken} \times 100$$

Moisture increases the transport cost and also reduces the effective calorific values of coal. Much amount of heat is wasted in evaporating the moisture available in coal during combustion. The lesser the moisture content, the better is the quality of coal as fuel.

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 925^0C. 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. By knowing the weight of volatile matter removed from coal, its percentage can be calculated as:

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

Volatile matter is not a constituent of coal but consists of a complex mixture of gaseous and liquid products resulting from the thermal decomposition of the coal substance. Hence, stipulated conditions should be followed during its determination. The greater the volatile matter lowers the calorific value, and the lesser the volatile matter, the better is the rank of coal.

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 750^0C for half an 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.

The residue produced is reported as ash on percentage basis. By knowing the weight of ash formed, its percentage can be calculated as:

$$\% \ of \ Ash = \frac{weight \ of \ ash \ left}{weight \ of \ coal \ taken} \times 100$$

Ash is useless, non-combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hinderance to the flow of air and heat, thereby lowering the temperature. The presence of ash also increases transporting, handling and storage costs. It also involves additional cost in ash disposal. Hence, the formation of ash by burning coal is undesirable. The lower the ash content, the better is the quality of coal.

4. **Determination of fixed Carbon:** It is determined indirectly by deducting the total of percentage of moisture, volatile matter and ash from 100. It gives the percentage of fixed carbon.

$$\% \ \boldsymbol{of \ fixed \ Carbon = 100} - (\% \ \boldsymbol{of \ moisture} + \% \ \boldsymbol{of \ volatile \ matter} + \% \ \boldsymbol{of \ ash})$$

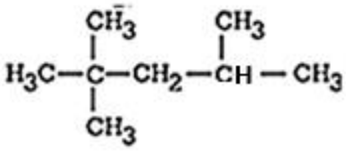
Higher the percentage of fixed carbon, greater is its calorific and better the quality of coal. Greater the percentage of fixed carbon, smaller is the percentage of volatile matter. Hence high percentage of fixed carbon is desirable.

Knocking: Knocking is the sharp metallic sounds in an internal-combustion engine which is caused by premature combustion of part of the compressed air-fuel mixture in the cylinder. Knocking damages the engine and reduces the efficiency of the engine.

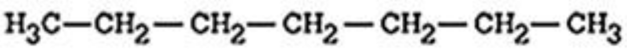
Fuel rating of Petrol and Diesel (Octane number and Cetane number)

Octane number: The octane number of gasoline is percentage of iso-octane in a mixture iso-octane and n-heptane which has the same knocking characteristics as that of the test fuel under similar experimental condition.

It has been found that n-heptane knocks very badly, its anti-knock value has arbitrary been given zero and iso-octane gives very little knocking, so its anti-knock value has been given as 100.


$H_3C-C(CH_3)_2-CH_2-CH(CH_3)-CH_3$

iso-octane
Octane No. =100

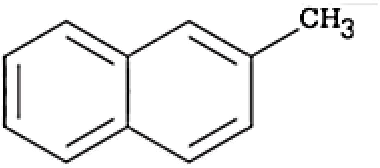

$H_3C-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3$

n-heptane
Octane No. = 0

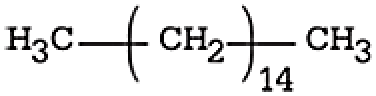
Fuel of octane number 80 and fuel mixture of 80% iso octane and 20% n-heptane produces same amount of knock. The higher the octane number lesser is the knocking. The octane number of gasolines may be increased by the addition of fuels of higher knock value. The anti-knock properties of gasoline are usually enhanced by adding tetra ethyl lead (TEL) [$Pb(C_2H_5)_4$] and the process is called doping. The addition of a small amount of TEL to a gasoline of low anti-knock values usually increases the octane number to a very considerable extent. About 0.5mL of tetra ethyl lead per litre is added for motor spirits and about 1 mL TEL per litre is generally added to aviation petrol.

Cetane Number: The knocking characteristics of diesel oil are expressed in terms of cetane number. Cetane[$C_{16}H_{34}$] is a saturated hydrocarbon with a very short ignition lag than any commercial diesel fuel. Hence its cetane rating is taken as 100. On the other hand, α-methyl naphthalene [$C_{11}H_{10}$], an aromatic hydrocarbon has very long ignition lag as compared to any commercial diesel oil. Hence, the cetane rating is taken as zero.

Cetane number of a diesel fuel is the percentage by volume of cetane in a mixture of cetane and liquid alpha-methylnaphthalene, which exactly matches its knocking characteristics with diesel oil under test.



α methyl naphthalene
(Cetane No.=0)



Cetane or n-Hexadecane
(Cetane No.=100)

The higher the cetane number, the better is the quality of the fuel. The cetane number of diesel oil can be improved by adding substances called dopes. For example, ethyl nitrile, ethyl nitrate, isoamyl nitrate and acetone peroxide can be used as dopes. The dopes are added only in small amounts, and they are not effective on low cetane number fuels.

In petrol engines knocking is due to the spontaneous combustion of the last portions of the fuel, whereas knocking in a diesel engine is due to delay in the spontaneous combustion of the first part of the fuel. Thus, oil of high octane number has low cetane number and vice- versa. Furthermore, crude oil which gives petrol of high octane number gives a diesel oil of low cetane number.

Chemical Composition, Calorific Values and Applications of Fuels:

SN	Fuel	Chemical Composition	Calorific Value	Applications
1	Liquefied Petroleum Gas (LPG)	Propane, n-butane, isobutane, propylene, butylene, small quantity of ethane, pentane, ethylene and pentene may also be present.	11,850 Kcal/Kg	Domestic fuel, industrial fuel, heating appliances and vehicles, motor fuel in internal combustion engine (IC-engine)
2	Compressed Natural Gas (CNG)	Methane – 95% Ethane and Nitrogen – 4% Propane and Carbon monoxide – 1%	12,600 Kcal/Kg	Automotive Fuel
3	Water Gas (Blue Gas)	Carbon monoxide and Hydrogen	2670 Kcal/m^3	Synthesis of Ammonia, methyl alcohol, illuminating gas, heating and lighting purpose, welding purpose.
4	Coal Gas	Hydrogen, Methane, Ethylene, Acetylene, Carbon monoxide and Nitrogen	4500 Kcal/m^3	Lighting, heating, fuel for cooking, illuminant.
5	Producer Gas	Carbon monoxide and Nitrogen	1300 Kcal/m^3	Heating open hearth furnace, muffle furnace, reducing agent in metallurgical operation.
6	Biogas	Methane, Carbon dioxide,	5300 Kcal/m^3	Domestic fuel, lighting, water pumps,

		Hydrogen and Nitrogen		cutting machines.

