# Module-I

## Water and its treatment

# Water

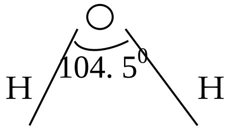
## Introduction:

Water is a natural gift on the earth is essential for human animal and plants. Human being used for all domestic purposes like drinking, cooking bathing, cleaning and washing. Water is not only essential for the survival of life, but it is also used for the operation in a large number of industries as coolant, solvent, for steam generation, for air conditioning, fire-fighting etc.Without food human can survive for a number of days, but water is such an essential that without it one cannot survive.

It has a wide role in industries also. Probably, its most important use as an engineering material is in the **"steam generation".**

Chemically, water has two atoms of hydrogen and one atom of oxygen having the molecular formula $H_2O$. In several chemical reactions, water is formed along with the main product, e.g. acid reacts with base to give salt and water. Alcohols and organic acids react to give ester and $H_2O$

Water molecule is a bent triatomic molecule with the bond angle $104.5^0$ the oxygen atom present in the water molecule has $sp^3$ – hybridization, state having two bond pairs and two lone pairs.



Water is found in three physical states, liquid (water), solid (ice) and gas (vapour). The freezing point of water is $0^0$C and the boiling point is $100^0$C. Several special behaviors found in water due to hydrogen bond present in it. In nature, water is present 3//4 of the earth surface.

The process of removing of all types of impurities from water and making fit for domestic or industrial purposes is called **Water Technology** or **Water Treatment**.

The main sources of water are,
1. Rain water
2. Surface water (Rivers and lakes)
3. Underground water (wells and springs)
4. Lake water
5. Sea water

**Rainwater**: It is the purest form of natural water. But unfortunately it dissolves the toxic gases like $CO_2$, $SO_2$, $NO_2$ etc. and other solids, which pollute the atmosphere.

**Sea water:** It is the most impure form of water containing about 3.5% dissolved salts of which about 2.6% is sodium chloride. Other salts present include sulphates, bicarbonates, bromides of sodium, potassium, magnesium etc. Other impurities are carried to sea through rivers.

**River water:** The sources of river water are the springs and the rainwater. River water while flowing through the land collects lots of organic matters from falling trees and nearby habitats and also other soluble and suspended matters from the lands, soils etc. The dissolved matters

include the salts like sulphates, bicarbonates and bromides of sodium, potassium and magnesium.
**Lake water:** It is much purer than river water, dissolved impurities are less but contains lots of organic matter.

**Underground water**: The rainwater and other surface water percolate down through the soil and rocks and get filtered and finally collected on rocky surface or again come out as spring. Though it contains less suspended matter but the dissolved mineral content is quite high and is of high organic purity.

**Impurities in Water**

Impurities in water are of three types
1. Physical impurities:
    A. Suspended impurities:
    B. Colloidal impurities
2. Chemical impurities
    A. Dissolved salts
3. Biological impurities
    A. Microorganisms

**<u>HARDNESS OF WATER:</u>** Most of the inorganic salts are soluble in water. The $Ca^{+2}$ and $Mg^{+2}$ salts are dissolved in the water causes hardness of water. When water passes through the rocks (dolomite **$MgCO_3$** and limestone **$CaCO_3$**) and flows on the ground. The $Ca^{+2}$ and $Mg^{+2}$ salts are present in the rocks are dissolved in water in the presence of atmospheric $CO_2$ and it make hard.

$$MgCO_3+CO_2+H_2O \longrightarrow Mg(HCO_3)_2$$

$$CaCO_3+CO_2+H_2O \longrightarrow Ca(HCO_3)_2$$

**Types of water:**
a) Hard Water b) Soft Water

**Hard Water:** Water, which does not produce lather with soap solution, but produces white precipitate is called **Hard water.** This is due to presence of dissolved calcium and magnesium salts. A soap is a sodium salt or potassium salt of higher fatty acid such as **stearic acid (**$C_{17}H_{35}COOH$). When soap is contact with hard water, sodium stearate will react with dissolved $Ca^{+2}$ and $Mg^{+2}$ salts and produce insoluble Ca-stearate (or) Mg-stearate precipitates.

$$2C_{17}H_{35}COONa + Ca^{2+} \longrightarrow (C_{17}H_{35}COO)_2Ca + 2Na^{+}$$

Soap (Water soluble) — hardness Causing Substance — calcium stearate (water insoluble)

# Water

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

Soap (Water soluble) hardness Causing Substance magnesium stearate (water insoluble)

**Soft water:** Water, which produce lather with soap solution is called **Soft water**. This is due to the absence of Ca & Mg salts.

