CHAPTER-I

MOLECULAR STRUCTURE AND SPECTROSCOPY

Syllabus: Molecular structure and Spectroscopy (9L): Introduction, Concept of atomic and molecular orbitals, LCAO, Molecular orbitals of diatomic molecules, Molecular orbital energy level diagrams of diatomic molecules (N_2, O_2 and F_2). Pi-molecular orbitals of butadiene and benzene.

Spectroscopic techniques: Principles of spectroscopy, selection rules and applications of electronic spectroscopy (UV & Visible). Vibrational and rotational spectroscopy (IR spectroscopy) - Applications.

Atom: A smallest indivisible particle of an element/matter/substance is called atom. In an atom, subatomic particles like protons and neutrons are present inside the nucleus and negatively charged electrons are present outside the nucleus.

Orbit: A fixed path in which electrons revolve around the nucleus of an atom is called orbit.

Orbital: A region *having the highest probability* of finding electrons (outside the nucleus) in an orbit called orbital.

Atomic orbital: A mathematical function describing the location and wave-like behavior of *an electron in an atom* called atomic orbital. This mathematical function can be used to calculate the probability of finding any electron at any specific region around the atom's nucleus.

Atomic orbitals are labelled as s, p, d and f orbitals. All four orbitals have different shapes. The energies of orbitals are in order of s<p<d<f

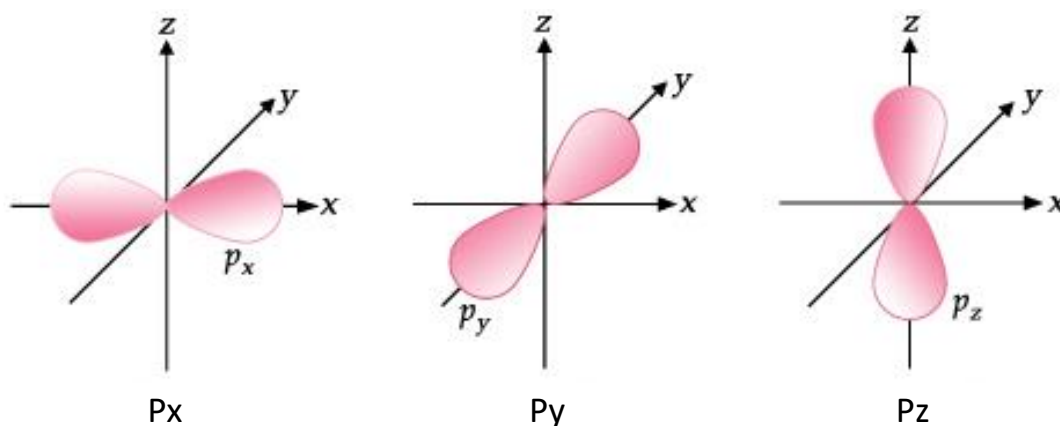**The shapes of atomic orbitals** are as follows

- 🞣   s-orbital: Spherical (it has one sub energy level)
- 🞣   p-orbital: Dumbbell (it has three sub energy levels)
- 🞣   d-orbital: Double dumbbell (it has five sub energy levels)
- 🞣   f-orbital: Diffused (complex) (it has seven sub energy levels)

➢ s-Orbital has only one sub energy level
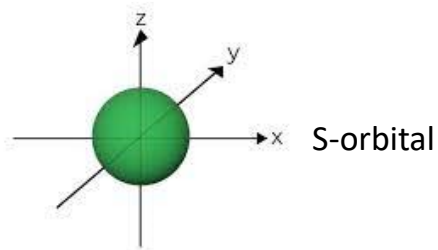
S-orbital

➤ p- Orbital has three sub-energy levels (Px, Py and Pz).

Px   Py   Pz

➤ d-Orbital has five sub-energy levels, i.e., dxy, dyz, dzx, dx^2-y^2 and dz^2.

dxy   dyz   dzx dx^2-y^2 dz^2
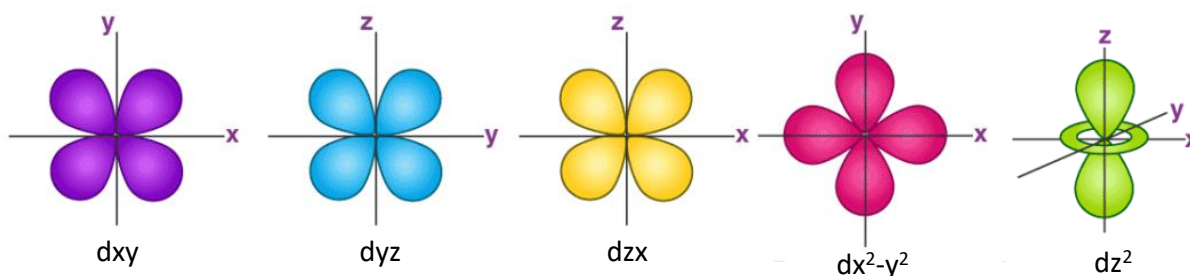
QUANTUM NUMBERS

Position and energy of electrons is completely described by four sets of quantum numbers.

1. Principal quantum number (n):

Principal quantum number was proposed by Neils Bohr and denoted by "n".

It tells about the ***distance from the nucleus (or size of orbit) and energy of electron***.

n = Integer with positive value

If, n = 1, i.e., 1st orbit; n = 2, i.e., 2nd orbit; n = 3, i.e., 3rd orbit; n = 4, i.e., 4th orbit.

Total no of electrons presents in a shell = $2n^2$

2. Azimuthal or Angular quantum number (l):

Azimuthal or Angular quantum number was proposed by Sommerfeld and it is denoted by 'l'.

It describes the ***shape of orbitals*** (s, p, d and f).

Value of l is from 0 to (n-1).

l = 0 for s-orbital, l = 1 for p-orbital, l = 2 for d-orbital, l = 3 for f-orbital.

**3. Magnetic quantum number (m or m_l):**

Magnetic quantum number was proposed by Lande and indicated by 'm or m_l'.

It describes about the ***number of orbitals and orientation of subshell***.

Magnetic quantum number values are (2l+1) and they are from –l····0····+l (including zero).

If, l = 0, then m = 1, i.e., 0

l = 1, then m = 3, i.e., -1, 0, +1

l = 2, then m = 5, i.e., -2, -1, 0, +1, +2

l = 3, then m = 7, i.e., -3, -2, -1, 0, +1, +2, +3

4. Spin quantum numbers (s or m_s):

Spin quantum number was proposed by Beck (George Uhlenbeck)) and Goudsmit (Samuel Goudsmit) and denoted by m_s.

It describes the spin of electrons. Spin quantum numbers are only two, those are +1/2 and –1/2.

Clockwise direction ↑ $+\frac{1}{2}$ Anticlockwise direction ↓ $-\frac{1}{2}$

FILLING OF ATOMIC ORBITALS WITH ELECTRONS

1. Aufbau principle: Aufbau principle states that the electrons are filled into atomic orbitals from lowest energy orbital to highest energy orbitals.

Example, carbon has 6 electrons. Electronic configuration is $1S^2\ 2S^2\ 2P^2$.

2. Hund's rule: All degenerate orbitals in a subshell occupy with one electron before any orbital occupy with two electrons, and all electrons in singly occupied orbitals have same spin.

Example: 3d: ↑ ↑ ↑ ↑ ↑

3. Pauli Exclusion Principle: Pauli exclusion principle states that, any two electrons do not have four same quantum numbers in an atom.

Examples: Hydrogen   ↑   Helium   ↑↓   Lithium   ↑↓ ↑

$1S^1$ $1S^2$ $1S^2$ $2S^1$

Molecule: Two or more atoms connected through chemical bonds is called molecule.

Molecular orbitals: A mathematical function describing **the location and wave-like behavior of an electron in a molecule** called molecular orbital.

Shapes of Molecular Orbitals

Molecular orbitals are two types, σ-molecular orbitals and π-molecular orbitals. σ-Molecular orbitals are formed when two atomic orbitals overlap along the internuclear axis. π-Molecular orbitals are formed when two atomic orbitals overlap in sideways.
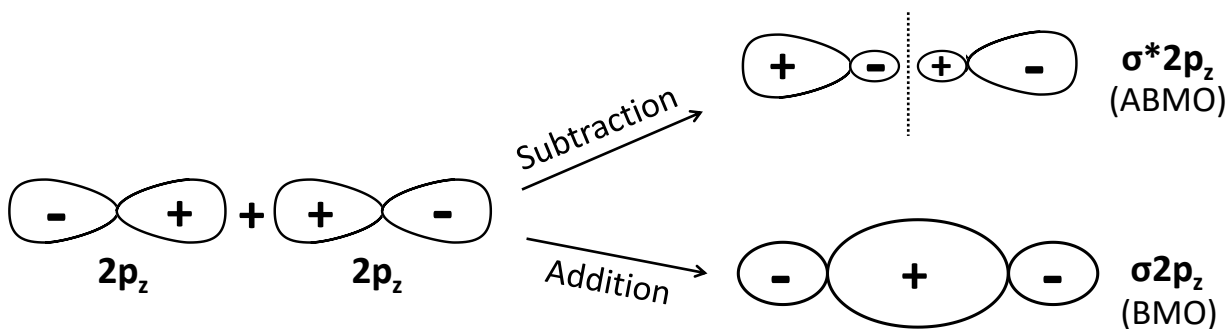
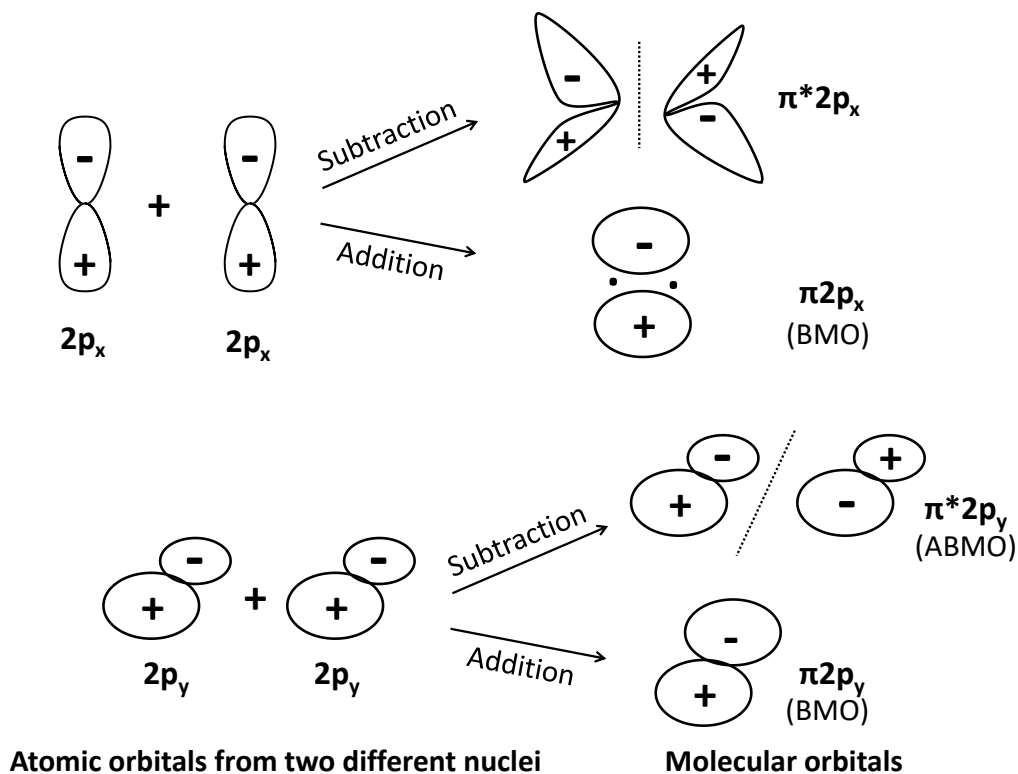## 1. Molecular orbitals from s-atomic orbitals (s-s overlap)

s-Atomic orbitals can overlap only through internuclear axis. Therefore, s-atomic orbitals produce only σ-molecular orbitals and cannot give π-molecular orbitals. Molecular orbitals which are formed through **addition method are called as bonding molecular orbitals (BMO)**. Molecular orbitals which are formed through **subtraction method are called as antibonding molecular orbitals (ABMO)**.

(electron density between nucleus is low)

(electron density between nucleus is high)
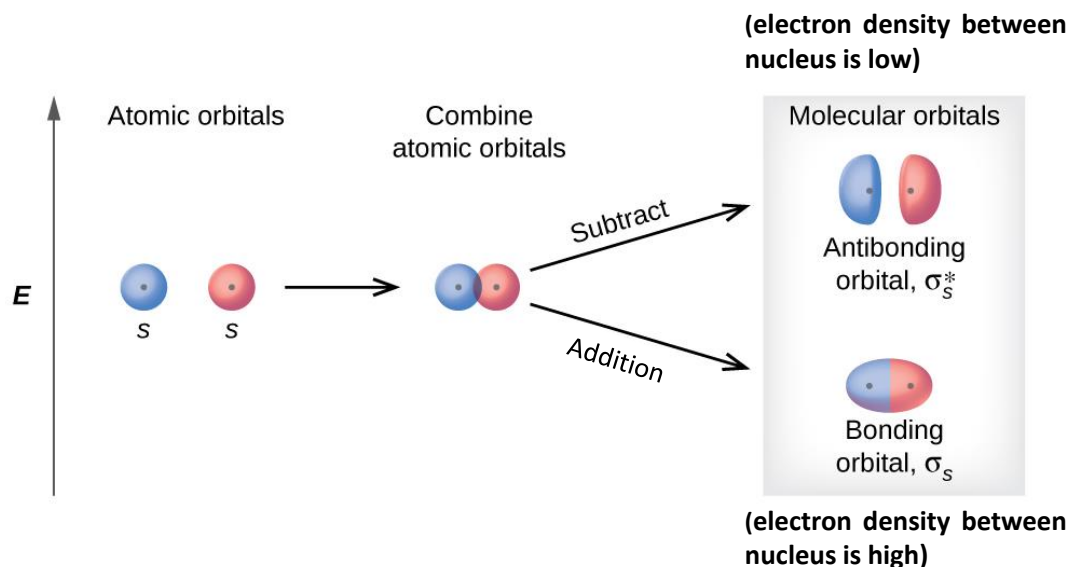
2. Molecular orbitals from 2p-atomic orbitals (p-p overlap)

p-Atomic orbitals can overlap through internuclear axis as well as in sideways. Therefore, p atomic orbitals can produce both σ and π-type molecular orbitals. When p-atomic orbitals overlap through internuclear axis produce σ-molecular orbitals, and when p-atomic orbitals overlap through sideways produce π-molecular orbitals. The strongest overlap occurs between the $2p_z$ orbitals.

Atomic orbitals from two different nuclei   **Molecular orbitals**

MOLECULAR ORBITAL THEORY (MOT)

Molecular orbital theory (MOT) was developed by F. Hund and R. S. Mulliken. MOT clearly describes the **structure and properties** of different molecules.

The important postulates of MOT are as follows

1. Only atomic orbitals having similar energy and proper symmetry combine each other to form molecular orbitals.

2. Total number of molecular orbitals formed is equal to the total number of atomic orbitals combined.

3. When n-number of atomic orbitals combine to form n-molecular orbitals, the wave functions are combined both *in phase* and *out of phase* to create $\left(\frac{n}{2}\right)$ bonding molecular orbitals (BMO), and $\left(\frac{n}{2}\right)$ antibonding molecular orbitals (ABMO), respectively.

4. Molecular orbitals which have lower energy than the corresponding atomic orbitals are called bonding molecular orbitals (BMO). BMOs are formed through addition method.

5. Molecular orbitals which have higher energy than the corresponding atomic orbitals are called antibonding molecular orbitals (ABMO). ABMOs are formed through subtraction method.

6. The electrons are filled in molecular orbitals following Aufbau rule, Hunds rule and Paulis exclusion principle.

5

7. Bond order **(BO) = $[Nb - Na]/2$**. Where, N_b is number of electrons present in BMO, and N_a is number of electrons present in ABMO.

8. A positive value of bond order reveals that the molecule exists and is stable. When the bond order is zero, the molecule is unstable and does not exist.

9. If a molecule possesses **one or more unpaired electrons** in its molecular orbitals that molecule will have **paramagnetic** property.

10. If a molecule doesn't have any **unpaired/lone pair electrons**, it will have **diamagnetic** property.

LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)

Atomic orbitals can be expressed by wave functions (ψ) which represents the amplitude of electron waves, but it may not be easy to solve for molecules.

To overcome this problem researchers developed an approximate method to obtain wave functions for molecular orbitals known as linear combination of atomic orbitals (LCAO) method.

Consider the hydrogen molecule (H_2) consisting of two hydrogen atoms H_A and H_B. Each hydrogen atom in the ground state has one electron in 1s orbital, then the overall wave function of H_2 molecule is as follows. Here, orbitals are represented by wave function (ψ).

$$\psi_{M.O} = \psi_A \pm \psi_B$$

$$\psi_{BMO} = \psi_A + \psi_B \text{ and } \psi_{ABMO} = \psi_A - \psi_B$$

A molecular orbital formed by addition of atomic orbitals is called bonding molecular orbitals (BMO). Indeed, the probability of finding electron is in square form,

$$\text{i.e., } \psi^2_{BMO} = (\psi_A + \psi_B)^2 \text{ and } \psi^2_{ABMO} = (\psi_A - \psi_B)^2$$

$$\psi^2_{BMO} = \psi^2_A + \psi^2_B + 2\ \psi_A\psi_B \text{ and } \psi^2_{ABMO} = \psi^2_A + \psi^2_B - 2\ \psi_A\psi_B$$

A molecular orbital formed by subtraction of atomic orbitals is called antibonding molecular orbitals (ABMO).

MOLECUALR ORBITAL ENERGY LEVEL DIAGRAN (MOED) OF VARIOUS DIASTOMIC MOLECULES

The relative energies of molecular orbitals in increasing order are found to be as follows.

For lighter molecules (having electrons ≤ 14):

σ1s < σ*1s < σ2s < σ*2s < **(π2P$_x$ = π2P$_y$)** < σ2p$_z$ < (π*2P$_x$ = π*2P$_y$) < σ*2p$_z$.

For heavier molecules (having electrons >14).

σ1s <σ*1s < σ2s < σ*2s **< σ2p$_z$ < (π2P$_x$= π2P$_y$)** < (π*2P$_x$=π*2P$_y$) < σ*2p$_z$.

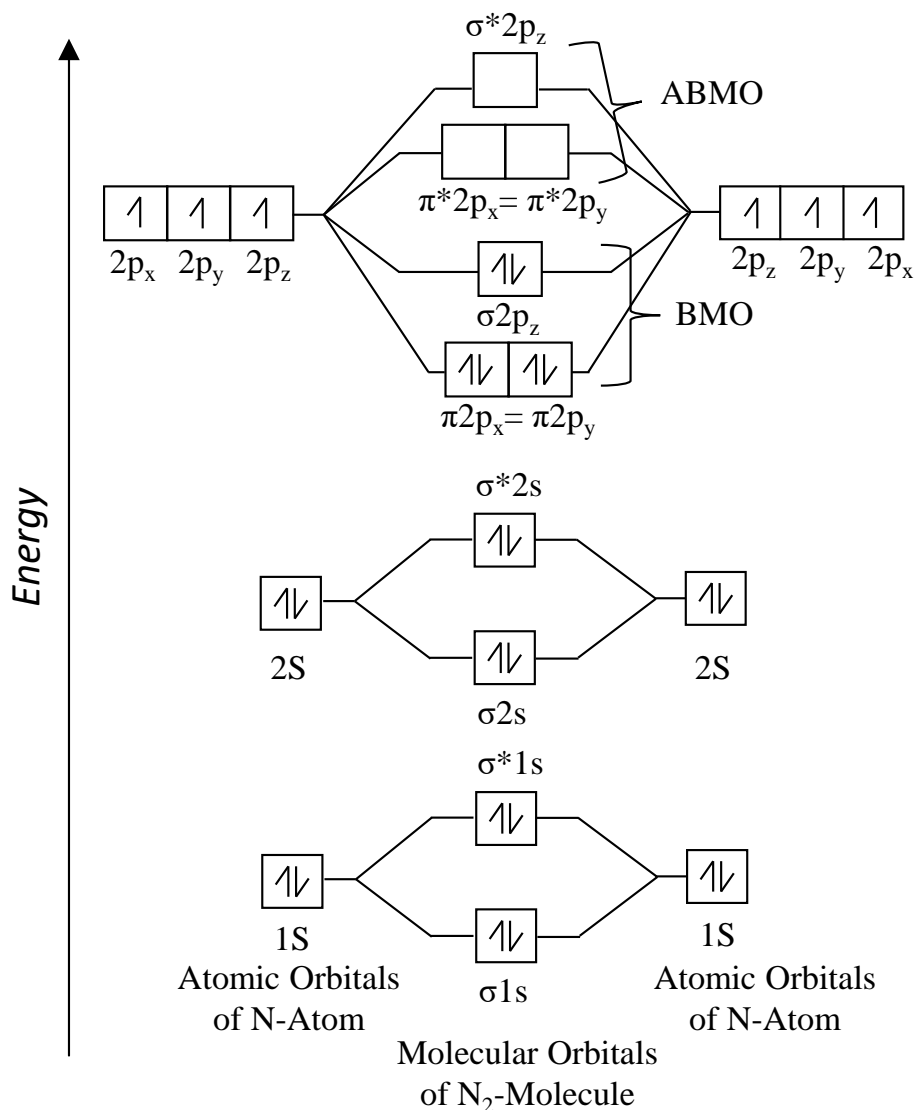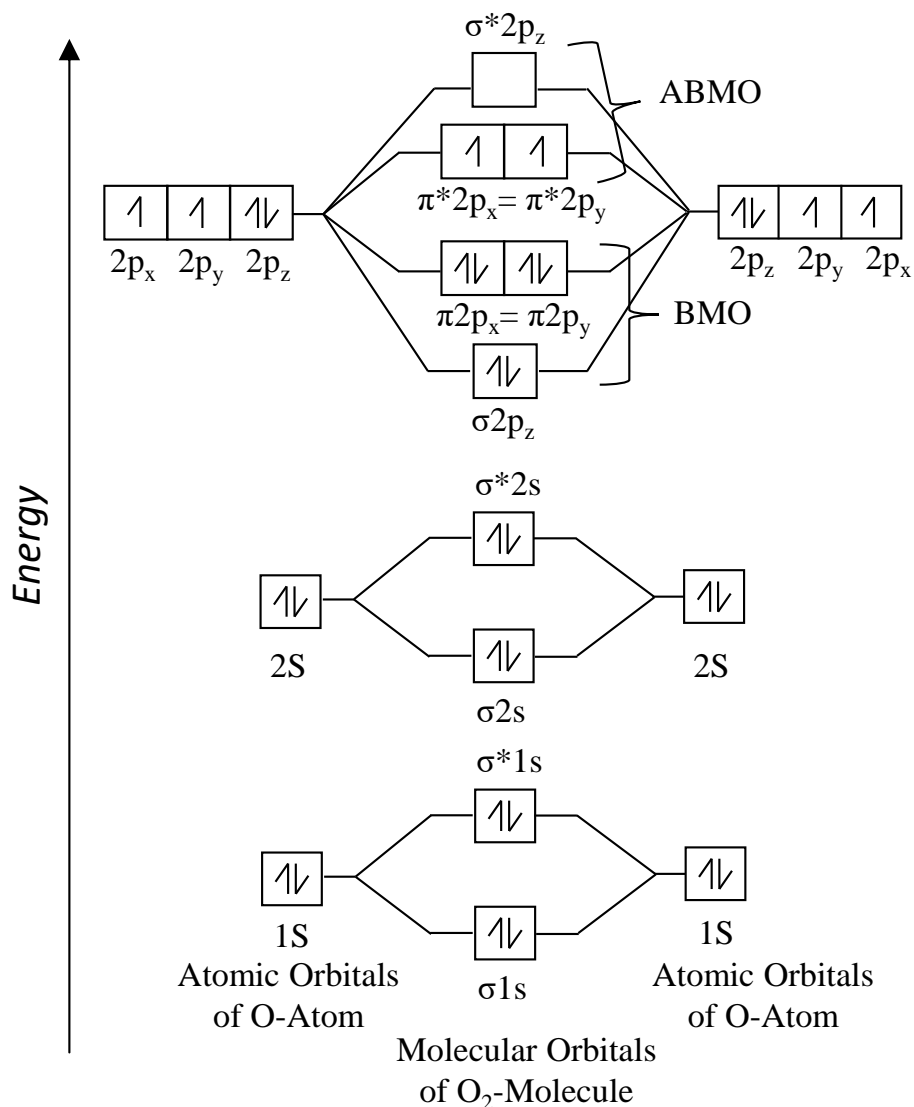## ** MOLECULAR ORBITAL ENERGY LEVEL DIAGRAM OF NITROGEN MOLECULE (N_2) **

➢ Atomic number of nitrogen (N) is 7. No of electrons in nitrogen atom (N) = 7. No of electrons in nitrogen (N_2) molecule = 14.

➢ Electronic configuration of Nitrogen atom is $1s^2\ 2s^2\ 2p^3$.

➢ The electronic configuration of N_2 is: **$\sigma 1s^2\ \sigma^*\ 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ (\pi 2Px^2 = \pi 2Py^2)\ \sigma 2pz^2$.**

➢ Bond order = $(N_b - N_a)\ /\ 2$

Where, N_b = no of bonding electrons & N_a = no of antibonding electrons.

Then, BO = (10-4)/2 = 3

In N_2 molecule BO is three means a triple bond is present between two nitrogen atoms.

➢ N_2 does not have any unpaired electrons, so, N_2 has **diamagnetic property**.

** MOLECULAR ORBITAL ENERGY LEVEL DIAGRAM OF OXYGEN MOLECULE (O_2) *

➤ Atomic number of oxygen (O) is 8. No of electrons present in oxygen atom (O) = 8. No of electrons present in oxygen molecule (O_2) = 16

➤ Electronic configuration of oxygen atom is $1s^2\ 2s^2\ 2p^4$

➤ The electronic configuration of oxygen molecule (O_2) is

$\sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \sigma 2p_z^2\ (\pi 2P_x^2 = \pi 2P_y^2)\ (\pi^*2P_x^1 = \pi^*2P_y^1)$

➤ Bond order = $(N_b - N_a)/2$, Where, N_b = no of bonding electrons & N_a = no of antibonding electrons.

Then, **BO = (10-6)/2 = 2.**

In O_2 molecule BO is two means a double bond is present between two oxygen atoms.

➤ O_2 molecule has two unpaired electrons, therefore O_2 has **paramagnetic property**.

Molecular Orbitals
of O_2-Molecule

** MOLECULAR ORBITAL ENERGY LEVEL DIAGRAM OF FLUORINE MOLECULE (F_2)

✓ Atomic number of fluorine (F) is 9. No of electrons present in fluorine atom (F) = 9. No of electrons present in fluorine molecule (F_2) = 18.

✓ Electronic configuration of oxygen atom is $1s^2\ 2s^2\ 2p^5$.

✓ The electronic configuration of oxygen molecule (F_2) is:

$\sigma 1s^2\ \sigma^*1s^2\ \sigma 2s^2\ \sigma^*2s^2\ \sigma 2p_z^2\ (\pi 2P_x^2 = \pi 2P_y^2)\ (\pi^*2P_y^2 = \pi^*2P_x^2)$.

✓ Bond order = $(N_b-N_a)/2$, Where, N_b = no of bonding electrons & N_a = no of antibonding electrons.

Then, **BO = (10-8)/2 = 1**.

✓ In F_2 molecule the BO is one means a single bond is present between two fluorine atoms.

✓ F_2 molecule doesn't have unpaired electrons, so, F_2 has **diamagnetic property**.
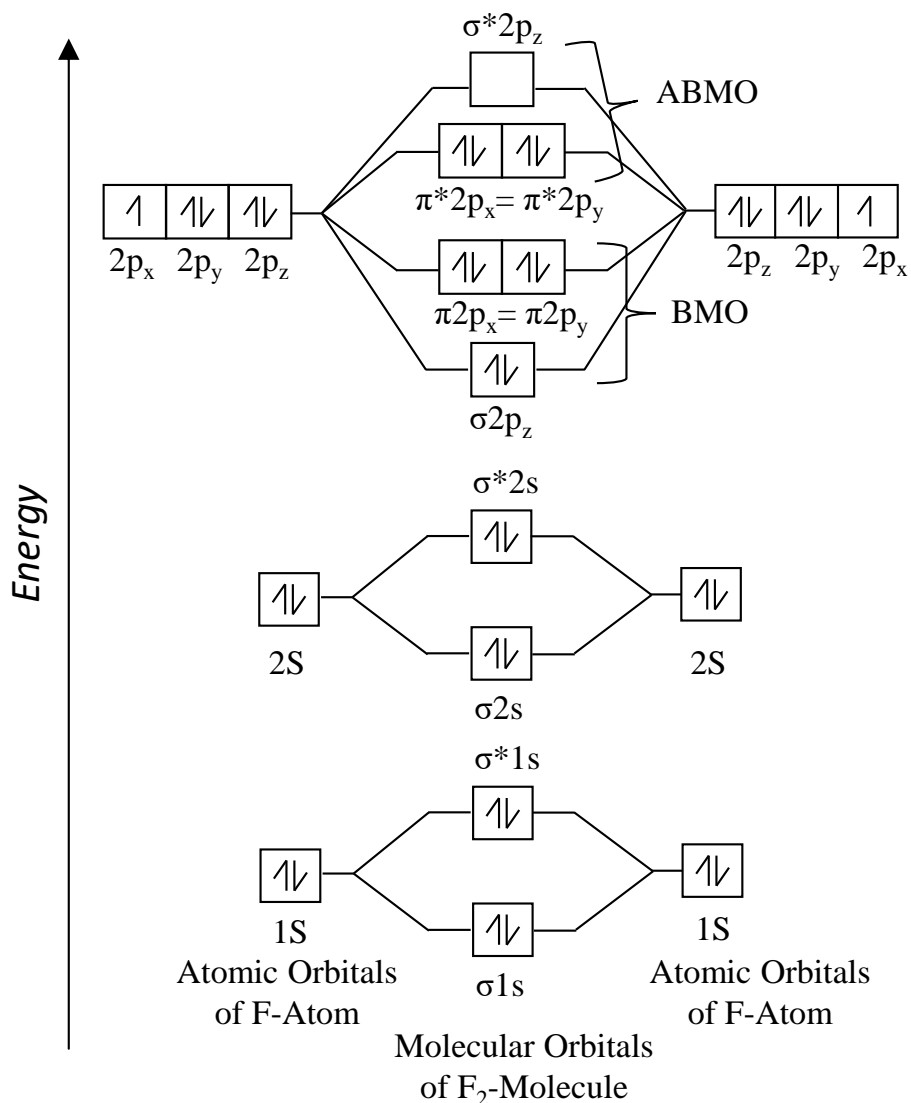
Pi (π) MOLECULAR ORBITALS OF 1,3-BUTADIENE

The structure of 1,3-butadiene is $CH_2=CH–CH=CH_2$

Node: The probability of finding electron zero is called as node.

1,3-butadiene contains two double bonds that are in conjugation. It is built from 4 sp^2 hybridized carbon atoms, each contributing one p-atomic orbital containing one electron.
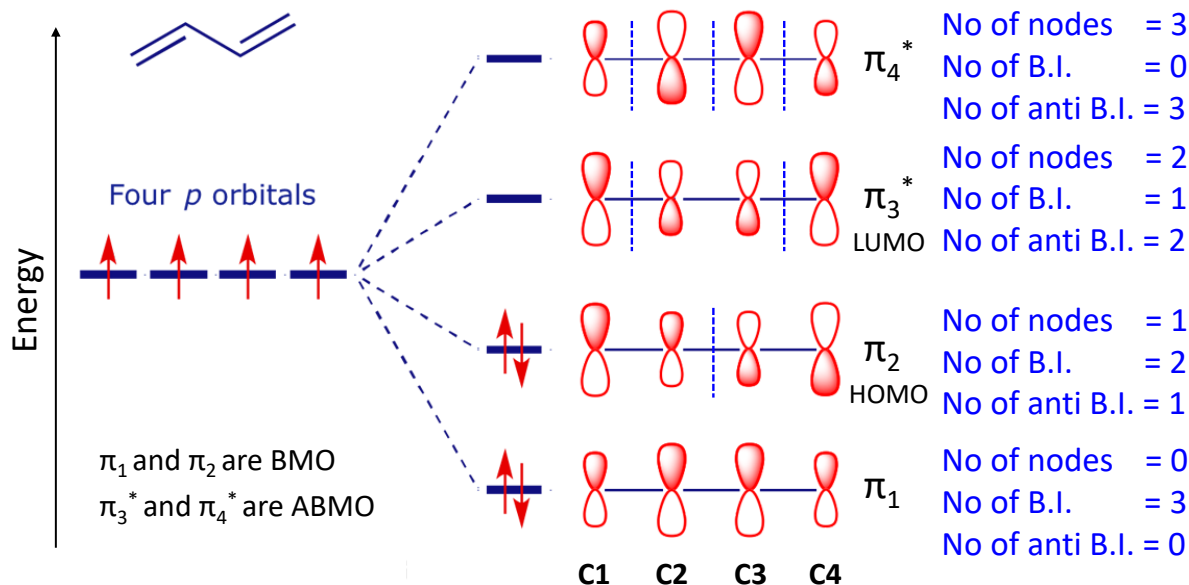
π_4^*	No of nodes = 3
	No of B.I. = 0
	No of anti B.I. = 3
π_3^* LUMO	No of nodes = 2
	No of B.I. = 1
	No of anti B.I. = 2
π_2 HOMO	No of nodes = 1
	No of B.I. = 2
	No of anti B.I. = 1
π_1	No of nodes = 0
	No of B.I. = 3
	No of anti B.I. = 0

Four *p* orbitals

π_1 and π_2 are BMO
π_3^* and π_4^* are ABMO

C1   C2   C3   C4

HOMO : Highest Occupied Molecular Orbital & LUMO : Lowest Unoccupied Molecular Orbital

B. I. = Bonding Interactions & anti B.I. = anti bonding interactions

- The number of molecular orbitals for π-system is equal to the number of contributing p-orbitals.
- Since butadiene consists of 4 individual p-orbitals, butadiene will contain 4 π-molecular orbitals.
- The number of nodes between p-orbitals increases by one for each successive energy level, such that the highest energy orbital has (n-1) nodes.
- **π_1 Molecular orbital:** π_1 Molecular orbital is the lowest energy orbital, that has **zero nodes** between the p-atomic orbitals. π_1 MO has three bonding interactions between C_1-C_2, C_2-C_3 and C_3-C_4. π_1 -MO has zero antibonding interactions.
- **π_2 Molecular orbital:** π_2-MO has **one nodal** plane between C_2-C_3. It has two bonding interactions between C_1-C_2 and C_3-C_4 but one antibonding interaction between C_2-C_3.
- **π_3^* Molecular orbital:** π_3^* has **two nodal** planes between C_1-C_2 & C_3-C_4. It has one bonding interactions between C_2-C_3 and two antibonding interactions between C_1-C_2 & C_3-C_4.
- **π_4^* Molecular orbital**: π_4^* MO has **three nodal** planes between C_1-C_2, C_2-C_3 and C_3-C_4. It has no bonding interactions but three antibonding interactions between C_1-C_2, C_2 –C_3 and C_3-C_4.

- The highest occupied molecular orbital (HOMO) is π_2 in 1,3-butadiene.
- In contrast, the anti-bonding π_3* orbitals contain no electrons. The lowest unoccupied orbital (LUMO) is π_3* in 1,3-butadiene.

π-MOLECULAR ORBITALS OF BENZENE

Benzene (C_6H_6) is the simplest aromatic hydrocarbon. Benzene has a planar hexagonal structure. All the carbon atoms are sp^2 hybridized, each contributing one p-atomic orbital and one electron. Since benzene contributes 6 individual p-orbitals, the π-system of benzene will contain 6-π molecular orbitals.
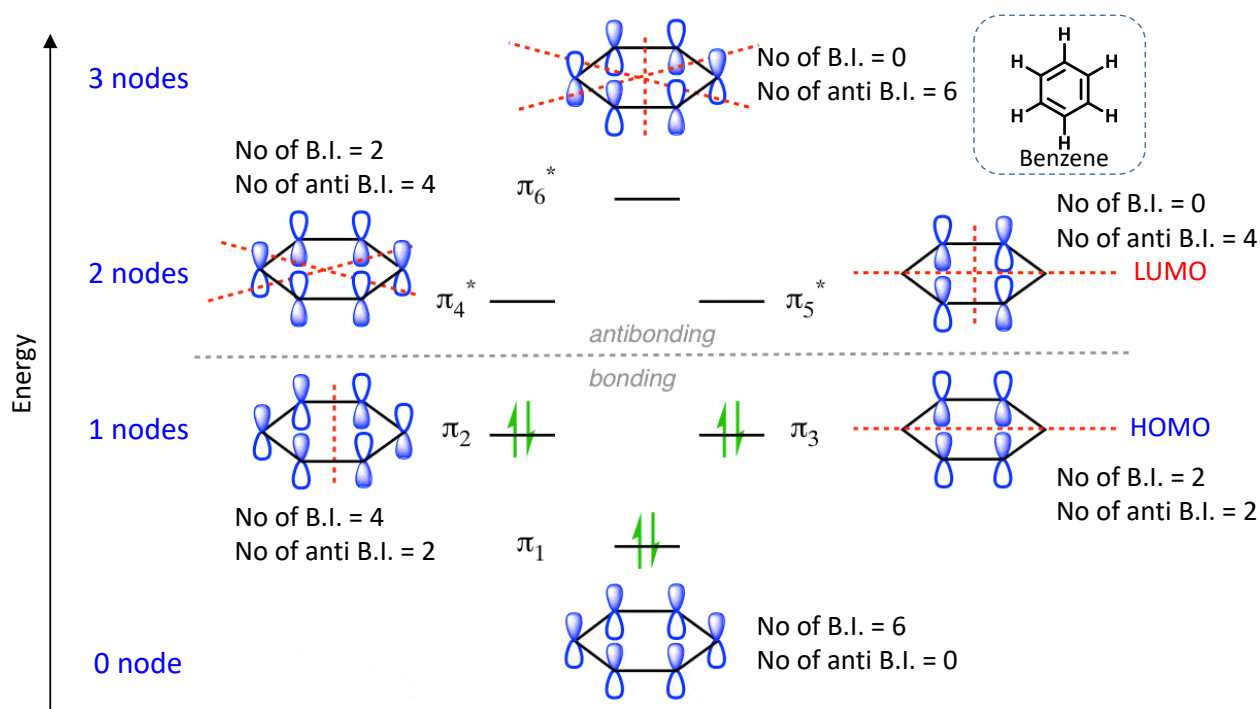
HOMO : Highest Occupied Molecular Orbital & LUMO : Lowest Unoccupied Molecular Orbital

B. I. = Bonding Interactions & anti B.I. = anti bonding interactions

- ❖ The molecular orbitals of benzene: π_1, π_2 and π_3 are bonding molecular orbitals (BMO). π_4*, π_5* and π_6* are antibonding molecular orbitals (ABMO).
- ❖ **π_1-Molecular orbital**: π_1-MO is the lowest-energy orbital. It has **zero nodes** between the p-atomic orbitals. π_1 MO has **six bonding interactions** and **zero antibonding interactions**.
- ❖ **π_2 & π_3 Molecular orbitals:** π_2 and π_3 Mos are degenerate molecular orbitals (means same energy orbitals) and each has one nodal plane. π_2 has four bonding interactions and two antibonding interactions. π_3 has two bonding interactions and two antibonding interactions.

- ❖ **π_4^* & π_5^* Molecular orbitals:** π_4^* and π_5^* are degenerate molecular orbitals and have two nodal planes. π_4^* has two bonding interactions and four antibonding interactions. π_5^* has zero bonding interactions and four antibonding interactions.

- ❖ **π_6^* Molecular orbitals:** π_6^* MO has three nodal planes. It has zero bonding interactions and six antibonding interactions.

- ❖ Benzene has 6π electrons which are filled in π_1, π_2 and π_3 molecular orbitals.

- ❖ The highest occupied molecular orbital (HOMO) is π_2 and π_3 in benzene & the lowest unoccupied molecular orbital (LUMO) is π_4^* and π_5^* in benzene.

SPECTROSCOPY

Aim: Spectroscopy is an analytical tool to determine molecular structure and concentration of unknown compounds.

Spectroscopy: Spectroscopy is the study of interaction between electromagnetic radiation (EMR) and sample/compound/matter.

Electromagnetic radiation (EMR)

Electromagnetic radiation (EMR) consists of electromagnetic waves which are synchronized oscillations of electric and magnetic fields. It is a type of energy, commonly known as *light* which is produced by the movement of electrically charged particles travelling through a space or vacuum. The electric and magnetic components are mutually perpendicular (90⁰) to each other.

EMR contains a range of wavelengths. Based on wavelength or energy EMR classified into different categories as follows.

1) Gamma (γ) rays; 2) X-rays; 3) Ultraviolet (UV)-Visible; 4) Infrared (IR); 5) Microwave and 6) Radio waves.
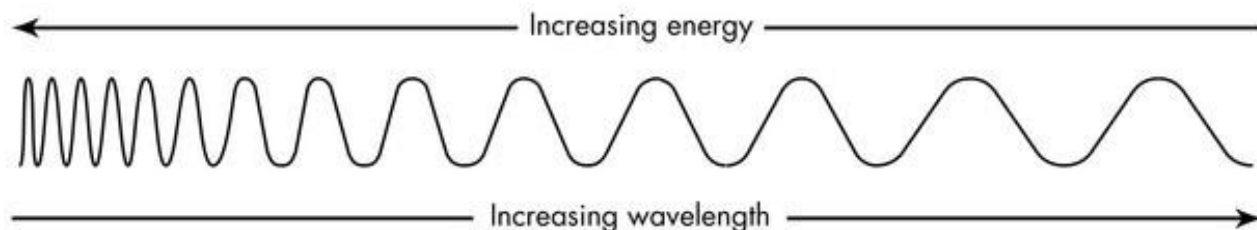
1. Gamma-rays 2. X-rays 3. Ultra-violet (UV)-Visible 4. Infrared (IR) 5. Microwave 6. Radio waves

Wavelength (λ): The distance between two successive crests or troughs is known as wavelength. Wavelength can be represented by λ. Units for wavelength: Å (10^{-8} cm), nm (10^{-9}m), μm, cm.

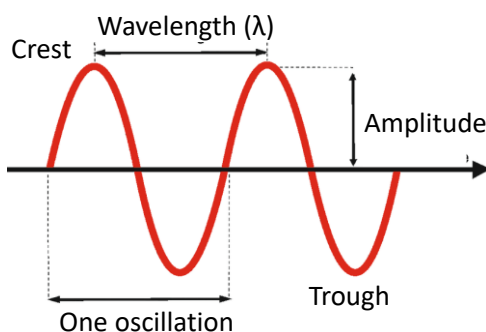**Amplitude (A):** Height of crest or depth of trough is called amplitude.

Wavenumber (γ): The number of waves present in unit length (cm) is known as wavenumber. It is reciprocal of wavelength. Wavenumber can be represented by γ.

$$\gamma \propto \frac{1}{\lambda}$$

Units: cm^{-1}

Frequency (ν): The number of waves passed through a specific point in a given time (sec) is called frequency. $\nu = c/\lambda$.

Units: Hertz (Hz) or cycles/sec.

Various spectroscopic methods available for solving wide range of analytical problems.

The spectroscopy can be classified into two types:

1) *Absorption spectroscopy*: The absorbed radiation by molecule in the form of spectra.

Ex: UV-Visible spectroscopy, infrared (IR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, colorimetry, *etc.*

2) *Emission spectroscopy*: The emitted radiation by the molecules in the form of spectra.

Ex: Fluorescence and phosphorescence spectroscopy.

EMR used for analysis

UV-radiation (UV-Vis Spectroscopy)

IR-radiation (IR Spectroscopy)

Radio-radiation (NMR Spectroscopy)

UV-VISIBLE SPECTROSCOPY (ELECTRONIC SPECTROSCOPY)

Wavelength Range: UV-Visible radiation wavelength is 200-800 nm.

UV region is 200-400 nm & Visible region is 400-800 nm.

Source for UV-Visible radiation: Tungsten lamp, Deuterium lamp, Mercury arc lamp, Xenon lamp.

Solvents: The most commonly used solvents are ethanol, water and hexane. The other solvents like methanol, chloroform and ether can also be used.

In UV-Vis spectrum instead of sharp peaks broad bands will appear because of rotational and vibrational transitions.