Lubrication:

Lubricants are the substances applied in between the sliding/rolling surfaces with a view to reduce the frictional resistance between them.

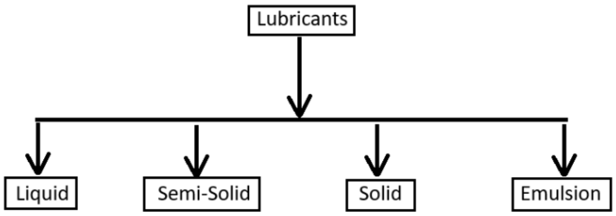
Lubrication is crucial for machinery, reducing friction, wear, and heat, thus extending equipment lifespan and improving efficiency.

Functions of Lubricants:

The main functions of lubricants are as follows:

1. It reduces friction in machines.
2. It reduces wearing and tearing of machinery parts.
3. It reduces loss of energy.
4. It reduces noise pollution.
5. It reduces the expansion of metals.
6. It increases the efficiency of engines.
7. It enhances the durability of machinery parts.
8. It acts as a coolant by removing frictional heat.
9. It prevents foreign material penetration, rust, and corrosion.
10. It reduces maintenance costs.
11. It reduces power loss in IC engines.

Classification of Lubricants



Liquid Lubricants, classification and Properties

Liquid lubricants are classified into three categories i.e.

(1) Natural or animal or Vegetable oil

(2) Mineral or Petroleum oil

(3) Synthetic or Blended oil.

Liquid Lubricants: Classification and Properties

Type of Liquid Lubricant	Examples	Composition and Properties
Natural/Vegetable/Animal 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.	➢ Animal oils contain saturated fatty acids and monounsaturated fatty acids, ➢ Vegetable oils contain polyunsaturated fatty acids and oleic acids. ➢ Unstable in oxidative and thermal environment. ➢ Costly, undergo easy oxidation to give gummy products and hydrolyze easily on contact with moist air or water. Hence, it is rarely used as blending agents in petroleum-based lubricants to get improved oiliness.
Mineral Oil 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 -6^0C to -60^0C. ➢ Lower flash may provide sludge and vamish deposits.
Synthetic or Blended Oil	Hydrocarbons produced by polymerization. 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 to .50'C. ➢ Higher flash point to non-flammable. ➢ Generally free of sludge and varnish deposits. They are of two types a) Chemically active additives-e.g. detergents. Anti-wear agent, dispersant, oxidation inhibitors. b) 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. The thickeners may be special soaps of Li, Na, Ca, Ba, Al etc.

Non soap thickeners include carbon black, silica gel, polyurea 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.

Types of Semi Solid Lubricants	Properties	Uses
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^{0}C	➢ When a machine works at slow speeds and high pressures. ➢ Where spilling or spurting oil from the bearings is detrimental to the product being manufactured, for example in textile mills, paper and food product manufacture. ➢ Where oil cannot be maintained in position due to bad seal. ➢ Where the bearing has to be sealed against entry of dirt, water, dust and grit.
Lithium Based	Lithium soaps are emulsifying with petroleum oil. They are water resistant and used up to 15^{0}C.	
Calcium Based	Calcium soaps are emulsifying with petroleum oil. They are water resistant and used up to 80^{0}C.	

Solid Lubricants: Classifications and Properties:

A solid lubricant is a material that separates two moving surfaces under boundary conditions and decreases the amount of wear. Graphite, molybdenum disulphide (MoS_2), 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 high temperature (around 450°C) condition.
- **Molybdenum disulphide (MoS_2):** It is sandwich-like structure in which hexagonal layer of molybdenum (Mo) lies between two hexagonal layers of sulfur (S) atom. Like graphite the layers are held together with weak Vander Waals forces. It is stable up to 400^{0}C. It is used in high vacuum. It adheres even more strongly to the metal or other surfaces.

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 continuous adherent film on the rubbing surfaces and reduce the wear. Example: Metals and plastics are characterized 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 defense programs 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.

MECHANISM OF LUBRICATION:

Sl.No	Thick film/Fluid film/ Hydrodynamic Lubrication	Thin film/ Boundary Lubrication
1	The lubricating oil forms a uniform film of a thickness of more than 10,000 A^0 in between two moving or sliding surfaces.	The lubricating oil forms a uniform film of a thickness of about 1,000 A^0 in between two moving or sliding surfaces.
2	Hydrocarbon oils of lower molecular weight with about 12 to 50 carbon atoms are considered to be satisfactory lubricants for thick-film lubrication.	Vegetable oil, animal oil and mineral oil are suitable for this type of lubrication. Graphite and molybdenum disulphide are also suitable for thin film lubrication.
3	In this case, the coefficient of friction ranges from 0.001 to 0.03.	In this case, the coefficient of friction ranges from 0.05 to 0.15.
4	The lubrication should have minimum viscosity.	The lubricant should have more oiliness.
5	The lubricant neither gets adsorbed on nor chemically reacts with a metallic surface.	The lubricants may be absorbed on or chemically reacts with metallic surfaces
6	This lubrication is used in machines working under light load and at high speed.	This lubrication is used in machines working under heavy load and slow speed.
7	Useful in delicate and light machines like watches, clocks, guns, scientific equipment.	Useful in Bearing, gears, tractor rollers, lathes, railway track joints, concrete mixture etc.

Physical Properties of Lubricants:

1. **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. 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. 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. 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.

2. **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. Hence, a lubricant should have high viscosity index.

Viscosity Index Improvers (VII) or Viscosity Modifiers (VM)

Viscosity Index Improvers, or Viscosity Modifiers influence the viscosity temperature trend. VIIs are polymers with a variable molecular weight belonging to the following main categories:

- Hydrogenated ethylene-propylene copolymers (also called Olefin Co-Polymers, (OCP)).
- Hydrogenated polyisoprenes.
- Poly-metacrylates (PMA).
- Hydrogenated styrene-isoprene copolymers.
- Poly-isobutenes (PIB).

3. **Oiliness:**
   - Oiliness 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.
   - The 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.

4. **Flash Point:**
   - ☞ The flash point of a lubricant is the lowest temperature at which vapours of the material gives a flash for a moment when an ignition source brought near to it.
   - ☞ The lubricating oil should have flash point reasonably higher than its working temperature.