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

Soap (Water soluble) (water soluble)

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

(Sodium stearate ) (Stearicacid)

## Types of Hardness :

Hardness of water is of two types

(a) Temporary hardness (carbonate hardness)
(b) Permanent hardness (non – carbonate hardness)

### (a) Temporary hardness (carbonate hardness)

**Temporary Hardness** is due to the presence of magnesium and calcium bicarbonates [$Ca(HCO_3)_2$ and $Mg(HCO_3)_2$]. It is also called **carbonate hardness** (CH). It can be removed by **Boiling**. During boiling, the soluble $Mg(HCO_3)_2$ is converted into insoluble $Mg(OH)_2$ and $Ca(HCO_3)_2$ is changed to insoluble $CaCO_3$. These insoluble precipitates can be removed by filtration. Filtrate thus obtained will be soft water.

$$\underset{\text{Calcium bicarbonate}}{Ca(HCO_3)_2} \xrightarrow{\text{Boiling}} \underset{\text{Calcium carbonate (Insoluble)}}{CaCO_3\downarrow\ H_2O + CO_2}$$

$$\underset{\text{Magnesium bicarbonate}}{Mg(HCO_3)_2} \xrightarrow{\text{Boiling}} \underset{\text{Magnesium hydroxide (Insoluble)}}{Mg(OH)_2\downarrow + 2CO_2}$$

### Permanent (or) Non – carbonate hardness:

**Permanent Hardness** is due to the presence of soluble salts of magnesium and calcium in the form of chlorides, nitrates and sulphates in water ($CaCl_2$, $CaSO_4$, $MgCl_2$, $Ca(NO_3)_2$, $Mg(NO_3)_2$and $MgSO_4$). Permanent hardness is not removed by boiling. It is also called **non-carbonate hardness** (NCH). Only chemical treatment method can remove this hardness.

# Water

**Total Hardness:** Temporary hardness and permanent hardness constitute the total hardness which is also expressed as the sum of the concentration of calcium and magnesium ions

Total Hardness = Temporary Hardness + Permanent Hardness

Total Hardness = $[Ca^{2+}] + [Mg^{2+}]$

**Disadvantages of Hard Water:** The following are the disadvantages of hard water:

**In domestic use:** (a) Hard water is not useful for various domestic purposes, viz. washing, bathing and drinking. The hardness producing ions convert soluble soaps to insoluble precipitates. This results in wastage of soaps in washing and bathing.

(b) Due to the presence of dissolved hardness producing salts, the boiling point of water is elevated. Hence, more fuel and time are required for cooking.

(c) Hard water causes bad effect on our health. Calcium form oxalate crystals in urinary tract.

**In industrial use:** (a) The dissolved $Ca^{+2}$, $Mg^{+2}$ and Iron salts in hard water will react with dyes to form undesirable precipitates which gives improper shade.

(b) In sugar refineries must be free from sulphates, nitrates, alkali, carbonates and bacteria, these impurities sugar may not crystalline well.

(c) If hard water is fed directly in to the boilers for steam generation, it results in various boiler troubles viz. Scales, sludges, priming, foaming and caustic embrittlement.

(d) Hard water is not suitable for laboratory analysis, because hardness produces ions interferes (disturbs) in various reactions.

(e) Any water sample with hardness less than 150 ppm is good and portable while beyond 350 ppm is not suitable for consumption.

**Degree of Hardness:** The total hardness of water is caused by **8** different salts of $Ca^{2+}$ and $Mg^{2+}$, $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $CaCl_2$, $CaSO_4$, $MgCl_2$, $Ca(NO_3)_2$, $Mg(NO_3)_2$ and $MgSO_4$. The hardness of water is expressed in terms of $CaCO_3$ equivalents. $CaCO_3$ is selected for the expression of degree of hardness is due to (**a**) Its molecular weight is 100, which is easy for calculation (**b**) It is most in soluble in water.