Energy levels of molecules: Molecules have different energy levels like, Electronic energy level (E), Vibrational energy level (V) and Rotational energy level (R). The energy order of energy levels in the molecules is as follows: $\Delta E > \Delta V > \Delta R$ Absorption of radiation in UV-Visible region causes transition between electronic energy levels. Therefore, this is also called as **electronic spectroscopy.**
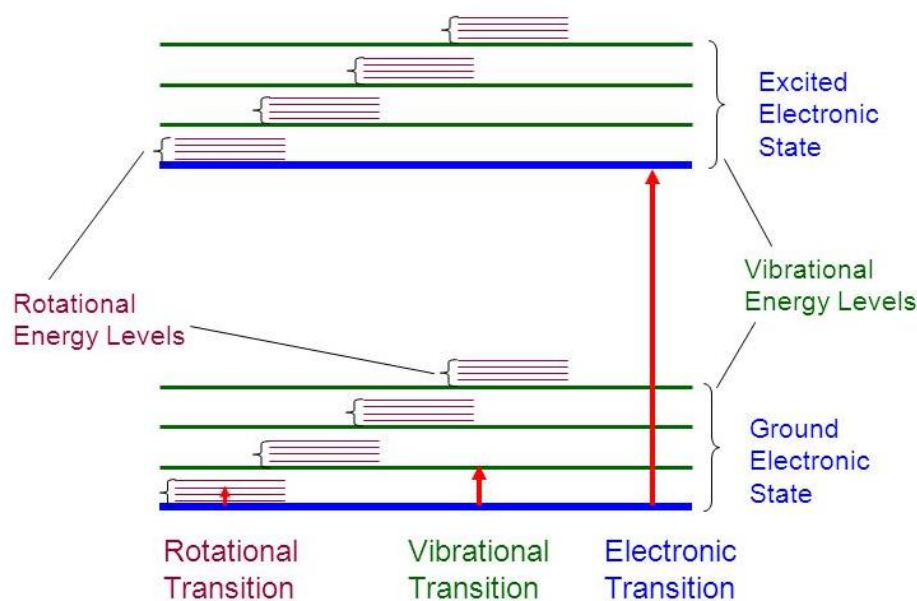
Principle of UV-Visible spectroscopy: When a molecule is exposed to UV-Visible radiation, electron present in the electronic ground state (E_0) absorbs the UV-visible radiation and travels into the higher energy electronic state (E_n). The transportation of electron from electronic ground state to electronic excited state is called as electronic transitions.

Absorption Laws:

Monochromatic light is a **single-wavelength light**, where mono refers to single, and chroma means color.

Beers Law: When a monochromatic light passed through a sample solution, the absorption of light (A) is directly proportional to the concentration (c) of the solution. This law was proposed by Pierre Bouguer. **A ∝ c**
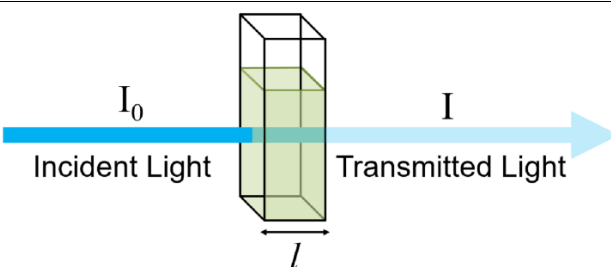
Lamberts Law: When a monochromatic light passed through a sample solution, the absorption of light (A) is directly proportional to the path length (*l*) of the sample solution. This law was proposed by Johann Heinrich Lambert. **A $\propto$ *l***

Beer-Lamberts law: When a monochromatic light passed through a solution, absorption (A) of radiation is directly proportional to the concentration of the solution (c) and the path length (*l*) of the sample solution.

$$A \propto cl$$

$$A = \varepsilon cl$$

$$A = \log_{10}\left(\frac{I_o}{I}\right) = \epsilon cl$$

I_0 = Intensity of incident light;   ε = Molar extinction coefficient;

I = Intensity of transmitted light; c = Concentration of the solution;

l = path length of solution.

*** POSSIBLE ELECTRONIC TRANSITIONS IN UV-VISIBLE SPECTROSCOPY ***

The possible electronic transitions can be graphically shown as follows:
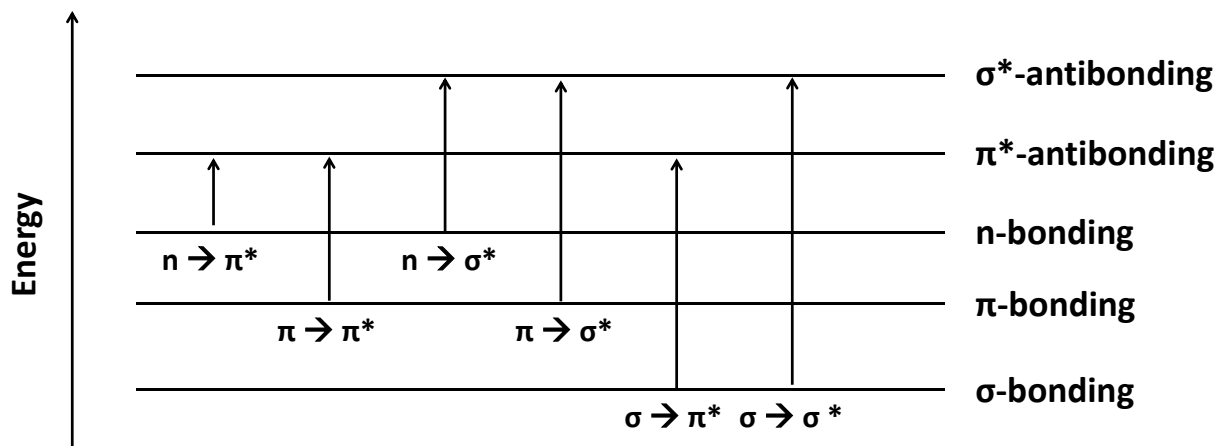
1. σ → σ* transition	4. n → π* transition
2. π → π* transition	5. σ → π* transition
3. n → σ* transition	6. π → σ* transition

Energy order: n - π* < π - π* < n - σ* < σ - σ*

1. σ → σ* transition: Molecules which are having only σ-electrons.

Examples: Alkanes (CH_3-CH_3) and cycloalkanes.

2. π → π* transition: Molecules having σ and π electrons.

Examples: Alkenes ($CH_2=CH_2$), alkynes (CH≡CH) and aromatics.

3. n → σ* transition: Molecules having σ and n electrons.

Example: Alcohols (-CH_2OH), alkyl halides (-CH_2Cl), amines (-CH_2NH_2), etc.

4. n → π* transition: Molecules having σ, π and n electrons.

Examples: Carbonyls (-C=O), carboxylic acids (-COOH), esters (-COOR) and amides (-$CONH_2$).

5. σ → π* transition and 6. π → σ* transitions: These transitions are only theoretically possible but practically not allowed due to symmetry criteria.

Examples for different electronic transitions

1) CH_3-CH_3: Only σ → σ* transition is possible

2) $CH_2=CH_2$: π → π* and σ → σ* transitions are possible

3) Benzene.
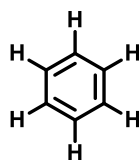
 π → π* and σ → σ* transitions.

4) CH_3-CH_2-Cl: n → σ* and σ → σ* transitions.

5) Amines (CH_3CH_2-NH_2): n → σ* and σ → σ* transitions.

6) Acetic acid
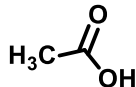
 π → π*, σ → σ*, n → σ* and n → π* transitions.

7) Acetone (CH_3COCH_3): n → π*, n → σ*, π → π*, and σ → σ* transitions.

Absorption spectrum

The intensity of the absorption varies as a function of wavelength is called as absorption spectrum.

The wavelength which corresponding to the maximum absorption intensity is called maximum absorption wavelength (λ_{max}). λ_{max} depends on various factors like Chemical structure of the molecule and solvent used to record spectrum.
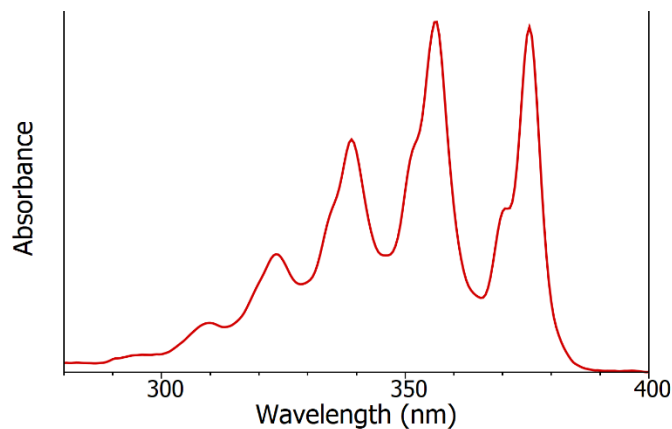
BASIC TERMINOLOGY IN ABSORPTION SPECTROSCOPY

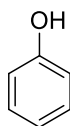**Chromophore:** Chromophore is a group of atoms or a part of a molecule that absorbs light.

Examples: C=C (λ_{max} = 190 nm), C≡C (λ_{max} = 205 nm), C=N (λ_{max} = 207 nm), C≡N and N≡N, NO_2, N=O, C=O, *etc*.

Auxochrome: A group attached to chromophore that can change the absorption characteristics of the chromophore is called auxochromes.
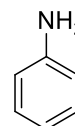
Examples: -OH, NH_2, NR_2, NHR, SH, OR, etc.

Benzene (λmax = 255 nm)

Phenol (λmax = 275 nm)
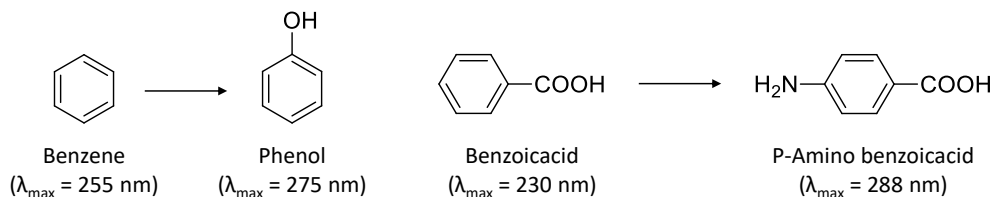
Aniline (λmax = 275 nm)

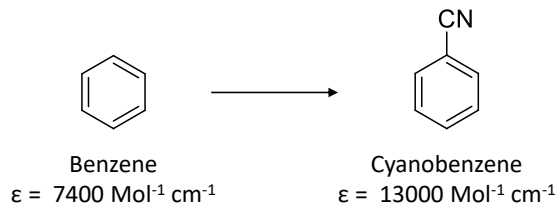**SHIFTS IN ABSORPTION SPECTRUM**
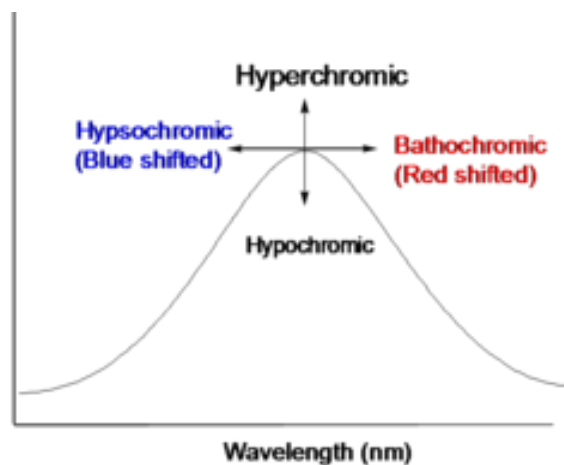
a) Bathochromic shift or Red shift: Shift of maximum absorption wavelength (λ_{max}) towards longer wavelength due to substitution or solvent is called as bathochromic shift or red shift.

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Benzene
(λ_{max} = 255 nm)

Phenol
(λ_{max} = 275 nm)

Benzoicacid
(λ_{max} = 230 nm)

P-Amino benzoicacid
(λ_{max} = 288 nm)

b) Hypsochromic shift or Blue shift: Shift of maximum absorption wavelength (λmax) towards shorter wavelength due to substitution or solvent is called as hypsochromic shift or blue shift.

Aniline
(λ_{max} = 275 nm)

Anilinium chloride
λ_{max} = 265 nm
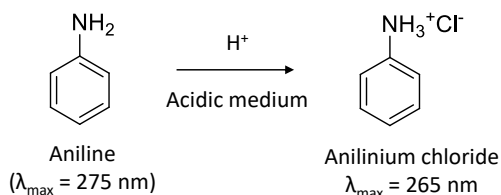
c) Hyperchromic shift: Increase in absorption intensity (ε) of a compound is called Hyperchromic shift.

Benzene
ε = 7400 Mol^{-1} cm^{-1}

Cyanobenzene
ε = 13000 Mol^{-1} cm^{-1}

d) Hypochromic shift: Decrease in absorption intensity (ε) of a compound is called as Hypochromic shift.

Naphthalene
ε = 19000 Mol^{-1} cm^{-1}

2-Methylnaphthalene
ε = 10250 Mol^{-1} cm^{-1}
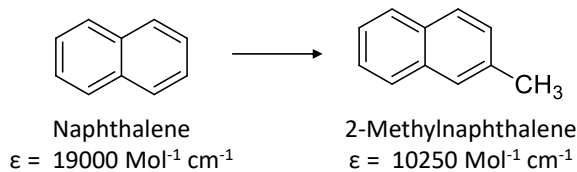
SELECTION RULES FOR UV-VISIBLE SPECTROSCOPY

1) The transition of only one electron from lower electronic energy level to higher electronic energy level by the absorption of UV-Visible radiation is allowed, means provide more intense band. Transitions involving two or more electrons are forbidden means provide less intense band or not detected.

2) $\pi - \pi^*$ transitions are allowed because π & π^* orbitals are in plane; thus, they readily overlap. n $- \pi^*$ transitions are forbidden because n & π^* orbitals are out of plane. So, they undergo poor overlapping.

3) **Spin selection rule:** During electronic transition retention of spin of electron is allowed. Inversion of spin of electron is forbidden. Means $\Delta S = 0$.

4) **Angular momentum rule:** The change in angular momentum should be 0 or ±1.

5) **Multiplicity rule***:* Electron transition between the *same spin multiplicity* allowed (i.e., singlet to singlet or triplet to triplet), whereas, singlet to triplet or triplet to singlet is forbidden.

6) **Laporte rule:** Electronic transitions involving molecular orbitals with same symmetry are forbidden (less probable). Electronic transitions involving molecular orbitals with different symmetry are highly probable.

   Gerade (g) means molecular orbital having center of symmetry.

   Ungerade (u) means the molecular orbital without center of symmetry.

   i.e., allowed. g → u or u → g is allowed.

   σ - g, π - u, σ* - u, π* - g

Applications of UV-Visible absorption spectroscopy

1. *Structure elucidation of organic compounds:* UV-Visible absorption spectroscopy is useful in the structure elucidation of organic compounds such as the presence or absence of unsaturation or hetero atoms etc.

2. *Detection of impurities:* Impurities present in organic compounds can be detected by UV-Visible absorption spectroscopy.

3. UV-Visible absorption spectroscopy is used to find the conjugation in a molecule.

4. UV-Visible absorption spectroscopy can be used to find the molar concentration of the solution.

5. *Detection of functional groups*: UV-Visible absorption spectroscopy is used to detect the presence of certain functional groups present in compounds.

6. *Detection of geometrical isomers (Trans and Cis)*: In the case of geometrical isomers, trans isomers exhibit slightly longer wavelength than the corresponding cis isomers.

INFRARED (IR) SPECTROSCOPY

Infrared (IR) spectroscopy is also called as *rotational vibrational spectroscopy*.

The spectroscopy which deals with the infrared (IR) radiation is called as IR spectroscopy.

IR spectroscopy is particularly used to identify different functional groups present in organic molecules. IR spectroscopy is also useful in molecular structure determination.

A common laboratory instrument that uses this technique is a Fourier Transform Infrared (FTIR) spectrometer.

Range: In terms of wavenumber IR region is from **12500 cm^{-1} to 50 cm^{-1}**. (The wavelength region from 0.8 μm to 200 μm. But representation in wavelength is not common for IR spectroscopy).

Near IR region: 12500 – 4000 cm^{-1} (0.8 – 2.5 μm).

Mid IR region: 4000 – 667 cm^{-1} (2.5 – 15 μm), this is the main important region. Almost all functional groups absorb in this region.

4000 – 1450 cm^{-1} is functional group region.

1450 – 667 cm^{-1} is fingerprint region.

Far IR region: 667 – 50 cm^{-1} (15 – 200 μm)

Source: Nernst glover, Mercury arc, IR-LEDs and Lasers, etc.

PRINCIPLE OF IR SPECTROSCOPY

When molecules absorb IR radiation, molecular vibrations and rotations takes place. That means the molecules undergo lower vibrational, rotational energy level to higher vibrational rotational energy level. Hence it is called as vibrational rotational spectroscopy.
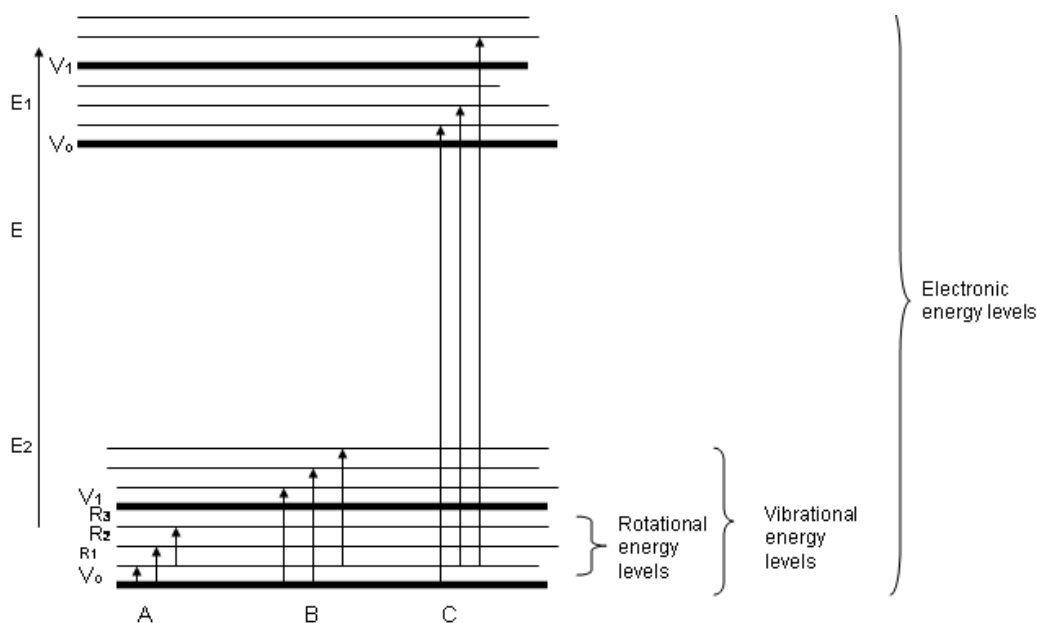
Selection rules of IR Spectroscopy

➢ The most fundamental requirement for IR activity is that a vibration must cause change in the dipole moment of the molecule. Means, the molecules which change their dipole moments is IR active. Means the molecules having dipole moment is not equal to zero then those molecules are IR active.

➤ If dipole moment is equal to zero then those molecules are IR inactive.

$$\frac{D\mu}{Dr} \neq 0$$

Examples: HCl, NaOH, KOH, $CHCl_3$, NH_3, H_2O, C_2H_5OH, H_2S: $\mu \neq 0$, Therefore IR active.

➤ The molecule which does not change their dipole moment during IR absorption is IR inactive.

H_2, N_2, Cl_2, $CH_2=CH_2$, HC≡CH etc. are IR inactive.

❖ **Exception:** Carbon dioxide (CO_2) though it is a linear molecule and $\mu = 0$, but it changes its dipole moment due to **asymmetric stretching and asymmetric bending** hence it is IR active.

O=C=O
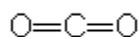
Asymmetric stretching (IR active)

****Types of Molecular Vibrations

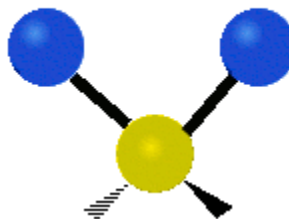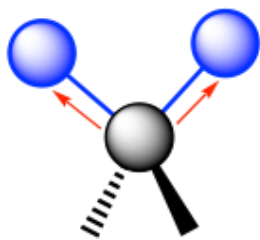| 1. Stretching vibrations	2. Bending vibrations
a) Symmetrical stretching vibrations	A) In plane bending vibrations
b) Asymmetrical stretching vibrations	a) Scissoring bending vibrations
	b) Rocking bending vibrations
	B) Out of plane bending vibrations
	a) Wagging bending vibrations
	b) Twisting bending vibrations

1. Stretching vibrations

In stretching vibrations occurs a change in inter-atomic distance along the bond axis. That **means bond length changes in stretching vibrations**.

Occurs at higher frequency 4000-1450 cm^{-1}.

Depending on the movement of atoms stretching vibrations are two types: Symmetrical stretching vibrations and asymmetrical stretching vibrations.

A) Symmetrical stretching vibration: Both the atoms in a molecule either move towards or away from the central atom, but in the same direction.

B) Asymmetrical stretching vibration: In asymmetric stretching vibration, one atom approach towards the central atom, while the other atom goes away from the central atom.
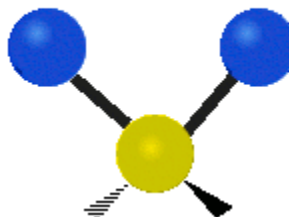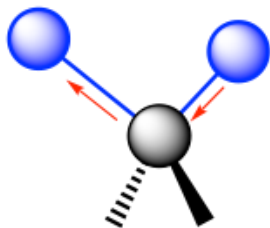
2. Bending vibrations

The position of the atoms changes relative to the original bond axis. Vibration or oscillation not along the line of bond. In **bending vibrations bond angle is altered**.

Bending vibrations occur at lower frequency 1450 – 667 cm^{-1}.

Bending vibrations are two types: (A) In plane bending vibration and (B) Out of plane bending vibration.

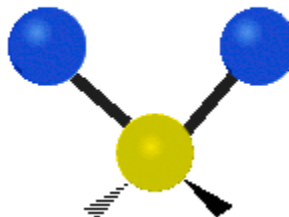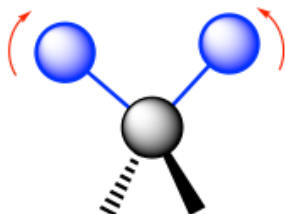| A) In plane bending vibration	B) Out of plane bending vibration
a) Scissoring	a) Wagging
b) Rocking	b) Twisting

A) In plane bending: In plane bending again two types.

a) Scissoring: In this type two atoms approach towards each other or go away from each other.

b) Rocking: In this type, the moment of atoms moves in same direction.

B) Out of plane bending:

a) Wagging: In this type, two atoms move up or down the plane with respect to the central atom.

b) Twisting: In this type, one of the atoms move up to the plane, while the other atom moves down the plane with respect to the central atom.

Calculation of no of molecular vibrations in molecules

For linear molecules: No of vibrations = 3N-5.

Where N is the number of atoms present in molecule.

Eg: 1) CO_2: N = 3, 3x3-5 = 4 vibrations

   2) $BeCl_2$: N = 3, 3x3-5 = 4 vibrations.

       3) HC≡CH: N = 4, 3x4-5 = 7 vibrations.

For nonlinear molecules: No of vibrations = 3N-6.

Example: 1) NH_3: N = 4, 3x4-6 = 6 vibrations.

2) H_2O: N = 3, 3 x3-6 = 3. Therefore, water molecule has 3 vibrations.

Applications of IR spectroscopy

1. **Identification of functional groups**: IR spectroscopy is used to identify functional groups like alkenes, alkynes, aldehyde, ketones, amines. i.e., C=C, C≡C, C=O, C-OH, CO-NH_2, NH_2, etc.

2. **To distinguish geometrical isomers (Cis-trans):** Geometrical isomers like Cis and Trans isomers can be determined using IR spectroscopy. Generally, trans-isomers are IR inactive and cis-isomers are IR active.
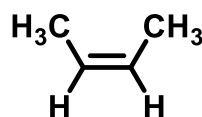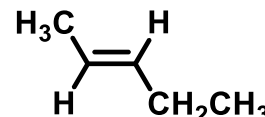

Cis-2-butene
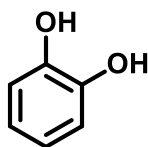$\mu \neq 0$
IR active
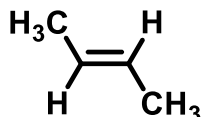
Trans-2-butene
μ =0
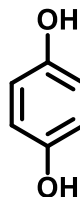IR inactive
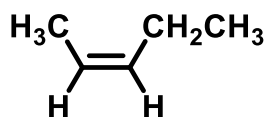
Cis-2-pentene
C-H bending
700 cm^{-1}.

Trans-2-pentene
C-H bending
900 cm^{-1}.

3. Distinguish between two types of hydrogen bonding (Intramolecular and intermolecular hydrogen bonding).

o-dihydroxy benzene
Intramolecular H-bonding
3570 cm^{-1}

p-dihydroxy benzene
Intermolecular H-bonding
3400 cm^{-1}

4. Study of reaction progress:

Progress of the chemical reaction can be determined by examining the small portion of the reaction mixture withdrawn from time to time. The rate of disappearance of a characteristic absorption band of the reactant functional group and/or the rate of the appearance of the characteristic absorption band of the product group to formation of product is observed.

5. *Detection of impurities:* IR spectroscopy is used to determine the impurities present in the sample.

6. IR spectroscopy is also useful in measuring the degree of polymerization in polymer manufacture.

7. IR spectrum is also useful in measuring in forensic analysis in both criminal and civil cases. For example, in identifying in polymer degradation. It can be used in determining the blood alcohol content of a suspected drunken driver.

8. IR spectroscopy has been successfully used in analysis and identification of pigments present in paintings.

9. IR spectroscopy can also use in the food industry to measure the concentration of various compounds in different food products.

CHAPTER-II

WATER TECHNOLOGY

Syllabus: Causes and effects of hardness of water, expression of hardness ($CaCO_3$ equivalent), units and types of hardness. Estimation of temporary and permanent hardness of water by EDTA method. Numerical problems based on hardness of water. Potable water: characteristics, treatment of water for domestic supply. Desalination of brackish water: Reverse osmosis. Alkalinity of water and its determination. Boiler feed water: Boiler troubles (scale and sludge, priming, foaming, caustic embrittlement and boiler corrosion) and its treatment: Internal treatment (colloidal, phosphate, calgon conditioning of water). External treatment (ion –exchange process).

Chemical formula of water is H_2O.

PH of water is neutral. Pure water is a colorless and odorless.

On the earth 70-75% of water is existing in the form of lakes, rivers and oceans and only 20-25% of land is existing. Among these only 1% of water, we are using.

Sources of water

1) Rain fall

2) Surface water: Seas, Oceans and Rivers.

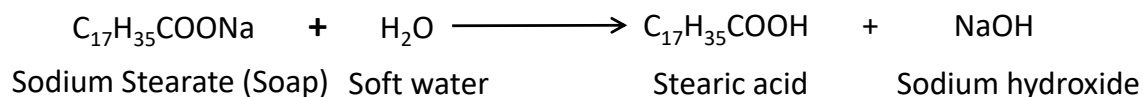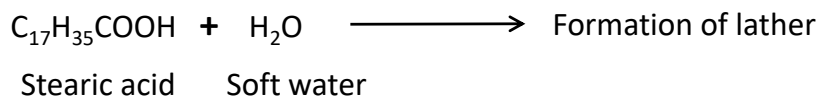3) Underground water: Springs, Well and Borewell.

Impurities in water

Impurities present in water can be broadly classified into the following types.

1. **Dissolved impurities:** Inorganic salts like bicarbonates (HCO_3^-), chlorides (Cl^-), sulphates (SO_4^{-2}), and nitrates (NO_3^-) of Sodium (Na^+), Calcium (Ca^{+2}), Magnesium (Mg^{+2}), and Iron (Fe^{+2}) ions.

2. **Dissolved gases:** Oxygen, nitrogen, carbon dioxide (CO_2), oxides of nitrogen, oxides of Sulphur, ammonia and hydrogen sulfide (H_2S), etc.

3. **Suspended impurities**: Sand or clay and decayed organic substances.

4. **Microorganisms**: These include bacteria, fungi, and algae.
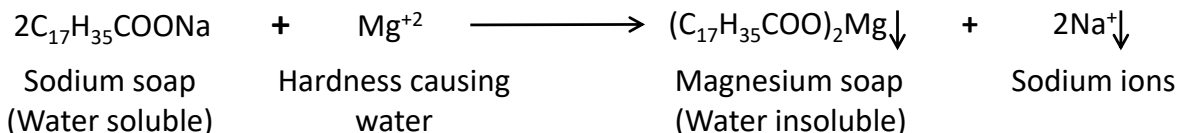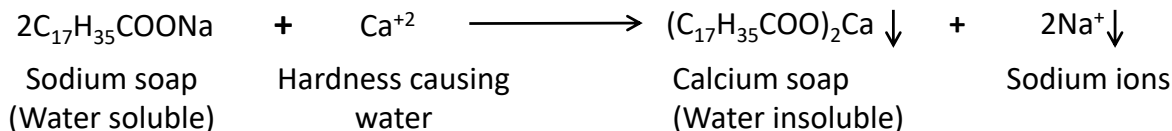
Types of water: Water can be broadly classified into two types, i.e., soft water and hard water.

1) *Soft water:* Water which gives lather readily with soap solution called soft water.

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

Sodium Stearate (Soap) Soft water   Stearic acid   Sodium hydroxide

$$C_{17}H_{35}COOH \ + \ H_2O \longrightarrow \text{Formation of lather}$$

Stearic acid   Soft water

2) Hard water: Water which does not give lather with soap solution, but produce only white insoluble precipitate (or scum) called hard water.
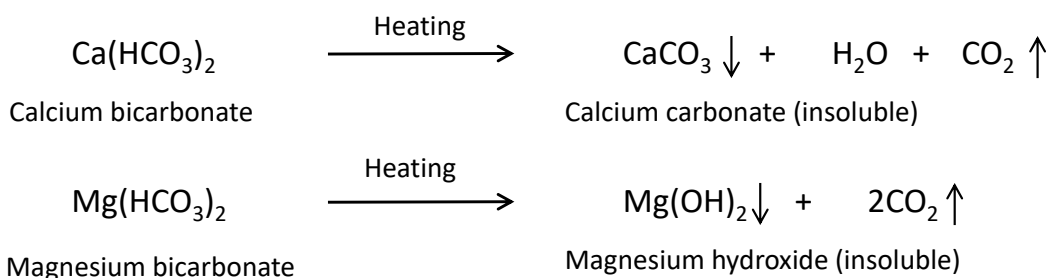
$$2C_{17}H_{35}COONa \ + \ Ca^{+2} \longrightarrow (C_{17}H_{35}COO)_2Ca \downarrow \ + \ 2Na^+\downarrow$$

Sodium soap   Hardness causing   Calcium soap   Sodium ions
(Water soluble)   water   (Water insoluble)

$$2C_{17}H_{35}COONa \ + \ Mg^{+2} \longrightarrow (C_{17}H_{35}COO)_2Mg\downarrow \ + \ 2Na^+\downarrow$$

Sodium soap   Hardness causing   Magnesium soap   Sodium ions
(Water soluble)   water   (Water insoluble)

Causes for hardness of water

Hardness: Hardness is the characteristic property of water, which prevents the lathering of soap. It caused due to the presence of dissolved calcium (Ca^{+2}) and magnesium (Mg^{+2}) salts such as bicarbonates (HCO_3^-), sulphates (SO_4^{-2}), chloridesb(Cl^-), and nitrates (NO_3^-).

Types of hardness: Hardness is two types i.e., temporary and permanent hardness.

1. Temporary hardness: Temporary hardness caused due to the presence of **bicarbonate (HCO_3^-) salts of Calcium(Ca^{+2}) and Magnesium (Mg^{+2})**, that is $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ in water. Temporary hardness can be removed by boiling and filtering the water.

$$Ca(HCO_3)_2 \xrightarrow{\text{Heating}} CaCO_3 \downarrow \ + \ H_2O \ + \ CO_2 \uparrow$$

Calcium bicarbonate   Calcium carbonate (insoluble)

$$Mg(HCO_3)_2 \xrightarrow{\text{Heating}} Mg(OH)_2\downarrow \ + \ 2CO_2 \uparrow$$

Magnesium bicarbonate   Magnesium hydroxide (insoluble)

2. Permanent hardness: Permanent hardness causes due to the presence of chlorides (Cl^-), sulphates (SO_4^{-2}) and nitrates (NO_3^-) of Calcium (Ca^{+2}) and Magnesium (Mg^{+2}) ions, that is $CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $Ca(NO_3)_2$, and $Mg(NO_3)_2$. Permanent hardness can be removed by i) Ion exchange process, ii) Lime soda process, and iii) Zeolite method.

Total Hardness = Temporary Hardness + Permanent Hardness

Units of hardness of water: Four types of units are available to express hardness of water.

1) ppm; 2) mg/L; 3) °F (Degree French); 4) °Cl (Degree Clark).

1. ppm (parts per million): No of parts of $CaCO_3$ equivalents hardness causing salts present in 10^6 parts of water.

2. mg/L: 1 milli gram of $CaCO_3$ equivalents of hardness causing salts present in 1 liter (or 10^6 mg) of water.

   1ppm = 1mg/Lit.

3. Degree French (°F): 1 Part of $CaCO_3$ equivalents of hardness causing salts present in 10^5 parts of water.

4. °Cl (Degree Clark): 1 part of $CaCO_3$ equivalents of hardness causing salts present in 70,000 parts of water. 1ppm = 0.07 °Cl.

> Relationship among the units of hardness: 1ppm = 1mg/L = 0.1 $^\circ$F = 0.07 $^\circ$Cl

Any water sample with hardness less than 150 is good and potable, while beyond 350 ppm is not suitable for consumption.

Degree of hardness:

The hardness of water can be expressed in terms of **equivalent amount of $CaCO_3$.** Because of two reasons. i.e., i) $CaCO_3$ is insoluble in water and doesn't contribute hardness and ii) the molecular weight of $CaCO_3$ is 100 and its equivalent weight is 50, which is easy for calculation. The concentration of hardness producing salts is calculated as

> The hardness of water in terms of $CaCO_3$ equivalents $= \dfrac{\text{Weight of salt}}{\text{Molecular weight of salt}} \times 100$

Equivalent weight = Molecular weight / total positive or negative charge

Problems

1) Calculate the total hardness in calcium carbonate equivalents ($CaCO_3$) for the following water sample. The water sample contains 81 mg/L of $Ca(HCO_3)_2$ (Molecular weight is 162).

The hardness of water in terms of equivalent amount of $CaCO_3 = \dfrac{81}{162} \times 100 = 50$ mg/L

2) Calculate the total hardness in calcium carbonate equivalents ($CaCO_3$) for the following water sample. Sample water contains 11.1 mg/L of $CaCl_2$ (Molecular weight is 111).

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The hardness of water in terms of equivalent amount of $CaCO_3$ = $\dfrac{11.1}{111}$ X 100 = 10 mg/L

3) Sample water contains 9.5 mg/L of $MgCl_2$ (Molecular weight is 95).

The hardness of water in terms of equivalent amount of $CaCO_3$ = $\dfrac{9.5}{95}$ X 100 = 10 mg/L

4) Sample water contains 136 mg/L of $CaSO_4$ (Molecular weight is 136).

The hardness of water in terms of equivalent amount of $CaCO_3$ = $\dfrac{136}{136}$ X 100 = 100 mg/L

5) Sample water contains 40 mg/L of $MgSO_4$ (Molecular weight is 120).

The hardness of water in terms of equivalent amount of $CaCO_3$ = $\dfrac{40}{120}$ X 100 = 33.3 mg/L

6) Sample water contains 164 mg/L of $Ca(NO_3)_2$ (Molecular weight is 164).

The hardness of water in terms of equivalent amount of $CaCO_3$ = $\dfrac{164}{164}$ X 100 = 100 mg/L

7) Sample water contains 148 mg/L of $Mg(NO_3)_4$ (Molecular weight is 148).

The hardness of water in terms of equivalent amount of $CaCO_3$ = $\dfrac{148}{148}$ X 100 = 100 mg/L

8) Calculate the temporary, permanent and total hardness for the water containing $Ca(HCO_3)_2$ = 162 mg/L, $CaCl_2$ = 111 mg/L, $MgSO_4$ = 120 mg/L. *HCS is hardness causing salt.

HCS	Amount of HCS	M.Wt.	Hardness in terms of $CaCO_3$
$Ca(HCO_3)_2$	162	162	$\dfrac{162}{162}$ X 100 = 100 mg/L
$CaCl_2$	111	111	$\dfrac{111}{111}$ X 100 = 100 mg/L
$MgSO_4$	120	120	$\dfrac{120}{120}$ X 100 = 100 mg/L

| Temporary hardness | = Hardness due to Ca(HCO₃)₂ |

Temporary hardness   = Hardness due to $Ca(HCO_3)_2$

                           = 100 mg/L

Permanent hardness   = Hardness due to Cl_2, SO_4

                           = 100 + 100 = 200 mg/L

Total hardness   = Permanent hardness + Temporary hardness

                           = 100 + 200 = 300 mg/L

9) Calculate the temporary, permanent and total hardness of a sample of hard water containing the following dissolved salts per liter.

$Mg(HCO_3)_2$ = 14.6 mg/L, $Ca(HCO_3)_2$ = 16.2 mg/L, $MgCl_2$ = 9.5 mg/L, $CaSO_4$ = 13.6 mg/L.

HCS	Amount of HCS	M.Wt.	Hardness in terms of $CaCO_3$
$Mg(HCO_3)_2$	14.6	146	$\dfrac{14.6}{146} \times 100$ = 10 mg/L
$Ca(HCO_3)_2$	16.2	162	$\dfrac{16.2}{162} \times 100$ = 10 mg/L
$MgCl_2$	9.5	95	$\dfrac{9.5}{95} \times 100$ = 10 mg/L
$CaSO_4$	13.6	136	$\dfrac{13.6}{136} \times 100$ = 10 mg/L

Temporary hardness   = Hardness due to $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$

                           = 10 + 10 = 20 mg/L

Permanent hardness   = Hardness due to Cl_2, SO_4

                           = 10+10 = 20 mg/L

Total hardness   = Permanent hardness + Temporary hardness

                           = 20 + 20 = 40 mg/L

10) Calculate the total, temporary and permanent hardness of a sample of hard water containing the following dissolved salts per liter.

$Mg(HCO_3)_2$ = 7.3 mg/L, $Ca(HCO_3)_2$ = 32.4 mg/L, $CaCl_2$ = 11.1 mg/L, $MgCl_2$ = 19 mg/L, $MgSO_4$ = 60 mg/L.

HCS	Amount of HCS	M.Wt.	Hardness in terms of CaCO$_3$
Mg(HCO$_3$)$_2$	7.3	146	$\dfrac{7.3}{146} \times 100 = 5$ mg/L
Ca(HCO$_3$)$_2$	32.4	162	$\dfrac{32.4}{162} \times 100 = 20$ mg/L
CaCl$_2$	11.1	111	$\dfrac{11.1}{111} \times 100 = 10$ mg/L
MgSO$_4$	60	120	$\dfrac{60}{120} \times 100 = 50$ mg/L
MgCl$_2$	19	95	$\dfrac{19}{95} \times 100 = 20$ mg/L

Temporary hardness   = Hardness due to Ca(HCO$_3$)$_2$ and Mg(HCO$_3$)$_2$

= 20 + 5 = 25 mg/L

Permanent hardness   = Hardness due to Cl$_2$, SO$_4$

= 10 + 50 + 20 = 80 mg/L

Total hardness   = Permanent hardness + Temporary hardness

= 25 + 80 = 105 mg/L

Quality of water for different uses:

| Purpose	Quality requirement
Drinking	Tasty, clear and free from color, odor, turbidity and pathogens
Domestic washing	Soft water producing lather readily.
Textile dying	Free from color, turbidity, organic matter, Iron (Fe) and Magnesium (Mg)
Boiler feed water	Free from dissolved salts, suspended impurities, silica and dissolved gases.
Drugs and pharmaceuticals	Soft and clear, free from pathogens, color, odor and suspended impurities.
Construction	Not too hard, should contain less amount of chlorides.

Paper industry	Free from color, turbidity, organic matter, iron (Fe), manganese (Mn), silica and alkalinity.

ESTIMATION OF HARDNESS OF WATER BY EDTA METHOD

➢ EDTA is Ethylene Diamine Tetra Acetic acid

➢ EDTA method is used to determine total temporary, permanent and hardness of water.

➢ Involves the volumetric titration. It is a complexometric titration (colored complex is used to determine the end point of the titration)

➢ Titrant: EDTA (Ethylene Diamine Tetra Acetic acid). The structure is shown below
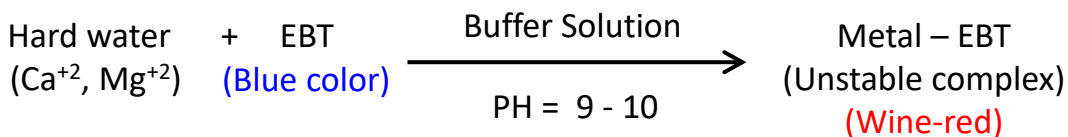

EDTA Structure
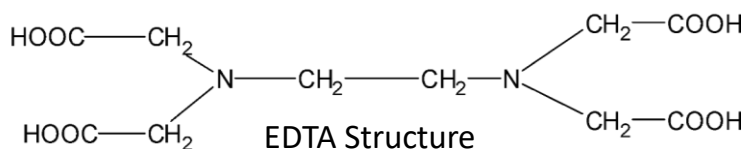
➢ Indicator: Eriochrome Black-T (EBT)

➢ Analyte: Water

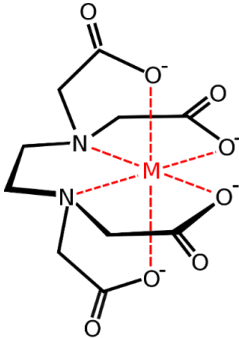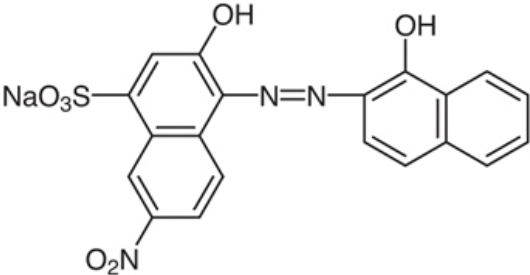➢ Buffer: Ammonium chloride (NH_4Cl) + Ammonium hydroxide (NH_4OH) (PH: 9-10)

Principle: EDTA has low solubility in water, but its disodium salt dissolves in water quickly & completely. EDTA is a hexa dentate ligand. It binds the metal ions in water to give stable chelate complex. Hence it is called as complexometric titration method. This method has greater accuracy, convenience & more rapid.

Initially buffer solution (NH_4Cl + NH_4OH) is added to the hard water to maintain the PH at 9-10. When 3 drops of Eriochrome Black-T (EBT) indicator is added to the hard water sample at PH 9-10, water turns to wine-red colored solution due to the formation an **unstable complex of EBT with Ca^{+2} and Mg^{+2} present** in hard water. When wine-red colored solution is titrated with EDTA, **wine-red color gets converted into blue color due to the formation of colorless stable complex and free EBT indicator**. The liberated free indicator has blue color at pH 9-10. So, the color changes from wine-red to blue is considered as the end point.

Indicator EBT becomes wine red in color when bound with metal ions while remaining blue in color when free from metal ions. While EDTA (which is ethylene diamine tetra acetic acid) is colorless whether it's bound to metal ions or not. So, the addition of the EBT indicator in the sample (water containing metal) makes it wine red in color as EBT binds with metal ions. EBT indicator binds with metal ions loosely, while EDTA binds with metal ions strongly. So, when all metal ions are bound to

EDTA, indicator EBT remains free in the water sample, therefore the solution turns blue. Wine red color to blue color is considered as an end point.

Hard water + EBT
(Ca^{+2}, Mg^{+2}) (Blue color) $\xrightarrow[\text{PH = 9 - 10}]{\text{Buffer Solution}}$ Metal – EBT (Unstable complex) (Wine-red)

M – EBT + EDTA (Wine-red) $\xrightarrow[\text{PH = 9 - 10}]{\text{Buffer Solution}}$ Metal – EDTA (color less) (Stable complex) + EBT (Blue color)
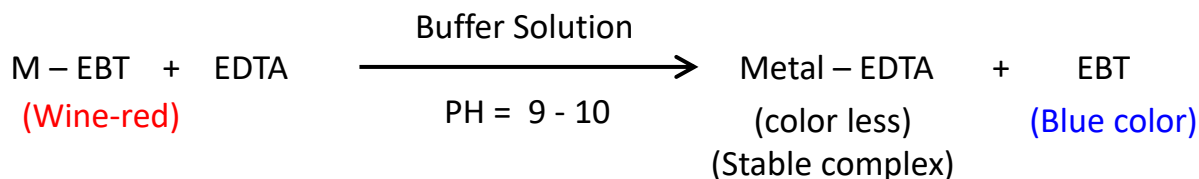
Metal-EDTA structure	**Eriochrome black-T (EBT)**

Procedure: 5 steps are involved in EDTA method.

1) Preparation of standard hard water (SHW)

2) Standardization of EDTA.

3) Estimation of total hardness

4) Estimation of permanent hardness

5) Estimation of temporary hardness.

1) Preparation of standard hard water (SHW) (M_1)

Standard solution means a solution for which the concentration is accurately known. 1.0 g of $CaCO_3$ is dissolved in 1L distilled water and few drops of HCl is added. It is known as a 0.1 N standard hard water.

2) Standardization of EDTA (M_2): Take 50 ml of standard hard water into a conical flask + add 10 ml of buffer solution + 3- drops of eriochrome black-T (EBT), then it turns to wine-red color. Then titrate with EDTA. When wine-red color converted to blue color will be considered as an end point.

$M_1V_1 = M_2V_2$

M_1 = Molarity of standard hard water (0.1 N)

V_1 = Volume of standard hard water taken into conical flask (50 mL)

M_2 = Molarity of EDTA to be measured

V_2 = Volume of EDTA (Burette reading)

3) Estimation of Total hardness of hard water sample: Take 50 mL of sample hard water (i.e., tap water) in a conical flask + add 10 mL of buffer solution (NH_4Cl + NH_4OH) + 3-drops of EBT indicator, then it turns to wine-red color. Then titrate with EDTA. When wine-red color converted to blue color will be considered as an end point.