5. **Fire Point:**
   - The fire point of a lubricant is the lowest temperature at which the vapour of the lubricant continues to burn for at least 5 seconds when an ignition source brought near to it.
   - In most cases, the fire points are 40°C to 50°C higher than the flash points.
   - A good lubricant should have fire point much above the working temperature.

6. **Cloud Point:**
   - When the lubricant oil is cooled slowly, the temperature at which lubricating oil becomes cloudy in appearance is called cloud point.
   - Cloud point of a lubricant indicates the suitability of lubricant oil when the machines are working under cold conditions.
   - The cloud point of a lubricant should be much lower than the working temperature.

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

- The pour point indicates the suitability of lubricant oil when machine is working under cold condition.
- The pour point of a lubricant should be much lower than the working temperature.

Chemical Properties of Lubricants:

1. Coke Number or Carbon Residue

Coke number or Carbon residue of lubricant is the tendency to form carbon deposits after heating under high-temperature conditions under specific conditions.

A high coke number suggests a lubricant's tendency to form carbon deposits, which can lead to engine problems, such as reduced efficiency, increased wear, and even engine damage. A low coke number is generally desirable, indicating that the lubricant is less prone to forming deposits. The type of base oil, additives used, and operating conditions of the lubricant can all influence the coke number.

2. 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.
TAN is determined by the amount of potassium hydroxide in milligrams that is needed to neutralise the acids in one gram of oil. TAN is a crucial parameter for assessing the quality and condition of oils and lubricants, as increased acidity can lead to corrosion, degradation, and reduced performance.

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.
- 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.

3. Saponification Value (SV) or Saponification Number (SN)

Saponification value of lubricating oil is the number of milligrams of potassium hydroxide (KOH) required to saponify one gram of fatty oil.

The saponification value is a measure of the average molecular weight (or chain length) of the fatty acids present in the lubricant sample, specifically those in the form of triglycerides.

- A high saponification value suggests shorter fatty acid chains (lower molecular weight).
- A low saponification value indicates longer fatty acid chains (higher molecular weight).
- Saponification value can indicate the presence of vegetable and animal oil additives in blended lubricating oils.

UNIT –5

ELECTROCHEMISTRY

Electrochemistry is the branch of chemistry which deals with the study of inter conversion of electrical energy and chemical energy.

Electronic concept of Oxidation, Reduction and Redox reactions:

Oxidation: Oxidation may be defined as the loss of electron/s by an atom, ion or molecule.

Examples:

$Na - e^- \rightarrow Na^+$

$Ca - 2e^- \rightarrow Ca^{2+}$

$Fe^{2+} - e^- \rightarrow Fe^{3+}$

Reduction: Reduction may be defined as the gain of electron/s by an atom, ion or molecule.

Examples:

$Na^+ + e^- \rightarrow Na$

$Ca^{2+} + 2e^- \rightarrow Ca$

$Fe^{3+} + e^- \rightarrow Fe^{2+}$

Redox Reaction or Net reaction: The chemical reaction in which both oxidation and reduction takes place simultaneously is called a redox reaction. Oxidation and reduction go side by side.

Examples:

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

$Cl_2 + 2Fe^{2+} \rightarrow 2Cl^- + 2Fe^{3+}$

$H_2 + F_2 \rightarrow 2HF$

Electrolytes: The chemical substances which allow electricity to pass through their molten, fused or solution state are called electrolytes. Examples:

- All acids: HCl, HNO_3, H_2SO_4, H_2CO_3, CH_3COOH, etc.
- All alkalis: NaOH, KOH, $Ca(OH)_2$, NH_4OH, etc.
- All salts: NaCl, KCl, $CaCl_2$, $NaNO_3$, etc.

Electrolytes undergo dissociation/ionization in to ions in aqueous solution.

Non-electrolytes: The chemical substances which do not allow electricity to pass through their molten, fused or solution state are called non-electrolytes. Examples: Uera, Sugar, glucose, fructose, sucrose, etc.

Non-electrolytes do not ionise in aqueous solution.

Classification of Electrolytes: Depending upon the degree of ionisation/dissociation electrolytes may be classified into two types. (a) Strong electrolytes and (b) weak electrolytes.

(a) Strong Electrolytes: The electrolytes which undergo almost complete ionisation in aqueous solution are called strong electrolytes. Examples:

- Acids like: HCl, HNO_3, H_2SO_4, etc.
- Alkalis like: NaOH, KOH, etc.
- All salts: NaCl, KCl, $CaCl_2$, $NaNO_3$, etc.

(b) Weak Electrolytes: The electrolytes which undergo partial ionisation in aqueous solution are called weak electrolytes. Examples:

- Acids like: H_2CO_3, HCOOH, CH_3COOH, etc.
- Alkali like: NH_4OH

Faraday's 1st Law of Electrolysis: The law may be stated as "During electrolysis, the amount of substances deposited/liberated at an electrode is directly proportional to the quantity of electricity passed through the electrolyte".

Mathematically,

$$W \propto Q$$

But, $Q = I \times T$

$$\Rightarrow W \propto I \times T$$

$$\Rightarrow W = Z \times I \times T$$

Where, W = Amount of substance in gram

Q = Quantity of electricity or Charge in coulomb

I = Current in ampere

t = time of flow of current in second.

Z = Electrochemical equivalent (ECE)

When, I = 1 ampere; t = 1 second,

W = Z

Thus, electrochemical equivalent is numerically equal to the amount of substance deposited or liberated at the electrode when 1 ampere of current is passed through an electrolyte for 1 second. Or it is the amount of substance deposited or liberated at the electrode when 1 coulomb of charge is made to flow through an electrolyte.

A bigger unit of charge is Faraday.

1 Faraday = 96500 coulomb

Experimentally it is observed that when 1 Faraday (96500 C) of charged is passed through an electrolyte 1gram equivalent of the substance is deposited at the electrode.

96500 Coulomb of charge deposits 1 gram equivalent

$\Rightarrow$ 1 coulomb of charge deposits $\frac{1\,gram\,equivalent}{96500C}$

Hence, Electrochemical Equivalent (Z) = $\frac{1\,gram\,equivalent}{96500C} = \frac{Atomic\,mass/Valency}{96500}$

Unit of 'Z' is gram equivalent/coulomb.

Note: 1 mole of electrons carries 1 Faraday or 96500 Coulomb of charge.

Question 1: How many grams of silver will be deposited at the cathode by the passage of 10 ampere of current through an aqueous solution of $AgNO_3$ for 1 hour?