Hardness causing salt (H.C.S) In terms of $CaCO_3$ equivalents

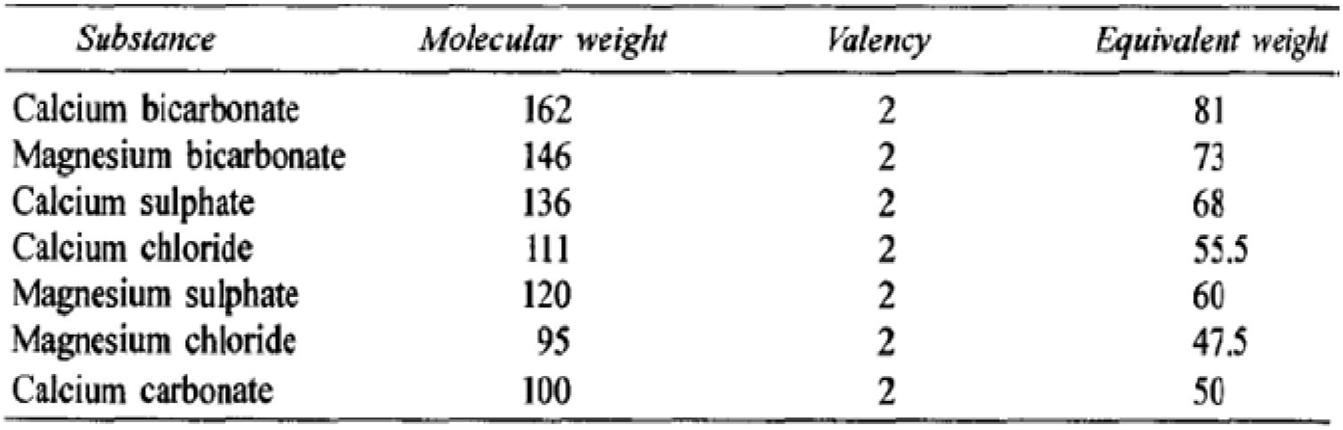
$$= \frac{\textbf{Weight of the hardness causing salt}}{\textbf{Molecular weight of the hardness causing salt}} \times \textbf{Molecular weight of CaCO3}$$

OR

Hardness causing salt (H.C.S) In terms of $CaCO_3$ equivalents

$$= \frac{\textbf{Weight of the hardness causing salt}}{\textbf{Equivalent weight of the hardness causing salt}} \times \textbf{Eqivalent weight of CaCO3}$$

# Water



| Substance | Molecular weight | Valency | Equivalent weight |
|---|---|---|---|
| Calcium bicarbonate | 162 | 2 | 81 |
| Magnesium bicarbonate | 146 | 2 | 73 |
| Calcium sulphate | 136 | 2 | 68 |
| Calcium chloride | 111 | 2 | 55.5 |
| Magnesium sulphate | 120 | 2 | 60 |
| Magnesium chloride | 95 | 2 | 47.5 |
| Calcium carbonate | 100 | 2 | 50 |
| **Calcium nitrate** | **164** | **2** | **82** |
| **Magnesium nitrate** | **148** | **2** | **74** |

**Problem 1: Calculate $CaCO_3$ equivalent of hardness causing salts present in 1000 liters of sample of water containing 16.2 mg/l of $Ca(HCO_3)_2$, 11.1 mg/l of $CaCl_2$, 60mg/l of $MgSO_4$ and 19 mg/l of $MgCl_2$.**

| salt | Quantity of the salt | M.W | Equivalent to **$CaCO_3$(mg/l)** | Equivalent hardness causing salt in 1000 L of water |
|---|---|---|---|---|
| **$Ca(HCO_3)_2$** | 16.2 | 162 | $\frac{16.2X100}{162} = 10$ | 10X1000=10,000 mg |
| **$CaCl_2$** | 11.1 | 111 | $\frac{11.1X100}{111} = 10$ | 10X1000=10,000 mg |
| **$MgSO_4$** | 60 | 120 | $\frac{60X100}{120} = 50$ | 50X1000=50,000 mg |
| **$MgCl_2$** | 19 | 95 | $\frac{19X100}{95} = 20$ | 20X1000=20,000 mg |

**UNITS OF HARDNESS:** The following are the common units used in hardness measurements.

[1] **Parts per million (ppm):** It is defined as the number of parts of $CaCO_3$ equivalent hardness causing salts present in million parts ($10^6$) of water.