$M_2V_2 = M_3V_3$ → $M_3 = M_2V_2/V_3$

M_2 = Molarity of EDTA, V_2 = Volume of EDTA (Burette reading)

M_3 = Molarity of hard water to be measured

V_3 = Volume of hard water taken into conical flask (i.e., 50 mL).

By multiplying M_3 with 10^5 gives total hardness in ppm units.

4) Estimation of permanent hardness: Take 100 mL of sample hard water and boil it continuously to get to 50 mL. Then filter it and add 50 mL of distilled water to the filtered water and make it to 100 mL.

100 mL of hard water sample $\xrightarrow{\Delta}$ 50 mL of hard water + 50 mL of distilled water
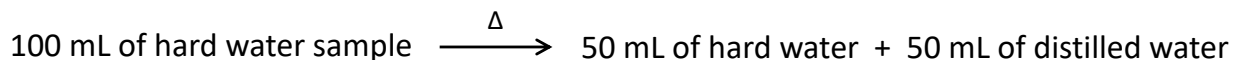
Take 50 mL of the above prepared hard water sample into 250 mL conical flask + add 10 mL of buffer solution (NH_4Cl + NH_4OH) + 3 drops of EBT indicator, then it turns to wine-red color. Then titrate with EDTA. When wine red color converted to blue color will be considered as an end point.

$M_2V_2 = M_4V_4$

$M_4 = M_2V_2/V_4$

M_2 = Molarity of EDTA

V_2 = Volume of EDTA (Burette reading)

M_4 = Molarity of hard water to be measured

V_4 = Volume of hard water taken into conical flask (i.e., 50 mL)

By multiplying M_4 with 10^5 gives permanent hardness (in ppm units).

5) Estimation of temporary hardness:

Total hardness = Permanent hardness + Temporary hardness

Temporary hardness = Total hardness – Permanent hardness.

Result: The hardness of the given water sample has been found to be as follows:

Total hardness = ----------------------------------- ppm

Permanent hardness = ----------------------------- ppm

Temporary hardness = ---------------------------- ppm

Potable Water and it's Characteristics

Water which is safe for drinking is called as potable water.

Characteristics of Potable water

❖ Should be clean, colorless and odorless

❖ PH must be between 6.5 – 8.0

❖ Should be free from pathogenic bacteria

❖ Should not contain dissolved gases like CO, CO_2, NH_3, H_2S etc

❖ The optimum hardness of water must be 125 ppm

❖ Turbidity should not exceed 25 ppm

❖ The maximum concentration of total dissolved solids (TDS) must not exceed 500 ppm

❖ Must be free from heavy metals like Lead (Pb), Arsenic (As), Chromium (Cr) and Manganese (Mn), *etc*.

❖ Water should not be corrosive.

TREATMENT OF WATER FOR DOMESTIC SUPPLY

This treatment involves the removal of colloidal impurities, suspended impurities and pathogenic bacteria. Municipal water treatment method involves the following several steps.

1. Screening, 2. Aeration, 3. Sedimentation, 4. Coagulation, 5. Filtration, 6. Sterilization and disinfection, 7. Storage and supply distribution of water.

1. Screening: All the floating impurities like leaves, sticks, bio-related impurities can be removed in the screening process

Raw water $\longrightarrow$ (≡) $\longrightarrow$ Removes floating materials

Screen with holes
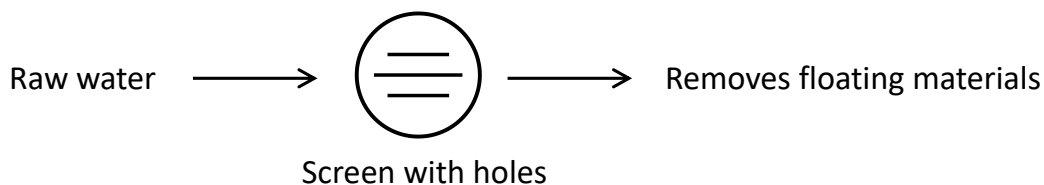
2. Aeration: In this process air will be sent into the water. Then the hazardous gases like carbon monoxide (CO), carbon dioxide (CO_2), NH_3, H_2S etc will be removed. Further, it removes certain metal ion impurities like Iron (Fe^{+3}) and Manganese (Mn^{+2}) by precipitating as metal hydroxides ($Fe(OH)_3$ and $Mn(OH)_2$.

3. Sedimentation: Water is allowed to stand undisturbed for 3-6 hours. Suspended particles settle down and clear water raises to top which can be drawn out with pumps. Almost 75% of suspended impurities can be settled down. Sedimentation step is carried out without adding any chemicals.

4. Coagulation: Helps in the removal of colloidal and suspended impurities by adding coagulants like Alum (K_2SO_4, $Al_2(SO_4)_3$) and $NaAlO_2$, etc. Coagulants can interact with impurities and increase the particle size and facilitate to easy settlement.

5. Filtration: This also helps in the removal of colloidal and suspended impurities which are not removed by sedimentation method. Also, color, smell and most of the bacteria can be removed.

Two types of sand filters are used here.

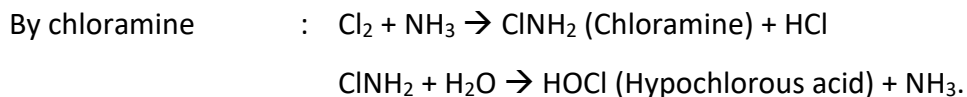Slow sand filter and Rapid sand filter/pressure sand filter.
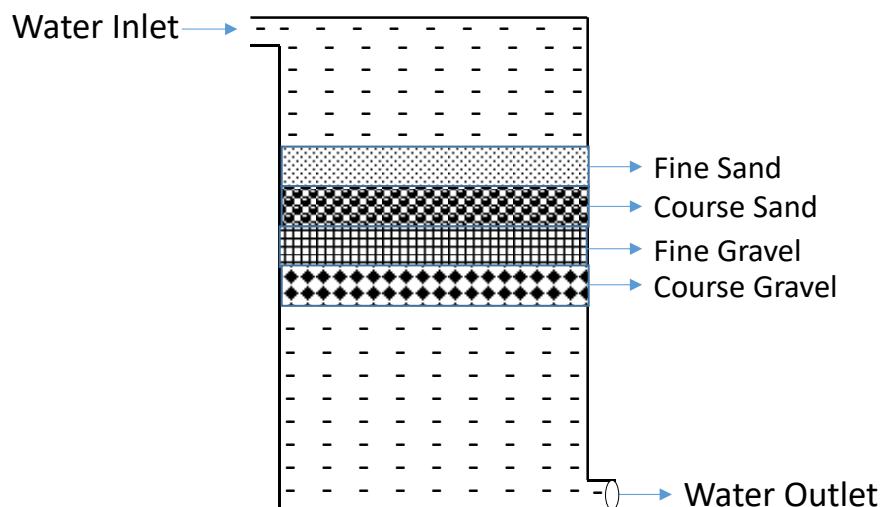
6. Sterilization and disinfection:

The process of removing harmful bacteria is called sterilization. Methods adopted for sterilization are as follows

a) Boiling

b) By passing ozone $O_3 \rightarrow O_2 + [O]$ (Nascent oxygen disinfectant)

c) Chlorination: There are three chlorinating agents.

    By chloramine   : $Cl_2 + NH_3 \rightarrow ClNH_2$ (Chloramine) + HCl

                                  $ClNH_2 + H_2O \rightarrow HOCl$ (Hypochlorous acid) + NH_3.

    By   bleaching : $CaOCl_2 + H_2O \rightarrow Cl_2 + Ca(OH)_2$
powder $Cl_2 + H_2O \rightarrow HOCl + HCl$
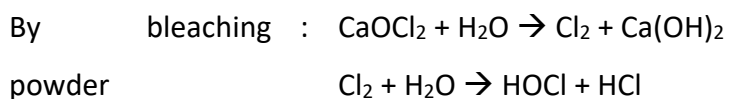
By chlorination   :   Process of addition of calculating amount of Cl_2 to water to kill the bacteria.

$$Cl_2 + H_2O \rightarrow HOCl + HCl.$$
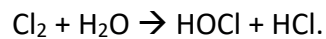
Only calculated amount of Cl_2, must be added, otherwise excess of present as residual Cl_2, which causes bad taste, bad odor and toxicity.

Break point of chlorination: The minimal amount of chlorine which is required to kill pathogenic bacteria.
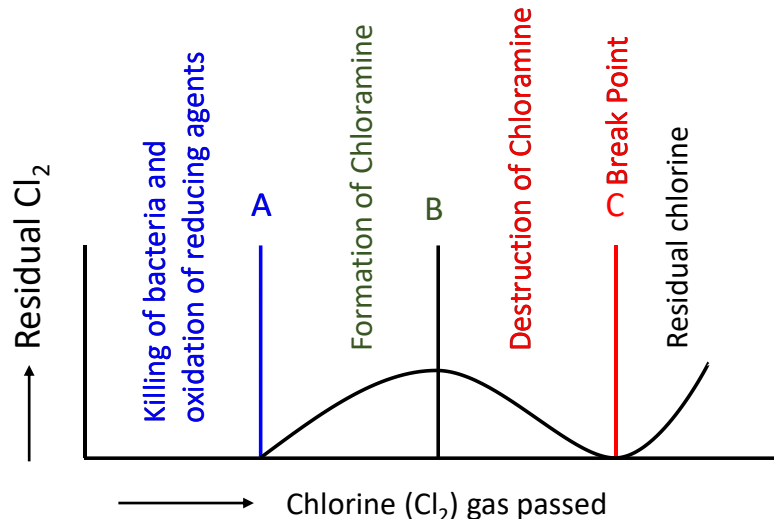
A = Killing of bacteria and oxidation of reducing the impurities

B = Formation of chloramine; C = Destruction of chloramine; D = Residual chlorine.

Advantages of breaking point of chlorine:

It destroys all types of pathogenic bacteria. Color, taste and organic impurities can be removed.

DESALINATION OF BRACKISH WATER

Brackish means salty. Water having dissolved salts with an average of 3.5% is known as brackish water. Such water is not useful for drinking.

Desalination: The process of removal of dissolved salts (e.g., NaCl) from water.

Water quality is usually graded as

Fresh water   :   Less than 100 mg/L of dissolved salts

Brackish water :   10 g – 35 g/L of dissolved salts

Sea water   :   > 35 g/L of dissolved salts

The following techniques are carried out for desalination of Brackish water:

1) Reverse Osmosis, 2) Electrodialysis & 3) Distillation.

1) REVERSE OSMOSIS*

Osmosis: When two solutions of different concentrations are separated by a semi permeable membrane (SPM), **solvent flows from a lower concentration region to a higher concentration region is called as Osmosis**. This process is a natural process. This natural process can be **reversed by applying a pressure** higher than the osmatic pressure on the high concentration side. Then, **the solvent flows from higher concentration solution to lower concentration solution, which is called reverse osmosis**.

The external pressure which is required to stop the flow of solvent from low concentration region to high concentration region is called osmatic pressure.

Semi permeable membranes having the pores in the range of (0.0001 – 0.001 mm in diameter) and these are made by cellulose triacetate or cellulose butyrate or polyamide.

Osmosis — Direction of Water Flow

Reverse Osmosis — Direction of Water Flow
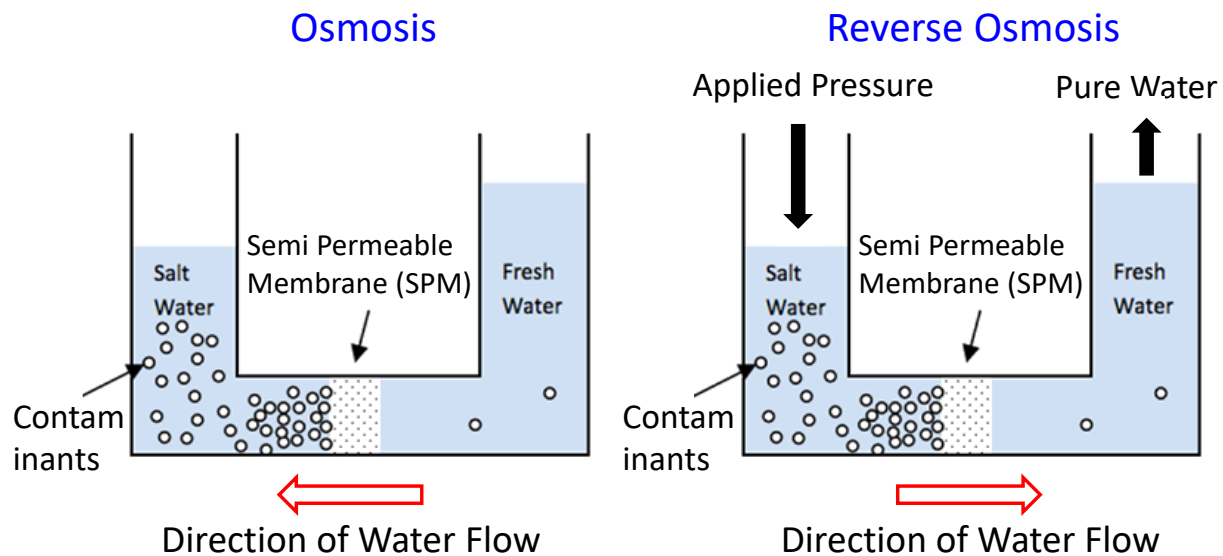
Advantages of RO technique are as follows

1. It can remove ionic and non-ionic, inorganic, colloidal and high molecular weight organic impurities.

2. The lifetime of membrane is quite high (>1 year).

3. The maintenance cost is only the replacement of membrane.

4. Reverse osmosis is the final category of membrane filtration (also known as *super-filtration or hyper-filtration*). It removes particles with size up to 0.1 nm

BOILER FEED WATER

Boilers are two types, steam boilers (generates steam) and hot water boilers. Steam boilers can be used in Power generation, Food processing industry, Textile industry, Paper industries, Building materials, *etc*. The water which is used in boilers called boiler feed water. The water has to meet specific requirements. **If hard water is used in boilers, those boilers get the following troubles.**

Boiler troubles: Boilers troubles are as follows

1) Scales and sludges (formation of deposits)

2) Priming and foaming (carry over)

3) Boiler corrosion

4) Caustic embrittlement

1) Scales and sludges (formation of deposits)

On continuous evaporation of water in boilers the concentration of insoluble matters increases progressively, which leads to boiler troubles.

Scale: A hard and sticky precipitate, which stick on the inner wall of the boiler called Scale. These are formed by $CaCO_3$, $CaSO_4$, $Ca(HCO_3)_2$, $Mg(OH)_2$ etc. in *hot portion of boiler*.

Disadvantages of scale formation

➕ Scale is a poor conductor of heat, so they tend to waste time and heat.

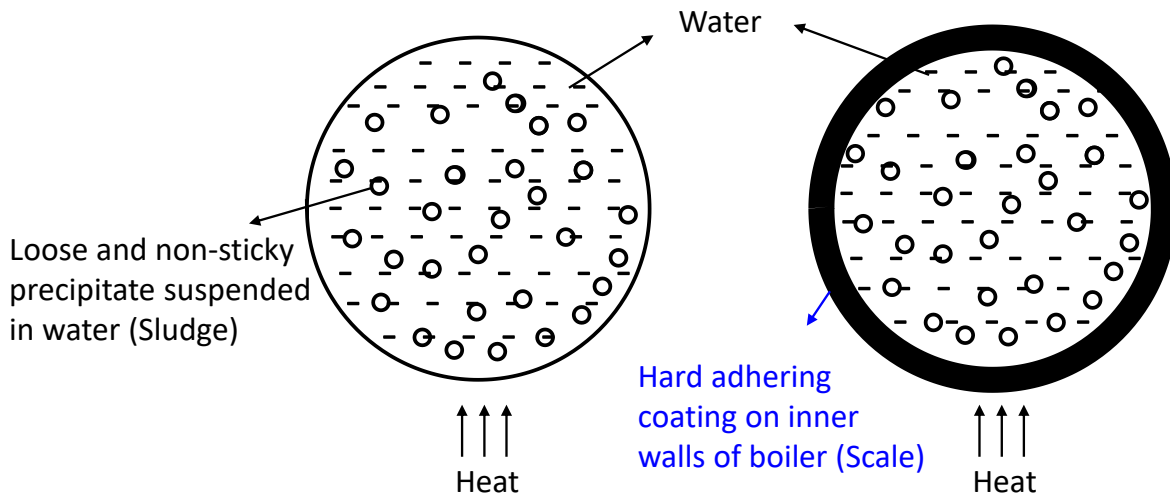➕ It decreases the efficiency and safety of boilers. May lead to explosion.

Removal of scales

    i.   With the help of scraper or piece of wood or wire brush, if they are loosely adhering.

    ii.   By giving thermal shocks, if they are brittle.

    iii.   By dissolving them in chemicals like 5-10% HCl or EDTA solution.

Sludge: Sludges are loose, soft and non-sticky precipitate. The sludge formed by the $CaCl_2$, $MgCl_2$, $MgCO_3$, $MgSO_4$ etc.

Disadvantages of Sludge formation

➕ Sludge is poor conductor of heat, so they tend to waste time and heat.

➕ It decreases the efficiency and safety of boilers.

➕ Excessive sludge formation disturbs the working of boiler.

Water

Loose and non-sticky precipitate suspended in water (Sludge)

Hard adhering coating on inner walls of boiler (Scale)

Heat   Heat

*Prevention of **Scale and Sludge** formation*

➢ By using well softened water and Blow-down operation (replacing the concentrated water with fresh water).

2) Priming and foaming

Priming: When a boiler is steaming (i.e., producing stream) rapidly, some particles of the liquid water are carried along-with the stream. This process of wet-stream formation is called priming.

Reasons

(a) Due to the presence of huge dissolved solids. (b) Improper boiler design. (c) Sudden boiling. (d) Sudden increase in steam-production rate.

Priming can be avoided by

i) Fitting "mechanical steam purifiers", maintaining of low water levels in boilers.

ii) By using well softened water and Blow-down operation.

Foaming: The production of persistent foam or bubbles along with stream in boilers is called as foaming.

Reasons: Foaming is due to the presence of substances like oils (which greatly reduce the surface tension of water).

Foaming can be avoided by adding anti-foaming chemicals like castor oil.

When, priming or foaming happens dissolved salts may enter the parts of other machinery, where stream is being used, thereby decreasing the life of the machinery.

3. Boiler corrosion

Damage of boilers by its environment is called as boiler corrosion. Corrosion in boilers is due to the presence of (i) Dissolved O_2, (ii) Dissolved CO_2 and (iii) Dissolved mineral acids (HCl and H_2SO_4).

I) Dissolved oxygen (O_2): Water usually contains about 8 mL of dissolved oxygen per liter at room temperature. That oxygen interacts with Iron (Fe) and produces rust.

$$2Fe + 2H_2O + O_2 \rightarrow 2Fe(OH)_2$$

$$4Fe(OH)_2 + O_2 \rightarrow 2Fe_2O_3.2H_2O \text{ (Rust)}$$
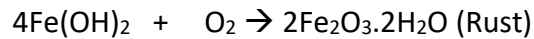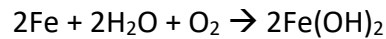
Removal of dissolved oxygen:

1) By adding calculated quantity of hydrazine (N_2H_4)

$$\underset{\text{(Hydrazine)}}{N_2H_4} + O_2 \rightarrow N_2 \uparrow + 2H_2O$$
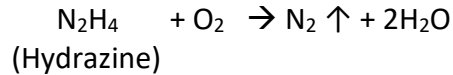
2) By mechanical de-aeration means without adding chemicals also can remove the dissolved gases.

4. Caustic Embrittlement:

Caustic embrittlement is the phenomenon in which *the boiler material becomes brittle due to the accumulation of caustic substances.* Caustic Embrittlement is a type of boiler corrosion.

The NaOH containing water flows into the hair-cracks, always present in the inner side of boiler by capillary action.

$$Fe + 2NaOH \rightarrow Na_2FeO_2 \text{ (Sodium Ferroate)} + H_2O$$
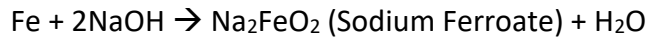
This causes embrittlement of boiler parts, particularly stressed parts (like bends, joints, rivets, etc.) causing even failure of the boiler.

Caustic Embrittlement can be avoided by

- By using *sodium sulfate (Na_2SO_4)* as the softening agent, instead of *sodium carbonate*. *Sodium sulfate* prevents the infiltration of caustic soda solutions.

- By adding Tannin or Lignin to boiler water, since these blocks the hair-cracks, thereby preventing infiltration of caustic soda solution.

TREATMENT OF BOILER FEED WATER OR SOFTENING OF WATER:

There are two types of treatments

1) Internal treatment

2) External treatment.

1) Internal treatment: The principle involved in internal treatment is the conversion of scale forming salts into sludges. Internal treatment methods are generally followed by blow-down operation. So that an accumulated sludge is removed. Important internal condition methods are:

a) **Colloidal conditioning**: In low pressure boilers scale formation can be avoided by adding organic substances like kerosene, tannin, agar-agar (a gel) etc, which get coated over the forming

precipitates, thereby yielding non-sticky and loose deposits which can be easily removed by blow-down operators.

b) Carbonate conditioning: Scale formation in low pressure boilers can be avoided by adding sodium carbonate to boiler water, where $CaSO_4$ is converted into calcium carbonate, a sludge which can be removed by blow don operation.

$$CaSO_4 + Na_2CO_3 \leftrightarrow CaCO_3 + Na_2SO_4$$
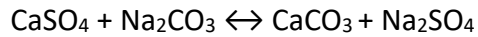
c) Phosphate conditioning: In high pressure boilers, scale formation can be avoided by adding sodium phosphate, which reacts with calcium and magnesium salts forming non-adherent and easily removable soft sludge of calcium and magnesium phosphates, which can be removed by blow-down operation.

$$3CaCl_2 + 2Na_3PO_4 \rightarrow Ca_3(PO_4)_2 + 6NaCl$$
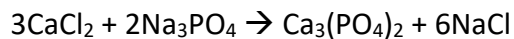
The main phosphates employed are (a) NaH_2PO_4, sodium dihydrogen phosphate (acidic); (b) Na_2HPO_4, disodium hydrogen phosphate (weakly alkaline); (c) Na_3PO_4, trisodium phosphate (alkaline).

d) Calgon conditioning: The word Calgon means Calcium gone, i.e., the removal of Ca^{+2}. Sodium hexameta phosphate $\{Na_2[Na_4(PO_3)_6]\}$ is Calgon. When we add Calgon to boiler water, it prevents the scale and sludge formation by forming soluble complex compound with $CaSO_4$.

$$Na_2[Na_4(PO_3)_6] + 2CaSO_4 \rightarrow Na_2[Ca_2(PO_3)_6] + 2Na_2SO_4$$

(Calgon)   (Soluble complex ion)
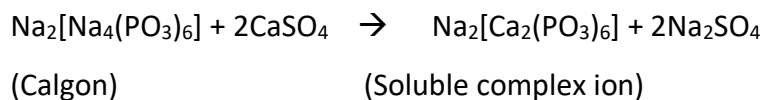
2. EXTERNAL TREATMENT OF BOILER FEED WATER

Treating the water before feeding it into boiler is called external treatment.

i) ION EXCHANGE PROCESS (DEIONIZATION OR DE-MINERALIZATION)

This process removes almost all the ions present in water. Ion exchangers are resins (Polymers).
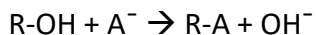
Based on the functional groups, resins are two types: (These functional groups are responsible for the ion exchanging process).

Cations are *the positively charged ions* and Anions are *the negatively charged ions.*

(i) Cation exchange resin: In this step cations (Na^+, K^+, Ca^{+2}, Mg^{+2}, etc) present in hard water are exchanged with H^+ ions of resin. Cation exchange resins contain **acidic functional groups like -SO₃H or -COOH**. Example: Sulphonated polystyrene

$$R\text{-}H + M^+ \rightarrow R\text{-}M + H^+$$
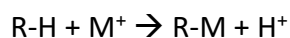
(ii) Anion exchange resin: In this step, anions (Cl^-, SO_4^{-2}, HCO_3^-) present in hard water are exchanged with OH^- of the resins. Anion exchange resins contain basic functional groups like quaternary ammonium salts etc. Example: Polystyrene with quaternary ammonium salt.

$$R\text{-}OH + A^- \rightarrow R\text{-}A + OH^-$$

| Step-I	Step-II
Water passed through cation chamber Na^+, K^+, Ca^{+2}, Mg^{+2}, etc are exchanged with H^+ ions of resin.	Water passed through anion chamber, then Cl^-, SO_4^{-2}, HCO_3^- etc. ions are exchanged with OH^- of the resin.
$R\text{-}H + Na^+ \rightarrow R\text{-}Na + H^+$	$R\text{-}OH + Cl^- \rightarrow R\text{-}Cl + OH^-$
$2R\text{-}H + Mg^{+2} \rightarrow R_2\text{-}Mg + 2H^+$	$2R\text{-}OH + SO_4^{-2} \rightarrow R_2SO_4 + 2OH^-$
$2R\text{-}H + Ca^{+2} \rightarrow R_2\text{-}Ca + 2H^+$	Free from almost all the ions and it is neutral
Water is acidic in nature.	(deionized or demineralized water)
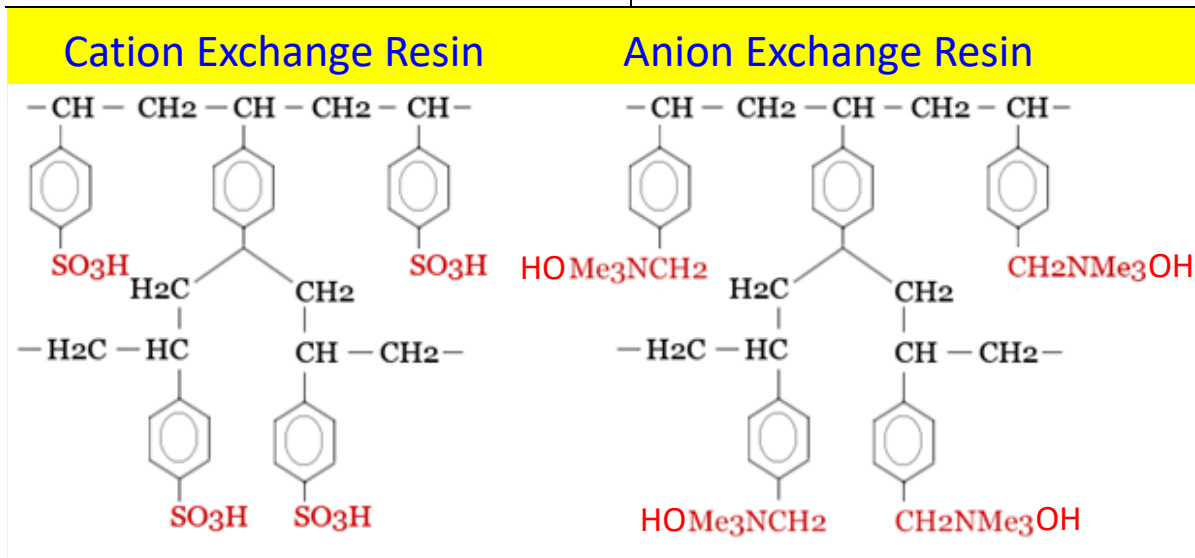
Diagram of Ion Exchange Method

Cation exchange column | Anion exchange column
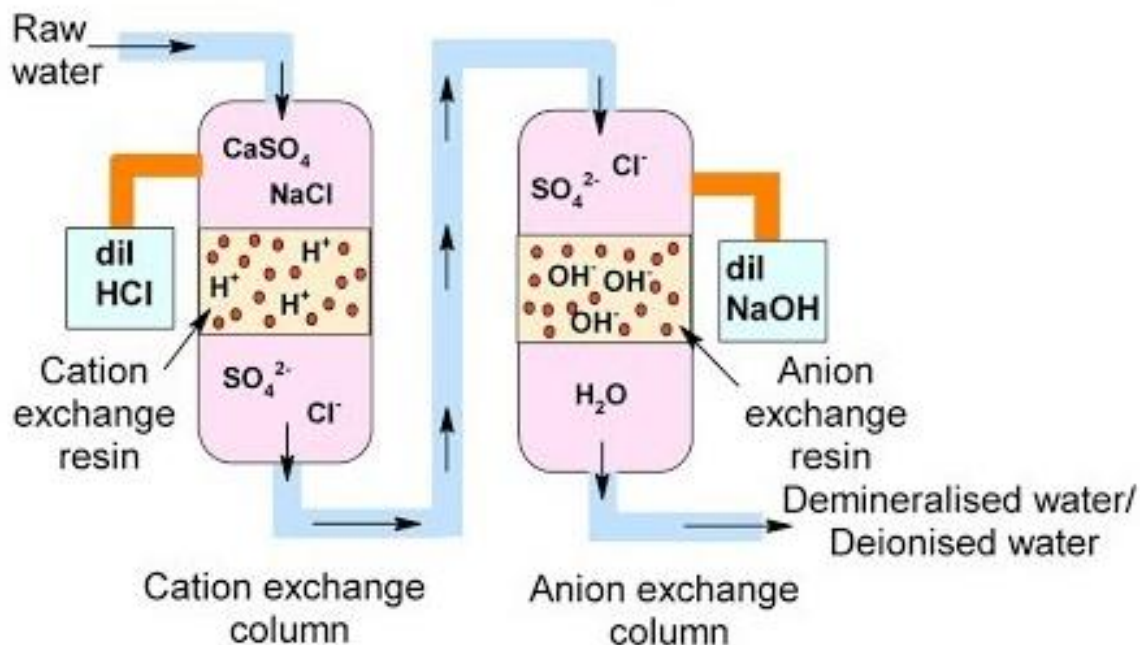
REGENERATION OF RESINS:

The exhausted cation exchange resin is regenerated by passing dilute HCl solution through it.

$$R\text{-}Ca + 2HCl \rightarrow R\text{-}H_2 + CaCl_2$$

$$R\text{-}Na + HCl \rightarrow R\text{-}H + NaCl$$
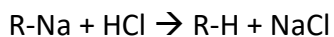
The exhausted anion exchange resin is regenerated by passing dilute NaOH solution through it.

$$R\text{-}Cl + NaOH \rightarrow R\text{-}OH + NaCl$$
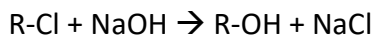
Advantages

✓ The water hardness can be reduced up to 2 ppm, hence it is suitable for use in high pressure boilers.

✓ Highly acidic or highly basic water can be softened by using this process.

Limitations

▪ The resins used in the process are quite expensive.

▪ If water contains turbidity, the efficiency of the process will be reduced.

▪ Water containing Fe and Mn cannot be treated because they form stable product with the resins.

LIME SODA PROCESS

In this process lime [$Ca(OH)_2$] and soda [Na_2CO_3] are used to precipitate the dissolved salts of Ca^{+2} and Mg^{+2} as insoluble $CaCO_3$ and $Mg(OH)_2$, which can be removed by settling or filtration. **Lime reacts with Ca-based temporary hardness salts, Mg-based permanent salts, CO_2, acids, bicarbonates and alum. However, lime cannot remove Ca-based permanent salts.**

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2CaCO_3 \downarrow + 2H_2O$$

$$Ca(OH)_2 + MgCl_2 \rightarrow Mg(OH)_2 \downarrow + CaCl_2$$

$$Ca(OH)_2 + MgSO_4 \rightarrow Mg(OH)_2 \downarrow + CaSO_4$$
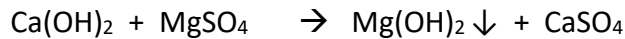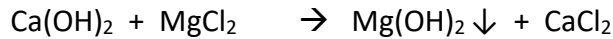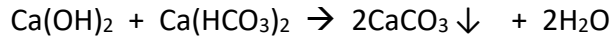
Soda can remove all Calcium (Ca) based permanent hardness causing salts.

$$Na_2CO_3 + CaCl_2 \rightarrow CaCO_3 \downarrow + 2NaCl$$

$$Na_2CO_3 + CaSO_4 \rightarrow CaCO_3 \downarrow + Na_2SO_4$$
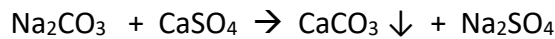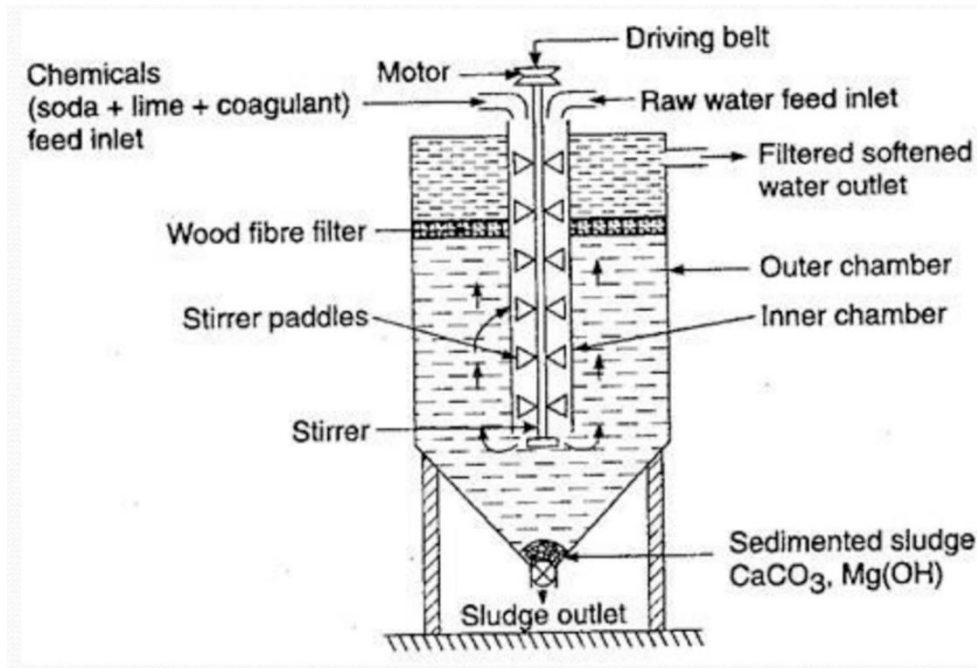
Precautions to be followed

- Only calculated amounts of lime and soda should be added. Because the excess amount of reagents causes boiler troubles like corrosion and caustic embrittlement.
- Proper time must be given to complete the reactions.

Lime soda process is of two types: Cold lime soda process & Hot lime-soda process

1) Cold lime soda process: If the entire process is carried out at **room-temperature** it is called cold lime soda process. However, at room temperature the precipitates formed are finely divided, so they do not settle down easily. Therefore, a small amount of coagulants [$NaAlO_2$ or $Al_2(SO_4)_3$] should be added.
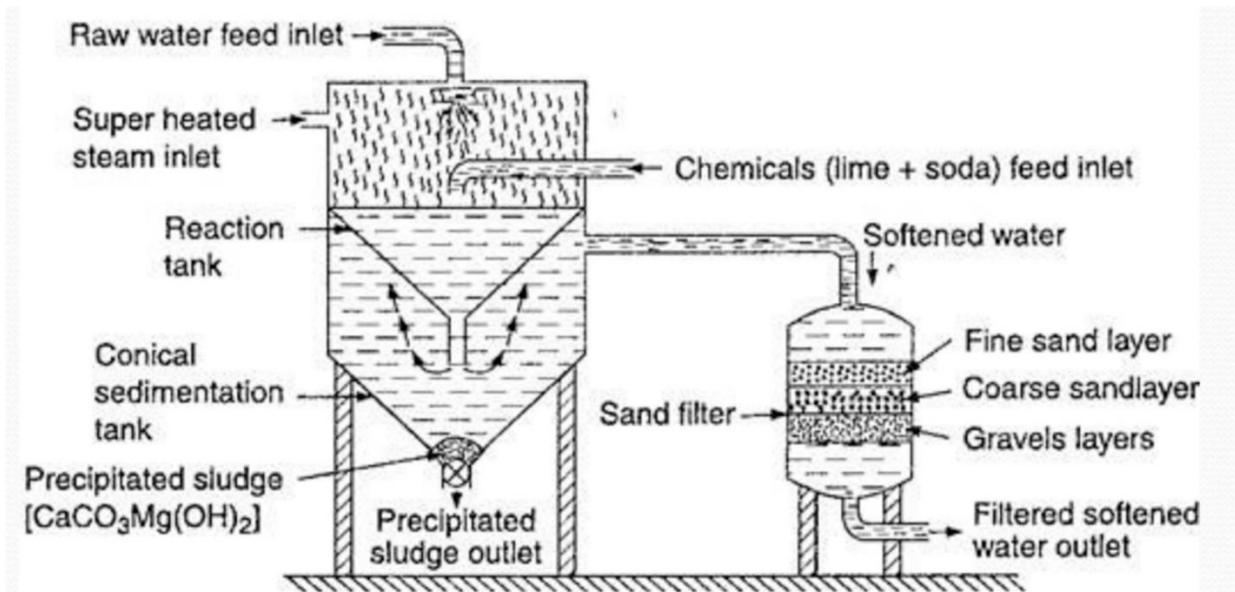
$$NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3$$
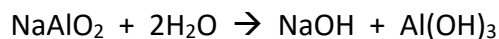
In this process, raw water and required amount of lime, soda and coagulants are pored at room temperature from the top in to the inner chamber. A fitted paddle stirrer can vigorously stir the water, then the raw and chemicals flow down. The softened water rising up and passes through a wood fiber filter.

Driving belt
Motor
Chemicals (soda + lime + coagulant) feed inlet
Raw water feed inlet
Filtered softened water outlet
Wood fibre filter
Outer chamber
Inner chamber
Stirrer paddles
Stirrer
Sedimented sludge $CaCO_3$, $Mg(OH)$
Sludge outlet

2) Hot-lime soda process

In hot lime soda process, water is treated with lime $[Ca(OH)_2]$ and soda $[Na_2CO_3]$ **at 80 − 150 ºC**. Coagulant is not needed.

Raw water feed inlet
Super heated steam inlet
Chemicals (lime + soda) feed inlet
Reaction tank
Softened water
Conical sedimentation tank
Fine sand layer
Coarse sandlayer
Sand filter
Gravels layers
Precipitated sludge $[CaCO_3Mg(OH)_2]$
Precipitated sludge outlet
Filtered softened water outlet

In hot lime soda process, three steps are taken.

(a) Reaction tank: Raw water, chemicals and superheated steam are passed into reaction tank, where all three are mixed thoroughly. The beginning and ending reaction occur in this tank.

(b) Conical sedimentation tank: From the reaction tank, the contents go to this tank, so hot sludge settle down.

(c) Sand filter: It acts as filter and ensure complete removal of sludge from the softened water.

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Cold Lime Soda Method	Hot Lime Soda Method
Carried at room temperature	Carried at 80 – 150 °C
Coagulant is added.	No need of coagulant.
Dissolved gases are not removed.	Dissolved gases are also removed.
Obtained water hardness is of 60 ppm	Obtained water hardness is of 15-20 ppm
Slow process	Fast process

Advantages of lime soda process

- It is more economical.
- Less amount of coagulant is needed.
- It increases the pH value, thereby corrosion is reduced.
- Fe, Mn and minerals are reduced.

Disadvantages of lime soda process

- For efficient and economical softening careful operation is required.
- Disposal of large amount of sludge is a problem.
- This can remove hardness up to 15 ppm which is not good for boilers.

Alkalinity of water

Alkalinity: The capacity of water to neutralize acids called alkalinity. It can measure the presence of the hydroxide (OH^-), carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) ions which are naturally present in water. Three types of ions (OH^-, CO_3^{2-} and HCO_3^-) are mainly responsible for alkalinity. Different ions cause different pH.

Alkalinity of water can be determined using titrimetric analysis.

Principle: $OH^- + H^+ \rightarrow H_2O$ (complete neutralization of OH^-)

$CO_3^{2-} + H^+ \rightarrow HCO_3^-$ (half neutralization of carbonate)

$HCO_3^- + H^+ \rightarrow H_2CO_3$ (complete neutralization of carbonate)

OH^- and CO_3^{2-}: Basic PH (>7) Phenolphthalein indicator is used.

HCO_3^-: Acidic PH (<7) Methyl orange indicator is used.

Phenolphthalein: Colorless

Pink to light yellow

Methyl orange: Light yellow to red.

CHAPTER-III

ELECTROCHEMISTY, BATTERIES and CORROSION

SYLLABUS: Electrode, electrode potential, galvanic cell, cell reactions and cell notation, cell EMF, types of electrodes (Normal Hydrogen Electrode, calomel electrode), Determination of pH, Nernst equation, Numerical problems.

Electrochemistry is an important branch of chemistry. It deals with the relation between the electrical energy and chemical entity. It is the study of "conversion of electrical energy into chemical energy and chemical energy into electrical energy".

Electrode: A metal rod dipped in its own salt solution is called as electrode.

Examples for metal electrode:

Zinc electrode: $Zn/ZnSO_4$

Copper electrode: $Cu/CuSO_4$

Magnesium electrode: $Mg/MgSO_4$

Silver electrode: $Ag/AgNO_3$

Zn Electrode   Cu Electrode   Ag Electrode

$Zn/ZnSO_4$ $Cu/CuSO_4$ $Ag/AgNO_3$
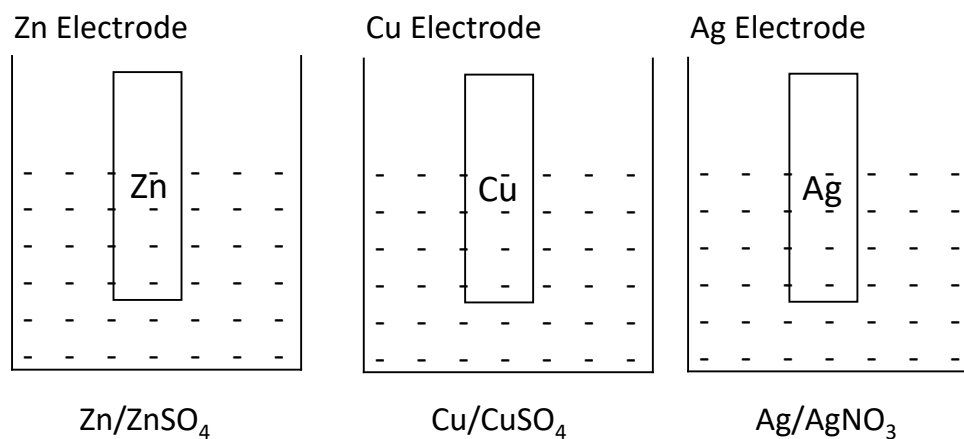
Electrode potential (E_{cell}): The tendency of a metal to loosen electrons (oxidation) or taken electrons (reduction) when it is placed in its own salt solution called electrode potential. Means, when a metal [M] placed into its own salt solution containing its own ions [M^{n+}], then the metal may undergo either oxidation or reduction.

If metal undergoes oxidation, then the positive metal ions will pass into the solution

$M \rightarrow M^{n+} + ne^-$ (Oxidation)
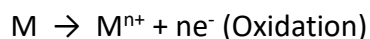
If the metal undergoes reduction, then the negative ions may get deposited over the metal.

$M^{n+} + ne^- \rightarrow M$ (Reduction)

Standard electrode potential (E_{cell}^0): The tendency of metal to loosen electrons (oxidation) or taken electrons (reduction) when it is placed in its own salt solution **having 1.0 M** (unimolar) concentration **at 25 ^oC** is called as standard electrode potential.

Cell (Galvanic Cell or Electrochemical cell): Cell is made up of **two electrodes**, i.e., anode half-cell and cathode half-cell. Oxidation reaction takes place at one electrode called as anode half-cell and reduction reaction takes place at another electrode called as cathode half-cell.

Cell = Anode half-cell + Cathode half-cell.

Cell reactions: In an electrochemical cell, flow of electrons takes place from one electrode to another electrode due to the oxidation reaction at anode and reduction reaction at cathode. So, the net chemical change can be obtained by adding the two half-cell reactions called as cell reaction. Cell reaction = Anode half-cell reaction + Cathode half-cell reaction

Example, Galvanic cell [Zn/ZnSO$_4$//CuSO$_4$/Cu]

Anode half-cell reaction: $Zn \rightarrow Zn^{+2} + 2e^-$ (Oxidation)

Cathode half-cell reaction: $Cu^{+2} + 2e^- \rightarrow Cu$ (Reduction)

Cell reaction or net reaction: $Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$

Electromotive Force (EMF) or Cell Potential: In an electrochemical cell, a potential difference which is required to flow of electricity from anode to cathode is called as electromotive force (emf) or cell potential.

Representation and notation of electrochemical cells

The Galvanic cell or electrochemical cells are represented on the paper with the help of symbolic representation of single electrodes.

Example: Galvanic cell is represented as Zn/ZnSO$_4$//CuSO$_4$/Cu

Steps for construction of Cell:

(i)   Single vertical line (/): It represents a phase boundary between metal and its salt solution.

Zn/ZnSO$_4$ (Anode half-cell), CuSO$_4$/Cu (Cathode half-cell).

(ii) Anode half-cell is written on left side and cathode half-cell is written on right side.

(iii) Anode half-cell and cathode half cells are separated by two vertical lines (//) called salt bridge.

Example: Zn/ZnSO$_4$//CuSO$_4$/Cu

(iv) Symbolic formation electrode, like the Platinum electrode is often enclosed in a bracket.

Mg/Mg^{+2}//H$^+$/H$_2$ (Pt)

(v)   The emf value of a cell is written on the right side of the cell diagram.

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Zn/ZnSO$_4$//CuSO$_4$/Cu E = 1.12 eV
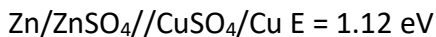
NERNST EQUATION: This equation gives the relationship between electrode potential, concentration of the products and reactants, and absolute temperature.