Solution:

Given Data: I = 10 Ampere

t = 1 hr = 3600 Sec.

$$Z = \frac{1\,gram\,equivalent}{96500C} = \frac{Atomic\,mass/Valency}{96500} = \frac{108/1}{96500} = \frac{108}{96500} = 0.0011$$

Applying Faraday's 1st Law of electrolysis

W = ZIt = 0.0011 X 10 X 3600 = 39.6 gram.

Question 2: How many coulombs are required for the following changes?

- **i.** One mole Ca^{2+} into Ca.
- **ii.** Two moles of Al^{3+} into A*l.*

Solution:

i. $Ca^{2+} + 2e^{-} \rightarrow Ca$

1 mole of electrons carries 96500 coulombs.

$\Rightarrow$ 2 moles of electrons carry (2 x 96500) coulomb = 193000 Coulombs.

ii. $2Al^{3+} + 6e^{-} \rightarrow 2Al$

1 mole of electrons carries 96500 coulombs.

$\Rightarrow$ 6 moles of electrons carry (6 x 96500) coulomb = 579000 Coulombs.

Question 3: How many coulombs of charge are required to get 10 grams of calcium from molten $CaCl_2$?

Solution:

W = 10 gm, Q =?

W = Z Q

$$= \frac{Eq.mass/Valency}{96500} \times Q$$

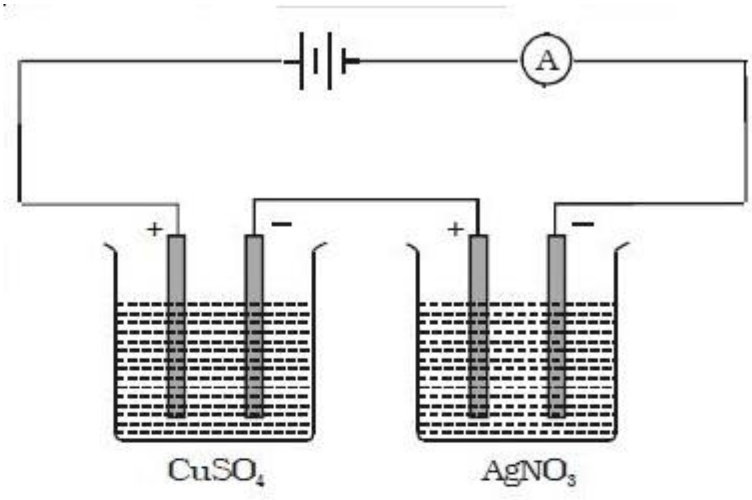
$$\Rightarrow 10 = \frac{40/2}{96500} \times Q \quad \Rightarrow \quad Q = 10 \times \frac{96500}{20} = 48250\,Coulomb$$

Faraday's 2nd Law of Electrolysis:

The law may be stated as "when the same quantity of electricity is passed through different electrolytes connected in series, the amounts (W) of substances deposited at various electrodes are directly proportional to their equivalent masses (E)".

Mathematically,

$$W \propto E$$



Let us consider two electrolytic solutions $AgNO_3$ and $CuSO_4$ taken in two different electrolytic cells. Both the cells are connected in series and the same quantity of electricity is passed through the electrolytes.

Applying Faraday's 2nd law of electrolysis,

$$W_{Ag} \propto E_{Ag} \text{ -----------(1)}$$

$$W_{Cu} \propto E_{Cu} \text{ ---------(2)}$$

From equation (1) and (2), we have

$$\Rightarrow \frac{W_{Ag}}{W_{Cu}} = \frac{E_{Ag}}{E_{Cu}} \quad \Rightarrow \quad \frac{W_{Ag}}{W_{Cu}} = \frac{\frac{E_{Ag}}{96500}}{\frac{E_{Cu}}{96500}} = \frac{Z_{Ag}}{Z_{Cu}}$$

In general, $\boxed{\frac{W_1}{W_2} = \frac{E_1}{E_2} = \frac{Z_1}{Z_2}}$ or $W \propto E \propto Z$

Question: 1. The same quantity of electricity is passed simultaneously through acidulated water and copper sulphate solution. Weights of hydrogen and copper liberated are 0.0132 and 0.4164 gram respectively. Find out the equivalent weight of copper.

Solution: Weight of hydrogen W_{H_2} = 0.0132 gm

Weight of copper W_{Cu} = 0.4164 gm

Equivalent weight of hydrogen E_{H_2} = 1.008

Equivalent weight of copper E_{Cu} = ?

Applying Faraday's 2nd law of electrolysis,

$$\frac{W_{H_2}}{W_{Cu}} = \frac{E_{H_2}}{E_{Cu}} \Rightarrow E_{Cu} = E_{H_2} \times \frac{W_{Cu}}{W_{H_2}} = 1.008 \times \frac{0.4164}{0.0132} = 31.79$$

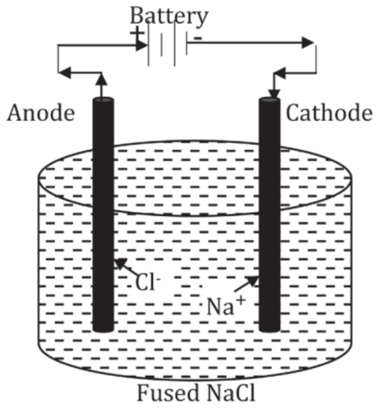
Industrial Application of Electrolysis:

The significant industrial applications of electrolysis are as follows
1. Electrometallurgy
2. Electroplating
3. Electrolytic Refining

1. **Electrometallurgy:** The process of extraction of metals from their ores by electrolysis is called electrometallurgy. 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. The fused metal salt (acts as electrolyte) is taken in an electrolytic cell with suitable electrodes. When electricity is passed through the electrolyte, metal gets deposited at the cathode.

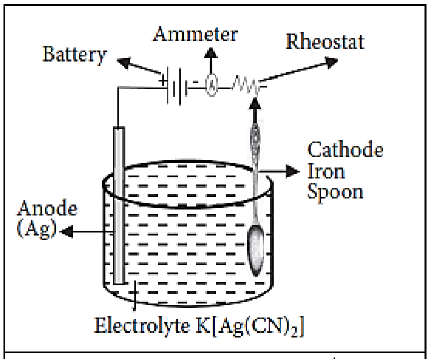
   Example: Extraction of sodium metal from fused NaCl.
   The fused NaCl is taken in an electrolytic cell using graphite electrodes. When electricity is passed through the fused NaCl, the following changes take place at different electrodes.
   $NaCl \rightarrow Na^+ + Cl^-$
   At Anode: $2Cl^- - 2e^- \rightarrow Cl_2$ (liberated)
   At Cathode: $2Na + 2e^- \rightarrow 2Na$ (deposited)

   Thus, metallic sodium is collected at the cathode.