Let us consider a cell reaction

aA + bB → cC + dD
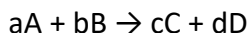
Where, a, b, c, d represent the number of moles of A, B, C and D components, respectively. The Nernst equation for the cell is

$$E_{cell} = E^o{}_{cell} - \frac{2.303\ RT}{nF} \log\left(\frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}\right)$$

$$E_{cell} = E^o{}_{cell} - \frac{0.0591}{n} \log\left(\frac{[C]^c\ [D]^d}{[A]^a\ [B]^b}\right)$$

Where, R = gas constant = 8.314 J K^{-1}mol^{-1}, T = 298 K, F = 96500 coulombs (Faraday), n = no of electrons involved in the cell reaction,

E^o_{cell} = Standard electrode potential & E_{cell} = Cell potential (EMF)

Nernst equation is used to determine **single electrode potential** and also **cell potential**.

Electrochemical cell: Cell which converts electrical energy into chemical energy or chemical energy into electrical energy called electrochemical cell.

Galvanic cell/Voltaic Cell/Daniel Cell: A device which converts chemical energy into electrical energy due to spontaneous redox reaction.

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

$$Zn(s)\,|\,ZnSO_4(aq)\,\|\,CuSO_4(aq)\,|\,Cu(s)$$
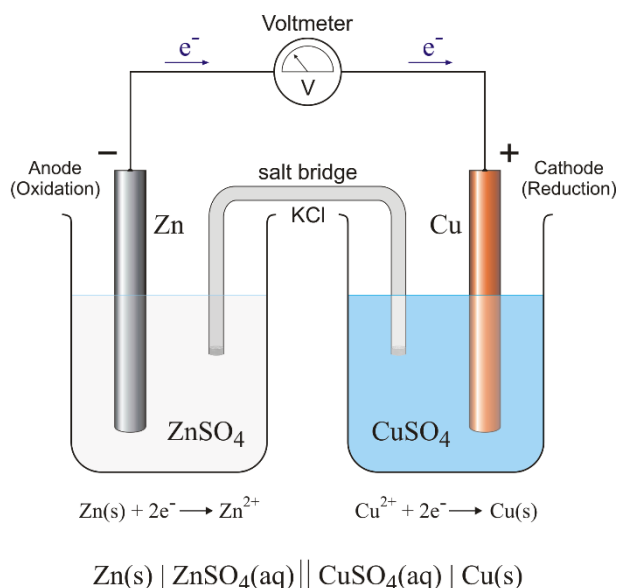
Salt bridge: It is an inverted U-shaped glass tube, which contains a paste of KCl or KNO_3 or NH_4NO_3 with Agar-agar.

Use of salt bridge: Salt bridge completes the circuit and allows the passage of electric current. It also maintains the electric neutrality in both half cells.

Types of electrodes:

1) Working electrode, 2) Reference electrode & 3) Counter electrode

Reference electrode: The electrode which is used to determine the electrode potential of another electrode is called reference electrode. The best example for reference electrode is standard hydrogen electrode (SHE), whose electrode potential at all temperatures is 'zero'.

The most commonly used reference electrodes are:

1) Standard Hydrogen Electrode (SHE) or Normal Hydrogen electrode (NHE)

2) Standard Calomel electrode (SCE)

1) Standard Hydrogen Electrode (SHE) or Normal Hydrogen Electrode (NHE):

(a) *Introduction*: Standard Hydrogen Electrode (SHE) is a **primary reference electrode** used to determine **electrode potential** and **pH of any unknown sample solution**.

(b) *Construction:* Standard Hydrogen Electrode (SHE) consists of Pt electrodes coated with Pt black immersed in a 1.0 M acidic solution (H^+ ions) maintained at 25 °C. A stream of pure hydrogen is bubbled around the platinum foil at a constant pressure of one atmosphere (1 atm). The gas at the Pt electrode forms H^+ ions and electrons.
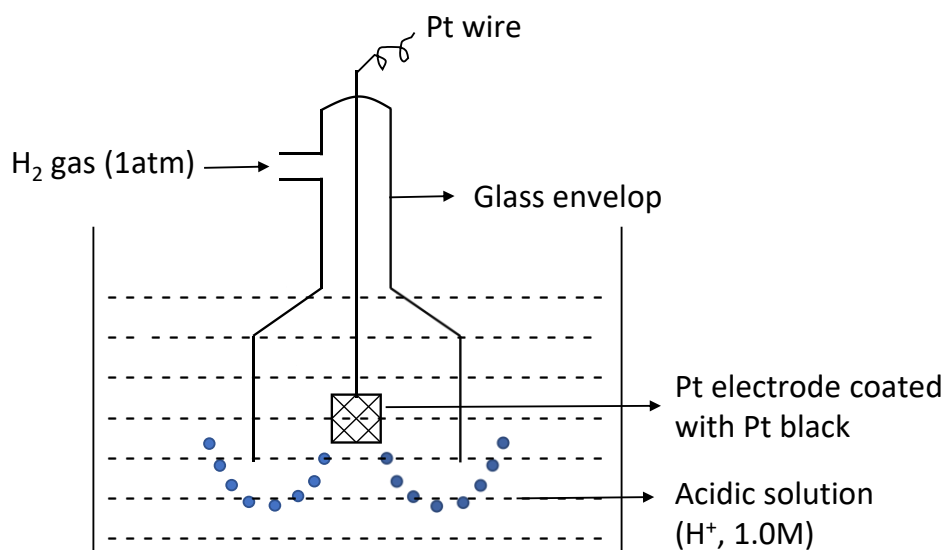
(c) *Cell Representaion:* (Pt), H_2 (g)/H^+ solution (1.0 M)
SHE acts as both anode and cathode.

If it acts as anode $H_2 \rightleftharpoons 2H^+ + 2e^-$

If it acts as cathode $2H^+ + 2e^- \rightleftharpoons H_2$

(d) Determination of pH of any sample solution using standard hydrogen electrode

Hydrogen electrode can be employed to find the pH value of an unknown solution. For this, the solution pH is to be determined is taken in a vessel and an electrode is half dipped in it. The half cell so formed is connected to a standard hydorgen electrode (having a solution of 1N HCl) through a salt bridge. The emf of the cell is determined by potentiometer. Since emf of the reference electrode is zero, the observed emf gives directly the emf of the half-cell containing the solution under test.

Hydrogen electrode (HE) (Anode)	Acidic solution (H⁺, pH to be determined)		Acidic solution (H⁺, 1.0M)	Standard Hydrogen electrode (SHE) (Cathode)
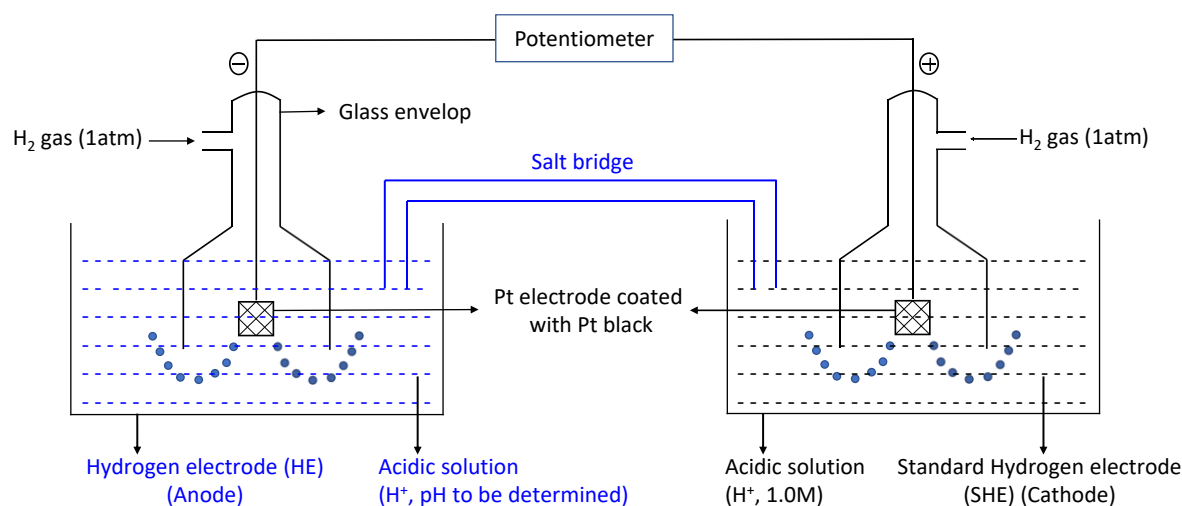
The cell represented as;

Anode (Pt), H_2 (g)/H^+ (pH to be determined)//Acidic solution (H^+ = 1M)/H_2 (g), (Pt) (Cathode)

$E_{cell} = E_{anode} + E_{cathode}$

$E_{cell} = E_{HE} + E_{SHE}$

$= (0.0591\ pH) + 0$

$= 0.0591 pH$

$$\boxed{pH = \frac{Ecell}{0.0591}}$$
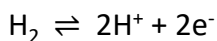
$H_2 \rightleftharpoons 2H^+ + 2e^-$

$$Ecell = E°cell - \frac{0.0591}{n} \log \frac{[P]}{[R]}$$

$$Ecell = E°cell - \frac{0.0591}{2} \log \frac{[H^+]^2}{[H_2]}$$

$$Ecell = 0 - \frac{0.0591}{2} \log \frac{[H^+]^2}{1}$$

$$Ecell = - \frac{0.0591}{2} \ 2 \times \log\ [H^+]$$

$$Ecell = 0.0591 p^H$$

(B) STANDARD CALOMEL ELECTRODE (SCE)

(a) *Introduction*: Standard calomel electrode (SCE) is a **secondary reference electrode** used to **determine electrode potential** and **pH of any unknown solution**.

(b) *Construction*:
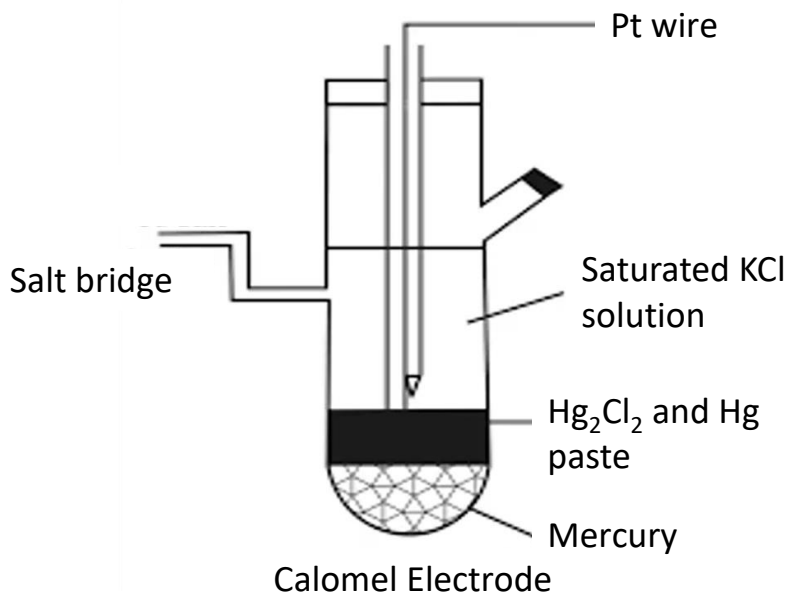
Calomel Electrode

(c) *Cell Representaion:* Standard calomel electrode representation: **Hg/Hg₂Cl₂, Saturated KCl**

Predominantly it acts as cathode. $Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$

$Hg_2Cl_2 \quad\quad \rightarrow 2Hg^+ + 2Cl^-$
$2Hg^+ + 2e^- \rightarrow 2Hg$
$Hg_2Cl_2 \rightarrow 2Hg + 2Cl^-$
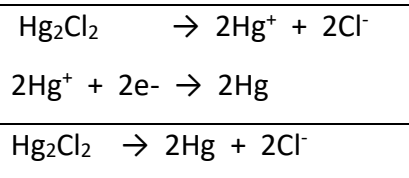
Electrode potential of calomel electrode depends on the concentration of electrolyte.

If saturated KCl is used as an electrolyte, the electrode potential is 0.241 V.

 If 1.0N KCl is used as an electrolyte, the electrode potential is 0.280 V.

If 0.1N KCl is used as an electrolyte, the electrode potential is 0.333 V.

Determination of pH of unknown solution using standard calomel electrode:

To determine the pH of an unknown solution, a Standard Hydrogen Electrode (SHE) containing solution of unknown pH is coupled with standard calomel electrode.
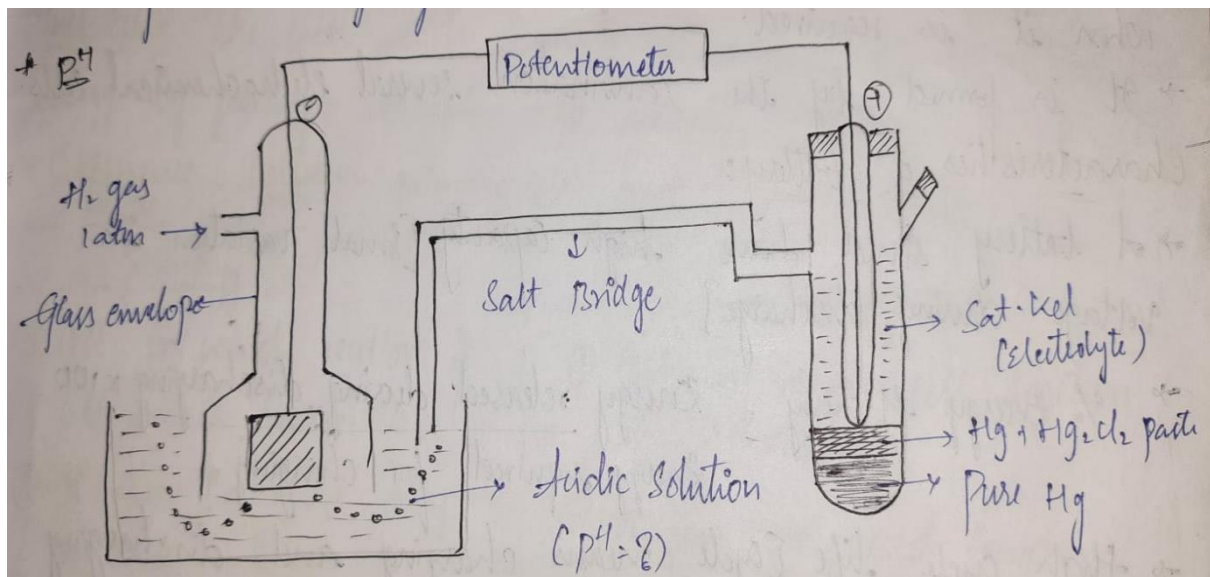
The above cell can be represented as

(Pt), $H_2(g)/H^+$ (pH to be determined) // Sat.KCl/ Hg_2Cl_2, Hg
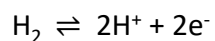
      (Anode)   (Cathode)

$E_{cell} = E_{cathode} + E_{Anode}$

$E_{cell} = E_{SCE} + E_{HE}$

$E_{cell} = 0.241 + 0.0591pH$

$0.0591pH = E_{cell} - 0.241$

pH	=	$\dfrac{E_{cell} - 0.241}{0.0591}$

$H_2 \rightleftharpoons 2H^+ + 2e^-$

$$E_{cell} = E°_{cell} - \frac{0.0591}{n} \log \frac{[P]}{[R]}$$

$$E_{cell} = E°_{cell} - \frac{0.0591}{2} \log \frac{[H^+]^2}{[H_2]}$$

$$E_{cell} = 0 - \frac{0.0591}{2} \log \frac{[H^+]^2}{1}$$

$$E_{cell} = - \frac{0.0591}{2} \; 2 \times \log [H^+]$$

$$E_{cell} = 0.0591 pH$$

Problems based on Nernst equation:

1) Calculate the single electrode potential of the following electrochemical cell reaction.

   Cu^{+2}/Cu where $E°_{Cu^{+2}/Cu} = 0.36V$
   (0.01M)

Ans: Net reaction: $Cu^{+2} + 2e^- \rightarrow Cu$ (Reduction)

        Nernt Equation: $E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{[P]}{[R]}$

$$E_{Cu^{+2}/Cu} \;=\; E^0_{Cu^{+2}/Cu} - \frac{0.0591}{n} \log \frac{[Cu]}{[Cu^{+2}]}$$

$$= \; 0.36 - \frac{0.0591}{2} \log \frac{[1]}{[0.01]}$$

$$= \; 0.36 - \frac{0.0591}{2} \log [10^2]$$

$$= \; 0.36 - \frac{0.0591}{2} \times 2 \log [10]$$

$$= \; 0.36 - 0.0591$$

$$E_{Cu^{+2}/Cu} \;=\; 0.3009V$$

2) Calculate the single electrode potential of the following electrochemical cell reaction.

Ag⁺/Ag   where   E⁰$_{Ag^+/Ag}$ = 0.8V
(0.01M)

Ans: Net reaction: $Ag^+ + e^- \rightarrow Ag$ (Reduction)

$$\text{Nernt Equation: } E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{[P]}{[R]}$$

$$E_{Ag^+/Ag} \;=\; E^0_{Ag^+/Ag} - \frac{0.0591}{n} \log \frac{[Ag]}{[Ag^+]}$$

$$= \; 0.8 - \frac{0.0591}{2} \log \frac{[1]}{[0.01]}$$

$$= \; 0.8 - \frac{0.0591}{2} \log [10^2]$$

$$= \; 0.8 - \frac{0.0591}{2} \times 2 \log [10]$$

$$= \; 0.8 - 0.0591$$

$$E_{Cu^{+2}/Cu} \;=\; 0.7409V$$

3) Calculate the single electrode potential of the following electrochemical cell reaction.

(Pt) Cl₂/Cl⁻   where   E⁰$_{Cl2/Cl^-}$ = 1.36V
(0.01M)

Ans: Net reaction: $Cl_2 + 2e^- \rightarrow 2Cl^-$ (Reduction)

$$\text{Nernt Equation: } E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{[P]}{[R]}$$

$$E_{Cl2/Cl^-} \;=\; E^0_{Cl_2/Cl^-} - \frac{0.0591}{n} \log \frac{[Cl^-]^2}{[Cl_2]}$$

$$= \; 1.36 - \frac{0.0591}{2} \log \frac{[0.01]^2}{[1]}$$

$$= \quad 1.36 - \frac{0.0591}{2} \log [10^{-2}]^2$$

$$= \quad 1.36 - \frac{0.0591}{2} \times (-4) \log [10]$$

$$= \quad 1.36 + 0.1182$$

$$E_{Cl2/Cl^-} \quad = \quad 1.4782V$$

4) Calculate the single electrode potential of the following electrochemical cell reaction.

Zn/Zn^{+2}   where   **E^0$_{Zn}$$^{+2}$$_{/Zn}$ = -0.76V**
    (0.1M)

Ans: Net reaction: Zn → Zn^{+2} + 2e$^-$ (Oxidation)

$$\text{Nernt Equation: } E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{[P]}{[R]}$$

$$E_{cell} \quad = \quad E^0_{cell} - \frac{0.0591}{n} \log \frac{[P]}{[R]}$$

$$E_{Zn/Zn}{}^{+2} \quad = \quad E^0_{Zn/Zn^{+2}} - \frac{0.0591}{n} \log \frac{[Zn^{+2}]}{[Zn]}$$

$$= \quad 0.76 - \frac{0.0591}{2} \log \frac{[0.1]}{[1]}$$

$$= \quad 0.76 - 0.0295 \log [10^{-1}]$$
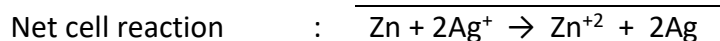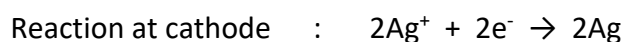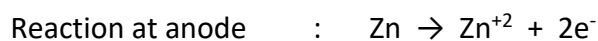
$$= \quad 0.76 + 0.0295$$

$$E_{Zn/Zn}{}^{+2} \quad = \quad 0.7895 \text{ V}$$

5) Calculate the EMF of cell potential of the following electrochemical cell reaction.

Zn/Zn^{+2}//Ag$^+$/Ag where   **E^0$_{Zn/Zn}$$^{+2}$ = 0.76V and E^0$_{Ag}$$^+$$_{/Ag}$ = 0.8V**
   (1.0M)   **(1.0M)**

Ans:

$$E^0_{cell} \quad = \quad E^0_{Anode} + E^0_{Cathode}$$

$$= \quad E^0{}_{Zn/Zn}{}^{+2} + E^0{}_{Ag}{}^+{}_{/Ag}$$

$$= \quad 0.76 + 0.80$$

$$E^0_{cell} \quad = \quad 1.56V$$

Reaction at anode   :   Zn → Zn^{+2} + 2e$^-$

Reaction at cathode   :   2Ag$^+$ + 2e$^-$ → 2Ag

Net cell reaction   :   Zn + 2Ag$^+$ → Zn^{+2} + 2Ag

$$\text{Nernt Equation: } E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{[P]}{[R]}$$

$$E_{cell} \quad = \quad E^0_{cell} - \frac{0.0591}{n} \log \frac{[Zn^{+2}] \, [Ag]^2}{[Ag^+]^2 \, [Zn]}$$

$$= \quad 1.56 \quad - \quad \frac{0.0591}{2} \quad \log \quad \frac{[1]\,[1]^2}{[1]^2\,[1]}$$

$$= \quad 1.56 \ - \ \frac{0.0591}{2} \log [1]$$

$$= \quad 1.56 \ + 0$$

$$E_{cell} \quad = \quad 1.56V$$

6) Calculate the EMF of cell potential of the following electrochemical cell reaction.

Fe/Fe^{+2}//Cu^{+2}/Cu where $\quad$ E^0$_{Fe}$$^{+2}$$_{/Fe}$ = -0.44V and E^0$_{Cu}$$^{+2}$$_{/Cu}$ = 0.34V
(0.1M)   (0.01M)

Ans: $\qquad\qquad E^0_{cell} \qquad = \quad E^0_{Anode} + E^0_{Cathode}$

$$= \quad E^0{}_{Fe}{}^{+2}{}_{/Fe} + E^0{}_{Cu}{}^{+2}{}_{/Cu}$$

$$= \quad 0.44 + 0.34$$

$$E^0_{cell} \qquad = \quad 0.78V$$

Reaction at anode $\quad$: $\quad$ Fe $\rightarrow$ Fe^{+2} + 2e$^-$

Reaction at cathode $\quad$: $\quad$ Cu^{+2} + 2e$^-$ $\rightarrow$ Cu

Net cell reaction $\qquad$: $\quad$ Fe + Cu^{+2} $\rightarrow$ Fe^{+2} + Cu

Nernt Equation: $E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{[P]}{[R]}$

$$E_{cell} \quad = \quad E^0_{cell} \ - \ \frac{0.0591}{n} \ \log \ \frac{[Fe^{+2}]\,[Cu]}{[Fe]\,[Cu^{+2}]}$$

$$= \quad 0.78 \quad - \quad \frac{0.0591}{2} \quad \log \quad \frac{[0.1]\,[1]}{[1]\,[0.01]}$$

$$= \quad 0.78 \ - \ \frac{0.0591}{2} \log [10]$$

$$= \quad 0.78 \ - \ 0.0295$$

$$E_{cell} \quad = \quad 0.7504V$$

7) Calculate the EMF of cell potential of the following electrochemical cell reaction.

Zn/Zn^{+2}//Ag$^+$/Ag where $\quad$ E^0$_{Zn/Zn}$$^{+2}$ = 0.76V and E^0$_{Ag}$$^+$$_{/Ag}$ = 0.8V
(0.1M) (0.01M)
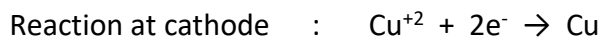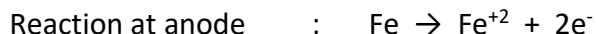
Ans: $\qquad\qquad\qquad E^0_{cell} \qquad = \quad E^0_{Anode} + E^0_{Cathode}$

$$= \quad E^0{}_{Zn/Zn}{}^{+2} + E^0{}_{Ag}{}^+{}_{/Ag}$$

$$= \quad 0.76 + 0.80$$

$$E^0_{cell} \quad = \quad 1.56V$$

Reaction at anode $\quad : \quad$ Zn $\rightarrow$ Zn^{+2} + 2e$^-$

Reaction at cathode $\quad : \quad$ 2Ag$^+$ + 2e$^-$ $\rightarrow$ 2Ag

Net cell reaction $\quad : \quad$ Zn + 2Ag$^+$ $\rightarrow$ Zn^{+2} + 2Ag
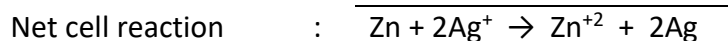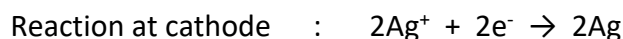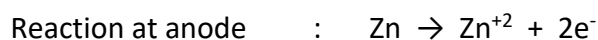
Nernt Equation: $E_{cell} = E^0_{cell} - \dfrac{0.0591}{n} \log \dfrac{[P]}{[R]}$

$$E_{cell} \quad = \quad E^0_{cell} - \frac{0.0591}{n} \log \frac{[Zn^{+2}]\,[Ag]^2}{[Ag^+]^2\,[Zn]}$$

$$= \quad 1.56 - \frac{0.0591}{2} \log \frac{[0.1]\,[1]^2}{[0.01]^2\,[1]}$$

$$1.56 - \frac{0.0591}{2} \log \frac{[10^{-1}]}{[10^{-2}]^2}$$

$$= \quad 1.56 - \frac{0.0591}{2} \log [10^3]$$

$$= \quad 1.56 - 0.0295 \times 3$$

$$= \quad 1.56 - 0.08865$$

$$E_{cell} \quad = \quad 1.47V$$

BATTERIES

Introduction to cell and battery, Primary (lithium cell) and secondary cells, (lead-Acid cell, and Lithium-ion cells). Fuel cells – Hydrogen – Oxygen fuel cell, advantages and engineering applications of fuel cells. Introduction to super capacitors.

Cell: A cell is a single unit of device that **converts chemical energy into electrical energy**.

Cells are **two types**:

Galvanic cell: Electrochemical cells which convert chemical energy to electrical energy. Here, Anode (-Ve charge) and Cathode (+Ve charge).

Electrolytic cell: Electrochemical cells which **convert electrical energy to chemical energy**. Here, Anode (+Ve charge) and Cathode (-Ve charge)

Battery: Battery is the **collection of cells that converts chemical energy into electrical energy**.

Cells and batteries can store chemical energy and release it as electrical energy when required.

Battery has 3 main components: **Anode (-Ve charge), Cathode (+Ve charge) & Electrolyte.**

Characteristics of Battery

a) A battery should have high capacity (very small variation of voltage during discharge).

b) Battery should have high energy efficiency.

c) A battery should have high cycle life means it should have more number of charging and discharging cycles before failure.

d) Long shelf-life is required.

e) High tolerance to different service conditions such as variation in temperature, vibration shock etc.

f) Cost should be affordable.

Types of batteries: Batteries are two types. Primary battery/cell and Secondary battery/cell.

Primary cells/battery	Secondary cells/battery
1. The cell in which all reactions are **not reversible** called as primary cell. Once reactants are converted to products, the cell becomes dead.	1. Cells in which reactions are **reversible**. It can be used for many cycles by charging and discharging.
2. These are not rechargeable	2. These are rechargeable
3. These can be used only once	3. These can be used for many times
4. These are cheap	4. These are expensive
5. Ex: Lithium cell, Dry cell	5. Ex: Lead acid storage cells, Lithium-ion cell

1) LITHIUM CELLS (A Primary cell):

In Lithium cell, **Lithium (Li) acts as anode**

Depending on the cathode and electrolyte Lithium cells are classified into two types.

a) Lithium Cell with Solid Cathode (LSC): Ex. **Li-MnO$_2$**

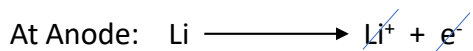b) Lithium cell with Liquid Cathode (LLC): Ex. **Li-SO$_2$** and **Li-SOCl$_2$**

a) Lithium Cell with Solid Cathode (LSC): In these cells the cathode is solid.

Li-MnO$_2$ is the example for LSC

Anode: **Li**

Cathode: **MnO$_2$**

Electrolyte: **Propylene carbonate and 1,2-dihydroxyehtane.**

At Anode: $Li \longrightarrow Li^+ + e^-$

At Cathode: $Li^+ + e^- + MnO_2 \longrightarrow LiMnO_2$

Net Cell reaction: $Li + MnO_2 \longrightarrow LiMnO_2$

Li-MnO₂ battery delivers voltage about 3V.

Applications:

(i) Cylindrical type of batteries is used in cameras and remotes etc.

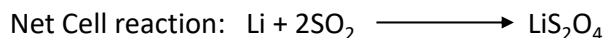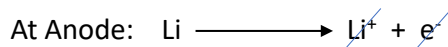(ii) Coin type batteries are used in wrist watches and calculators.

b) Lithium Cell with Liquid Cathode (LLC): In these cells the cathode is liquid.

Li-SO₂ and Li-SOCl₂ are the examples for LLC

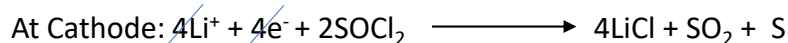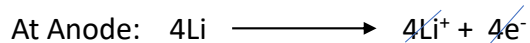**Li-SO₂:**   Anode: **Li**

Cathode: **SO₂**

Electrolyte: **Propylene carbonate or acrylonitrile**

At Anode: $Li \longrightarrow Li^+ + e^-$

At Cathode: $Li^+ + e^- + 2SO_2 \longrightarrow LiS_2O_4$

Net Cell reaction: $Li + 2SO_2 \longrightarrow LiS_2O_4$

Li-SOCl₂: Anode: **Li**

Cathode: **SOCl₂**

Electrolyte: **SOCl₂**

At Anode: $4Li \longrightarrow 4Li^+ + 4e^-$

At Cathode: $4Li^+ + 4e^- + 2SOCl_2 \longrightarrow 4LiCl + SO_2 + S$

Net Cell reaction: $4Li + 2SOCl_2 \longrightarrow 4LiCl + SO_2 + S$
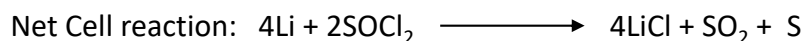
These batteries deliver voltage up to about 3.3 – 3.5 V

Applications:

They are used in electronic circuit boards.

They have many military and space applications.

They can be used in medical devices like neuro stimulations and drug delivery system.

SECONDARY CELLS

Secondary cells act as both galvanic/voltaic and electrolytic cells. When it converts **chemical energy into electrical energy** functions as **voltaic cell** and while converting **electrical energy into chemical energy** functions as **electrolytic cells**.

2) LEAD-ACID STORAGE CELL: Lead storage battery is also known as the lead acid battery. It is a kind of rechargeable battery. It is a secondary storage battery. This secondary storage battery can undergo reversible chemical reaction. Lead storage batteries are the energy storage device.
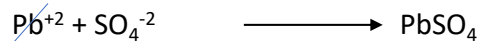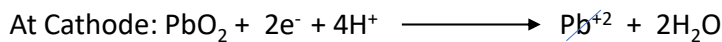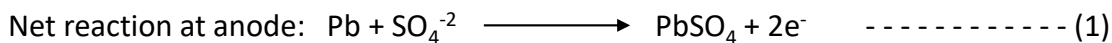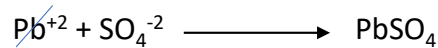
Anode: Lead (Pb) plates

Cathode: Pb plates coated with PbO_2

Electrolyte: Diluted H_2SO_4 (38%)

Construction:

Pb (Anode) ← $2H^+$ SO_4^{-2}
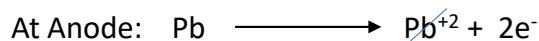
Pb plate coated with PbO_2 (Cathode)
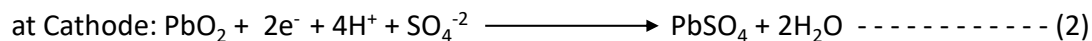
H_2SO_4 (38%)
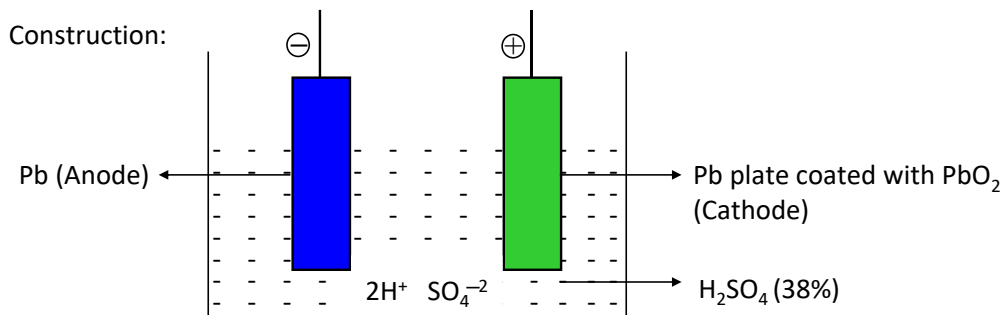
When Lead-Acid storage battery converting chemical energy into electrical energy it is said to be presenting discharging phase.
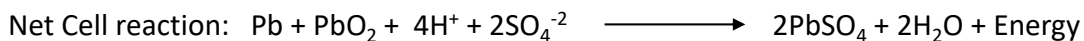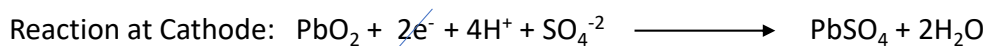
DISCHARGING PHASE

At Anode: $Pb \longrightarrow Pb^{+2} + 2e^-$

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

Net reaction at anode: $Pb + SO_4^{-2} \longrightarrow PbSO_4 + 2e^-$ - - - - - - - - - - - (1)

At Cathode: $PbO_2 + 2e^- + 4H^+ \longrightarrow Pb^{+2} + 2H_2O$

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

Net reaction at Cathode: $PbO_2 + 2e^- + 4H^+ + SO_4^{-2} \longrightarrow PbSO_4 + 2H_2O$ - - - - - - - - - - - - (2)

Overall reaction during discharging (1) + (2)

Reaction at anode: $Pb + SO_4^{-2} \longrightarrow PbSO_4 + 2e^-$

Reaction at Cathode: $PbO_2 + 2e^- + 4H^+ + SO_4^{-2} \longrightarrow PbSO_4 + 2H_2O$

Net Cell reaction: $Pb + PbO_2 + 4H^+ + 2SO_4^{-2} \longrightarrow 2PbSO_4 + 2H_2O + Energy$
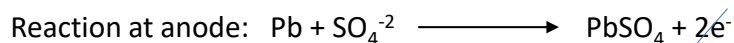
Lead-acid battery **delivers voltage 2V**.

In this case, $PbSO_4$ completely converts anode and cathode the cell stops functioning as voltaic cell, at this condition cell needs to be recharged.

Charging can be done by sending electricity with voltage more than 2V.

Charging Phase: When Lead-acid storage cell converts the electrical energy into chemical energy it is said to be in the charging phase, during charging, the chemical reactions taking place in the discharging phase will be reversed (Reverse to reactions 1 &2).

Net reaction at anode: $PbSO_4 + 2e^- \longrightarrow Pb + SO_4^{-2}$

Net reaction at Cathode: $PbSO_4 + 2H_2O \longrightarrow PbO_2 + 2e^- + 4H^+ + SO_4^{-2}$

Net Cell reaction: $2PbSO_4 + 2H_2O + Energy \longrightarrow Pb + PbO_2 + 4H^+ + 2SO_4^{-2}$

Car battery contains six Lead-acid storage cells that means car battery delivers voltage above 12V. Generally, by decreasing temperature by 1 ^oC, there will be decrease in voltage about 1.5×10^{-4} V. With this reason starting of car is quite difficult in cold climate. At that condition car battery needs to be heated.

Applications: Lead-acid batteries are used for supplying electricity for automobiles (all kind of vehicles), electronic devices, laboratories, hospitals, railways, broad-casting stations, etc.

3) LITHIUM ION CELL

Anode: $LiCoO_2$ ($LiNiO_2$ or $LiMnO_4$) mixed with conductor and binder

Cathode: Carbon mixed with binder.

Electrolyte: $LiPF_6$ in organic solution.

Voltameter

1st Metal foil coated with $LiCoO_2$ + binder + conductor (Anode)

2nd Metal foil coated with Carbon + binder (Cathode)

Electrolyte ($LiPF_6$)

DISCHARGING PHASE: When cell converts chemical energy into electrical energy is said to be present in discharging phase.
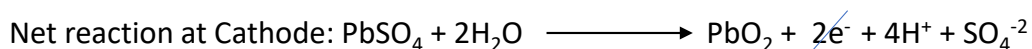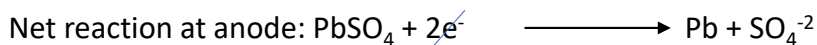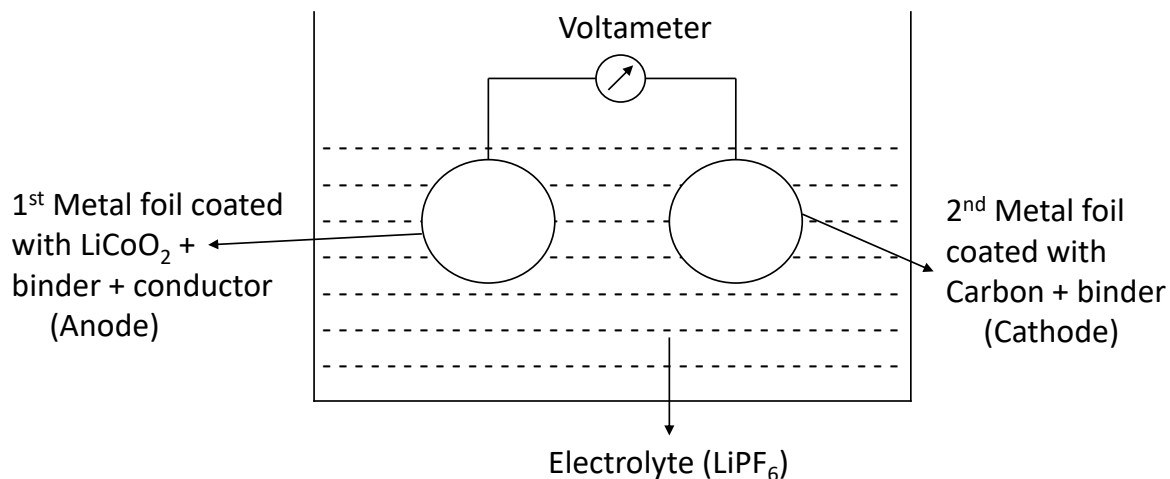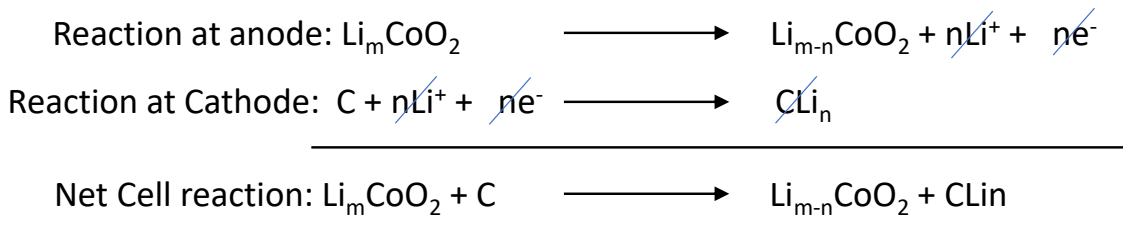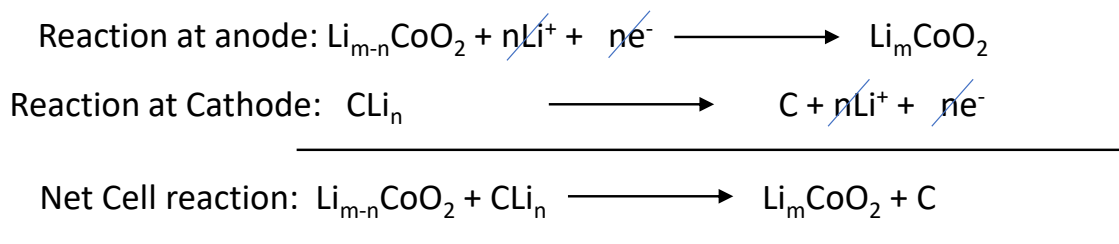
Reaction at anode: $Li_mCoO_2 \longrightarrow Li_{m-n}CoO_2 + n\cancel{Li^+} + \cancel{ne^-}$

Reaction at Cathode: $C + n\cancel{Li^+} + \cancel{ne^-} \longrightarrow C\cancel{Li}_n$

Net Cell reaction: $Li_mCoO_2 + C \longrightarrow Li_{m-n}CoO_2 + CLin$

Lithium-ion cell delivers voltage about 4.1V

RECHARGING PHASE: Charging can be done by sending current with voltage more than 4.1V, then chemical reaction taking place in discharging phase will be reversed.

Reaction at anode: $Li_{m-n}CoO_2 + n\cancel{Li^+} + \cancel{ne^-} \longrightarrow Li_mCoO_2$

Reaction at Cathode: $CLi_n \longrightarrow C + n\cancel{Li^+} + \cancel{ne^-}$

Net Cell reaction: $Li_{m-n}CoO_2 + CLi_n \longrightarrow Li_mCoO_2 + C$

Applications:

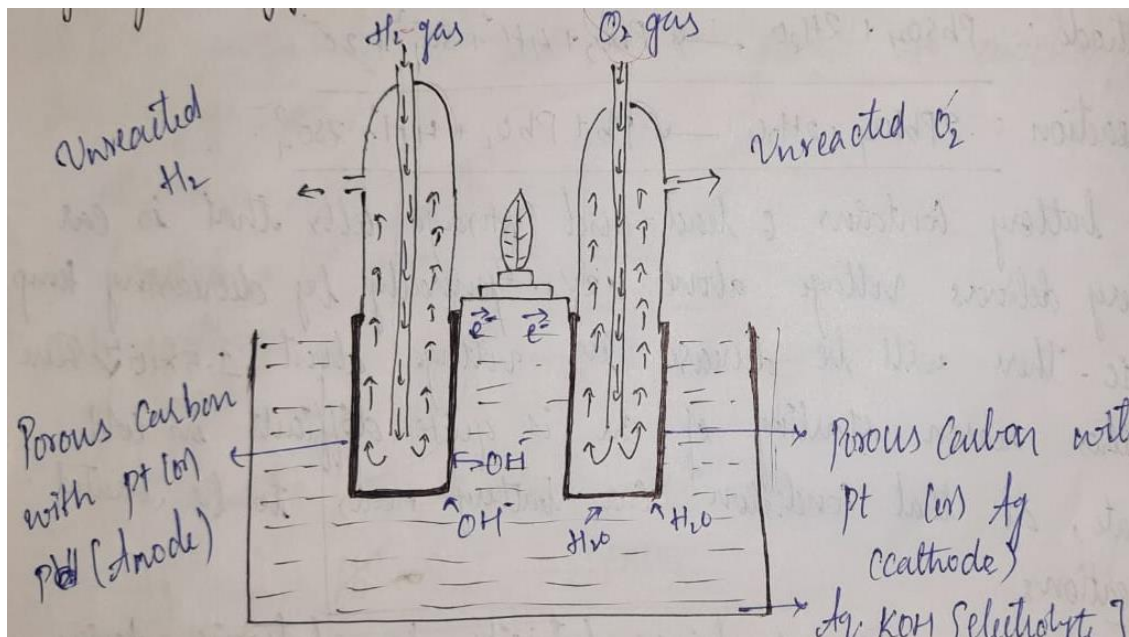Lithium-ion batteries used in laptops and mobile phones.

Fuel Cell

Fuel cell is an electrochemical cell, where chemical energy is converted into electrical energy by sending reactants into the battery. The basic principle of fuel cell is identical to that of an electrochemical cell. But only the difference is that chemical energy provided by **oxidant and fuel are stored outside of battery/cell**. Example: Hydrogen – oxygen fuel cells (H_2 - O_2).
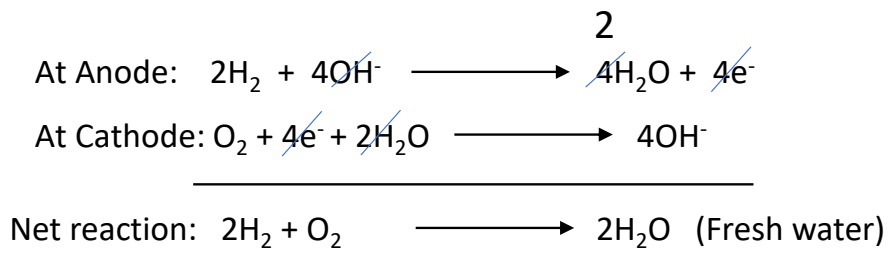
Characteristics of Fuel cells: Energy conversion is very high & thermal pollution is low.

Hydrogen-Oxygen Fuel Cell (H_2 - O_2)

Similar to a galvanic cell, fuel cell also has two half cells. Both half cells have porous carbon/graphite electrode with a catalyst (platinum or lead or silver). The electrodes are placed in the aqueous solution of NaOH or KOH which acts as an electrolyte. Hydrogen is supplied at anode and oxygen is supplied at cathode.

The two half-cell reactions are as follows:

$$\text{At Anode:} \quad 2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$$

$$\text{At Cathode:} \quad O_2 + 4e^- + 2H_2O \longrightarrow 4OH^-$$

$$\text{Net reaction:} \quad 2H_2 + O_2 \longrightarrow 2H_2O \quad \text{(Fresh water)}$$

The EMF of this cell is measured to be 1.23V. A number of such fuel cells are stacked together in series to make a battery.

Applications of Hydrogen-Oxygen Fuel Cell (H_2 - O_2):

1. The most important application of a fuel cell is its use in **Space Vehicles, Submarine or Military Vehicles**.

2. The product H_2O is valuable source of **fresh water by the Astronauts**.

3. It is hoped that fuel cell technology will bring a revolution in the area of energy production. 4. Fuel cell batteries for automotive will be a great boom for the future.

Advantages of Hydrogen-Oxygen Fuel Cell (H_2 - O_2):

🞣 **Energy conversion is very high** in Hydrogen-Oxygen fuel cell.

🞣 It has **low thermal pollution**.

🞣 Low maintenance cost.

🞣 It is an energy storage system for space applications.

🞣 Product H_2O is a drink water source for Astronauts.

Disadvantages of Hydrogen-Oxygen Fuel Cell (H_2 - O_2):

❖ The actual lifetime of Hydrogen-Oxygen *(H_2 - O_2)* fuel cell is not known.

❖ Initial cost of Hydrogen-Oxygen fuel cell is very high

❖ Storage of large amount of Hydrogen is difficult and the problems of durability.

CORROSION (MID-II Syllabus)

Introduction: (I) Types of corrosion: Chemical corrosion and Electrochemical corrosion. (ii) Factors affecting the rate of corrosion: Nature of the metal: Galvanic series, Anodic index, Purity of metal and Nature of corrosion-product & Nature of environment: Effect of temperature, Effect of pH, Humidity. (iii) Corrosion control methods: Cathodic protection: sacrificial anode method and impressed current cathode method. Protective coatings: metallic coatings (anodic and cathodic), methods of applications of metallic coatings: electroplating (of copper) and electroless plating (of Nickel).

INTRODUCTION

Metals and alloys (combination of two or more metals) are used for fabrication or construction of engineering materials. If the metals or alloy-based components are not properly maintained, they slowly decay by the action of atmospheric gases, moisture and other chemicals. "**The process of decay of metal by environmental attack is called as corrosion**".

When metals undergo corrosion they convert into their oxides, hydroxides, carbonates, sulphides, etc.

Examples: (i) Rusting of iron (Fe) – when Iron (Fe) is exposed to the atmospheric conditions, a layer of **Reddish-brown scale** formed is called as rusting of Iron [$Fe_2O_3.xH_2O$].
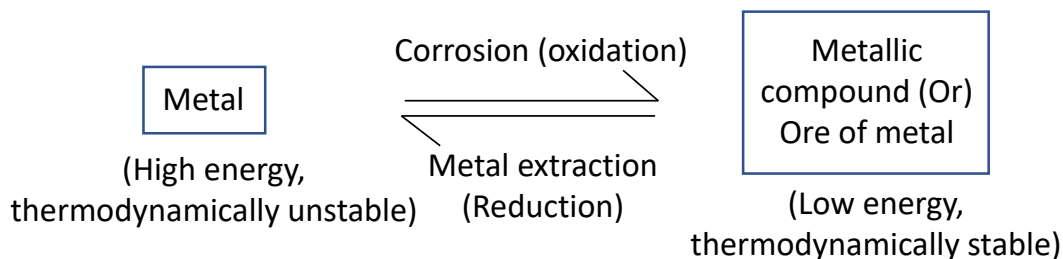
Reddish-brown film

Fe → Environment → Fe

(ii) Formation of **Green film** on the surface of Copper (Cu) when exposed to open atmosphere containing CO_2 due to the formation of basic carbonate [$CuCO_3$ + $Cu(OH)_2$].

Green film

Cu $\xrightarrow{\text{Environment}}$ Cu

Units for corrosion: mm/year or inches/year.

Reasons for corrosion

1. The metals exist in nature in the form of their "Raw materials or Ores" in the stable forms like oxides, chlorides, silicates, carbonates and sulphides.

2. Metals are extracted by giving some amount of energy to ore of the metal. So, the extracted metal has high energy and it is thermodynamically unstable. Hence, metals have natural tendency to go back to their stable ore form (oxides, chlorides, sulphides, carbonates and silicates).

Corrosion (oxidation)

Metal $\underset{\text{Metal extraction (Reduction)}}{\overset{\text{Corrosion (oxidation)}}{\rightleftarrows}}$ Metallic compound (Or) Ore of metal

(High energy, thermodynamically unstable)   (Low energy, thermodynamically stable)

[Corrosion is the reverse process of metal extraction]

Disadvantages

1. Life span and efficiency of metallic parts of machinery and fabrications is reduced.

2. Metals loss metallic properties like electrical conductivity, flexibility and elasticity.

3. Wastage of metal in the form of its compounds.

TYPES OF CORROSION

(1) Chemical corrosion (or) Dry corrosion

(2) Electrochemical corrosion (or) Wet corrosion

(1) CHEMICAL CORROSION (OR) DRY CORROSION

Attack of atmosphere on the surface of a metal **in the absence of moisture** is called Dry corrosion or chemical corrosion. This type of corrosion occurs mainly through the direct chemical action of atmospheric gases like O_2, N_2, halogens, H_2S, SO_2.
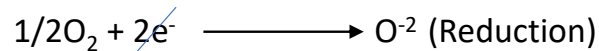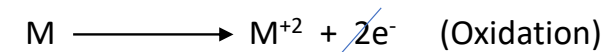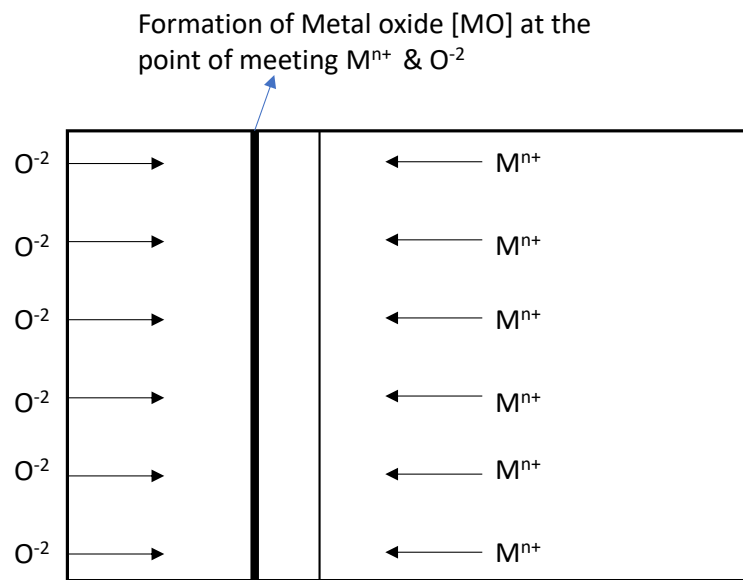
Dry corrosion is classified into three types.

(A) Oxidation corrosion, (B) Corrosion by other gases & (C) liquid metal corrosion.

(a) Oxidation corrosion: Attack of oxygen (O_2) on the surface of any metal in the absence of moisture called oxidation corrosion.

Generally, at low-temperature alkali and alkali earth metals undergo oxidation corrosion. At high temperature the remaining all metals undergo oxidation corrosion [except silver (Ag), Gold (Au) and Platinum (Pt)].

Mechanism:

Formation of Metal oxide [MO] at the point of meeting M^{n+} & O^{-2}

$$M \longrightarrow M^{+2} + 2e^- \quad \text{(Oxidation)}$$

$$1/2O_2 + 2e^- \longrightarrow O^{-2} \text{ (Reduction)}$$

_____

Net Reaction: $M + 1/2O_2 \longrightarrow M^{+2} + O^{-2} \longrightarrow$ MO (Metal Oxide)

_____

✓ The extent of corrosion depends upon the nature of the metal oxide formed on the surface.

Following are the types of metal oxides [MO] formed on metals.

(a) Stable metal oxide layer: The metal oxide layer formed is stable and it prevents further corrosion.
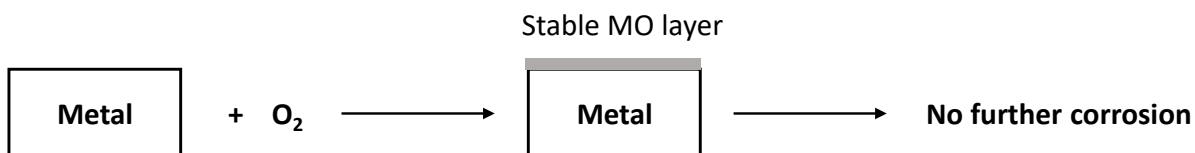
Stable MO layer

Eg.: Al, Cu, Sn, Pb, etc. form stable oxide layers on surface, thus preventing further oxidation.

(b) Unstable metal oxide layer: The oxide layer formed decomposes back to metal and oxygen. Therefore, oxidation corrosion is not possible in such cases. Ex: Ag, Au and Pt do not undergo oxidation corrosion.
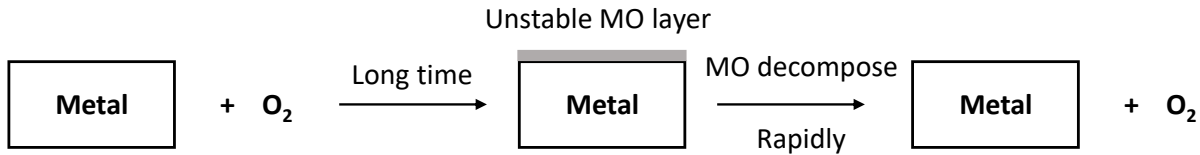
(c) Volatile metal oxide layer: The metal oxide layer formed is volatile in nature and evaporates as soon as it is formed. Example: Mo- molybdenum forms volatile MoO_3 layer.
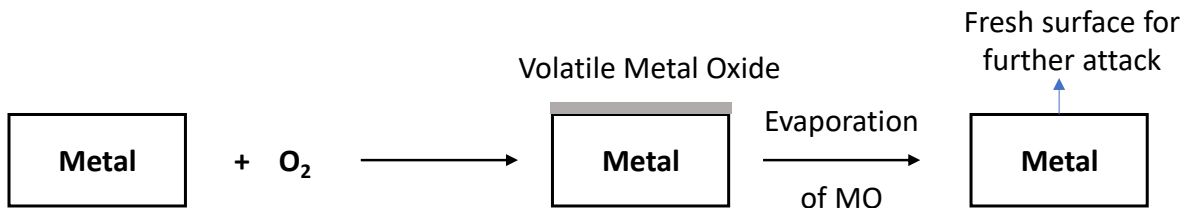
(d) Porous metal oxide layer: If the metal oxide layer is porous, that layer has pores or cracks. In this case the atmospheric oxygen penetrates through the pores or cracks and corrode the underlying metal surface. This cause continuous corrosion till the complete conversion of metal into its oxide. Example: Alkali and alkaline earth metals (Li, Na, K, Mg etc).
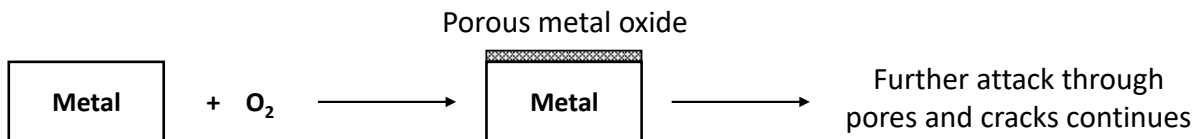
Pilling Bedworth rule

"The extent of protection given by the metal oxide layer to the parent metal" is Pilling Bedworth rule. It is expressed in terms of Specific Volume Ratio.

$$\text{Specific Volume Ratio} = \frac{Volume\ of\ Metal\ Oxide\ Layer}{Volume\ of\ Parent\ Metal}$$

Specific volume ratio increases the further oxidation corrosion decreases.

Specific volume ratio decreases the further oxidation corrosion increases.

Example. The specific volume ratio of W, Cr, and Ni are 3.6, 2.0 and 1.6, respectively. Ni has lower specific volume ratio, so it undergoes rapid oxidation corrosion.
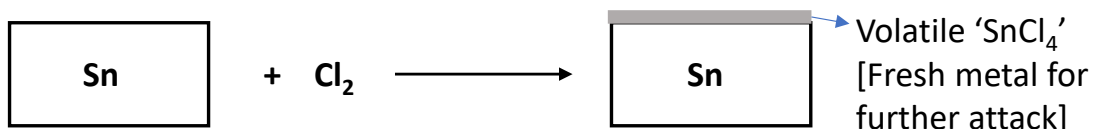
(B) Corrosion by other gases

Gases like CO_2, SO_2, Cl_2, F_2 and H_2S also cause corrosion of metals in absence of moisture.

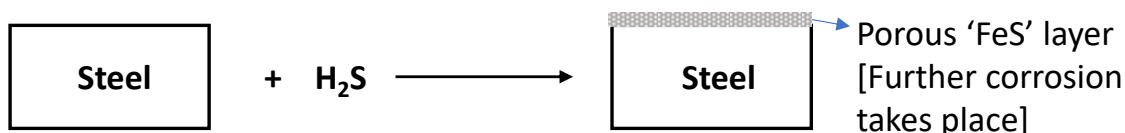The rate of corrosion depends on the reactivity of gases on metal surface.

Examples: (i) Attack of Cl_2 on Ag forms stable AgCl layer.
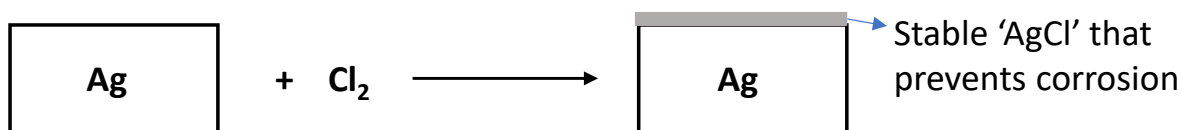
(ii) Attack of Cl_2 on Sn forms volatile $SnCl_4$ layer.

(iii) Attack of H_2S on steel forms porous 'FeS' layer.

(c) Liquid Metal Corrosion

"Attack of liquid metal on the surface of any solid metal in absence of moisture". It is due to inter penetration of liquid metal through the solid metal (or) dissolution of solid metal in liquid metal.

Example: Attack of Mercury (Hg) on any metal.

## 2) ELECTROCHEMICAL CORROSION OR WET CORROSION*****

Attack of atmosphere on the surface of a metal **in presence of moisture** is called as Electrochemical Corrosion or Wet Corrosion.

In this, formation of electrochemical cells takes place.

Electrochemical cell involves,

i) Anode and cathodes, which are separated by conducting medium (electrolyte)

ii) At anode, metal undergoes oxidation to form metallic ions

$$M \rightarrow M^{n+} + ne^-$$
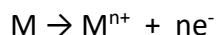
iii) At cathode, H^+ ions/H_2O/O_2 takes electrons and forms non-metallic ions like OH^- or O^{-2}

iv) Metallic ions formed at anode and non-metallic ions formed at cathode combines each other and forms corrosion product (like Rust) **between anode and cathode.**
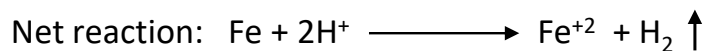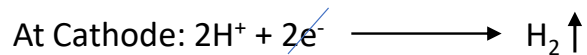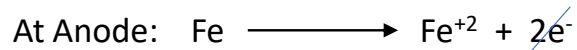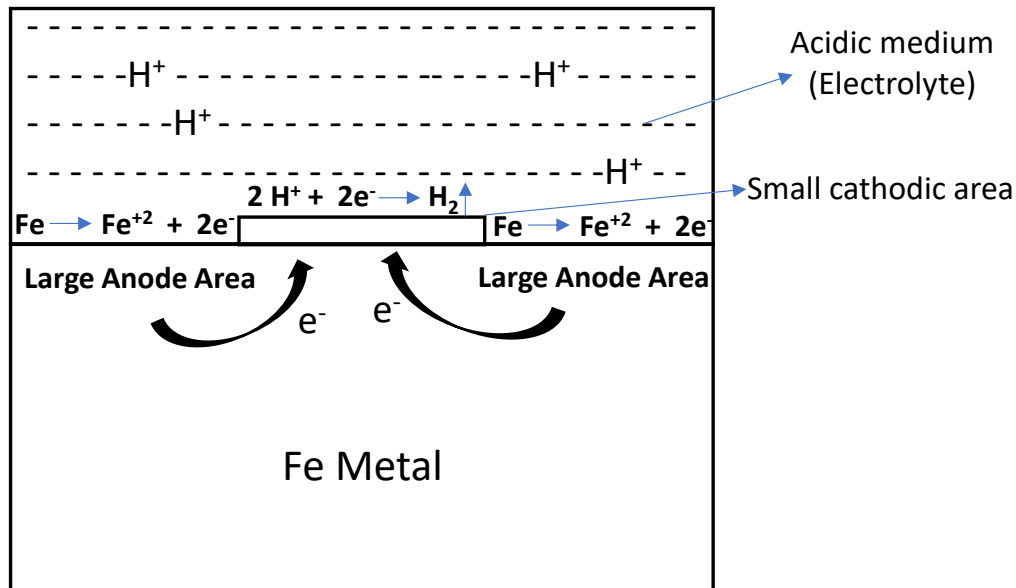
Wet corrosion takes place in two ways

a) Evaluation of Hydrogen (H_2) & b) Absorption of Oxygen (O_2)

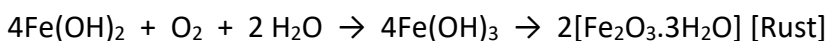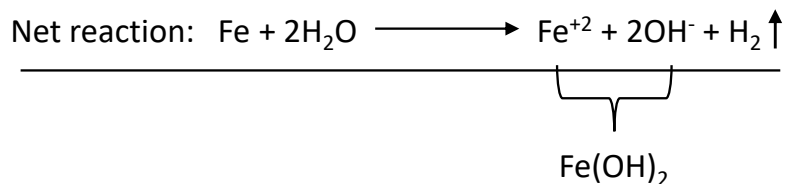**a) Evaluation of Hydrogen (H_2):**

This type of wet corrosion mainly occurs in "**acidic medium**" and also possible in **neutral medium (H₂O)**.

In hydrogen evolution type corrosion, **anodic areas are large** and **cathodic areas are small**.

In acidic medium:

At Anode: $Fe \longrightarrow Fe^{+2} + 2e^-$

At Cathode: $2H^+ + 2e^- \longrightarrow H_2 \uparrow$

Net reaction: $Fe + 2H^+ \longrightarrow Fe^{+2} + H_2 \uparrow$

In neutral medium (H_2O):

At Anode: $Fe \longrightarrow Fe^{+2} + 2e^-$

At Cathode: $2H_2O + 2e^- \longrightarrow 2OH^- + H_2 \uparrow$

Net reaction: $Fe + 2H_2O \longrightarrow Fe^{+2} + 2OH^- + H_2 \uparrow$

$Fe(OH)_2$

$4Fe(OH)_2 + O_2 + 2 H_2O \rightarrow 4Fe(OH)_3 \rightarrow 2[Fe_2O_3.3H_2O]$ [Rust]
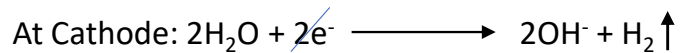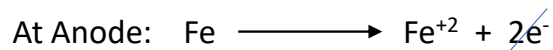
(b) Absorption of Oxygen (O_2):

- This type of corrosion takes place in **basic or neutral medium** in presence of oxygen.

- Usually, in presence of oxygen the surface of iron is coated with a thin film of iron oxide.
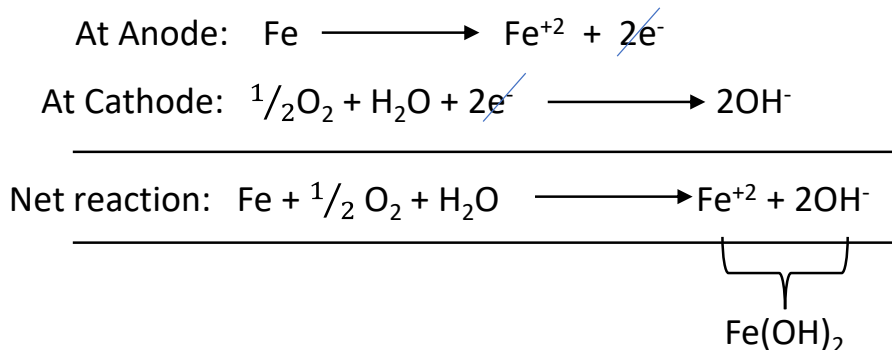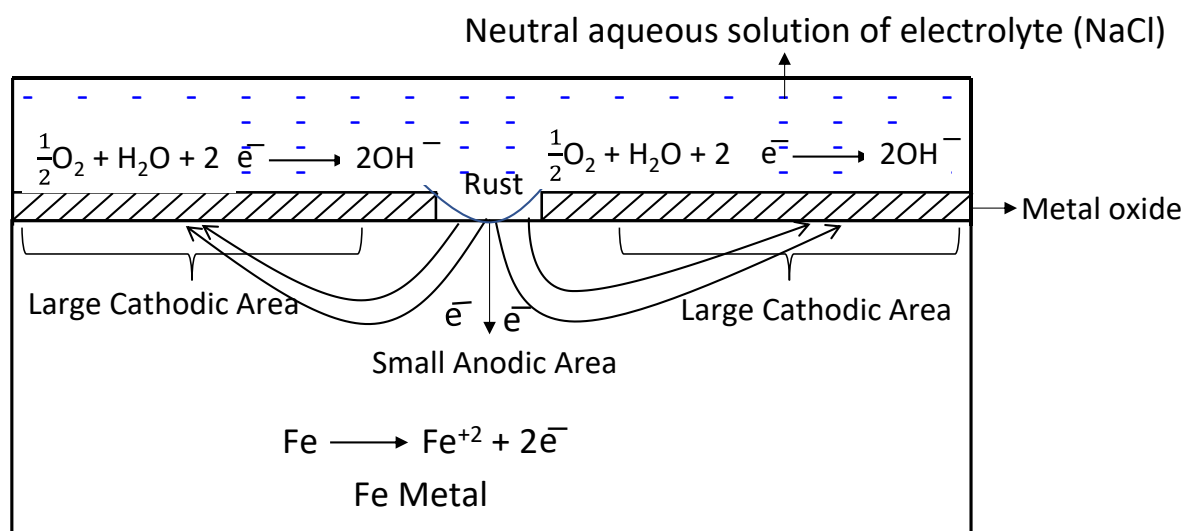
- If the film develops cracks, anodic areas are created on the surface and the rest of the metal surface acts as cathodes.
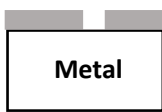
In absorption of oxygen type corrosion, anodic areas are small and cathodic areas are large.

Neutral aqueous solution of electrolyte (NaCl)

$\frac{1}{2}O_2 + H_2O + 2\ \bar{e} \longrightarrow 2OH^-$ Rust $\frac{1}{2}O_2 + H_2O + 2\ \bar{e} \longrightarrow 2OH^-$

Metal oxide

Large Cathodic Area $\bar{e} \downarrow \bar{e}$ Large Cathodic Area

Small Anodic Area

$Fe \longrightarrow Fe^{+2} + 2\bar{e}$

Fe Metal

At Anode: $Fe \longrightarrow Fe^{+2} + 2e^-$

At Cathode: $^1/_2 O_2 + H_2O + 2e^- \longrightarrow 2OH^-$

Net reaction: $Fe + ^1/_2\ O_2 + H_2O \longrightarrow Fe^{+2} + 2OH^-$

$Fe(OH)_2$

If there is enough oxygen is present, Ferrous hydroxides [$Fe(OH)_2$] will be converted to Ferric hydroxides [$Fe(OH)_3$] followed by rust.

$4Fe(OH)_2 + O_2 + 2\ H_2O \xrightarrow{(oxidation)} 4Fe(OH)_3 \xrightarrow{(oxidation)} 2[Fe_2O_3.3H_2O]$ [Rust]
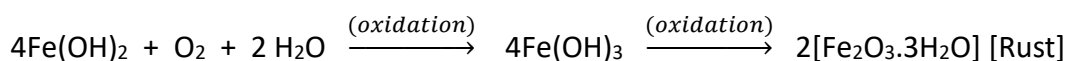
Differences between Dry corrosion and wet corrosion

Dry corrosion	Wet corrosion
1. The process of attacking of atmosphere on metal surface in absence of moisture	1. The process of attacking of atmosphere on metal surface in presence of moisture.

2. It is a slow process.	2. It is a rapid process
3. It is a uniform corrosion.	3. It is non-uniform corrosion.
Metal	**Metal**
4. It is explained by absorption mechanism	4. Explained by electrochemical mechanism
5. In this corrosion, product is formed at the place where corrosion is taking place.	5. In this process corrosion product takes place in between anode and cathode.

FACTORS EFFECTING THE RATE OF CORROSION

Always corrosion is the relation between METAL and ENVIRONMENT. Therefore, the rate of corrosion depends on the nature of metal and nature of environment.

1. Nature of Metal	2. Nature of Environment
(a) Position of metal in the Galvanic Series	(a) Temperature
(b) Purity of Metal	(b) Humidity
(c) Nature of surface film	(c) pH
(d) Nature of Corrosion product	

1. NATURE OF METAL

(a) Position of metal in the Galvanic Series:

Metals present at the **top of the Galvanic Series undergo rapid corrosion** due to high oxidation potential.

Metals present at **bottom of the Galvanic Series undergo less corrosion** due to low oxidation potentials.

Mg, Mg-alloy, Zinc, Al, Fe, Steel, Pb-Sn alloy, Pb, Sn, Brass, Cu, Bronze, Ag, Graphite, Ti, Au, Pt

Decreasing rate of corrision →

(b) Purity of Metal

As purity of metal decreases the rate of corrosion increases, and as purity of metal increases corrosion decreases.

$$\textbf{\% Of purity of Metal} \propto \frac{1}{\textit{Rate of Corrosion}}$$

Impurity presents in metal causes heterogeneity which results the formation of electrochemical cell. Hence, the rate of corrosion increases.

Example: Zinc metal.

% Of purity	99.999	99.99	99.9	99
Rate of Corrosion	1	2650	5000	7200

(c) Nature of surface film: According to Pilling Bedworth rule;
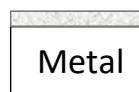
$$\text{Specific Volume Ratio (SVR)} \propto \frac{Volume\ of\ Metal\ Oxide\ Layer}{Volume\ of\ Parent\ Metal}$$

If SVR increases, the rate of corrosion decreases.

(Non porous, protective surface film

If SVR decreases, the rate of corrosion increases.

(Porous, non-protective surface film)

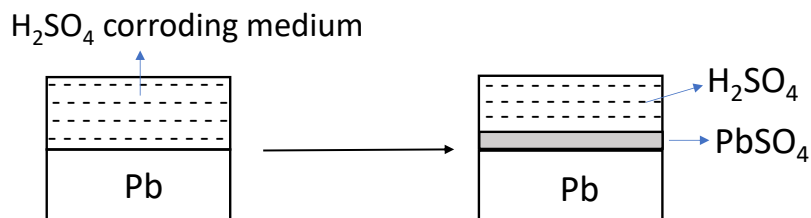**(d) Nature of corrosion product**

(i) Volatility of corrosion product: If the corrosion product is volatile, it evaporates as soon as it is formed and gives fresh metal to further attack.

Molybdenum + O₂ ⟶ Volatile Metal Oxide → Mo → Evaporation of MO → Molybdenum (Fresh surface for further attack)
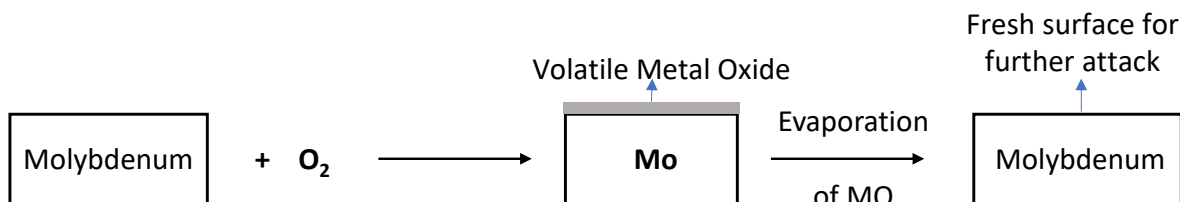
(ii) Solubility of corrosion product:

If corrosion product is **soluble in corroding medium, then the rate of corrosion is High**.

If corrosion product is **insoluble in corroding medium, then the rate of corrosion is Low**.

H_2SO_4 corroding medium

Pb → Pb (H_2SO_4, $PbSO_4$)

Corrosion product $PbSO_4$ is insoluble in H_2SO_4, so rate of corrosion of Pb is low.

2. NATURE OF ENVIRONMENT

(a) Temperature: The rate of corrosion increases with increase in temperature.

Rate of corrosion $\propto$ Temperature

Reasons: As temperature increases, the rate of reaction increases and diffusion of gases on metal surface increases.

(b) Humidity in air: The rate of corrosion increases with increase in humidity/moisture present in air.

Rate of corrosion $\propto$ Humidity of air.

Reasons: (i) Humidity present in atmosphere provides water to the electrolyte which is essential for setting up of an electrochemical cell.

(ii) The metal oxide film formed has the tendency to absorb moisture which creates another electrochemical cell.

Example: (i) Fe undergoes rapid corrosion in wet conditions than the case of dry conditions.

Critical Humidity: The humidity above which the rate of corrosion increases rapidly is called as critical humidity.

(c) pH: In acidic medium metals undergo rapid corrosion compared to neutral/basic medium.

$$pH \propto \frac{1}{Rate\ of\ corrosion}$$

Acidic medium: PH < 7 - Corrosion is More

Basic medium: PH > 7 - Corrosion is Less

Fe undergoes rapid corrosion in H_2CO_3 than H_2O and NaOH.

CORROSION CONTROLLING METHODS

Corrosion controlling methods are two types: (i) Cathodic protection & (ii) Metallic coatings.
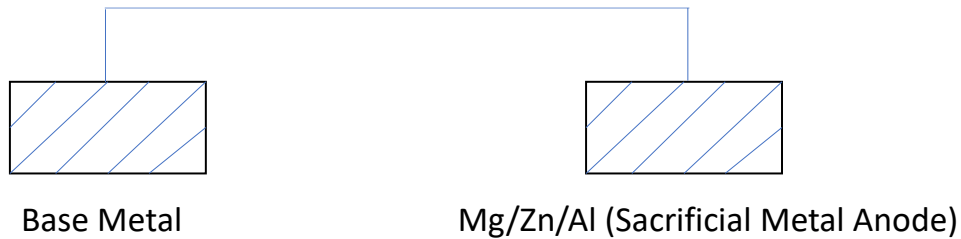
(I) CATHODIC PROTECTION

The method of protecting the base metal by forcibly making it to behave like a cathode there by preventing corrosion is called as Cathodic Protection. It is classified into two types.

(a) Sacrificial Anodic Protection & (b) Impressed Current Cathodic Protection.

(A) SACRIFICIAL ANODIC PROTECTION

In this method, the metal to be protected (base metal) is connected to a more anodic metal (having high oxidation potential metal) through a wire, then the newly introduced metal acts as anode and

undergoes corrosion, whereas the base metal acts as cathode i.e., that will be protected from corrosion. The attached more anodic metal is called Sacrificial Anode. Generally, sacrificial anodes are Mg, Al and Zn.

Base Metal   Mg/Zn/Al (Sacrificial Metal Anode)

APPLICATIONS

1) Marine structures and Ship hulls can be protected from corrosion.

Base Metal

Sacrificial Anode (Zn)
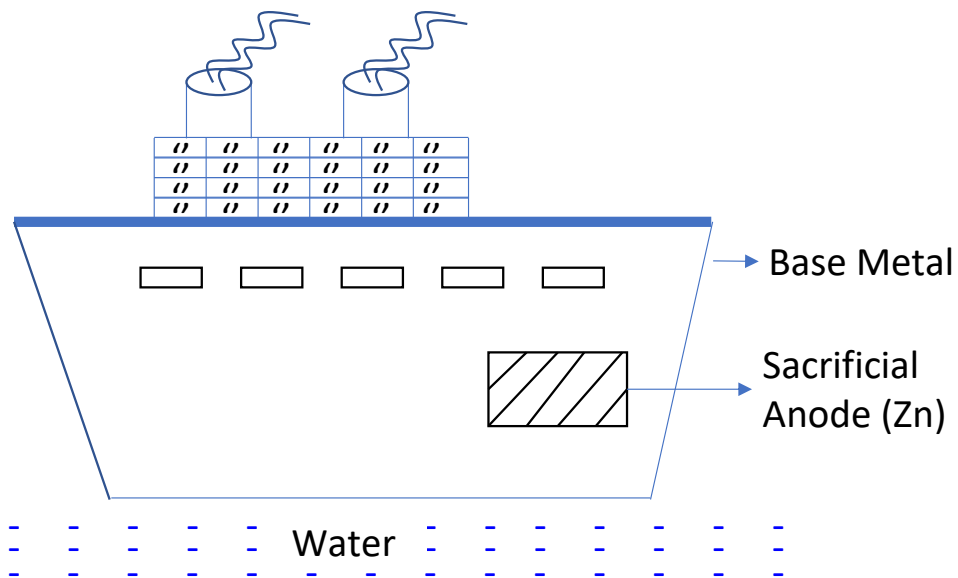
Water

2) Underground pipelines can be protected

Ground level

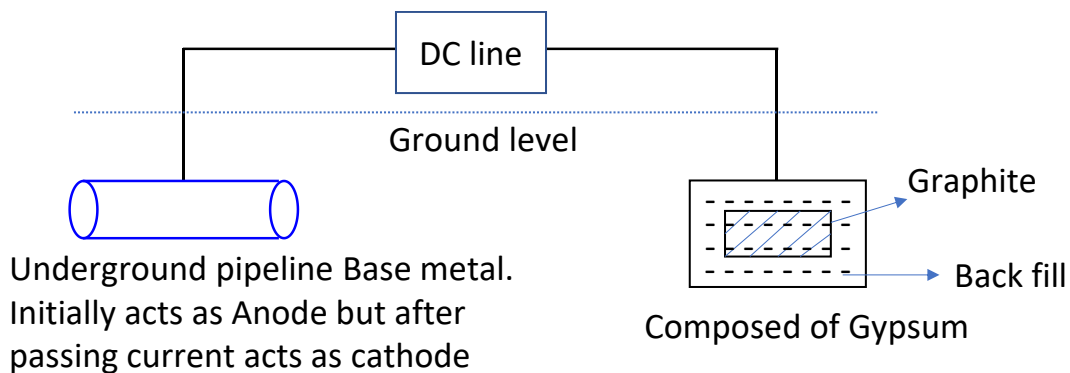Underground pipeline   Mg

Sacrificial Metal Anode
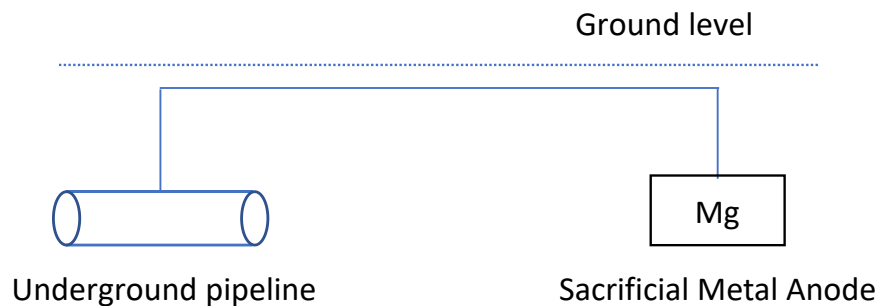
3) Industrial Hot Water tank can be protected.
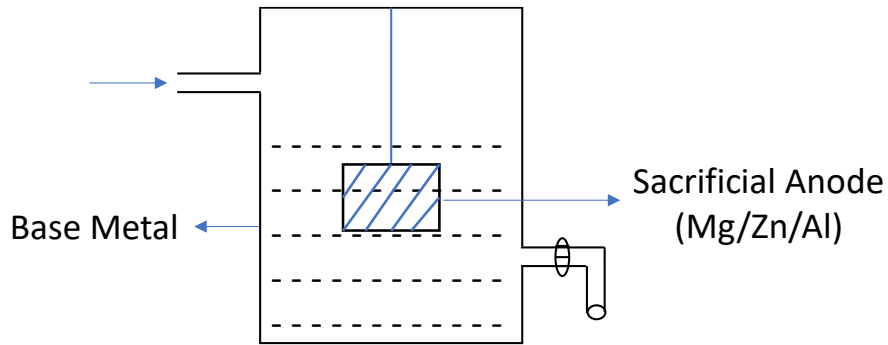
(B) IMPRESSED CURRENT CATHODIC PROTECTION

In this method, an impressed current is allowed through the circuit from an external DC source in the opposite direction to nullify the corrosion current. The result is that the anode metal is converted into cathode and protected from corrosion.

Applications

1. Underground pipelines can be prevented from corrosion

2. Marine structure can be prevented from corrosion

3. Hot water tanks can be prevented from corrosion

4. Condensers can be prevented from corrosion

5. Transmission line towers can be prevented from corrosion

Limitations

i) Capital investment and maintenance cost is very high

ii) Regular inspection is needed

iii) Industrial current using in this method ways correction of adjacent pipe lines.

(II) METALLIC COATINGS

The process of coating of a pure metal (coating metal) on the surface of the base metal which is to be protected (base metal) is called metallic coating.

Metal-II (Coating Metal)
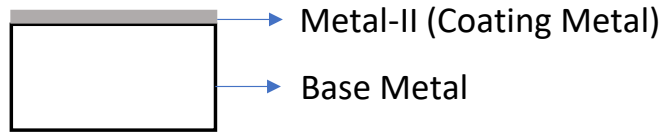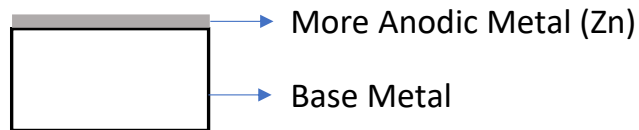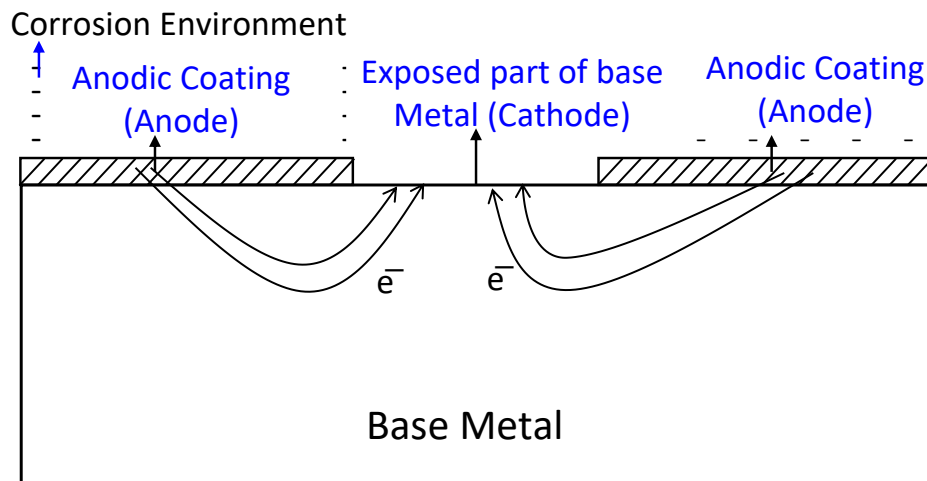
Base Metal

Based on coating, metallic coatings are classified into two types.

i) Anodic coating and ii) Cathodic coating.

A) ANODIC COATING: The process of coating more anodic metal (high oxidation potential metal) on the surface of the base metal is called anodic coating. Ex: Coating of Mg/Al/Zn on any base metal like Iron (Fe) or Steel.

More Anodic Metal (Zn)

Base Metal

Anodic coating prevents corrosion of base metal due to its high oxidation potential, i.e., anodic coating undergoes corrosion while base metal protected from corrosion.

Corrosion Environment

Anodic Coating (Anode) | Exposed part of base Metal (Cathode) | Anodic Coating (Anode)

e^- e^-

Base Metal

If anodic coating contains pores, breaks and discontinues the unexposed part of base metal acts as cathodic part (cathode). Hence, no corrosion takes place to the base metal until entire anodic coating gets corrosion.

B) CATHODIC COATING: The process of coating more cathodic metal (Low oxidation potential metal) on the surface of base metal is called cathodic coating.

Coating of Tin (Sn) on Iron (Fe) is known as Tinning.

More Cathodic Metal (Sn)
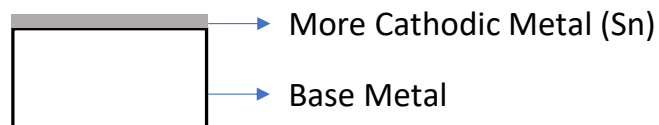
Base Metal

Cathodic coating prevents corrosion of base metal due to its noble behaviour towards corrosion, i.e., less tendency towards corrosion due to high reduction potential.
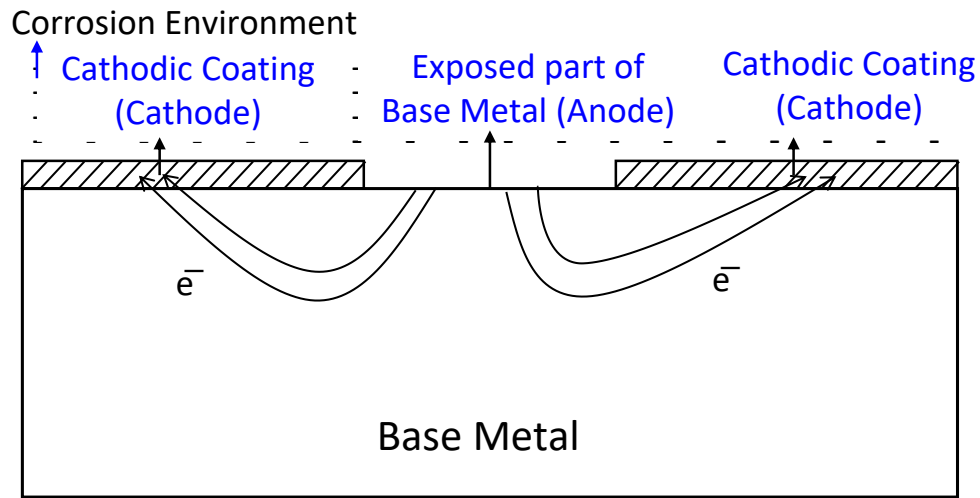
Corrosion Environment

If cathodic coating contains pores, breaks and discontinuity then unexposed part of base metal acts as anode and corrosion takes place of base metal. Hence, no corrosion takes place to base metal when cathodic coating free from pores, breaks and discontinuity.

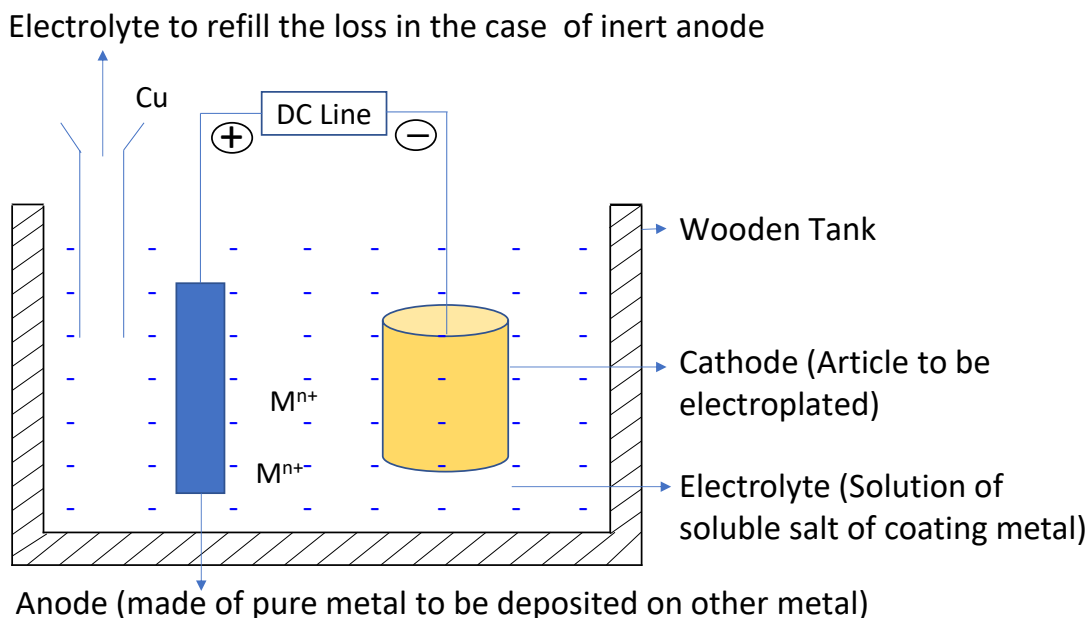Example: Tinning (coating of Sn on base metal)

Difference between anodic coating and cathodic coating	
Anodic coating	Cathodic coating
i) Coating of more anodic metal on the surface of base metal	i) Coating of more cathodic metal on the surface of base metal
ii) The coated metal should have high oxidation potential than the base metal	ii) The coated metal should have low oxidation potential than the base metal
iii) The coated metal should have low reduction potential than the base metal	iii) The coated metal should have high reduction potential than the base metal
iv) It prevents corrosion of base metals artificially	iv) It prevents corrosion of base metals by its noble behavior
v) If it contains pores, breaks and discontinuity, the base metal acts as cathode and prevents corrosion	v) If it contains pores, breaks and discontinuity, the base metal acts as anode and forms corrosion
vi) No corrosion forms until entire anodic coating gets corrosion	vi) No corrosion forms unless the coating contains pores, breaks and discontinues.
Ex: Galvanization	Ex: Tinning

METHODS AND APPLICATIONS OF METALLIC COATING

1) Electroplating, 2) Electroless plating & 3) Galvanisation.