2. **Electroplating:** The process of applying coating of one metal (superior) over another metal (inferior) by electrolysis is called electroplating. Electroplating is carried out for three main purposes: (a) protection, (b) decoration, and (c) repairing.
   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. A pure metal plate or rod whose coating is to be applied is used as anode. A suitable aqueous salt solution of the anodic metal is used as electrolyte.
   On passing electric current, the metallic ions from the electrolyte get deposited on the article made as a cathode. The equivalent amount of anode gets dissolved in the form of metal ions and passes into the electrolyte.
   Smooth and brighter deposits are obtained
   i) at low temperature,
   ii) high current density,
   iii) high metal ion concentration of electrolyte and iv)
   iv) at specific pH.

Example: Electroplating of silver on the iron spoon is carried out in a rectangular tank of steel. The iron spoon, which is to be electroplated, is cleaned thoroughly by boiling with caustic soda to remove dirt or grit or grease. Further, it is washed with water until it is free from caustic soda. Then it is placed in an acid tank containing dilute acid to remove the oxide layer present on the spoon. Further, it is washed with water to remove excess acid and polished with polishing paper. Then iron spoon is made as a cathode, and the anode is made up of a pure silver metal plate. The anode and cathode are suspended in the electrolyte in the cell of potassium



argentocynide $K[Ag(CN)_2]$. On passing the direct electric current, at applied voltage, the iron spoon gets plated with smooth and brighter deposits of silver. Silver anode gets slowly dissolved in solution by giving Ag^+ ions.

Reaction at Anode:

$Ag \quad - \quad e^- \quad \rightarrow \quad Ag^+$

(silver anode)

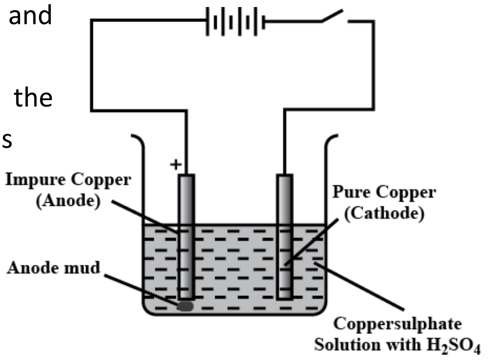
Reaction at Cathode:

$Ag^+ \quad + \quad e^- \quad \rightarrow \quad Ag$

(From Electrolyte)

3. **Electrorefining:** The process of purifying impure metals by electrolysis is called electrorefining. This method is employed to refine the less electro positive metals such as Zn, Pb, Al, Cu etc. The impure metal bar is used as anode while a pure metal (same metal) bar is taken as cathode. Both the electrodes are dipped in a suitable aqueous salt solution of the concerned metal. During the process of electrolysis, the impure metal dissolves in its aqueous salt solution providing metal ions which get discharged and deposited over the cathode.

   Example: Electrorefining of copper: In the electrorefining of copper, the impure copper is used as anode, while a pure copper plate is used as cathode. Both the electrodes are dipped in an acidified $CuSO_4$ solution which acts as an electrolyte. When electricity is passed, the copper ions present in the electrolyte migrate towards the cathode where they get discharged and deposited.



Reaction at Anode:

$Cu \quad - \quad 2e^- \quad \rightarrow \quad Cu^{2+}$

(Impure Copper anode)

Reaction at Cathode:

$Cu^{2+} \quad + \quad 2e^- \quad \rightarrow \quad Cu$

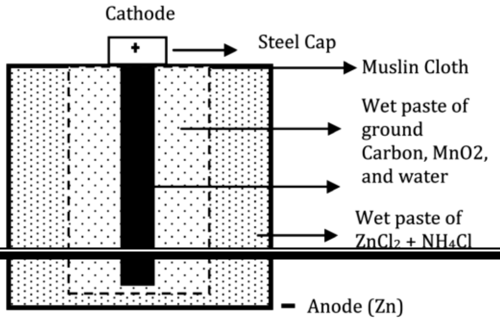
(From Electrolyte)

On the other hand, an equivalent quantity of copper dissolves to form copper ions. The impurities present in the impure copper bar settle down at the bottom of the electrolytic tank and is called anode mud. In this way pure copper is obtained at the cathode.

Primary Cell or Dry Cell

Primary cells are the electrochemical cells which are non-rechargeable. The electrochemical reactions in these batteries are non-reversible.

Construction:



The dry cell consists of a graphite rod at the centre surrounded by a paste of manganese dioxide (MnO_2), 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/brass cap is present, which represents the positive terminal. Around the muslin cloth, a paste of zinc chloride and ammonium chloride is covered with a metallic zinc container that acts as an anode representing a negative terminal.

Reaction at Anode (At Zn Electrode)

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

Reaction at Cathode

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

As a result of redox reaction in the cell, electrons flow from anode to cathode, which represents the generation of electricity. A primary cell develops 1.5 V of electricity. As chemical are responsible for electricity generation, this cell is known as an electrochemical cell, and hence spontaneous chemical reactions are taking place. The dry cell does not have a long life, as acidic ammonium chloride corrodes the zinc container, even when it is not in use.

Secondary Cell

A secondary cell, also known as a rechargeable battery, is a cell that can be recharged after use. In this type of cells chemical energy is converted into electrical energy when charged, and the chemical reaction can be reversed when discharged. They are used in many consumer electronics and electric vehicles.

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 like voltaic cells and as electric cells. When operating as a voltaic cell, it supplies electrical energy and is finally discharged. When being recharged, the cell operates as an electrolytic cell.

In a lead-acid storage cell, the cathodes are made of spongy lead (Pb), and the anodes are made of lead oxide (PbO_2).

The electrodes are 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 H_2SO_4 (with specific gravity 1.15 at 25°C).

During discharging:

During discharging, the lead electrodes enter into the solution with the formation of lead ions. Therefore, oxidation takes place at the lead electrode.

Reactions at Lead (Pb) Electrode

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

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

$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4\downarrow$ (Lead sulphate Precipitate)

Reactions at Lead oxide (PbO_2) 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. Here reduction takes place.