1) ELECTROPLATING/ELECTRODEPOSITION (of Copper)

Coating of a coat metal on the surface of any base metal by passing a direct current called Electroplating.

Electrolyte to refill the loss in the case of inert anode

Cu

DC Line

$+$ $-$

Wooden Tank

M^{n+}

Cathode (Article to be electroplated)

M^{n+-}

Electrolyte (Solution of soluble salt of coating metal)

Anode (made of pure metal to be deposited on other metal)

❖ In this method article to be electroplated subjected to solvent cleaning using trichloroethylene to remove oils and grease. Then the article is subjected to acid picking using dilute HCl to remove oxides.

❖ The cleaned article is made as the cathode of electrolytic cell.

❖ The pure metal to be deposited is made as the anode of the cell. Anode and cathodes are dipped into the electrolytic solution of soluble salt of coating metal.

❖ When electricity is passed through electrodes, the anode metal undergoes oxidation and forms metal ions. The liberated electrons accumulate at cathode. The formed metal ions migrate towards cathode and deposited on the surface of article (cathode) which results the formation of smooth, bright and thin layer of coating metal on the surface of base metal (article).

❖ Example: Electroplating of Copper (Cu) on the surface of article (base metal) with smooth and bright layer should maintain the following conditions.

   Anode   :   Cu pellets

Cathode	:	Article to be electroplated (Base metal)
Electrolyte	:	$CuSO_4$ or $AgCuCl_2$.
Temperature	:	$40 - 70\ ^oC$
Current density	:	$20 - 30\ mA/cm^2$

Applications

- Metals and non-metals can be electroplated.

- In this case of metals electroplating increases corrosion resistance and chemical resistance strength, hardness and surface properties.

- In the case of non-metals like plastic, glass and wood, electroplating increases strength and improves decorative values.

2) ELECTROLESS PLATING/AUTOCATALYTIC PLATING (OF NICKEL)

Coating of a coat metal on the surface of any base metal by using reducing agent instead of electricity is called electroless plating. In this process, the reducing agent supplies electrons for the reduction of Metal Ions into Metal.

$$M^+\quad +\quad R^-\quad \longrightarrow \quad M\ +\ R$$

Metal ion   Reducing agent   Metal
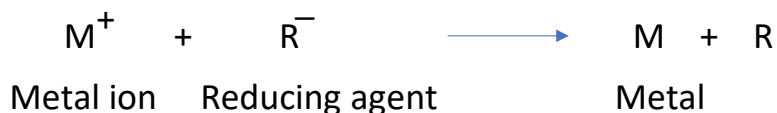
Following are the requirements for electroless plating

a) The coating metal should be in the form of salt soluble.

b) Reducing agents like Formaldehyde or Sodium Hypophosphite are used.

c) Accelerators like fluorides and Succinates are used to accelerate the reduction rate.

d) To improve the brightness of the coat, brighteners like Pb^{+2} and Cd^{+2} are added.

e) Buffer solution used to maintain PH and temperature.

Example: Electroless plating of Nickel (Ni) on the surface of ABS

ABS = Acrylonitrile Butadiene Styrene

Ni → (beaker)

ABS

NiSO$_4$ + Sodium hypophosphite (NaH$_2$PO$_2$) + Sodium succinate + Cd^{+2} + Sodium acetate
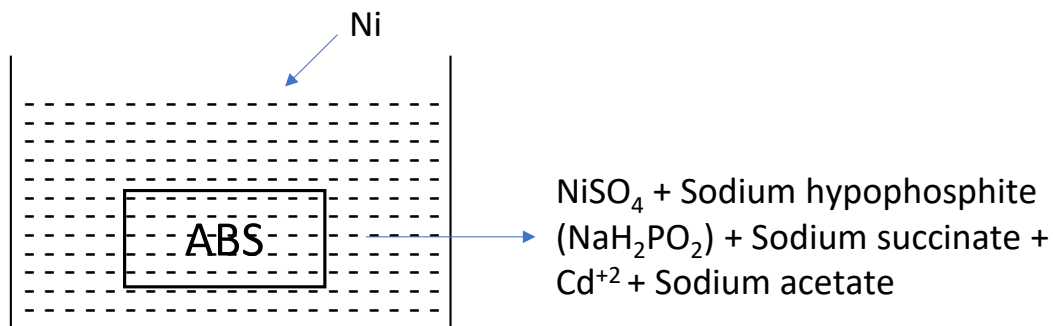
In this process, reducing agent (NaH$_2$PO$_2$) converts Ni^{+2} ions into Ni

$$Ni^{+2} + H_2PO_2^- + H_2O \rightarrow Ni + H_2PO_3^- + 2H^+$$
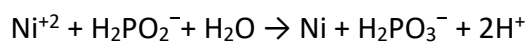
The formed (Ni) will be deposited on the surface of catalytically active ABS (non-metal) or (metal).

Applications

In the case of metals, electroless plating increases corrosion resistance, strength, hardness and surface properties.

In case of non-metals, electroless plating increases strength.

CHAPTER IV

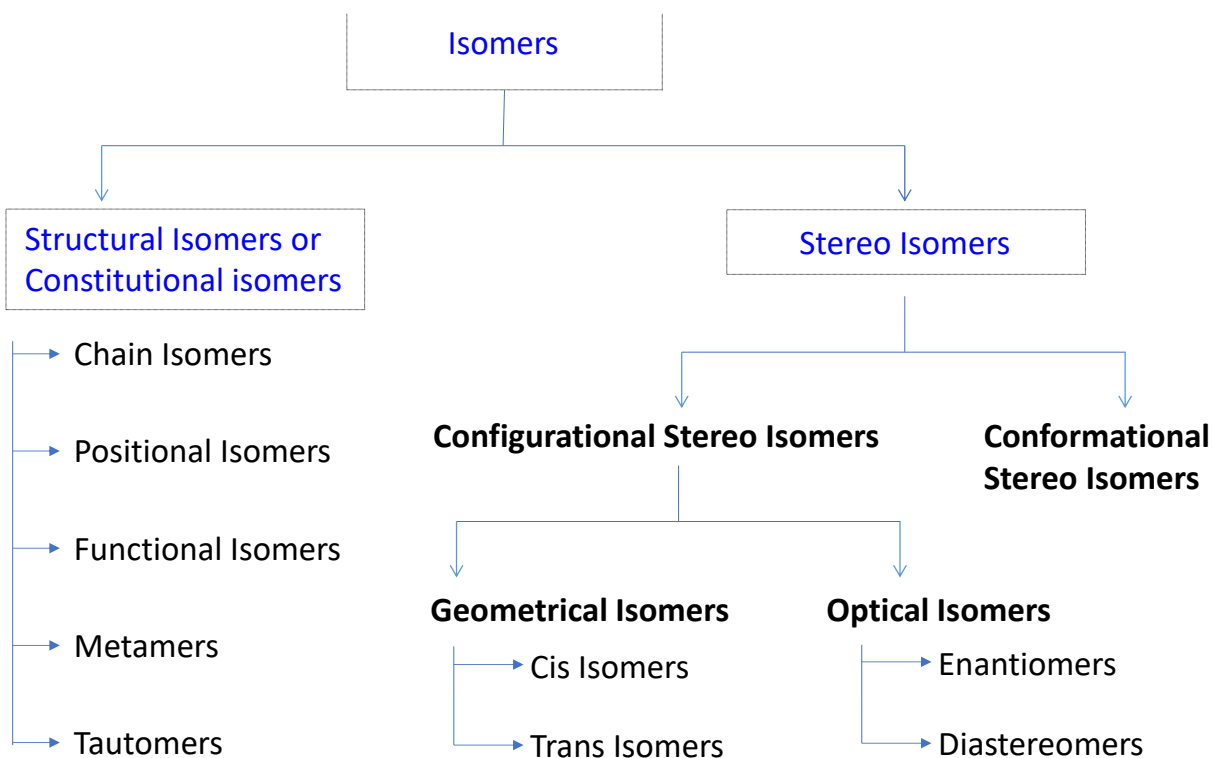 **Stereochemistry, Reaction Mechanism and Synthesis of Drug Molecules (9L)**

Structural isomers and stereoisomers, configurations, symmetry and chirality, enantiomers, diastereomers, optical activity. Conformational analysis of n-butane.

Organic reactions and synthesis of drug molecules:

Introduction to reactions involving substitution (SN^1 & SN^2), addition (addition of HBr to propene, Markownikoff and Anti Markownikoff addition), Elimination reactions: Dehydro halogenation of alkyl halides. Saytzeff rule. Redox reactions, oxidation (oxidation of alcohols using $KMnO_4$ & CrO_3), reduction (reduction of carbonyl compounds by $LiAlH_4$ & $NaBH_4$). Synthesis & uses of commonly used drug molecules: paracetamol and Asprin.

Stereo chemistry: "The study of properties (physical, chemical and biological) of molecules **with respective to spatial arrangement of atoms or groups in 3-dimensions**" is called as stereochemistry.

Or Stereochemistry is a branch of chemistry that deals with the three-dimensional arrangement of atoms/groups in molecules.

Isomers: Compounds having same molecular formula but different chemical and physical properties called isomers. This phenomenon is called as isomerism.
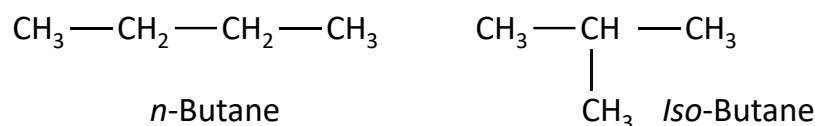
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                                    Isomers
                          ┌────────────┴────────────┐
         Structural Isomers or                    Stereo Isomers
         Constitutional isomers            ┌────────────┴────────────┐
    → Chain Isomers              Configurational Stereo Isomers   Conformational
                                 ┌──────────┴──────────┐          Stereo Isomers
    → Positional Isomers     Geometrical Isomers   Optical Isomers
                              → Cis Isomers         → Enantiomers
    → Functional Isomers
                              → Trans Isomers       → Diastereomers
    → Metamers

    → Tautomers
```
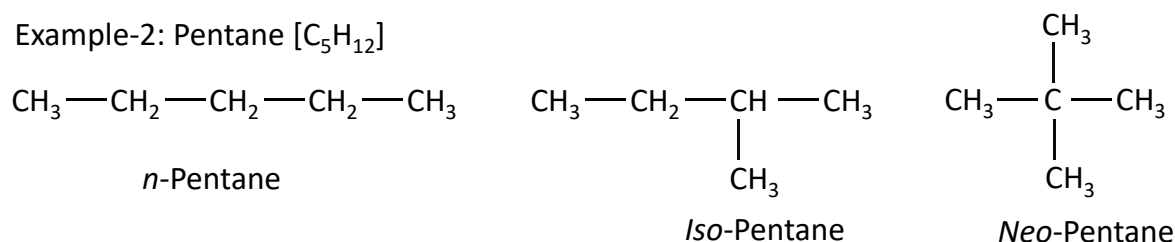
82

Structural Isomers:

Compounds having same molecular formula but different structures called as Structural isomers.

Chain Isomers: Compounds having same molecular formula but **differ in length/nature of carbon cain** is called as chain isomers. This phenomenon is called as chain isomerism.

Example-1: Butane [C_4H_{10}]

$$CH_3-CH_2-CH_2-CH_3 \qquad CH_3-CH-CH_3$$

$$n\text{-Butane} \qquad\qquad\qquad CH_3 \quad Iso\text{-Butane}$$

Example-2: Pentane [C_5H_{12}]

$$CH_3-CH_2-CH_2-CH_2-CH_3 \qquad CH_3-CH_2-CH-CH_3 \qquad CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3$$

$$n\text{-Pentane} \qquad\qquad\qquad\qquad CH_3$$

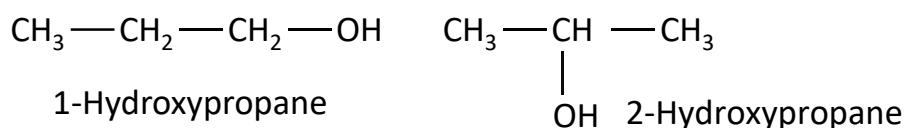$$Iso\text{-Pentane} \qquad\qquad Neo\text{-Pentane}$$

Positional Isomers: Compounds having same molecular formula but **differ in position of functional group** called Positional isomers. This phenomenon is called as positional isomerism.
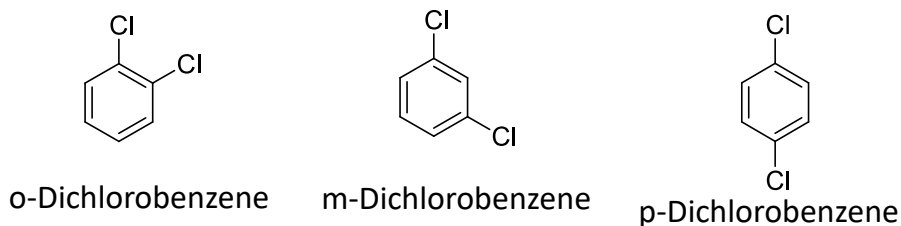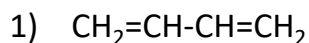
Example-1: Chloropropane [C_3H_7Cl]

$$CH_3-CH_2-CH_2-Cl \qquad CH_3-CH-CH_3$$

$$\text{1-Chloropropane} \qquad\qquad Cl \quad \text{2-Chloropropane}$$
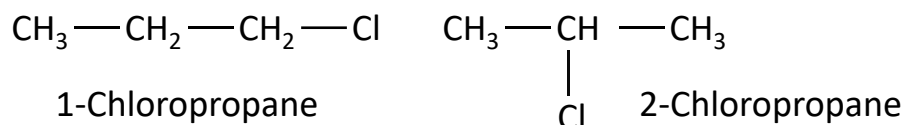
Example-2: Hydroxypropane [C_3H_7OH]

$$CH_3-CH_2-CH_2-OH \qquad CH_3-CH-CH_3$$

$$\text{1-Hydroxypropane} \qquad\qquad OH \quad \text{2-Hydroxypropane}$$

Example-3: Dichlorobenzene [$C_6H_4Cl_2$]

o-Dichlorobenzene   m-Dichlorobenzene   p-Dichlorobenzene
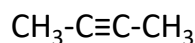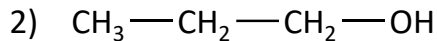
Functional isomers: Compounds having same molecular formula **but differ in functional groups** called as functional isomers and the phenomenon is called as functional isomerism.
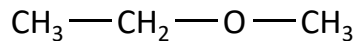
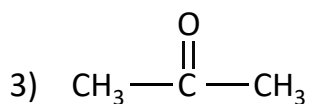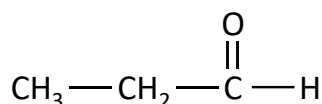1) $CH_2=CH-CH=CH_2$ $CH_3-C{\equiv}C-CH_3$

    1,3-Butadiene   2-Butyne

2) $CH_3-CH_2-CH_2-OH$ $CH_3-CH_2-O-CH_3$

    1-Hydroxypropane   Methoxyethane

3) $CH_3-\underset{\underset{\textstyle}{}}{\overset{\overset{\textstyle O}{\|}}{C}}-CH_3$ $CH_3-CH_2-\overset{\overset{\textstyle O}{\|}}{C}-H$
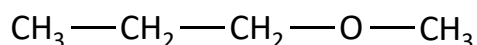
    Propanone   Propanal
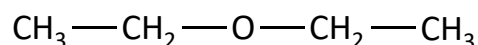
Metamers: Compounds having same molecular formula **but different alkyl groups around the same functional group** is called as metamers.
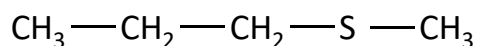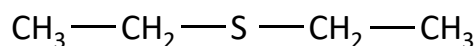
1. Ethers

$CH_3-CH_2-CH_2-O-CH_3$ $CH_3-CH_2-O-CH_2-CH_3$

Methyl propyl ether   Diethyl ether

2. Thioethers

$CH_3-CH_2-CH_2-S-CH_3$ $CH_3-CH_2-S-CH_2-CH_3$

Methyl propyl thioether   Diethyl thioether

Tautomers: Compounds having same molecular formula, **that are readily interconvertible** and exist dynamic equilibrium called tautomers and this phenomenon is called as tautomerism. (or) Compounds which are having same molecular formula, and **involves 1,3-proton transfer** called tautomers and this phenomenon is called tautomerism.

1) $CH_3-\overset{\overset{\textstyle O}{\|}}{C}-CH_3 \rightleftharpoons CH_3-\overset{\overset{\textstyle OH}{|}}{C}=CH_2$

    Keto form   Enol form
    (Propanone)   (Isopropenol)

2) $CH_3 - \overset{\overset{\displaystyle O}{\|}}{C} - NH_2 \rightleftharpoons CH_3 - \overset{\overset{\displaystyle OH}{|}}{C} = NH$

Amide form   Iminol form
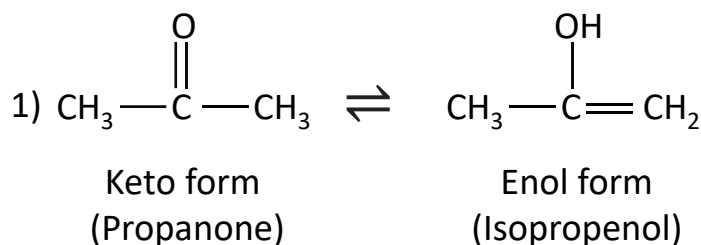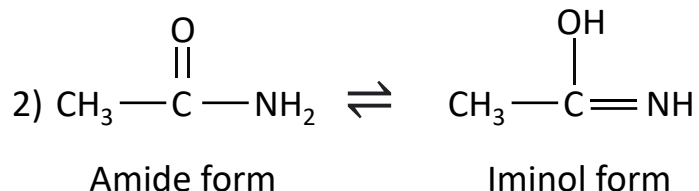
Stereo isomers

Compounds having same molecular formula **but different spatial arrangement of atoms or groups** called stereo isomers and this phenomenon is called as stereo isomerism.
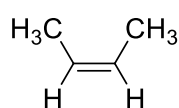
Configurational stereo isomers

The stereo isomers which are **not interconvertible by rotation** called configurational isomers. These are classified into two types.
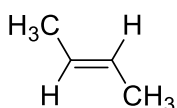
(i) Geometrical Isomers **

Compounds having same molecular formula **but different geometry** called as Geometrical isomers. These are two types.

(a) Cis Isomers: Compounds having same molecular formula and **both identical/similar groups are present on the same side of the double bond** called Cis isomers.

(b) Trans Isomers: Compounds having same molecular formula and **both identical/similar groups are present on the opposite side of the double bond** called Trans isomers.
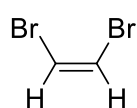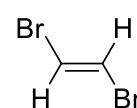
Cis 2-butene   Trans 2-butene   Cis-1,2-dibromoethene   Trans-1,2-dibromoethene
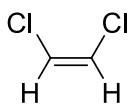
Cis-1,2-dichloroethene   Trans-1,2-dichloroethene   Cis-1,2-diFluoroethene   Trans-1,2-diFluoroethene

(ii) Optical isomers: Configurational isomers **which rotate plane polarized light** called optical isomers. These are two types.

(a) ***Enantiomers:*** Compounds having same molecular formula that are "**Non-Superimposable Mirror images**" called enantiomers.

(i)   Mirror   (ii)   Mirror   (iii)   Mirror

(i)   Mirror   (ii)   Mirror

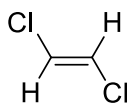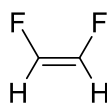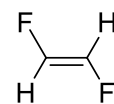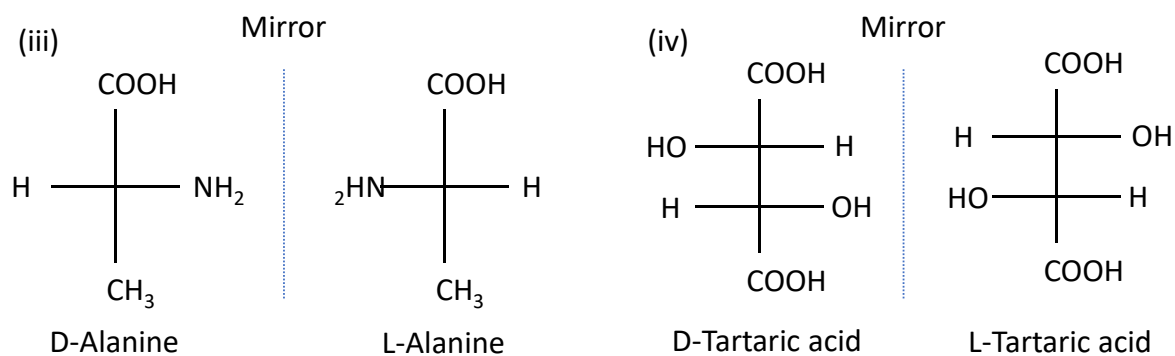| CHO | CHO |
| COOH | COOH |

H ——— OH   HO ——— H   H ——— OH   HO ——— H

CH_2OH CH_2OH CH_3 CH_3

D-Glyceraldehyde   L-Glyceraldehyde   D-Lactic acid   L-Lactic acid

(iii)   Mirror   (iv)   Mirror

COOH   COOH   COOH   COOH

H ——— NH_2 $_2HN$ ——— H   HO ——— H   H ——— OH

CH_3 CH_3 H ——— OH   HO ——— H

D-Alanine   L-Alanine   COOH   COOH

                                     D-Tartaric acid   L-Tartaric acid
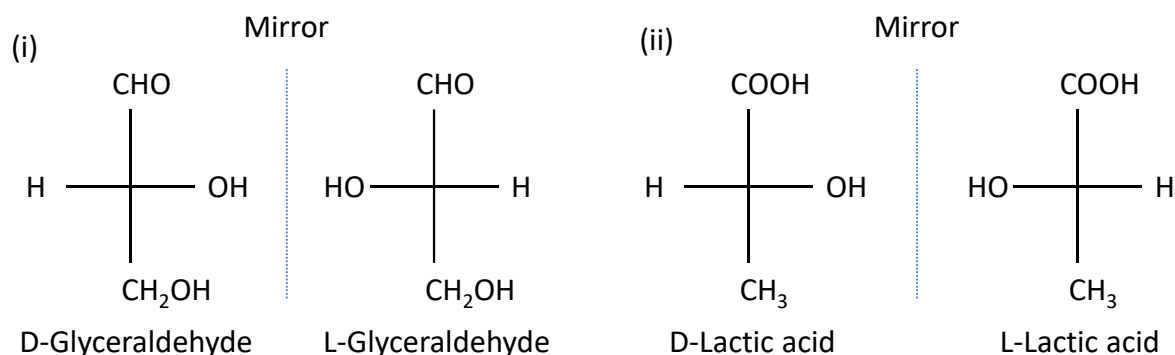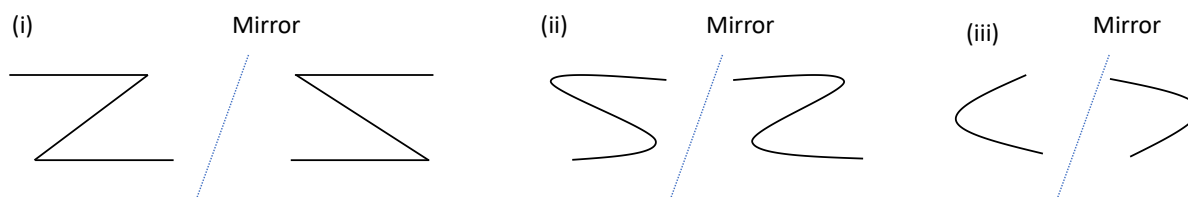
Properties of enantiomers

1. Enantiomers have **same physical properties**, means they have same melting point (MP), same boiling point (BP), same solubility, same density, same colour, etc.

2. Enantiomers have **same chemical properties**; means they have same reactivity towards acids and bases.

3. Enantiomers **should be optically active** (means they have chiral carbon).

4. Enantiomers have **same degree of rotation** of plane polarized light but they rotate light in **opposite direction**.

5. Mixture of enantiomers called **racemic mixture**.

6. Enantiomers can be separated from racemic mixture by **Mechanical Separation**.

(b) ***Diastereomers**: Compounds having same molecular formula, that are **Non-Superimposable and Non-Mirror images** called Diastereomers.

H₃C CH₃	H₃C H	Br Br	Br H

Cis 2-butene   Trans 2-butene   Cis-1,2-dibromoethene   Trans-1,2-dibromoethene

Non-Mirror   **Non**-Mirror

D-Tartaric acid   Meso-Tartaric acid   D-Tartaric acid   Meso-Tartaric acid
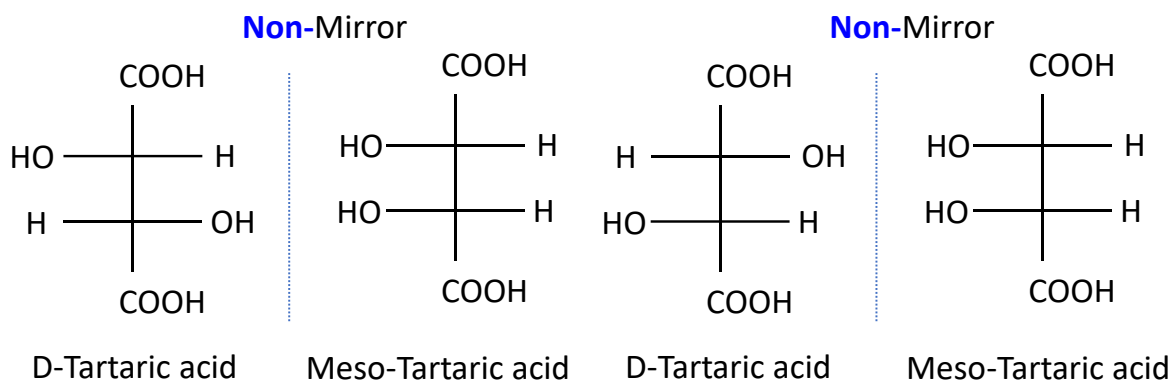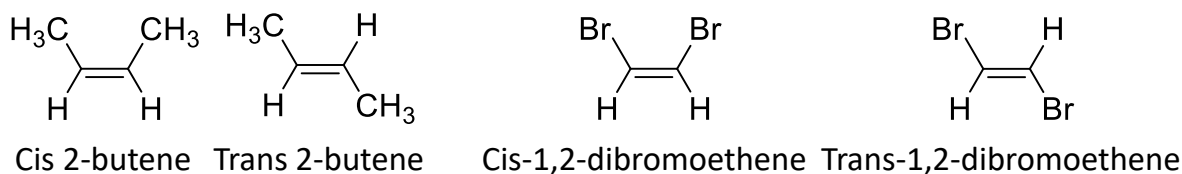
Properties of Diastereomers

1. Diastereomers have **different physical properties**, means they have different melting point (MP), different boiling point (BP), different solubility, different density, different colour, etc.

2. Diastereomers have **different chemical properties**; means they have different reactivity towards acids and bases.

3. Diastereomers **may or may not** optically active.

4. Diastereomers have **different degree of rotation** of plane polarized light.

5. Diastereomers can be separated by **Fractional Distillation**.

Chiral carbon/Chiral centre/Dissymmetric centre

Carbon which is **attached to four different atoms or groups** called as chiral carbon.

(i)   (ii)   (iii)

a
c *
b   d   e

* Chiral carbon   D-Glyceraldehyde   D-Lactic acid   D-Alanine

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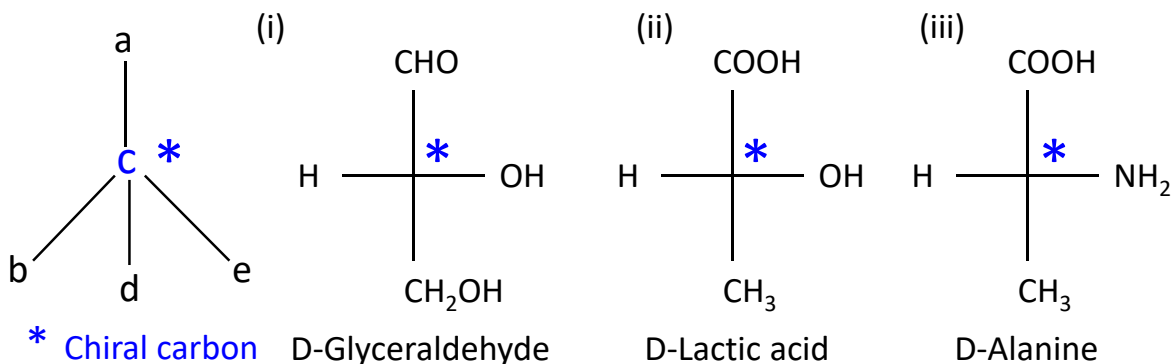
Chirality: Molecule which is **nonsuperimposable on its mirror image** called as chirality.

(i)   Mirror   (ii)   Mirror

CHO	CHO	COOH	COOH
H ——┼—— OH	HO ——┼—— H	H ——┼—— OH	HO ——┼—— H
CH$_2$OH	CH$_2$OH	CH$_3$	CH$_3$
D-Glyceraldehyde	L-Glyceraldehyde	D-Lactic acid	L-Lactic acid
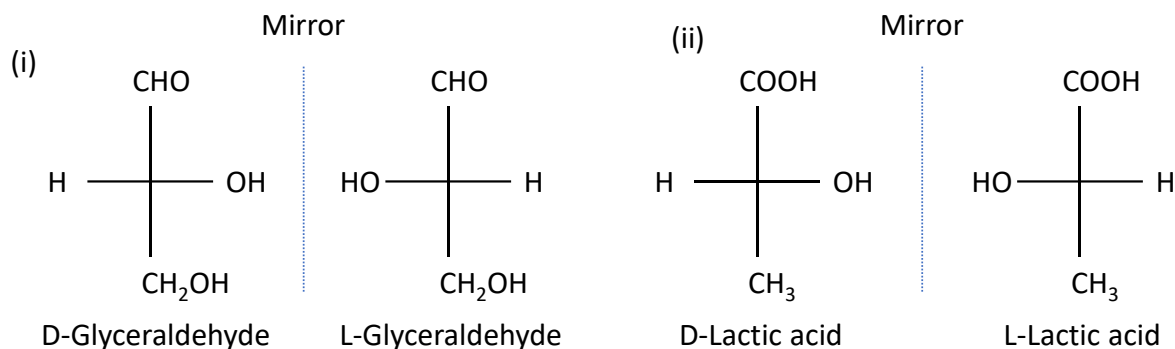
Optical activity

The ability of a substance to rotate the plane polarized light that is passed through it called optical activity. The compounds exhibiting optical activity are called as optically active compounds.

Note: Plane polarized light **consists of waves in which the direction of vibration is the same for all waves.**

Ordinary light → Prism → Plane polarized Light → Sample → Clockwise Or Anti clockwise
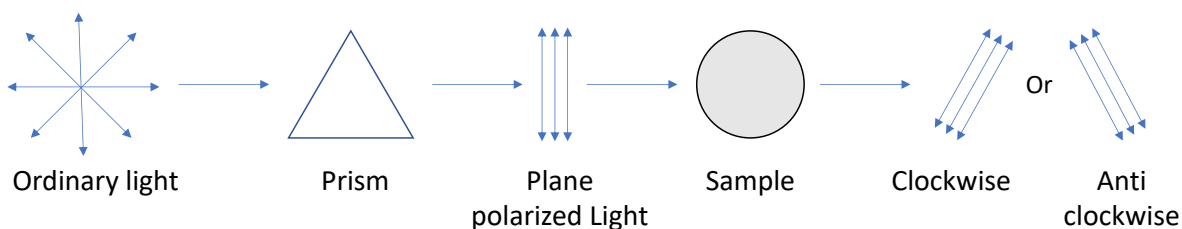
Optical activity of compounds can be measure using **Polarimeter**.

Conditions for optical activity

❖   Molecule **must contain chiral centre.**

If a compound rotates plane polarized light in the **clockwise** direction (or right side) called as **dextrorotatory (d).**

Plane polarized Light   Sample   Clockwise   Dextrorotatory
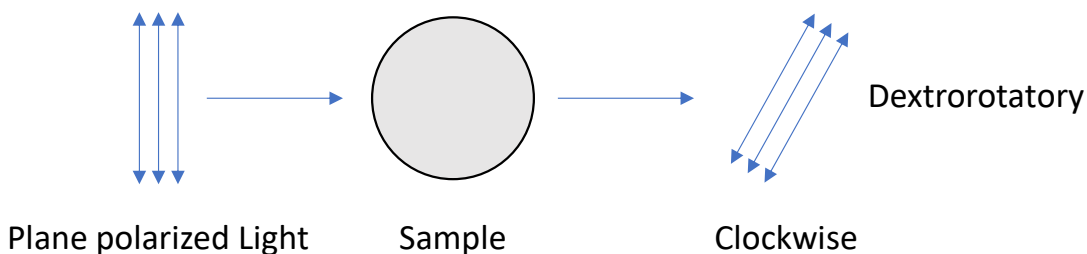
If a compound rotates plane polarized light in the **anti-clockwise** direction (or left side) called as **levorotatory (l).**

Plane polarized Light   Sample   Anti-clockwise

Levorotatory

Examples:

(i)	(ii)	(iii)	(iv)

(i)

CHO
|
H ——*—— OH
|
CH$_2$OH

D-Glyceraldehyde
(Optically Active)

(ii)

COOH
|
H ——*—— OH
|
CH$_3$

D-Lactic acid
(Optically Active)

(iii)

COOH
|
H ——*—— NH$_2$
|
CH$_3$

D-Alanine
(Optically Active)

(iv)

COOH
|
H ———— H
|
CH$_3$

(**Optically Inactive**)

CONFIGURATION

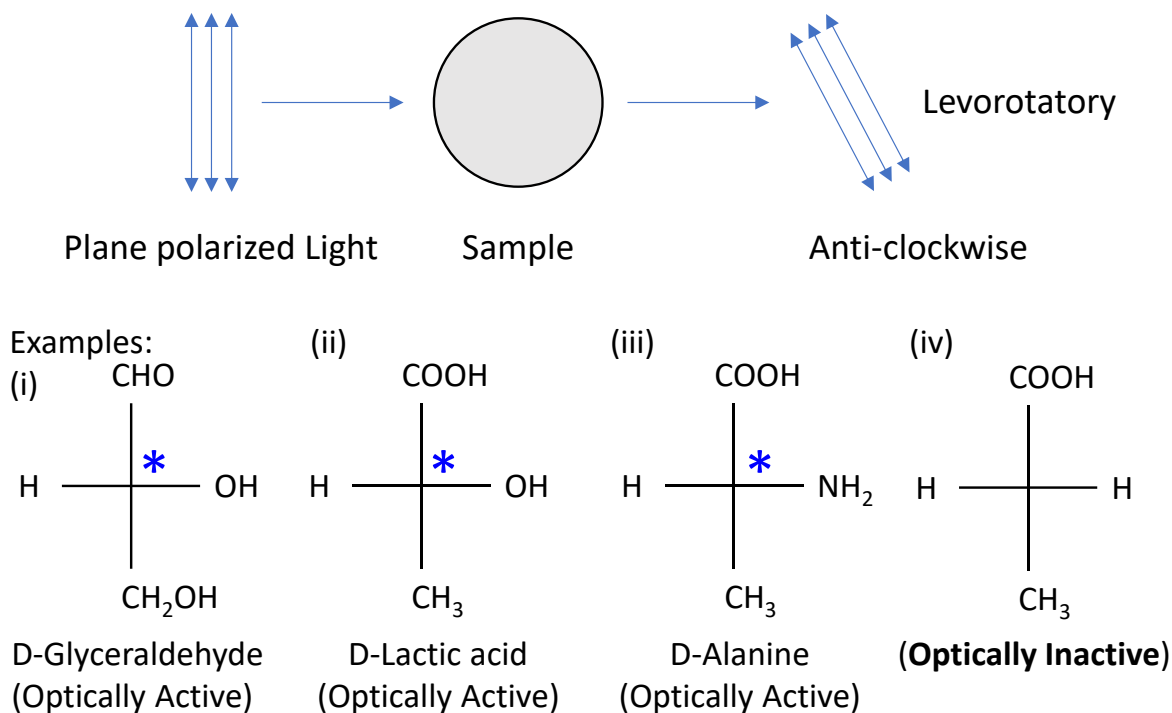The arrangement of atoms/groups at chiral centre or chiral carbon is known as configuration. Configuration is two types.

(i) Relative configuration/[DL] configuration & (ii) Absolute configuration/[RS] configuration

(I) RELATIVE CONFIGURATION/[DL] CONFIGURATION

In relative [or DL] configuration the arrangement of atoms or groups at chiral centre can be studied by taking reference isomer. Here, **Glyceraldehyde is used as reference isomer** to determine configuration of different isomers. Therefore, this configuration is called as relative configuration.

Rules for DL configuration

(i) Draw the molecule in Fischer Projection.

a
|
b ——+—— d
|
c
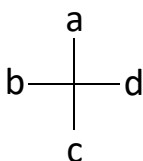
(ii) If the molecule contains more than two chiral centres, Identify the bottom most chiral centre from lower side.

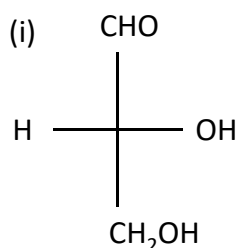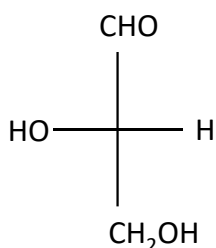(iii) Then at the chiral centre, if OH/NH$_2$ group or highly electronegative group present at Right Side of the Fischer projection of chiral centre, that configuration is said to be 'D'.

(iv) If OH/NH$_2$ group or highly electronegative group present at Left Side of the Fischer projection of chiral centre, that configuration is said to be 'L'
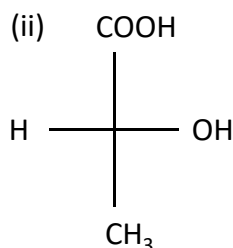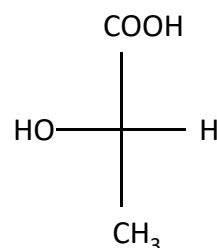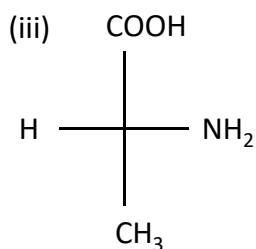
Examples

(i)

```
        CHO                    CHO
         |                      |
H ——————+—————— OH    HO ——————+—————— H
         |                      |
       CH₂OH                  CH₂OH
  D-Glyceraldehyde       L-Glyceraldehyde
```

(ii)

```
        COOH                   COOH
         |                      |
H ——————+—————— OH    HO ——————+—————— H
         |                      |
        CH₃                    CH₃
   D-Lactic acid          L-Lactic acid
```

(iii)

```
        COOH                   COOH
         |                      |
H ——————+—————— NH₂    H ——————+—————— NH₂
         |                      |
        CH₃                    CH₃
    D-Alanine              L-Alanine
```

(iv)
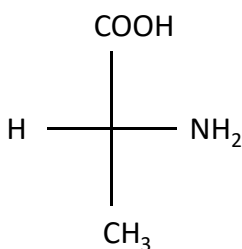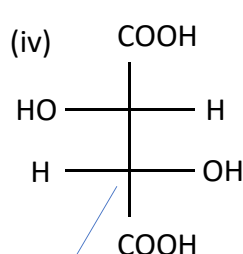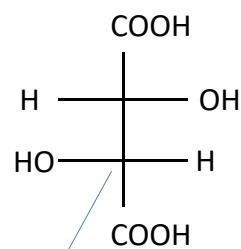
```
        COOH                   COOH
         |                      |
HO —————+————— H     H ——————+—————— OH
         |                      |
H ——————+————— OH    HO ——————+—————— H
         |                      |
        COOH                   COOH
   D-Tartaric acid        L-Tartaric acid
```

ABSOLUTE CONFIGURATION/[RS] CONFIGURATION

Cahn, Ingold, Prelog (CIP) rules are followed to assign the priorities at chiral carbon.

(i)   Draw the molecule in a Fischer projection.

```
        a
        |
b ——————+—————— d
        |
        c
```
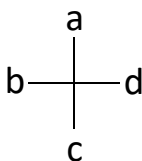
(ii) Give the priorities to the groups attached to chiral carbon based on atomic number. Priority: High atomic number > Low atomic number.

```
        Cl (3)
         |
(4) F ——+—————— Br (2)
         |
        I (1)
```

90
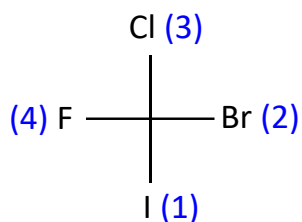
(iii) If isotopes (having same atomic number but different mass number) are attached to chiral carbon then give priority based on mass number.

Priority: High Mass number > Low Mass number.

$$\underset{\text{H (4)}}{\overset{\text{Cl (1)}}{\underset{|}{\overset{|}{\text{(2) CH}_3 - \!\!\!\!-\!\!\!\!- D \text{ (3)}}}}}$$

(iv) If first attached atom at chiral carbon is same then go to the next attached atom for deciding priority.

$$\underset{\text{(3) CH}_2\text{OH}}{\overset{\text{(1) NH}_2}{\underset{|}{\overset{|}{\text{(4) H} - \!\!\!\overset{\text{(2)}}{-} \!\!\!- \text{CH}_2\text{Cl}}}}}$$ $$\underset{\text{(1) OCH}_3}{\overset{\text{(3) NH}_2}{\underset{|}{\o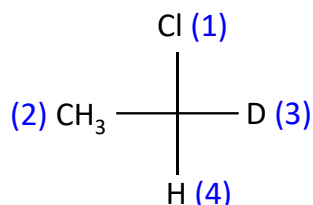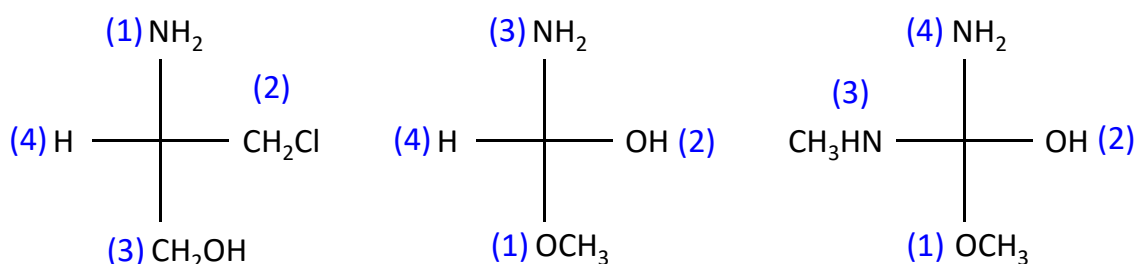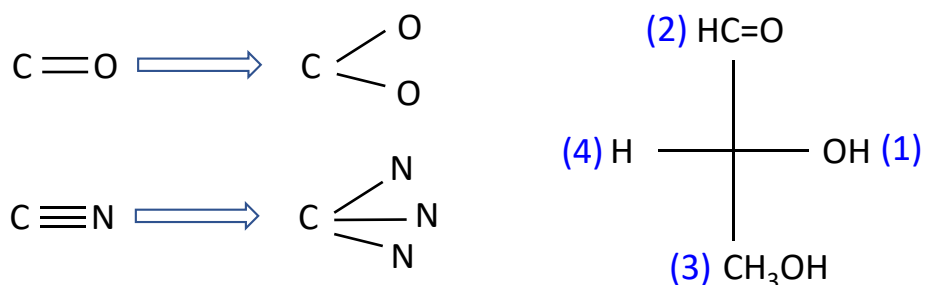verset{|}{\text{(4) H} - \!\!\!- \text{OH (2)}}}}}$$ $$\underset{\text{(1) OCH}_3}{\overset{\text{(4) NH}_2}{\underset{|}{\overset{|}{\text{CH}_3\text{HN} - \!\!\!\overset{\text{(3)}}{-} \!\!\!- \text{OH (2)}}}}}$$

(v) If chiral carbon attached to double or triple bonds, then that atom is considered as two and three single atoms, respectively.

$$C = O \implies C\!\!<\!\!\begin{matrix} O \\ O \end{matrix}$$

$$C \equiv N \implies C\!\!<\!\!\begin{matrix} N \\ N \\ N \end{matrix}$$

$$\underset{\text{(3) CH}_3\text{OH}}{\overset{\text{(2) HC=O}}{\underset{|}{\overset{|}{\text{(4) H} - \!\!\!- \text{OH (1)}}}}}$$

(vi) After given priority, the lowest priority group should be present on the vertical line. Then, if the priority of atoms at chiral carbon is clockwise direction that configuration is called "R". If the priority of atoms at chiral carbon is anticlockwise that configuration is "S".
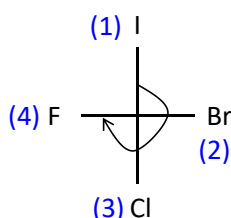
(vii) If the lowest priority group present on horizontal line, then the configuration will be reversed. Means R becomes S and S becomes R.
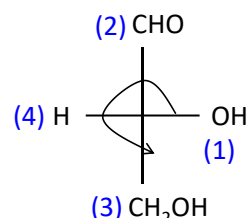
Examples
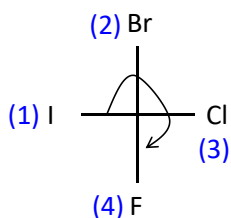
(2) Br — (1) I — Cl (3) — (4) F
Clockwise "R"

(1) I — (4) F — Br (2) — (3) Cl
Clockwise but least priority group is horizontal line. So, "S" Configuration

(2) CHO — (4) H — OH (1) — (3) CH₂OH
Anticlockwise but least priority group is horizontal line. So, "R" Configuration

(3) NH₂ — (1) H₃CO — OH (2) — (4) H
Anticlockwise but least priority group is horizontal line. So, "R" Configuration
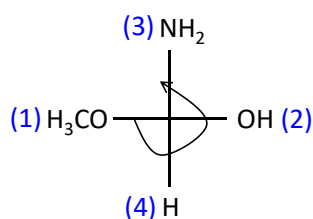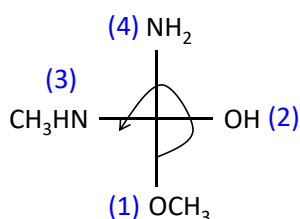
(4) NH₂ — (3) CH₃HN — OH (2) — (1) OCH₃
Anticlockwise. So, "R" Configuration
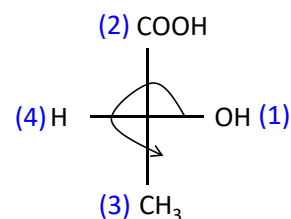
(2) COOH — (4) H — OH (1) — (3) CH₃
Anticlockwise but least priority group is horizontal line. So, "R" Configuration

(2) COOH — (1) Cl — CH₃ (3) — (4) H
Clockwise "R"

(2) COOH — (1) H — CH₃ (3) — (4) Cl
Clockwise but least priority group is horizontal line. So, "S" Configuration

(2) COOH — (1) HO — H (4) — S — (4) H — OH (1) — S — H (2)
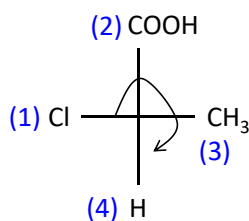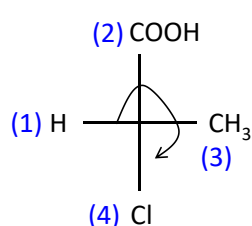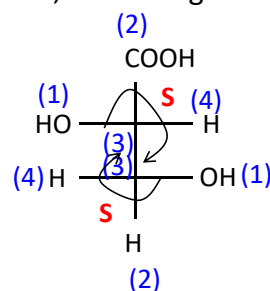
Conformational Isomers

Compounds having same molecular formula and which can be interconvertible by rotating the molecule around the single bond (C-C) are called conformational isomers.

**CONFORMATIONAL ANALYSIS OF n-BUTANE

Molecular formula of n-Butane is (C_4H_{10}): CH_3-CH_2-CH_2-CH_3

I, Fully Eclipsed
(0^0, 360^0)

II
Gauche (60^0)

III, Partially Eclipsed
(120^0)

VI
Gauche (300^0)

V, Partially Eclipsed
(240^0)

IV, Staggered/Anti
(180^0)
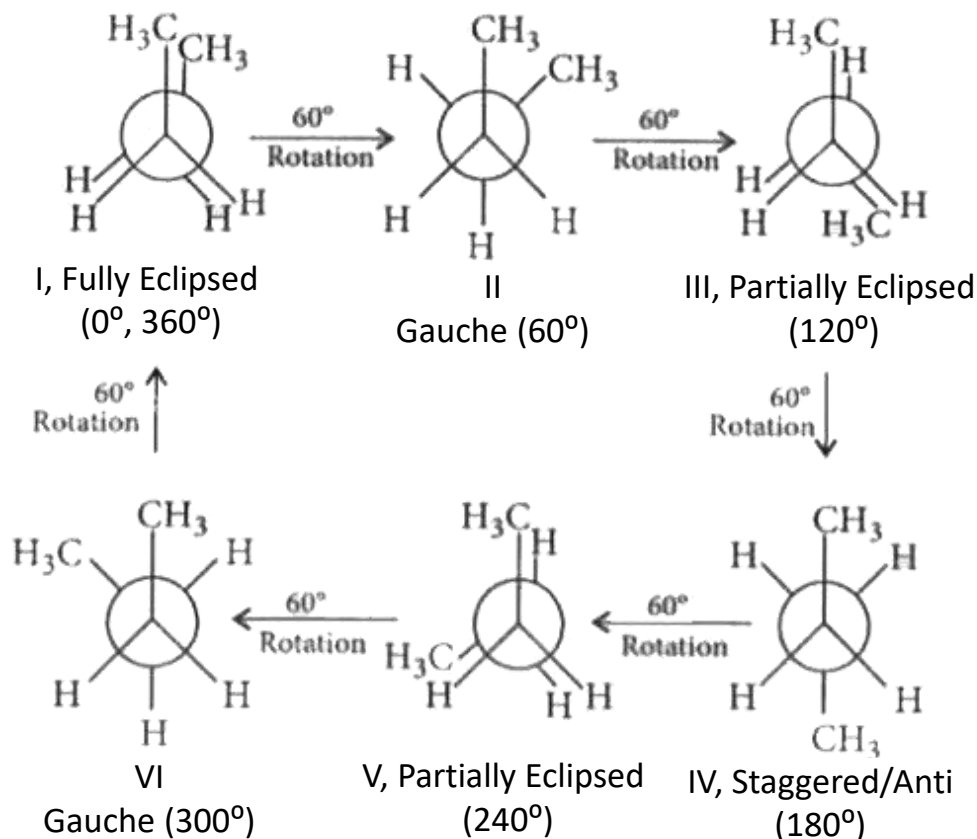
Steric hindrance between groups in conformations is $CH_3 - CH_3 > CH_3 - H > H - H$

Energy order of conformations of n-butane is **I > III, V > II, VI > IV**

Fully Eclipsed > Partially Eclipsed > Gauche > Staggered.

Energy is inversely proportional to the stability order of conformation of n-butane. Therefore, the

stability order of n-butane conformers is as follows.

IV > II, VI > III, V > I

Staggered > Gauche > Partially Eclipsed > Fully Eclipsed

Potential energy diagram of n-butane conformation is as follows.

93
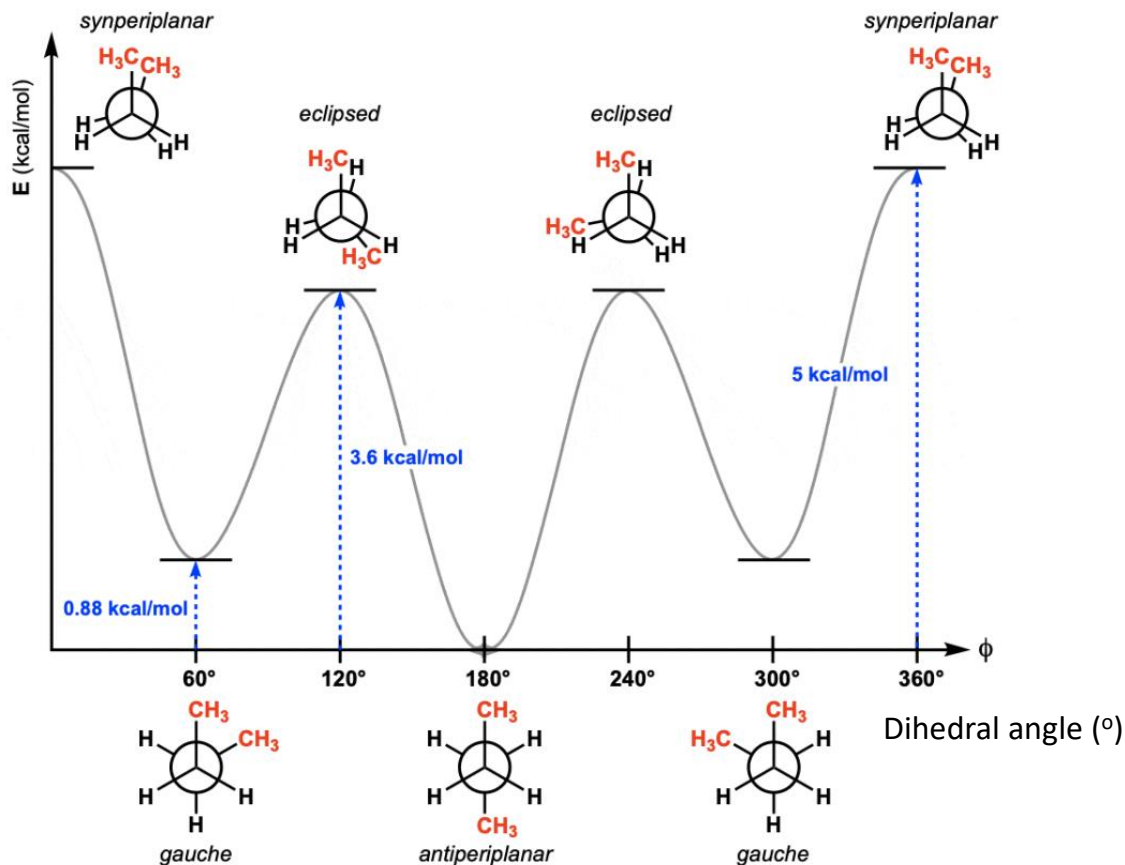
REACTION MECHANISM

Introduction: Organic reactions are chemical reactions involving organic compounds. Reaction mechanism is in chemical reactions the detailed process by which chemical substances are transformed into other substances. The reactions may involve the interaction of atoms, groups, ions, electrons and free radicals.

Organic reactions are mainly three types.

(i) Substitution reactions, (ii) Addition reactions & (iii) Elimination reactions.

1. SUBSTITUTION REACTIONS

The chemical reactions in which atoms or groups are replaced by another atom or groups called as substitution reactions. These are two types.

(A) Nucleophilic substitution reactions & (B) Electrophilic substitution reactions.

(A) NUCLEOPHILIC SUBSTITUTION REACTIONS

A chemical reaction in which one nucleophile is replaced by another nucleophile. These reactions may carried out in two ways.

(a) SN^1 reaction or Unimolecular Substitution Reaction.

(b) SN^2 reaction or Bimolecular Substitution Reaction.

(A) SN^1 REACTION OR UNIMOLECULAR SUBSTITUTION REACTION.

(i)   In SN^1, S means Substitution N means Nucleophilic and 1 means unimolecular reaction.

(ii) In SN^1, the rate of reaction depends only on the concentration of alkyl halide but not on Nucleophile.

Rate $\propto$ [Alkyl Halide]

(iii) The rate is depending on only alkyl halide, therefore it is called a First order reaction.

(iv) SN^1 is a two-step process.

(v)   Polar solvents (methanol or water) favour SN^1 reaction.

(vi) Carbocation is the reaction intermediate

(vii) SN^1 reactions are mainly shown by tertiary alkyl halides.

Example: Reaction between *tert*-butyl bromide with aq. KOH

Tert butyl bromide   Tert butyl alcohol
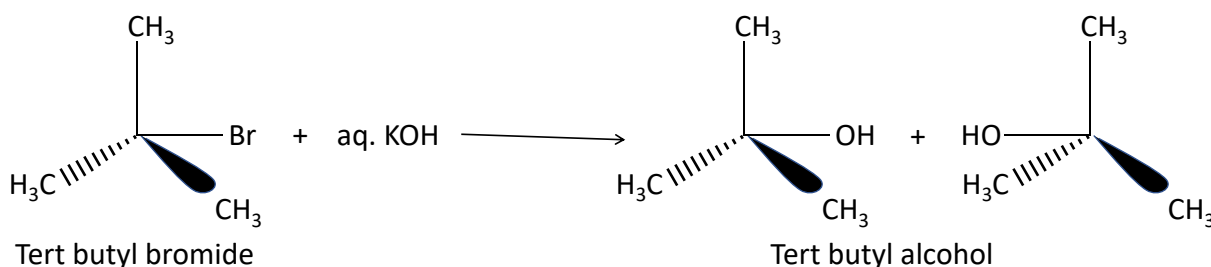
Mechanism: SN^1 reaction takes in two steps.

STEP-I: In first step, the carbon-halogen bond slowly breaks to from carbocation intermediate.

Tert butyl bromide   Carbocation

STEP-II: Carbo cation rapidly combines with nucleophile (OH⁻) from either side.

Carbocation   Tert butyl alcohol
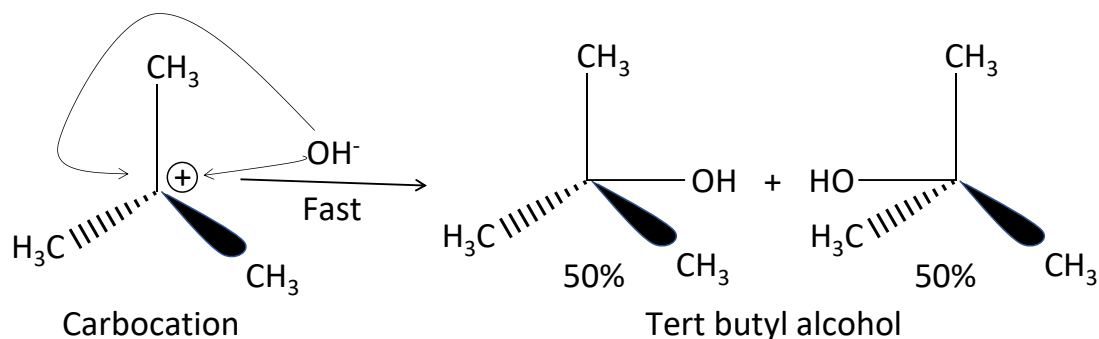
(B) SN² REACTION OR BIMOLECULAR SUBSTITUTION REACTION.

(i)   In SN², S means Substitution, N means Nucleophilic, and 2 means Bimolecular reaction.

(ii)   In SN², the rate of reaction depends on **both** that is **the concentration of alkyl halide and Nucleophile**.

Rate $\propto$ [Alkyl Halide] [Nucleophile]

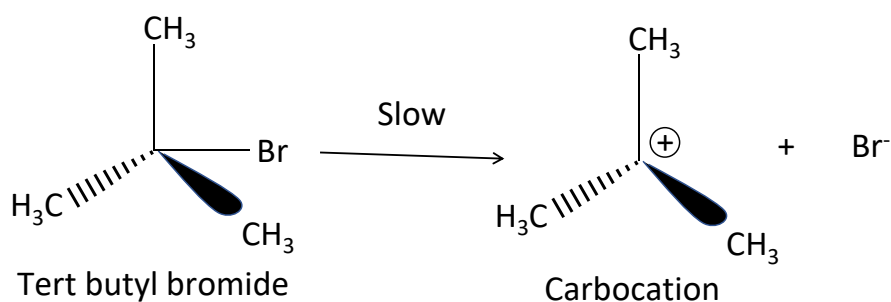(iii) The rate is depending on both; therefore, it is called a **Second order reaction**.

(iv) SN² proceeds in a **Single step** process.

(v) **Non-polar solvents** favour SN² reaction.

(vi) **A Transition state** is the reaction intermediate and 100% inversion product (also called as Walden Inversion)

(vii) SN² reactions are mainly shown by **Primary alkyl halides**.

Example: Reaction between Methyl bromide with aq. KOH

$$CH_3Br + OH^- \longrightarrow CH_3OH + Br^-$$
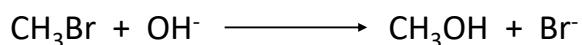
Mechanism: SN² reaction involves in a single step. Therefore, the breaking of carbon-halogen bond and making of carbon-nucleophile bond occurs simultaneously.

In SN² reaction, nucleophile attacks the carbon from opposite side to the halogen. In that stage, carbon atom is partially bonded to both nucleophile and leaving group. That state is called as **transition state** (or activated complex).

That transition state is highly unstable, so, it converts to alcohols as an **inversion product**.

Methyl Bromide   Transition state   Methyl alcohol (100% inversion product)
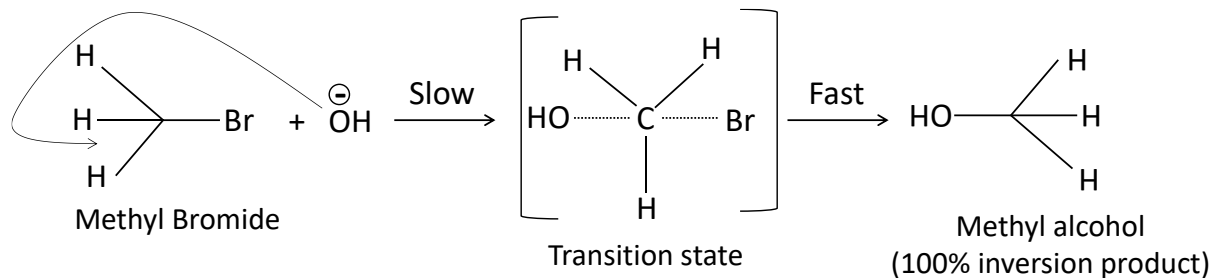
In SN^2 reaction inverted product is formed. This phenomenon is called **Walden Inversion**.

2. ADDITION REACTIONS

The Addition reaction in which two or more molecules combine and forms one product without the loss of any atom.

Unsaturated molecules like alkenes, alkadienes and alkynes involve addition reaction.

Addition reactions are initiated by electrophiles, nucleophiles or free radicals.

Depending on initiators, addition reactions are three types; (a) Electrophilic addition reactions, (b) Free radical addition reactions & (c) Nucleophilic addition reactions

(a) ELECTROPHILIC ADDITION REACTIONS

The addition reactions which are initiated by electrophiles (positively charged species or electron deficient) are called Electrophilic addition reactions.

$CH_2=CH_2$ + HBr → $H-CH_2-CH_2-Br$
(Ethene)   (Bromo ethene)

$HC≡CH$ + HBr → H-CH=CH-Br
Acetylene   (Bromoethene)
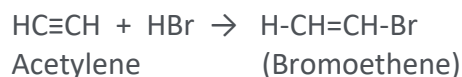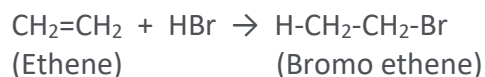
Addition of HBr to **unsymmetrical alkenes**

$CH_3-CH=CH_2$ + HBr

Propene

→ $CH_3-CH_2-CH_2-Br$
1-Bromopropane (Minor)

                    Br
                    |
→ $CH_3-CH-CH_3$
2-Bromopropane (Major)
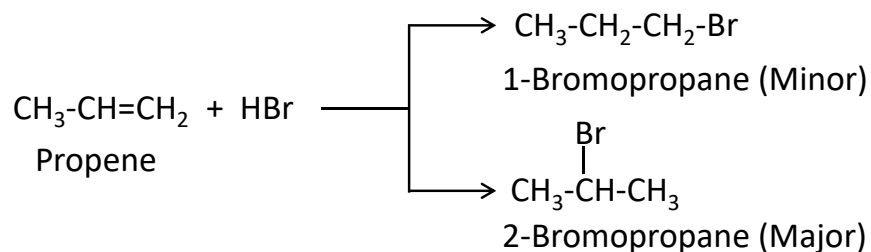
Formation of major product can be explained by **Markovnicov's Rule *****

"When an asymmetrical reagent is added to unsymmetrical alkene, then **negative half of the reagent will attach to the carbon atom containing lesser number of hydrogen atoms**" is Markovnicov's Rule.

Example: $CH_3\text{-}CH=CH_2$ + HBr $\longrightarrow$ $\underset{\displaystyle CH_3\text{-}CH\text{-}CH_3}{\overset{\displaystyle Br}{|}}$

                     Propene   2-Bromopropane (Major)
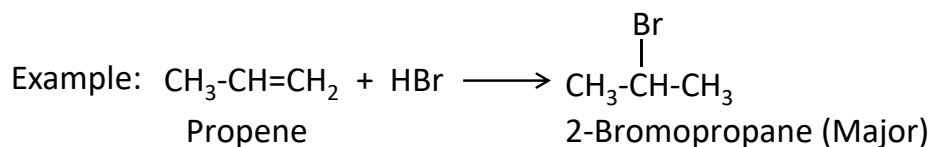
Mechanism: It involves **three** steps.

Step-1: HBr ionizes to form H$^+$ and Br$^-$ ions.   HBr $\xrightarrow{\text{Slow}}$ H$^+$ + Br$^-$

Step-2: Proton (H$^+$) reacts with π-bond of alkene and gives carbocation as follows.

$CH_3\text{-}CH=CH_2$ $\xrightarrow{\text{H}^+}$

$\longrightarrow$ $CH_3\text{-}CH_2\text{-}CH_2^{\oplus}$
1°-Carbocation (Less stable)

$\longrightarrow$ $CH_3\text{-}\overset{\oplus}{CH}\text{-}CH_3$
2°-Carbocation (**More stable**)

            Propene

Step-3: More stable 2°-carbocation reacts with Br$^-$ and forms 2-bromopropane as a major product.

$CH_3\text{-}\overset{\oplus}{CH}\text{-}CH_3$ $\longrightarrow$ $\underset{\displaystyle CH_3\text{-}CH\text{-}CH_3}{\overset{\displaystyle Br}{|}}$

  2°-Carbocation   2-Bromopropane (Major)
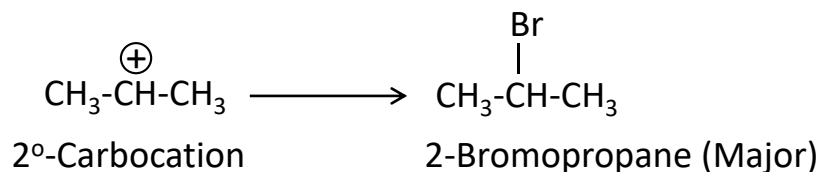
(b) FREE RADICAL ADDITION REACTIONS

Addition reactions which are initiated by free radicals called free radical addition reactions.

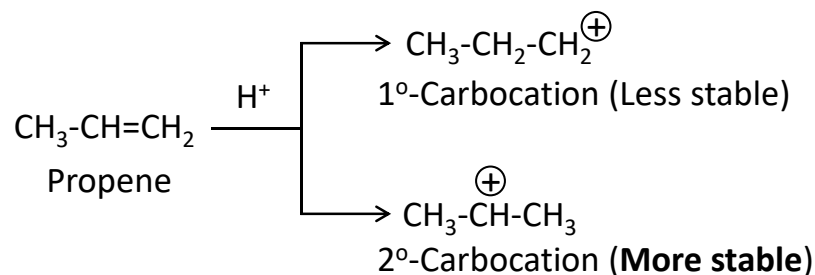## ANTI MARKOVNICOV'S RULE (OR) KHARASCH EFFECT (OR) PEROXIDE EFFECT***

When an asymmetrical reagent is added to unsymmetrical alkene, then **negative half of the reagent** will attach to the carbon atom containing **more number of hydrogen atoms** is Anti Markovnicov's Rule. This will occur in presence of peroxide; therefore, this is also called as **Peroxide effect** or **Kharasch effect**.

Example: $CH_3\text{-}CH=CH_2$ + HBr $\xrightarrow[\text{hv}]{\text{H}_2\text{O}_2}$ $CH_3\text{-}CH_2\text{-}CH_2\text{-}Br$

                     Propene   1-Bromopropane (Major)
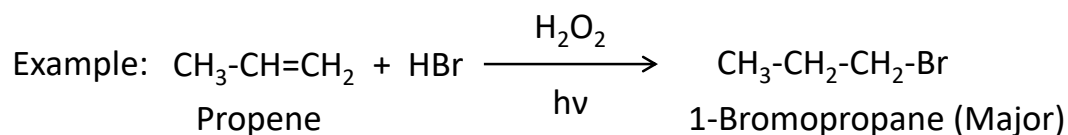
Mechanism: It takes in three steps.

Step-1: Peroxide cleaves and forms alkoxide free radical.

$$R-O-O-R \xrightarrow{\ h\nu\ } 2R\overset{\bullet}{O}$$

$$2R\overset{\bullet}{O} \ + \ HBr \longrightarrow ROH \ + \ \overset{\bullet}{Br}$$
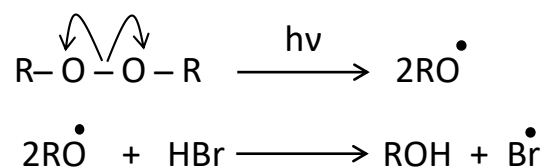
Step-2: Bromine radical (Br·) attacks at π-bond of propene and forms two types of free radicals.

$$CH_3-CH=CH_2 \ + \ \overset{\bullet}{Br}$$
Propene

$$\longrightarrow CH_3-\overset{\bullet}{C}H-CH_2-Br$$
2°-Free radical (**More stable**)

$$\longrightarrow CH_3-\underset{\overset{|}{Br}}{C}H-\overset{\bullet}{C}H_2$$
1°-Free radical (Less stable)

Step-3: 2° free radical reacts with HBr and forms 1-bromopropane as major product.

$$CH_3-\overset{\bullet}{C}H-CH_2-Br \xrightarrow{\ HBr\ } CH_3-CH_2-CH_2-Br \ + \ \overset{\bullet}{Br}$$
2°-Free radical   1-Bromopropane

3. ELIMINATION REACTIONS

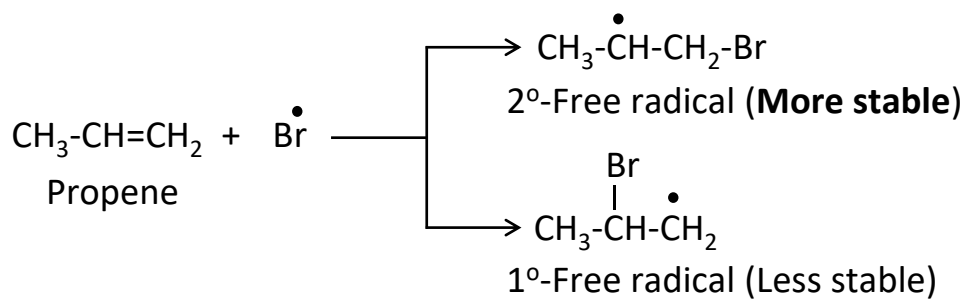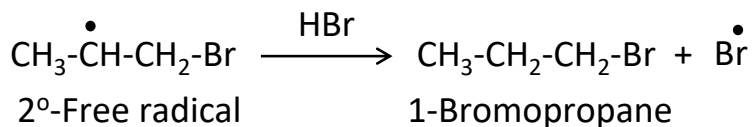The chemical reactions in which, two or more atoms/groups attached to adjacent carbons are eliminated to form double bond or triple bond called elimination reaction.

Example: Dehydrohalogenation: When alkyl halides react with alc. KOH dehydrohalogenation takes place.

$$R-\underset{}{\overset{\overset{\displaystyle H}{|}}{C}}H-CH_2-X \xrightarrow{\ alc.\ KOH\ } R-CH=CH_2$$
Alkyl halide   Alkene
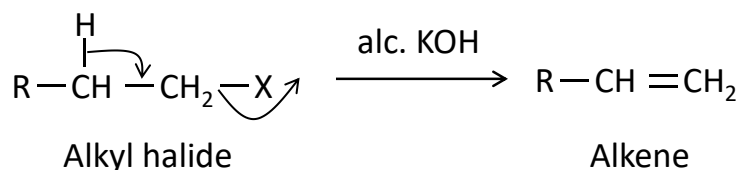
Elimination reactions are classified into two types.

(i) E_1 elimination reactions & (ii) E_2 elimination reactions.

(i) E_1 elimination reactions

E_1 stands for Unimolecular elimination. In this type, the rate of elimination depends on only alkyl halide but not on nucleophile. Therefore, it is a first order reaction.

This reaction is preferred in 2° and 3° alkyl halides.

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}-CH_3 \xrightarrow[\text{NaOH}]{\text{Ethanol}} CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2$$

2-Bromo-2-methylpropane   2-methylpropene

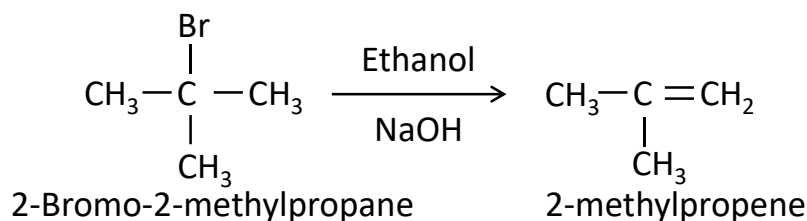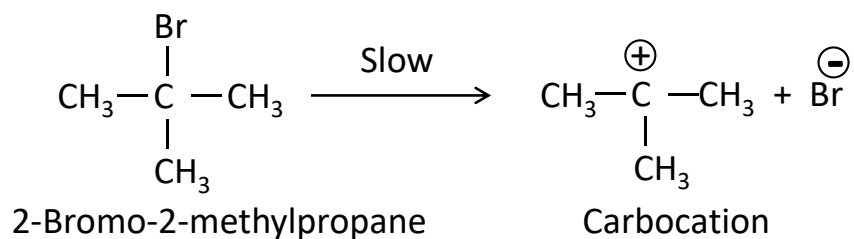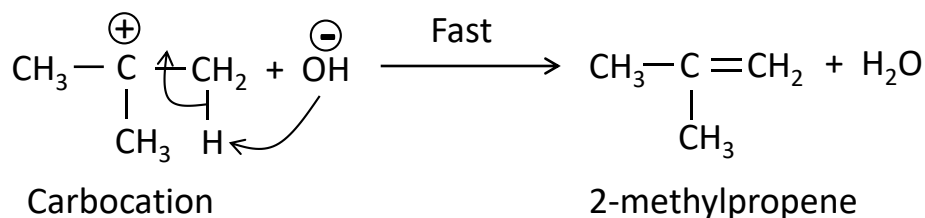**Mechanism**: This involves two steps

Step-1: Ionization of tert-butyl bromide and forms carbonium ion.

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}-CH_3 \xrightarrow{\text{Slow}} CH_3-\underset{\underset{CH_3}{|}}{\overset{\oplus}{C}}-CH_3 + \overset{\ominus}{Br}$$

2-Bromo-2-methylpropane   Carbocation

Step 2: Carbocation loses a proton from the adjacent carbon to give alkenes.

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\oplus}{C}}-CH_2 + \overset{\ominus}{OH} \xrightarrow{\text{Fast}} CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + H_2O$$

Carbocation   2-methylpropene

(ii) E_2 elimination reactions

E_2 stands for Bimolecular elimination. In this type, the rate of reaction depends on the concentration of **both alkyl halide and nucleophile**. Therefore, it is a second order elimination reaction.

    Rate $\propto$ [Alkyl Halide] [Nucleophile]

E_2 reaction preferentially occurs in 1°-alkyl halides.

Example: $R-CH_2-CH_2-Br \xrightarrow{\text{alc. KOH}} R-CH=CH_2 + HBr$

              Alkyl halide   Alkene
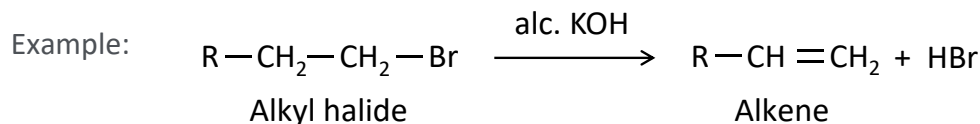
Mechanism: This is a one-step reaction.

In this type a proton is attracted by nucleophile and removal of halogen takes place simultaneously in a single step. At the same time double bond formation will be formed. That state is called as transition state.

Alkyl halide — Transition state — Alkene

$$R-CH_2 \text{ structure with } OH^-, H, Br \xrightarrow{\text{Slow}} \text{Transition state} \xrightarrow{\text{Fast}} R-CH=CH_2 + H_2O + Br^-$$
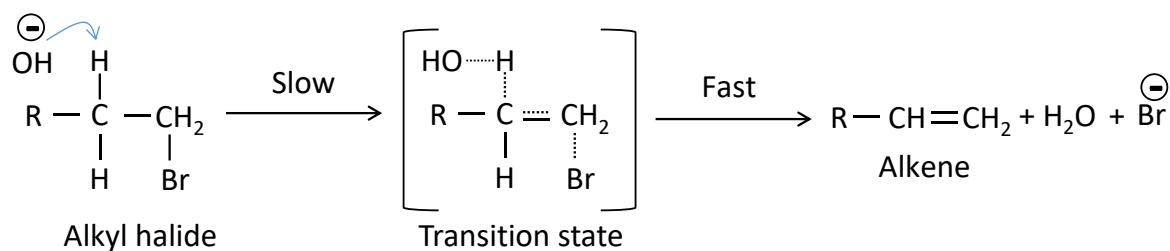
***Saytzeff rule

Saytzeff rule says that, in an elimination reaction if two types of products are possible, then **more substituted alkene** is the **major** product.

$$CH_3-CH=CH-CH_3 + HBr$$
2-Butene (Major) [Saytzeff Product]

$$CH_3-CH_2-CH=CH_2 + HBr$$
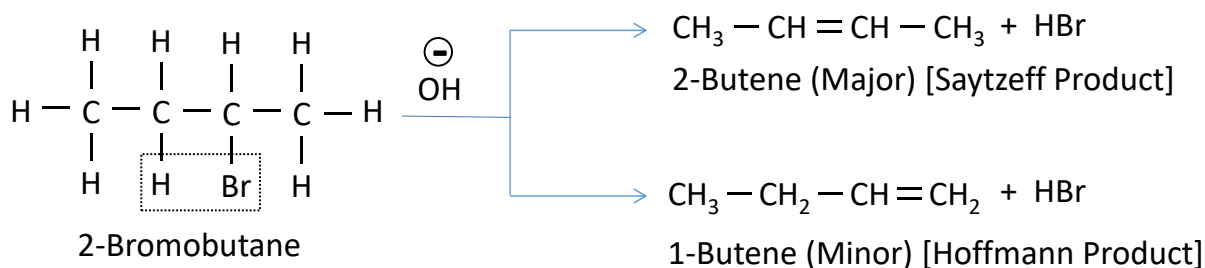1-Butene (Minor) [Hoffmann Product]

2-Bromobutane

2-Bromobutane on reaction with alcoholic KOH forms more substituted 2-butene as a major product, while less substitutes 1-butene is the minor product.

REDOX REACTIONS

An oxidation-reduction reaction called redox reaction.

Redox reaction is a type of chemical reaction that involves transfer of electrons between two species.

Oxidation of alcohols with KMnO₄ and CrO₃

(a) Oxidation of alcohols with KMnO₄ (Potassium permanganate)
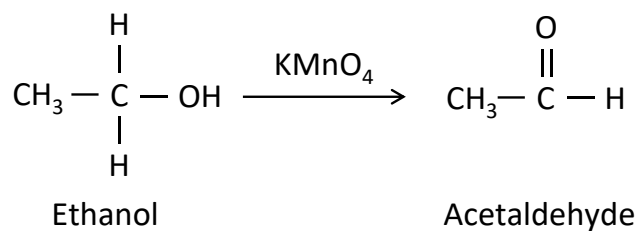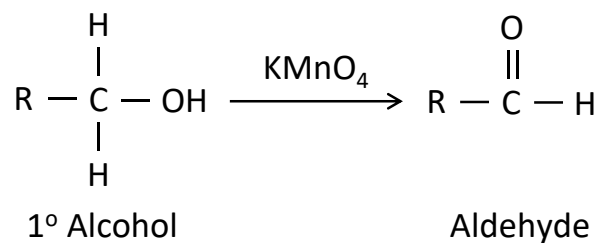
(i) Structure:
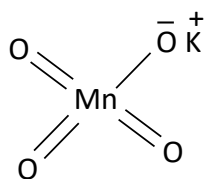
(ii) It is a crystalline substance

(iii) Soluble in water and alcohols

(iv) In soluble in organic compounds.

Applications: KMnO₄ converts 1° alcohols into aldehydes.

R — C — OH (1° Alcohol, with H above and H below) $\xrightarrow{KMnO_4}$ R — C — H (Aldehyde, with O double bond above)

CH₃ — C — OH (Ethanol, with H above and H below) $\xrightarrow{KMnO_4}$ CH₃ — C — H (Acetaldehyde, with O double bond above)

1° Alcohol → **Aldehyde**

Ethanol → **Acetaldehyde**

$KMnO_4$ oxidizes 2° alcohols into ketone

R — C — OH (with H above and R below) $\xrightarrow{KMnO_4}$ R — C — R (with O double bond above)

2° Alcohol → **Ketone**

CH₃ — C — OH (with H above and CH₃ below) $\xrightarrow{KMnO_4}$ CH₃ — C — CH₃ (with O double bond above)

2-Propanol → **Acetone**
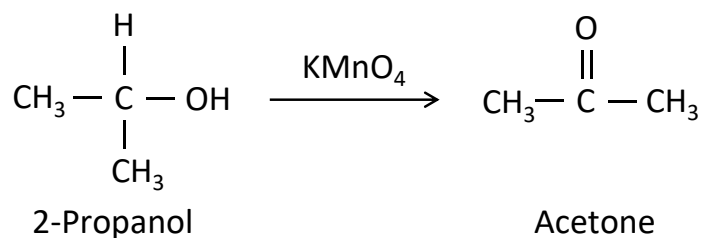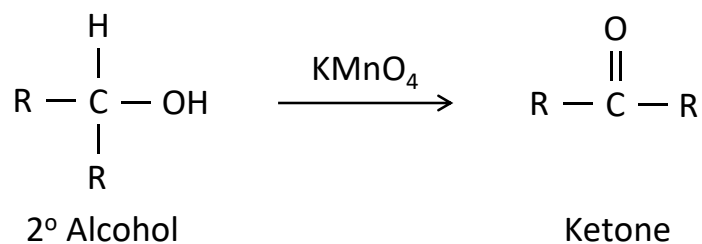
$KMnO_4$ cannot react with 3°-alcohols due to the absence of Hydrogens

CH₃ — C — OH (with CH₃ above and CH₃ below) $\xrightarrow{KMnO_4}$ **No reaction**

3° Butanol
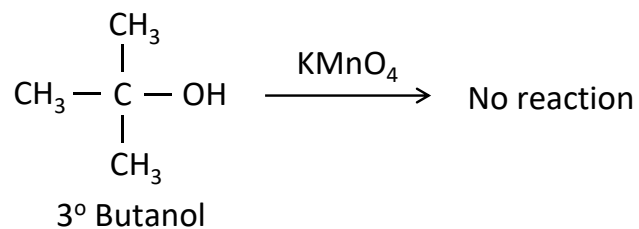
Oxidation of alcohols with Chromium trioxide (CrO₃)

(i) Structure

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$$\underset{\displaystyle O=Cr=O}{\overset{\displaystyle \overset{O}{\|}}{}}$$
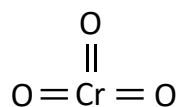
(ii) It is a crystalline substance

(iii) Soluble in organic solvents

(a) Jones reagent (CrO₃ + aq. H₂SO₄ + acetone)

➢ Jones reagent converts primary (1°) alcohols into Aldehydes.

$$\underset{\text{1° Alcohol}}{R-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-OH} \quad \xrightarrow[\text{Acetone}]{\text{CrO}_3 + \text{aq. H}_2\text{SO}_4} \quad \underset{\text{Aldehyde}}{R-\underset{}{\overset{\overset{O}{\|}}{C}}-H}$$

$$\underset{\text{Ethanol}}{CH_3-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-OH} \quad \xrightarrow[\text{Acetone}]{\text{CrO}_3 + \text{aq. H}_2\text{SO}_4} \quad \underset{\text{Acetaldehyde}}{CH_3-\underset{}{\overset{\overset{O}{\|}}{C}}-H}$$
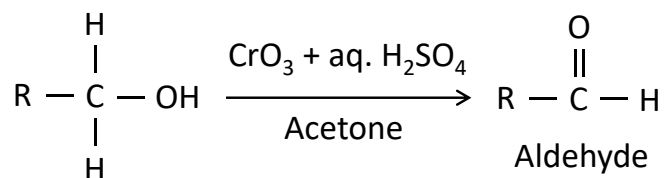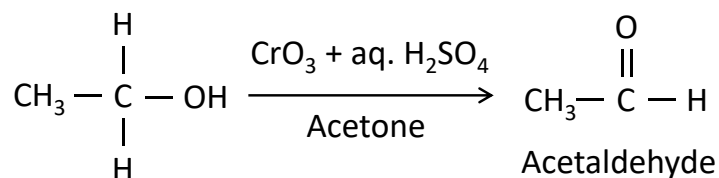
➢ Jones reagent converts secondary (2°) alcohols into Ketones.

$$\underset{\text{2° Alcohol}}{R-\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}-OH} \quad \xrightarrow[\text{Acetone}]{\text{CrO}_3 + \text{aq. H}_2\text{SO}_4} \quad \underset{\text{Ketone}}{R-\underset{}{\overset{\overset{O}{\|}}{C}}-R}$$

$$\underset{\text{2-Propanol}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}-OH} \quad \xrightarrow[\text{Acetone}]{\text{CrO}_3 + \text{aq. H}_2\text{SO}_4} \quad \underset{\text{Acetone}}{CH_3-\underset{}{\overset{\overset{O}{\|}}{C}}-CH_3}$$
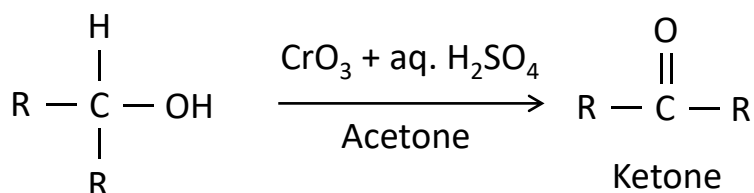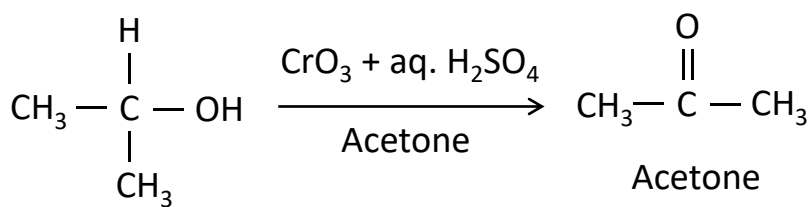
(b) Sarett reagent (CrO₃ + Pyridine)

➢ Sarett Reagent converts primary (1°) alcohols into Aldehydes.

$$\underset{\substack{\displaystyle | \\ \text{H} \\ \text{1° Alcohol}}}{\overset{\displaystyle \overset{\text{H}}{|}}{R-C-OH}} \xrightarrow{\text{CrO}_3 + \text{Pyridine}} \underset{\text{Aldehyde}}{\overset{\displaystyle \overset{\text{O}}{||}}{R-C-H}}$$

$$\underset{\substack{\displaystyle | \\ \text{H} \\ \text{Ethanol}}}{\overset{\displaystyle \overset{\text{H}}{|}}{CH_3-C-OH}} \xrightarrow{\text{CrO}_3 + \text{Pyridine}} \underset{\text{Acetaldehyde}}{\overset{\displaystyle \overset{\text{O}}{||}}{CH_3-C-H}}$$
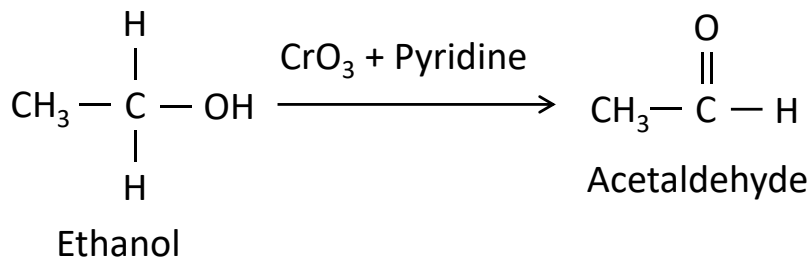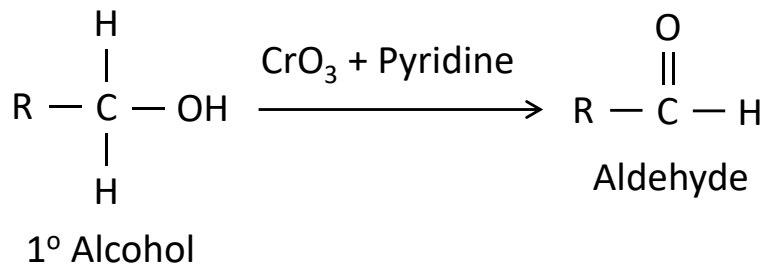
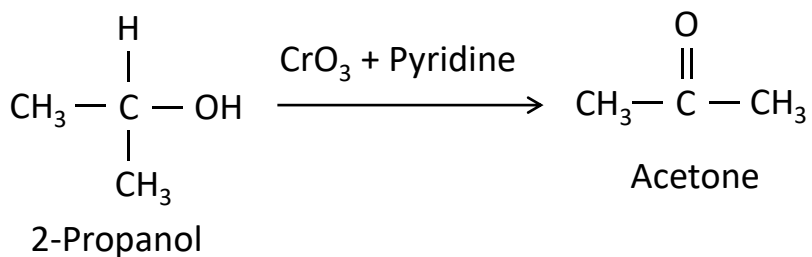➢ Sarette Reagent converts Secondary (2°) alcohols into Ketones.

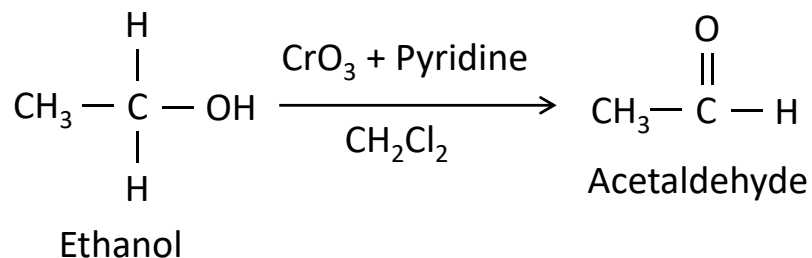$$\underset{\substack{\displaystyle | \\ \text{R} \\ \text{2° Alcohol}}}{\overset{\displaystyle \overset{\text{H}}{|}}{R-C-OH}} \xrightarrow{\text{CrO}_3 + \text{Pyridine}} \underset{\text{Ketone}}{\overset{\displaystyle \overset{\text{O}}{||}}{R-C-R}}$$

$$\underset{\substack{\displaystyle | \\ \text{CH}_3 \\ \text{2-Propanol}}}{\overset{\displaystyle \overset{\text{H}}{|}}{CH_3-C-OH}} \xrightarrow{\text{CrO}_3 + \text{Pyridine}} \underset{\text{Acetone}}{\overset{\displaystyle \overset{\text{O}}{||}}{CH_3-C-CH_3}}$$
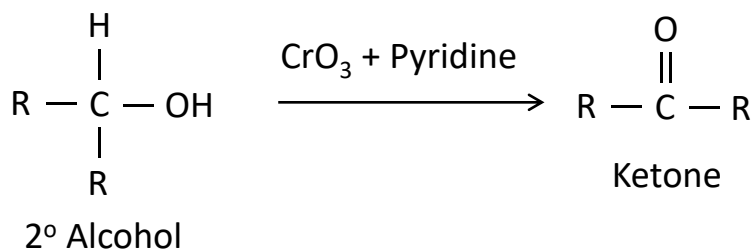
(c) Collins Reagent (CrO₃ + Pyridine + CH₂Cl₂)

➢ Collins Reagent converts primary (1°) alcohols into Aldehydes.

$$R - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - OH \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{CrO}_3 + \text{Pyridine}} R - \overset{\overset{\displaystyle O}{||}}{C} - H$$
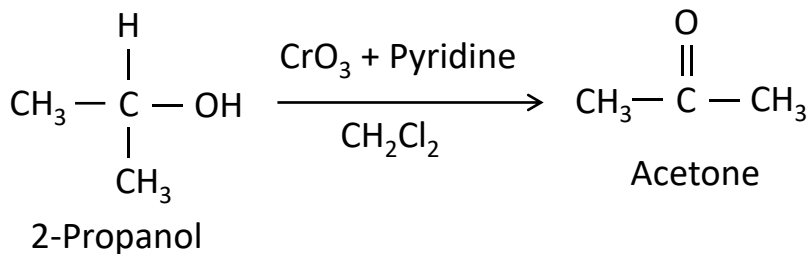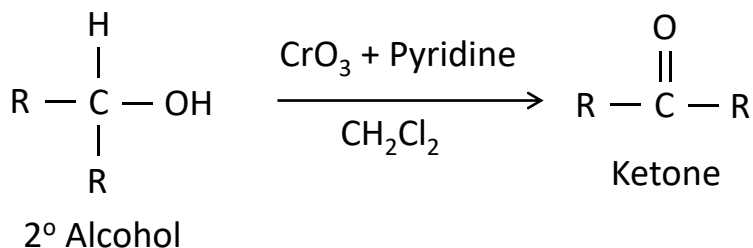
1° Alcohol → Aldehyde

$$CH_3 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}} - OH \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{CrO}_3 + \text{Pyridine}} CH_3 - \overset{\overset{\displaystyle O}{||}}{C} - H$$

Ethanol → Acetaldehyde

➤ Collins Reagent converts Secondary (2°) alcohols into Ketones.

$$R - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{C}} - OH \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{CrO}_3 + \text{Pyridine}} R - \overset{\overset{\displaystyle O}{||}}{C} - R$$

2° Alcohol → Ketone

$$CH_3 - \overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - OH \xrightarrow[\text{CH}_2\text{Cl}_2]{\text{CrO}_3 + \text{Pyridine}} CH_3 - \overset{\overset{\displaystyle O}{||}}{C} - CH_3$$

2-Propanol → Acetone
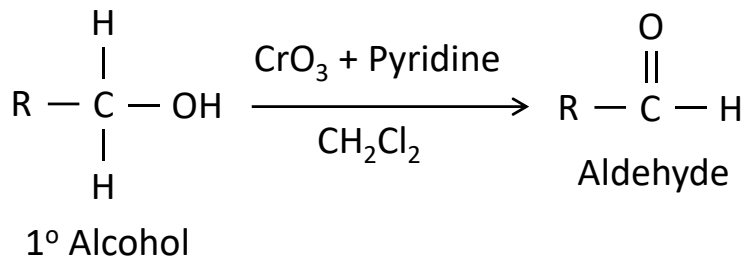
Note: Tertiary alcohols do not react with Jones, Sarette and Collins reagent due to absence of hydrogens.

$$CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}} - OH \xrightarrow[\text{Collins Reagent}]{\text{Jones, Sarette}} \text{No reaction}$$

3° Butanol
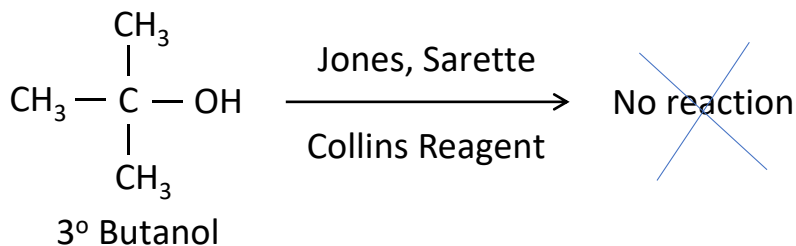
Reduction of carbonyl compounds (C=O) with Lithium Aluminium Hydride (LiAlH$_4$) and Sodium Borohydride (NaBH$_4$).

(a) Reduction of carbonyl compounds (C=O) with Lithium Aluminium Hydride (LiAlH$_4$)
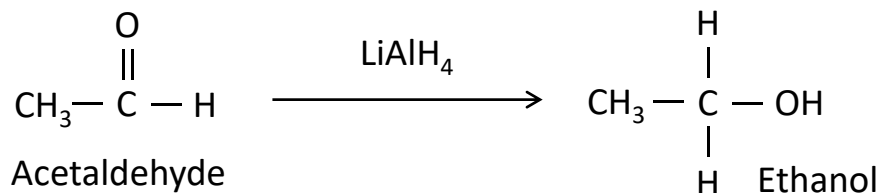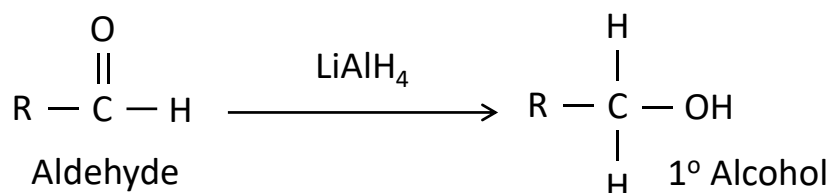
Structure
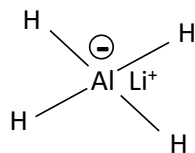
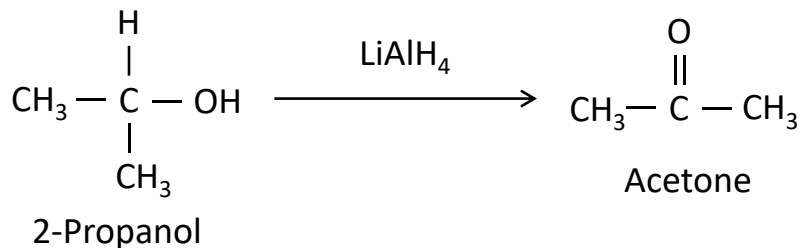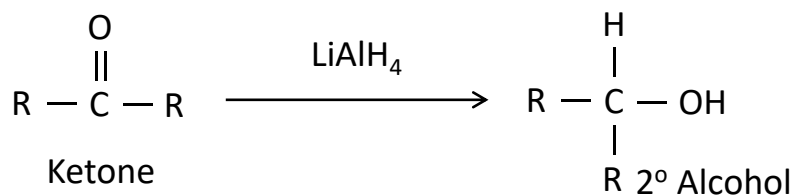It is a white crystalline substance

Solvents: Ether, Tetrahydrofuran.

Reaction with Carbonyl compounds (Aldehydes and Ketones)

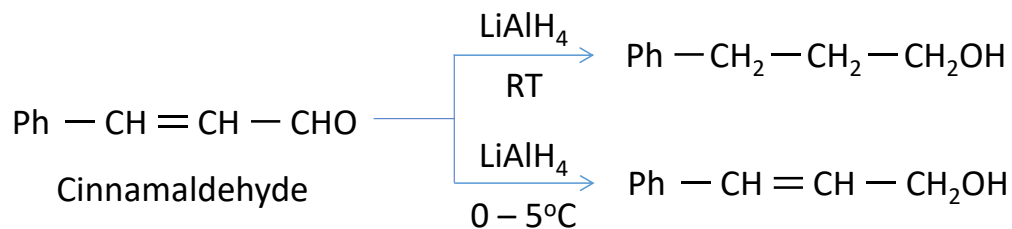(i) LiAlH$_4$ converts Aldehydes into 1°-Alcohols.
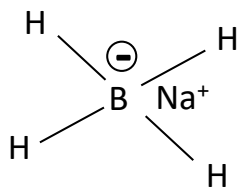

(ii) LiAlH$_4$ converts Ketones into 2°-Alcohols.

**** Cinnamaldehyde on reduction with LiALH4 forms following products.

$$Ph-CH=CH-CHO \quad \xrightarrow[\text{RT}]{\text{LiAlH}_4} \quad Ph-CH_2-CH_2-CH_2OH$$