$PbO_2 + 2e^- + 4H^+ \longrightarrow Pb^{2+} + 2H_2O$ (Reduction Reaction)

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

$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$

Lead Sulphate

So, the overall redox reaction in lead storage cell is:

$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4 + 2H_2O + \text{Energy}$

During discharging, lead and lead oxide electrodes slowly dissolve in the electrolyte, releasing Pb^{2+}. The amount of lead sulphate and water increases in the electrolytes during discharging while the percentage of H_2SO_4 decreases during discharging. A pair of Pb and PbO_2 gives 2 Volt of electricity. It gives 2 Volt of electricity during fully charged conditions, gradually decreasing during discharging up to 1.6 to 1.7 Volt.

During charging:

When both electrodes are covered with lead sulphate, the cell stops functioning as a voltaic. The reactions taking place during discharging are reversed by passing external electromotive force (e.m.f.) greater than 2 volts from an external supply.

Reactions at Pb (Lead) Electrode

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

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

Regeneration of electrode

Reactions at PbO_2 (Lead oxide) Electrode

$Pb^{2+} + 2H_2O \longrightarrow PbO_2 + 2e^- + 4H^+$ (Oxidation Reaction)

Regeneration of PbO_2 electrode

Hence net reaction during charging is

$$2PbSO_4 + 2H_2O + \text{Energy} \longrightarrow Pb + PbO_2 + 4H^+ + 2SO_4^{2-}$$

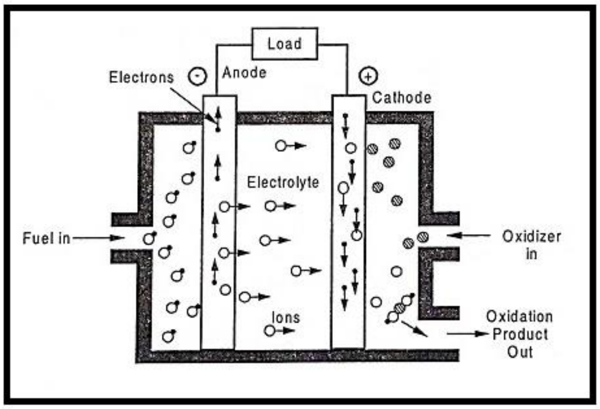
The redox cell reaction during discharging and charging can be shown as

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

Distinction between Electrolytic cell and Electrochemical cell		
1	It converts electrical energy into chemical energy.	It converts chemical energy into electrical energy.
2	Electricity is consumed. Require source of energy.	Produce electricity, it is a source of energy.
3	Redox reactions are non-spontaneous chemical reactions	Redox reactions are spontaneous chemical reactions.
4	Anode (+ve) terminal oxidation take place	Anode (-ve) terminal oxidation take place
5	Cathode (-ve) terminal reduction take place	Cathode (+ve) terminal reduction take place

(B) Fuel Cell

Fuel cells are electrochemical cells which can convert the chemical energy contained in a readily available fuel oxidant system into electrical energy by an electrochemical process, in which fuel is oxidized at the anode. A fuel cell consists of an electrolyte and two electrodes. However, the fuel and the oxidizing agent are continuously and separately supplied to the cell's electrodes at which they undergo reactions. Fuel cells have high efficiency and are pollution free.



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

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

One of the simplest and most successful fuel cell is the hydrogen-oxygen fuel cell. It consists 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

$$\begin{array}{lll}
\text{At Anode} & 2H_2 \longrightarrow & 4H^+ + 4e^- \\
 & 4H^+ + 4OH^- \longrightarrow & 4H_2O \\
\text{At Cathode} & O_2 + 2H_2O + 4e^- \longrightarrow & 4OH^- \\
\hline
\text{Redox} & 2H_2 + O_2 \longrightarrow & 2H_2O
\end{array}$$

The standard emf of the cell is 1.23 V

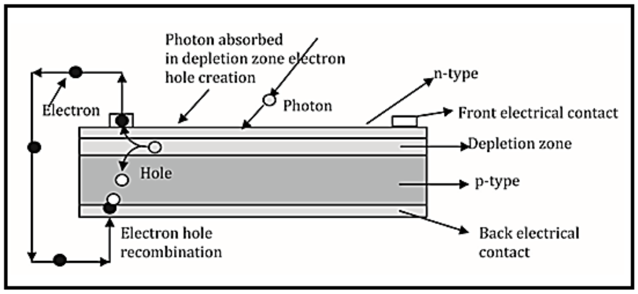
In actual practice, the emf of the cell is 0.8 to 1.0 V. Usually, large numbers of these cells are stacked together in series to make a battery called fuel cell battery or fuel battery.

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 O_2 reacts with two water to produce $4OH^-$ ions, taking up the four electrons from the outer circuit.

When hydrogen is used as fuel, the electrodes are made of either graphite impregnated with finely divided platinum, or an alloy of palladium and silver, or nickel. Electrolytes used most often are aqueous KOH or H_2SO_4 solution.

(C) Solar cell

Solar energy obtained from the sun is converted into electrical energy directly by using a photovoltaic cell. A photovoltaic cell consists of a p-type semiconductor (such as Si doped with B) in contact with an n-type semiconductor (such as Si doped with P).



The sunlight travels in packets of energy called 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.

Corrosion:

The process of deterioration or destruction and consequent loss of a solid metallic surface through an unwanted chemical, electrochemical and biochemical attack by its environment is called corrosion.

Examples:

(i) Rusting of Iron

(ii) Tarnishing of silver

(iii) Formation of Green Film on Copper/Bronze.

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 Corrosion or Chemical Corrosion:

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

Example:

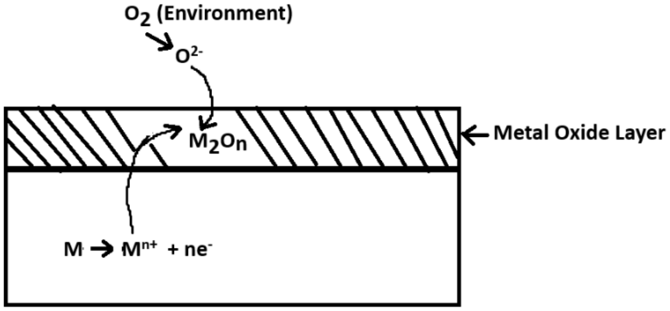
(i) Silver materials undergo chemical corrosion by atmospheric H_2S gas.
(ii) Iron metal undergoes chemical corrosion by HCl gas.

Types of dry or chemical corrosion

- Corrosion by Oxygen or Oxidation corrosion
- Corrosion by Hydrogen or other gases.