$$\text{Cinnamaldehyde} \quad \xrightarrow[\text{0}-5°C]{\text{LiAlH}_4} \quad Ph-CH=CH-CH_2OH$$

(a) Reduction of carbonyl compounds (C=O) with Sodium Borohydride (NaBH₄)

Structure

$$\begin{array}{c} H \\ H \end{array} \overset{\ominus}{\underset{H}{B}} \overset{H}{\underset{\quad}{\diagup}} Na^+$$
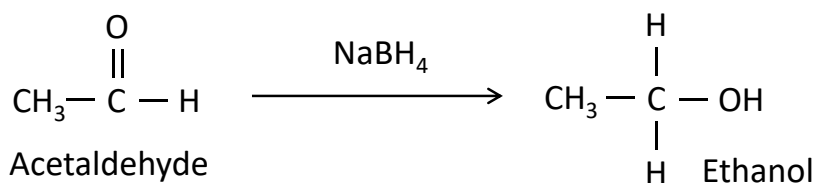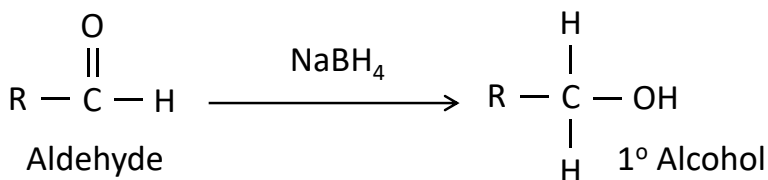
It is crystalline compound
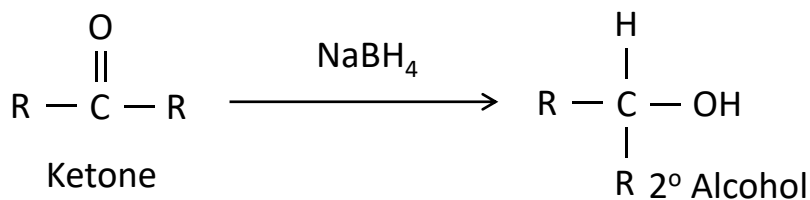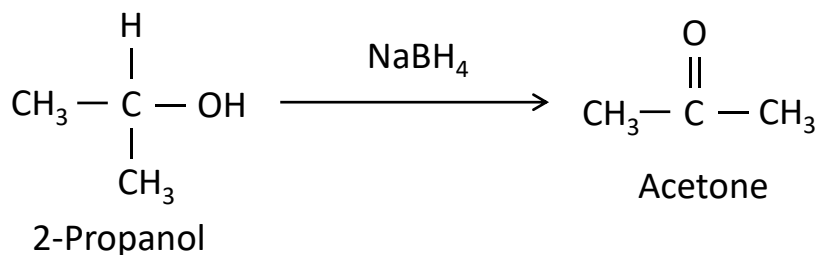
Solvent: Water, alcohol

Reaction with Carbonyl compounds (Aldehydes and Ketones)

(i) NaBH₄ converts Aldehydes into 1°-Alcohols.

$$\underset{\text{Aldehyde}}{R-\overset{\overset{\displaystyle O}{||}}{C}-H} \quad \xrightarrow{\text{NaBH}_4} \quad \underset{\text{1° Alcohol}}{R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH}$$

$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{\displaystyle O}{||}}{C}-H} \quad \xrightarrow{\text{NaBH}_4} \quad \underset{\text{Ethanol}}{CH_3-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH}$$

(ii) NaBH₄ converts Ketones into 2°-Alcohols.

$$\underset{\text{Ketone}}{R-\overset{\overset{\displaystyle O}{||}}{C}-R} \quad \xrightarrow{\text{NaBH}_4} \quad \underset{\text{2° Alcohol}}{R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle R}{|}}{C}}-OH}$$

2-Propanol $\xrightarrow{\text{NaBH}_4}$ Acetone

**** In Cinnamaldehyde NaBH4 reduces only aldehydes but not double bonds.

$$Ph - CH = CH - CHO \xrightarrow[\text{RT}]{\text{NaBH}_4} Ph - CH = CH - CH_2OH$$

Cinnamaldehyde   Cinnamyl alcohol
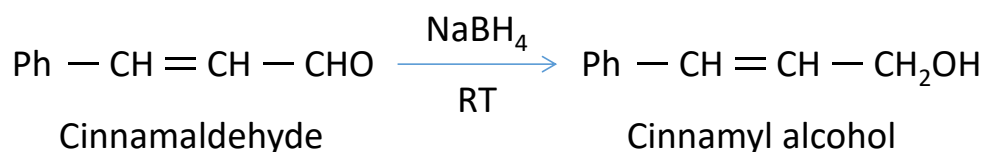
LiAlH$_4$ is more reactive, therefore less selective. But, NaBH$_4$ is less reactive, therefore more selective.

Synthesis and uses of commonly used drug molecules (Aspirin and Paracetamol)

ASPIRIN

Aspirin prepared by reaction of salicylic acid with acetic anhydride in presence of acid (H_3PO_4) as catalyst.

Salicylic acid   Acetic anhydride   Acetyl salicylic acid   Acetic acid
                                                   (Aspirin)
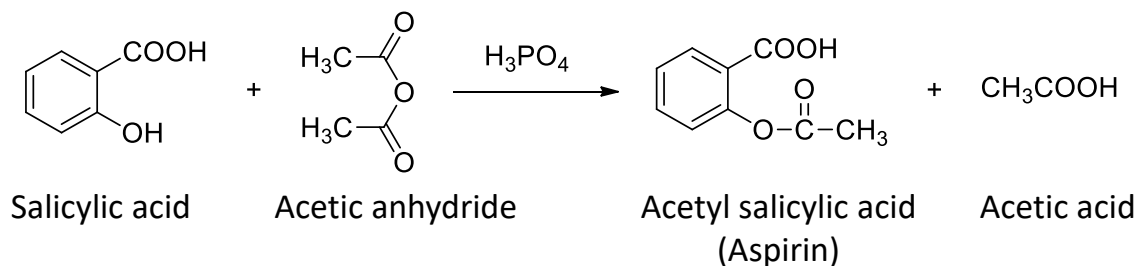
- It is an Electrophilic Substitution reaction.
- In this H$^+$ ions of Salicylic acid are substituted with acetyl group (CH$_3$-C=O). So, it is called as acetylation reaction.

Uses
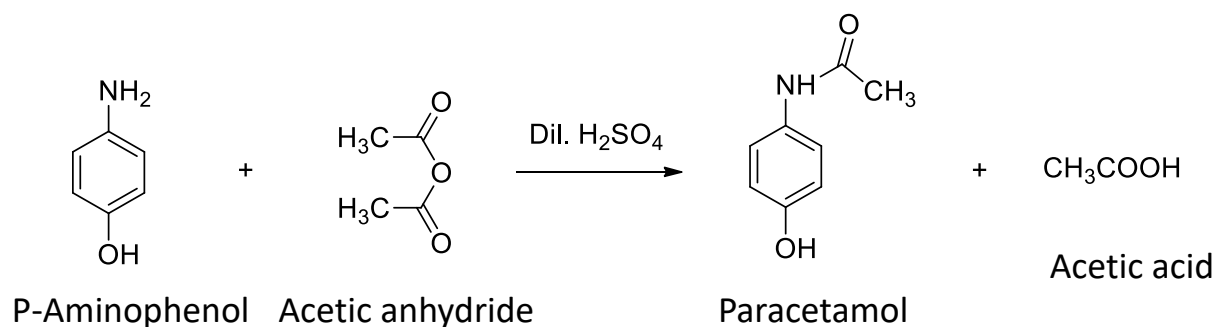
✓ Aspirin reduces Fever

✓ Aspirin is used as a pain killer, means it reduces headache, Muscle ache, Stomach ache, Tooth ache, etc.

✓ It also prevents blood clotting.

Side Effects

Upset of stomach. Kidney problems, Hearing problems, Yellowing of eyes and skin.

PARACETAMOL

It is prepared by the reaction between p-aminophenol and acetic anhydride in presence of dil. H_2SO_4 as a catalyst.

P-Aminophenol   Acetic anhydride   Paracetamol

- It is an electrophilic substitution reaction
- In this reaction H^+ ions of NH_2 in p-amino phenol substituted with acetyl group (CH_3-C=O). So, it is called as acetylation reaction.

Uses

✓ Paracetamol reduces Fever

✓ Paracetamol is used as a pain killer, means it reduces headache, Muscle ache, Stomach ache, Tooth ache, etc.

✓ Paracetamol also acts as anti-inflammatory (reduces swelling).

Side Effects

o It causes diarrhoea. Leads to vomiting.

o Low blood pressure.

o Over sweating.

UNIT-V: ENGINEERING MATERIALS(9L)

BIODEGRADABLE POLYMERS: Introduction, Preparation and properties of Polyhydroxy butyrate (PHB), Polyhydroxy butyrate-co-β-Hydroxy valerate (PHBV), Polyglycolic acid (PGA), Polylactic acid (PLA), Poly (Î-caprolactone) (PCL). Applications of biodegradable polymers.

LUBRICANTS: Introduction, Classification with examples, characteristics of a good lubricant and properties of lubricants: Viscosity and viscosity index, cloud point, pour point, flash & fire point.

REFRACTORIES: Classification with examples, characteristics and Properties of refractory materials (Refractoriness, RUL test & Thermal spalling).

CERAMICS: Introduction, chemical bonding and applications.

1. BIODEGRADABLE POLYMERS

A **polymer** is a molecule made up of numerous small molecules (called monomers) joined together to form a larger molecule. *Poly* which means *many*, and *mer* which means *unit*.

"The polymers which degrade by the enzymatic action of naturally occurring microorganism and bacteria" are called Biodegradable polymers.

Oxygen, water, heat and sunlight can also cause degradation of the polymers apart from enzymes and microbes.

(i) The degradation of the polymers may be due to breaking of chemical bonds (or)

(ii) Rearrangement of chemical bonds.

Properties of Biodegradable polymers

1. Until degraded, biodegradable polymers can retain good mechanical integrity.
2. Since biodegradable polymers have extremely strong carbon backbones that are difficult to crack. Degradation usually begins at the end-groups.
3. Biodegradable polymers should produce non-toxic materials.
4. The degradation rates of biodegradable polymers can be regulated.
5. Biodegradable polymers are hydrophilic (attracts water).

Biodegradable polymers are of two types, i.e., Natural Biodegradable Polymers and Synthetic Biodegradable Polymers.

Naturally occurring biodegradable polymers. These natural polymers are beautiful for environment degradation. The rate of degradation and the formation of metabolite depends on the structural complexity of material and the environment conditions related for degradation.

The biodegradable polymers which are found in nature called as Natural biodegradable polymers. These are generally nontoxic and easily available. Naturally biodegradable polymers are **four types**.

(a) Polysaccharides: Ex. Starch and Cellulose

(b) Proteins: Ex. Gelatin, Fibrin, Silk and Wool

(c) Polyesters: Ex: Polyhydroxyalkanoates
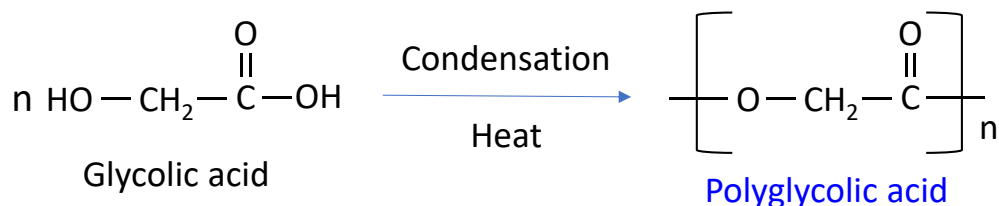
(d) Others: Ex. natural Rubbers and Lignin.

The biodegradable polymers which are preparing in laboratory or man-made called Synthetic biodegradable polymers. Synthetic biodegradable polymers have been developed in order to dispose them similar to that of naturally occurring polymers.

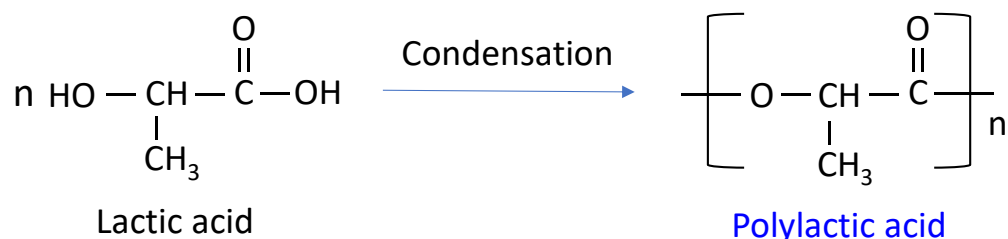The common examples of synthetic biodegradable polymers are given bellow.

(i) Poly Glycolic acid (PGA), (ii) Polylactic acid (PLA), (iii) Polyhydroxybutyrate (PHB)

(iv) Polyhydroxy butyrate-co-β-hydroxy valerate (PHBV) and (v) Polycaprolactone (PCL).

i) Polyglycolic acid (PGA): PGA polymer can be obtained by the self-condensation of Glycolic acid.

$$n \; HO-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow[\text{Heat}]{\text{Condensation}} \left[\!\!-O-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-\!\!\right]_n$$

Glycolic acid   Polyglycolic acid

ii) Polylactic acid (PLA): PLA polymer can be obtained by the self-condensation of Lactic acid.

$$n \; HO-\underset{\underset{\displaystyle CH_3}{|}}{CH}-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow{\text{Condensation}} \left[\!\!-O-\underset{\underset{\displaystyle CH_3}{|}}{CH}-\overset{\overset{\displaystyle O}{\|}}{C}-\!\!\right]_n$$

Lactic acid   Polylactic acid

iii) Polyhydroxy butyrate (PHB): PHB polymer can be obtained by the self-condensation of 3-hydroxybutanoic acid.

3-Hydroxybutanoic acid   PHB
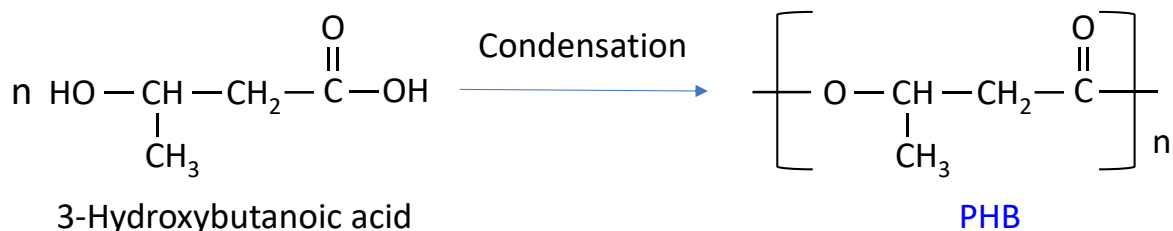
iv) Polyhydroxybutyrate-co-β-hydroxyvalerate (PHBV): PHBV is a copolymer formed by reaction between two different monomers. The condensation of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid produce PBHV polymer. In this polymer, the monomer units are joined by alternate linkages.

3-Hydroxybutanoic acid   3-Hydroxypentanoic acid

Condensation
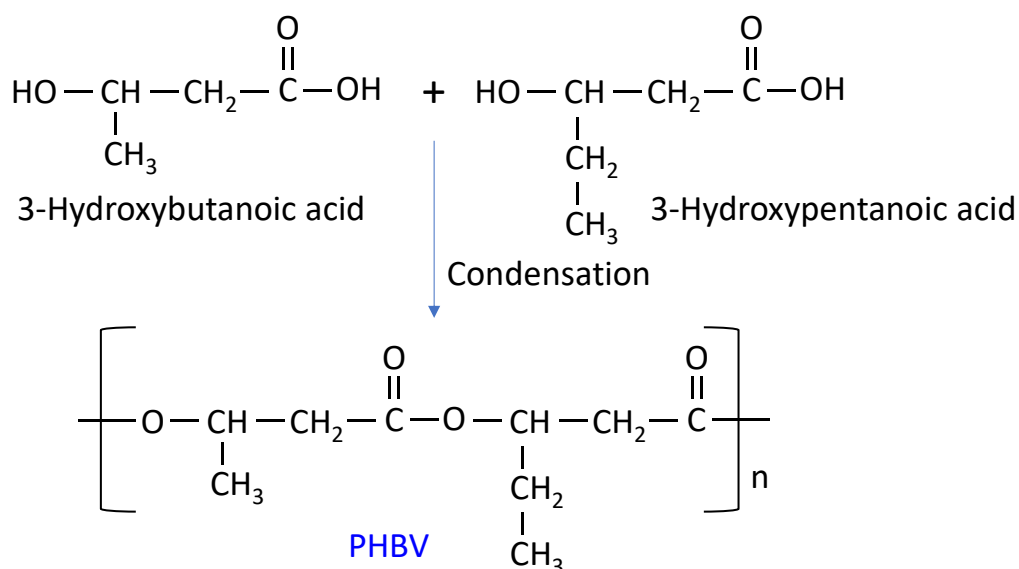
PHBV

The properties of PHBV depend on the ratio of both the monomers involved in polymerization. Presence of excess of 3-hydroxybutanoic acid provides stiffness and the presence of excess of 3-hydroxypentanoic acid provides flexibility.

v) Polycaprolactone (PCL): PCL polymer can be obtained by the condensation polymerization of caprolactone (6-hydroxy hexanoic acid).

Caprolactone   6-Hydroxyhexanoic acid   Polycaprolactone (PCL)
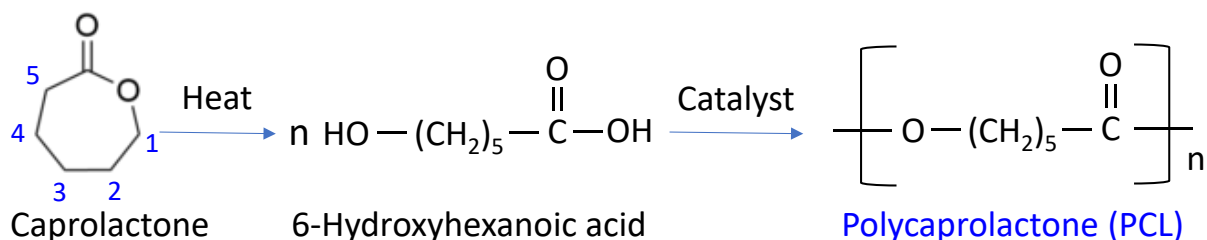
APPLICATION OF BIODEGRADABLE POLYMERS

1) Medical applications

a) Surgical sutures: The biodegradable polymers are used as surgical implants in blood vessels for controlled long term drug release and also used as absorbable surgical sutures for the treatment of eyes.

b) Bone fixation devices: It is proved that biodegradable polymers like PGA and PLA are used as bone fixation devices because they have better compatibility with bones and lignan compared to metal.

The other advantage is that sometimes the metal implants need to be removed while that is not the case with biodegradable polymers. Removal of metal sometimes may cause bone weakness and refractures. The biodegradable polymers when used for bone fixation allow free movement of ligaments and bones.

c) Vascular graft: Gelatin is used as a vascular graft in the treatment of cardiovascular diseases.

2) Agriculture

a) Biodegradable polymers are useful in manufacture of plant bags, pots etc.

b) In horticulture for making threads, fertilizer bags and seed bags.

c) They used to prepare ropes and fishing nets.

3) Packaging

Biodegradable polymers are used to prepare bags, cups and bottles etc.

2. REFRACTORIES

Refractories are inorganic materials that can resist at high temperature, without softening or without suffering a deformation in shape. Or any substance that is difficult to fuse is a refractory. A refractory is a material which doesn't melt easily because its fusion temperature is very high.

Refractories are widely used for providing high temperature resistant lining for furnace, rocket nozzles and for domestic heating appliances.

Classification of Refractories

Refractories are classified into three types as follows. 1) Based on Fusion Temperature

2) Based on Chemical Composition & 3) Based on Oxide Content.

1) On the basis of Fusion Temperature

a) Normal refractory: Refractories having fusion temperature of 1580 °C – 1780 °C are called as normal refractory. Example: Fire clay refractory

b) High refractory: Refractories having fusion temperature of 1780 °C – 2000 °C are called as High refractory. Example: Chromite refractory

c) Super refractory: Refractories having fusion temperature above 2000 °C are called as super refractory. Example: Zirconia refractory.

2) On the basis of Chemical Composition

a) Acidic refractories: Refractories consist of acidic materials like Alumina (Al_2O_3) and Silica (SiO_2) are called acidic refractories. They are not attacked or affected by acidic materials but are attacked by basic materials. Example: Alumina, Silica and Fireclay.

b) Basic refractories: Refractories consist of basic materials like CaO or MgO are called basic refractories. They are resistant to basic slags but are attacked by acidic slags.
Example: Magnesite and Dolomite bricks.

c) Neutral refractories: Refractories consist of weakly acidic or weakly basic materials are called neutral refractories. They are chemically stable towards both acids and bases. Example: Graphite, Zirconium and Silicon carbide (SiC) etc.

3) On the basis of Oxide Content

a) Single oxide refractories: Refractories having single oxide are called single oxide refractories. Example: Alumina, Magnesia and Zirconia.

b) Mixed refractories: Refractories having mixed oxides are called mixed refractories. Example: Chromite ($FeO.Cr_2O_3$).

c) Non-oxide refractories: Refractories are not having any oxides are called non-oxide refractories. Example: Borides, carbides, nitrides etc.

Characteristics of refractory materials

A good refractory material should have the following characteristics

1) The softening temperature should be much higher than the operating temperature.

2) They should have high refractoriness.

3) They should have high Refractoriness Under Load (RUL)

4) They should have Low Thermal Spalling (getting cracks or removing upper layer)

5) They should have Low Permeability (the ability of a substance to allow gases or liquids to go through it)

6) They should Not Crack at Operating Temperatures.

7) They should be chemically inert

PROPERTIES of REFRACTORIES

Refractories have the following properties

a) Refractoriness: The ability of a material to resist at high temperatures without appreciable deformation or softening under given working conditions called refractoriness. It is usually expressed in softening or fusion temperature of the material. Usually, as the temperature increases a material softens and deforms but a refractory should resist such a tendency. Higher the softening temperature more valuable is the refractory. So, a good refractory should possess high refractoriness.

b) Refractoriness Under Load (RUL): RUL is a measure of the resistance behaviour of a refractory body to the combined effects of rising temperature and load.

Since reactants are changed into the refractory lined furnaces, the refractory should resist such heavy loads at high temperatures.

Example: Fire clay refractories collapse at temperature below to their fusion temperature, when appreciable load is applied. On the other hand, Silica refractories withstand of heavy load even at high temperature. Hence, the RUL test is performed to know the safe upper temperature limit up to which the refractory can be used.

c) Thermal spalling: High temperature and its fluctuations induces uneven expansion and contraction of refractory material which ultimately leads to cracking and breaking of refractory bricks. This phenomenon is called as thermal spalling.

The spalling resistance order for some of the refractories is

Silicon carbide > Fireclay bricks > Magnesite > Silica bricks

Thermal spalling can be minimized by

(i) Avoiding sudden fluctuations in temperature

(ii) Proper furnace design.

(iii) Proper selection of refractory material with high thermal conductivity and low coefficient of thermal expansion.

3. LUBRICANTS

A substance which reduces the friction when introduced between two surfaces is lubricant. The phenomenon is known as lubrication.

Criteria of a good lubricant: Any substance which shows the process of lubrication must satisfy certain functions as follows

- A lubricant is to reduce the friction.
- The lubricant should keep moving parts apart.
- It should transfer heat and acts as coolant
- It should reduce the wear and tear as well as surface deformation caused due to rubbing action of a two sliding surfaces.
- It prevents rust and corrosion thereby reduces the maintenance and running cost of the machines.
- It acts as a seal
- It carries away contaminants, otherwise damage the surface of the machinery.
- It should also reduce the loss of energy in the form of heat.
- Lubricant minimizes the liberation of frictional heat, the expansion of metals can be reduced.

PROPERTIES OF LUBRICANTS

Mainly lubricant has three properties. 1) Viscosity, 2) Flash and Fire points & 3) Cloud and Pour points.

1) Viscosity: Viscosity is the property of a fluid that determines its resistance to flow. It is an indicator of flow ability of a lubricating oil. Viscosity is two types.

a) Absolute viscosity: It is the indirect force per unit area required to maintain a 'unit velocity gradient' between two parallel layers. Units in C.G.S. are 'Poise'.

b) Kinetic viscosity: It is the ratio of absolute viscosity to the density for any fluid. Units in C.G.S. are 'Stokes'.

Viscosity Index (VI): The variation of viscosity of a liquid with temperature is called viscosity index. For every 1 ^{o}C rise in the temperature viscosity index decreases by 2%. The mathematical expression for viscosity index is

$$VI = \frac{L-U}{L-H} \text{ X } 100$$

Where, L = Viscosity of standard oil having a viscosity index of zero at 38 ^{o}C. U = Viscosity of test oil at 38 ^{o}C, H = Viscosity of the standard oil having a VI of 100 at 38 ^{o}C.

Measurement of Viscosity

The instrument which is used for measuring viscosity is known as viscometer. The commonly used viscometer is Redwood Viscometer. This consists of the following essential parts.

i) Oil cup: It is a Silver (Ag)-plated brass cylinder. The upper end of the cup is open. The bottom of the cylinder is fitted with an agate jet. The jet is opened or closed by a "valve rod", which is a small silver-plated brass ball fixed to a short wire. A thermometer is fitted to the lid which gives the oil temperature.

ii) Heating bath: Oil cup is surrounded by a water bath fitted with a thermometer and a stirrer. the thermometer provides the temperature of the water.

iii) Stirrer: The stirrer has flour blades for stirring the water to maintain uniform temperature. The stirrer also has a circular shield at the top to prevent any water splashing into the oil present in cup.

iv) Levelling Screws: The entire apparatus rests on three legs provided at their bottom with levelling screws.
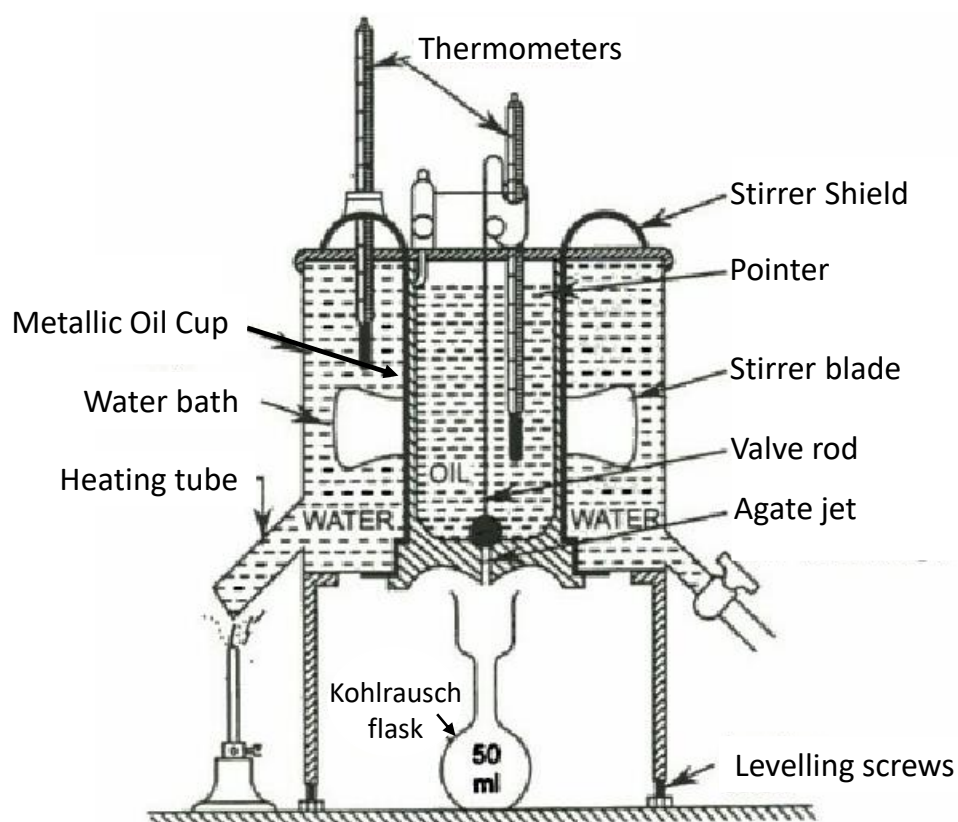
Working: Initially the oil cup is cleaned and valve rod is placed on the agate jet to close it. Oil to be tested is filled in the cup up to the pointer level. Kohlrausch flask is kept below the jet outlet to collect

the oil. Water is filled in the bath and side tube is heated slowly with constant stirring. At the desired temperature heating is stopped and the valve from jet hole is lifted. The time taken to collect 50mL oil in the Kohlrausch flask to be noted. Higher the time taken to flow, higher the viscosity of the oil.

2) Flash and Fire points

Flash point is the lowest temperature at which the lubricating oil gives enough vapours, when a test flame brought near to it.

Fire point is the lowest temperature at which the vapours of the lubricating oil burn continuously at least for 5 seconds, when a test flame brought near to it. Generally, fire point is 5 to 40 times higher than the flash point.

Measurement: Flash and Fire points are measured by "Pensky-Marten's apparatus".

Oil Cup: Pensky Marten's apparatus consists of an oil cup made up of brass with 5.0 cm depth and 5.5 cm diameter. The lid of the cup has four openings for introducing thermometer, stirrer, test flame and for passage of air.

Stirrer: The lid is provided with a stirrer having two blades.

Shutter: The shutter is provided at the top of the cup. By moving the shutter, the opening in the lid opens and flame from the flame exposure device is dipped into this opening. After introducing the test flame, the test flame returns back to its original position where it is lighted by a pilot burner.

Air bath: The oil cup is surrounded by an air-bath which is heated by a gas burner.
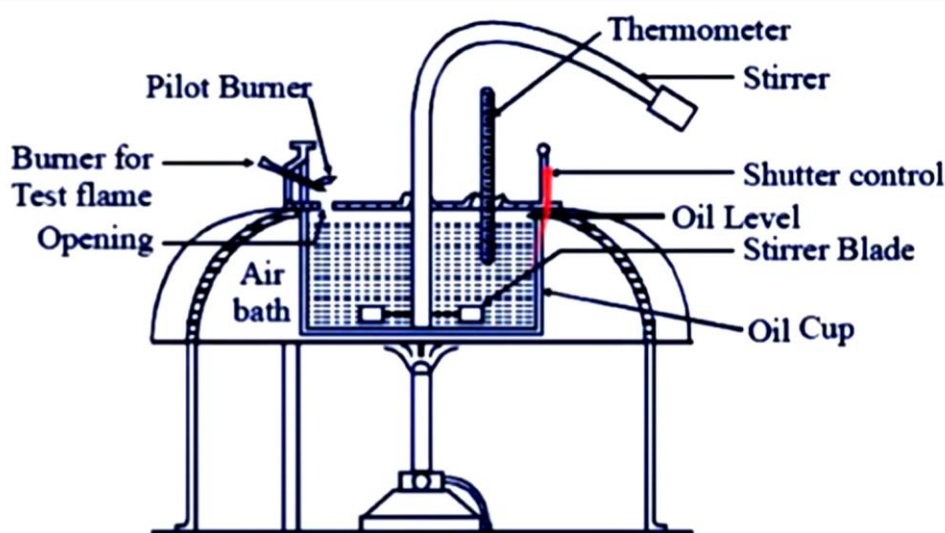
Working: The lubricating oil to be tested is filled into the oil cup up to the levelling mark and then heated by a burner. Stirring is done with the help of stirrer and heat is applied so as to raise the oil temperature of about 5°C per minute.

At every 1°C rise of temperature, test flame is introduced at the opening with the help of shutter for a moment. The temperature at which distinct vapours appear inside the cup is recorded as the Flash point. The procedure is continued till the oil vapour catches fire and burns for five seconds. That temperature is recorded as the Fire point.

3) Cloud point and Pour point

The temperature at which the lubricating oil becomes **cloudy or hazy upon cooling** is called cloud point.

The temperature at which the oil **ceases to flow or pour** is called as pour point.

The cloud and pour points indicate the suitability of lubricants in cold conditions. The lubricant used in machines should have low cloud and pour point than the operating conditions (means lower than the operating temperature).

Determination of cloud point and Pour point: It is determined by cloud point and pour point apparatus.
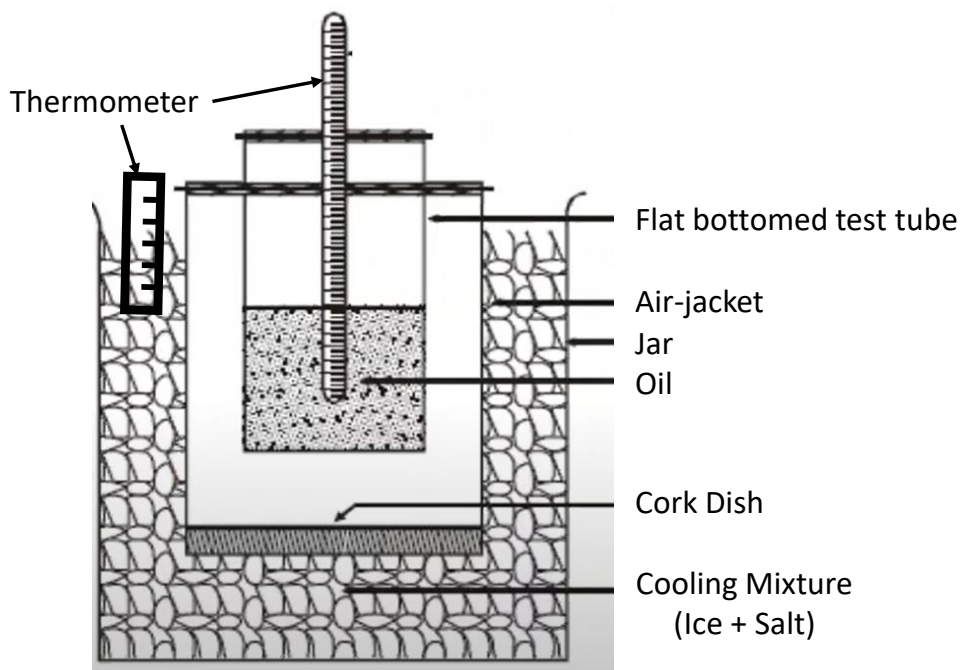
The apparatus consists of a flat-bottomed test tube kept in an air jacket. The jacket is surrounded by freezing mixture (Ice + $CaCl_2$) contained in a jar. The test tube is half filled with test oil. Two thermometers are introduced in the oil and in the freezing mixture for noting temperature. As the cooling proceeds slowly in jacket the temperature falls continuously with every degree fall of temperature of the oil. The tube is withdrawn from air jacket for a moment to check and then immersed immediately. The temperature at which cloudiness is noticed is recorded as a Cloud point.

After cloud point, the cooling is still continued the temperature at which oil doesn't flow in the test tube, even when kept horizontal for 5 sec is recorded as Pour point.

4. CERAMICS

Ceramics are inorganic non-metallic materials that are processed for use at high temperatures.

Example: Silica, Alumina, Fire clay, Glass etc.

Classification of Ceramics

1) Based on chemical composition

Oxides Ex: SiO_2, Al_2O_3

Carbides Ex: SiC

Nitrides Ex: Si_3N_4

Sulphides Ex: Ag_2S

2) Based on their applications

Clay products: Structural clay products (Tiles, Bricks etc)

White wares (Porcelain and China clay)

Chemical stone ware (Sanitary fixtures, Sinks, Bath tub).

Refractories: Fire clay, Dolomite, Zircon, Magnesia etc.

Glass: Insulated glass, Safety glass, Hard glass, Soft glass, Flint glass, Borosilicate glass or Pyrex glass, Vitreosil etc.

Advanced ceramics: Glazed ceramics, Porcelain.

Properties of Ceramics

Ceramics possess the following properties.

- Extreme hardness
- High wear resistance
- Corrosion resistance
- Heat resistance
- Low electrical conductivity
- Low thermal conductivity
- Low thermal expansion and contraction
- Low ductility (Flexibility)
- Low density

- High strength at elevated temperature
- Very brittle.

Applications of Ceramics

Consumer uses: Glassware, windows, tiles, lenses, microwave, home electronics, pottery, etc

Automotive: Catalytic converters, ceramic filters, sensors, ceramic rotors, pressure sensors, softly glass etc.

Aerospace: Thermal barriers, high temperature glass windows, fuel cells, etc.

Medical: Orthopaedic devices, dental restoration and bone implants.

Computers: Insulators, resistors, capacitors, super conductors, ferroelectric components etc.

Industries: Bricks, cement, membranes, filters and lab equipment.

Communications: Fiber optic/laser, TV, Radio components and Microphones, etc.

Yours Dr. Mallesham GODUMALA

All the very best