Corrosion by Oxygen or Oxidation Corrosion:

This type of corrosion occurs due to the direct attack of oxygen on the metallic surface at low or high temperatures in the absence of moisture. Alkali metals (Li, Na, K, etc.) and alkaline earth metals (Mg, Ca, etc.) are rapidly corroded by oxygen at low temperature. On the other hand, almost all metals (except Ag, Au and Pt) are oxidized.



(Dry Corrosion by Oxygen)

The nature of the oxide formed plays an important role in oxidation corrosion process.

Metal + Oxygen $\rightarrow$ Metal oxide (corrosion product)

When oxidation starts, a thin layer of oxide is formed on the metal surface and the nature of this film decides the further action. Different metals form different types of layers with oxygen.

(i) **Stable layer -** A Stable layer is fine grained in structure and can get adhered tightly to the parent metal surface. Hence, such a layer behaves as protective coating which prevents further attack of oxygen. The oxide films on Al, Sn, Pb, Cu, Pt, etc., are stable and tightly adhering in nature.

(ii) **Unstable Oxide layer:** This is formed on the surface of noble metals such as Ag, Au, Pt. The metallic state is more stable than oxide. Hence, it decomposes back into the metal and oxygen. Hence, oxidation corrosion is not possible with noble metals.

(iii) **Volatile Oxide layer:** The oxide layer volatilizes as soon as it is formed. Hence, always a fresh metal surface is available for further attack. This causes continuous corrosion. MoO_3 is volatile in nature.

(iv) **Porous layer:** In such a case, the atmospheric oxygen has access to the underlying surface of metal, through the pores or cracks of the layer, thereby the corrosion continues unobstructed, till the entire metal is completely converted into its oxide. Magnesium alloys undergo this type of corrosion.

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 the flow of electron-current between the anodic and cathodic areas.

At anodic area oxidation reaction takes place (liberation of free electron). Hence corrosion always occurs at anodic areas.

$$M(metal) \rightarrow M^{n+} + ne^-$$

The metal ions (M^{n+}) thus formed dissolves in solution and form compounds such as oxide.

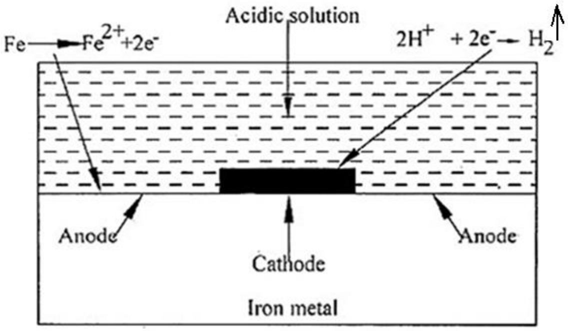
At cathodic area, reduction reaction takes place (gain of electrons). At the cathodic part, dissolved constituents in the conducting medium accepts the electrons to form some ions like OH^- and O^{2-}.

Depending on the nature of the corrosive environment, cathodic reaction consumes electrons with either by

(a) Evolution/Liberation of Hydrogen
(b) Absorption of Oxygen

(A) Hydrogen Evolution / Liberation Type:

All metals above hydrogen in the electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of hydrogen. It occurs in acidic environment. Consider the example of iron



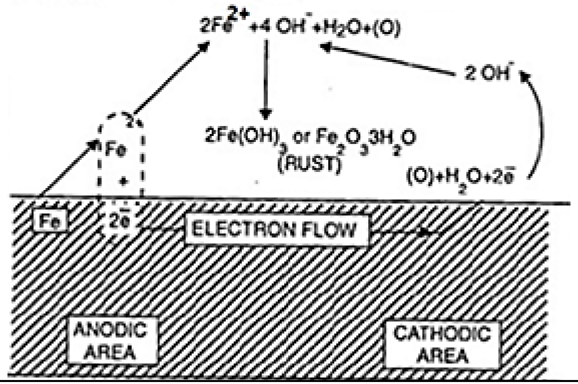
At Anode: $Fe \longrightarrow Fe^{2+} + 2e^-$

These electrons flow through the metal from anode to cathode, where H^+ ions of acidic solution are eliminated as H_2 gas.

At Cathode: $2H^+ + 2e^- \longrightarrow H_2$

(B) Oxygen Absorption Type:

Rusting of iron in neutral aqueous solution of electrolytes like NaCl solution in the presence of atmospheric oxygen is a common example of this type of corrosion. The surface of iron is usually coated with a thin film of iron oxide. However, if this iron oxide film develops some cracks, anodic areas are created on the surface; while the well metal parts act as cathodes.



At Anode: At the anodic area the metal get oxidized into metal ion with the liberation of electrons.

$Fe \rightarrow Fe^{2+} + 2e^-$

The free electrons flow towards the cathodic area where they react with moist air (oxygen) to form hydroxide ions.

At Cathode:

$\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$

The Fe^{2+} ions and OH^- ions diffuse and form, ferrous hydroxide.

$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$ (ppt)

If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide, which is nothing but rust.

$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3$ (Yellow rust $Fe_2O_3.H_2O$)

Difference between Dry Corrosion and Wet Corrosion

Aspect	Dry Corrosion	Wet Corrosion
Definition	Corrosion occurs in the absence of moisture.	Corrosion occurs in the presence of moisture or water.
Mechanism	Chemical reaction between metal and gases.	Electrochemical reaction involving an electrolyte.
Medium	Gaseous medium (e.g., oxygen, sulfur dioxide).	Aqueous medium (e.g., water, acids, salts).
Temperature Requirement	Usually occurs at high temperatures.	Can occur at room temperature or higher.
Rate of Corrosion	Slower compared to wet corrosion.	Faster due to electrochemical processes.
Surface Layer	Forms an oxide layer, which can be protective or non-protective.	Forms rust or other compounds, usually non-protective.
Examples	Oxidation of iron in a furnace.	Rusting of iron in humid air.

Factors affecting Rate of Corrosion:

The rate of corrosion depends upon the nature of metals and the nature of the corroding environment.

(A) Nature of metals

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

(i) **Position in Electrochemical Series:** The metal higher in electrochemical series is more active and suffers 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 small 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 the 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. Greater the specific volume ratio, lesser is the oxidation corrosion rate. For e.g. the specific volume ratio of Ni, Cr, W are 1.6, 2.0 and 3.6 respectively. Rate of oxidation corrosion is least for tungsten (W).

(v) **Nature of the Corrosion Product:** Following factors contribute to the nature of corrosion Product.

- **Solubility of Corrosion Products:** If the corrosion product is soluble in the corroding medium, then corrosion proceeds at a faster rate otherwise if it is insoluble, corrosion will be suppressed e.g. $PbSO_4$ formation in case of Pb in H_2SO_4.
- **Volatility of Corrosion Products:** If the corrosion product is volatile, it evaporates as soon as it is formed, thereby leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion. For example, Mo forms MoO_3 volatile oxide.

(vi) **Physical State** The rate of corrosion is influenced by physical state of the metal (such as grain size, orientation of crystals, stress, etc.). The smaller the grain size of the metal or alloy, the greater its solubility will be and hence greater the corrosion will be. Moreover, areas under stress, even in a pure metal, tend to be anodic and corrosion takes place at these areas.

(B) Nature of the Corroding Environment

(i) **Temperature:** The rate of corrosion increases with the increase in temperature, 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. If pH<3 rate of corrosion is high even in the absence of air due to evolution of hydrogen at the cathodic region.

(iv) **Presence of Impurities in Atmosphere:** Atmosphere in industrial areas contains corrosive gases like CO_2, H_2S, SO_2 and fumes of HCl, H_2SO_4 etc. In the presence of these gases, the acidity of the liquid adjacent to the metal surfaces increases and its electrical conductivity also increases, thereby the rate of corrosion increases.

(v) **Presence of Suspended Particles in Atmosphere:** In case of atmospheric corrosion:

- If suspended particles are chemically active in nature (like NaCl, Ammonium sulphate), they absorb moisture and act as strong electrolytes, thereby causing enhanced corrosion.
- If the suspended particles are chemically inactive in nature (e.g., charcoal), they absorb sulphur gases and moisture and slowly enhance corrosion rate.

(vi) **Conductance of medium:** The Conductivity rate of corrosion increases with the increase in conductance of medium. For example, the rate of corrosion of metal will be higher in wet atmosphere than dry atmosphere due to more conductance. Similarly, metal undergoes rapid corrosion in ocean water than in river water.

INTERNAL CORROSION PREVENTION MEASURES:

Some of the methods of internal prevention of corrosion are:

1. **Purification of metals**

   The impurities present in metal decrease 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 like Distillation, Liquation, Poling, Electrolysis, Zone Refining, Vapour Phase Refining, Chromatographic Methods, etc. are employed.

2. **Alloying**

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

3. **Heat Treatment**

   Heat treatment is found to affect 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 is 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. The 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.

The annealed specimen with coarser grain displayed better corrosion resistance. The corrosion rate results for annealed specimens were 35% lower than the other heat-treated specimens. Heat treatment can be defined as a combination of heating and cooling operations applied to a metal or alloy in its solid state to obtain desired properties.

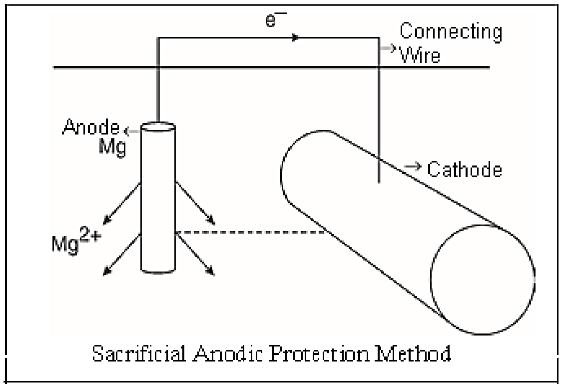
EXTERNAL CORROSION PREVENTION MEASURES:

1. Cathodic Protection

The basic principle of cathodic protection is that the metal structure is made preventing it from corrosion.

There are two types of cathodic protection.

(A) Sacrificial Anodic Protection method



Sacrificial Anodic Protection Method

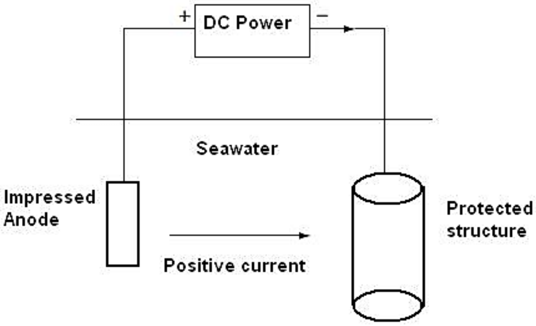
In this method the metallic structure to be protected is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal like Mg, Zn, Al and their alloys. The more active metal itself gets corroded slowly, while the parent structure which is cathodic is 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.

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 enhances 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.

2. Anodic Protection:

Galvanization is commonly used for anodic protection. Galvanization is the process of coating a layer of zinc on iron by hot dipping or by electrolysis process.

Hot dip galvanization process involves the following steps

(i) Iron sheet is passed through an 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 430^0 – 470°C.

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

Applications:

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 stuff, especially acidic ones since zinc gets dissolved in all acids forming highly toxic compounds.

3. 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

The substances which reduce or slow down the rate of anodic reaction (oxidation) are known as anodic inhibitors. Examples include alkalis, chromates, phosphates, molybdates, and nitrates. These inhibitors have high oxygen content. These inhibitors react with the newly formed metal ions to form insoluble precipitates which are adsorbed on the metal surface which makes a protective layer on the metal for which corrosion inhibited.

(B) Cathodic Inhibitors

The substances which reduce or slow down the rate of cathodic reaction (reduction) are known as cathodic inhibitors. They achieve this by either slowing the reaction itself or forming a barrier on the surface, like a protective film. Examples include organic compounds like amines and imidazoles, as well as inorganic compounds like Na_2SO_3, zinc, nickel and magnesium salts, which can form insoluble precipitates. 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 Na_2SO_3.

The diffusion of oxygen can be controlled by adding inhibitors like Mg, Zn or Ni salts.

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

(C) Vapour Phase Inhibitors

Vapor Phase Inhibitors (VPIs), also known as Vapor Corrosion Inhibitors (VCIs), are substances that release a corrosion-inhibiting vapor into the air to protect metal surfaces from corrosion. This vapor forms a protective layer on the metal, preventing contact with corrosive elements like moisture.

- VPIs are designed to release a non-toxic, non-hazardous vapor into the surrounding air.
- The released vapor condenses onto the surface of metal components, forming a thin, invisible layer.
- This protective layer acts as a barrier, preventing corrosion-causing elements like water vapor, moisture, and airborne contaminants from reaching the metal surface.
- VPIs can protect various types of metals, including ferrous and non-ferrous metals.

Examples are Dicyclohexyl ammonium nitrate, dicyclohexyl ammonium chromate, benzotriazole, phenylthiourea etc.