1 ppm = 1 part of $CaCO_3$ equivalent hardness in $10^6$ parts of water.

[2] **Milligram per litre:** It is defined as the number of milligrams of $CaCO_3$ equivalent hardness causing salts present in one litre of water.

1 mg/*l* = 1 mg of $CaCO_3$ equivalent hardness in one litre of water

Since weight of 1 litre of water = 1 kg = 1000 g

= 1000 x 1000 = $10^6$ mg

1 mg/*l* = 1 mg of $CaCO_3$ equivalent hardness causing salts per $10^6$ mg of water

= 1 part of $CaCO_3$ per $10^6$ parts of water = 1 ppm

Thus, mathematically both units are equal.

**[3] Degree Clarke ($^{O}$Cl):** It is the number of parts of $CaCO_3$ equivalent hardness per 70,000 parts of water.

$1^0$ clarke ($1^0$Cl) = 1 grain of $CaCO_3$ eq hardness per gallon of water or

$1^0$Cl = 1 part of $CaCO_3$ equivalent hardness per 70,000 parts of water.

**[4] Degree French ($^0$Fr):** It is the number of parts of $CaCO_3$ per $10^5$ parts of hard water thus,

$1^0$Fr = 1 part of equivalent $CaCO_3$ per $10^5$ parts of hard water.

**[5] Equivalent per Million : EPM [ mill equivalent per litre(meq/*l*)]:**

One Milligram equivalent of $CaCO_3$ per litre of hard water is called equivalent per million (or) Mill equivalent per litre is the number of milli equivalents of hardness present per litre Thus,

1Meq/L = 1 Meq of $CaCO_3$ per Litre of water

= $10^{-3} \times$ 50g of $CaCO_3$ eq per litre

= 50 mg of $CaCO_3$ eq per litre

= 50 mg / *l* of $CaCO_3$ eq

1mg = 50 ppm

(or) 1 epm = 50 ppm of $CaCO_3$

The hardness of water can converted in to all the 4 units by making use of the following interconversion.

**Relation between various units of hardness**

1 ppm = 1 mg/l = 0.1° Fr = 0.07° Cl

1° Cl = 1.43° Fr = 14.3 ppm = 14.3 mg/l

1° Fr = 10 ppm = 10 mg/l = 0.7° Cl.

**PROBLEM 1:** A sample of hard water contains 120 mg/l of hardness. Express hardness of water in ppm, degree of French and degree of clark?

Hardness of water sample= 120mg/l

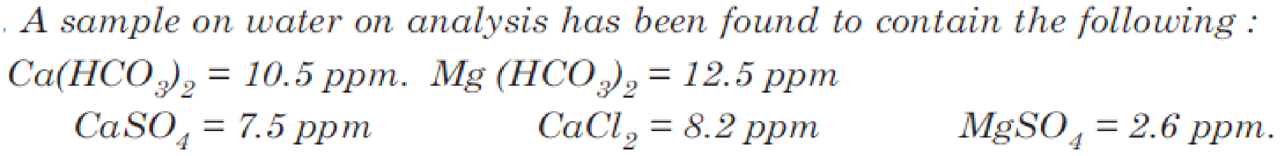
1 ppm = 1 mg/l = 0.1° Fr = 0.07° Cl

Hardness of water in degree of clark (**$^{O}$Cl)=** 120X0.07=8.4 **$^{O}$Cl**

Hardness of water in ppm=120 ppm

Hardness of water in degree of french (**$^{O}$Fr)=** 120X0.1=12 **$^{O}$Fr**

**PROBLEM:2**

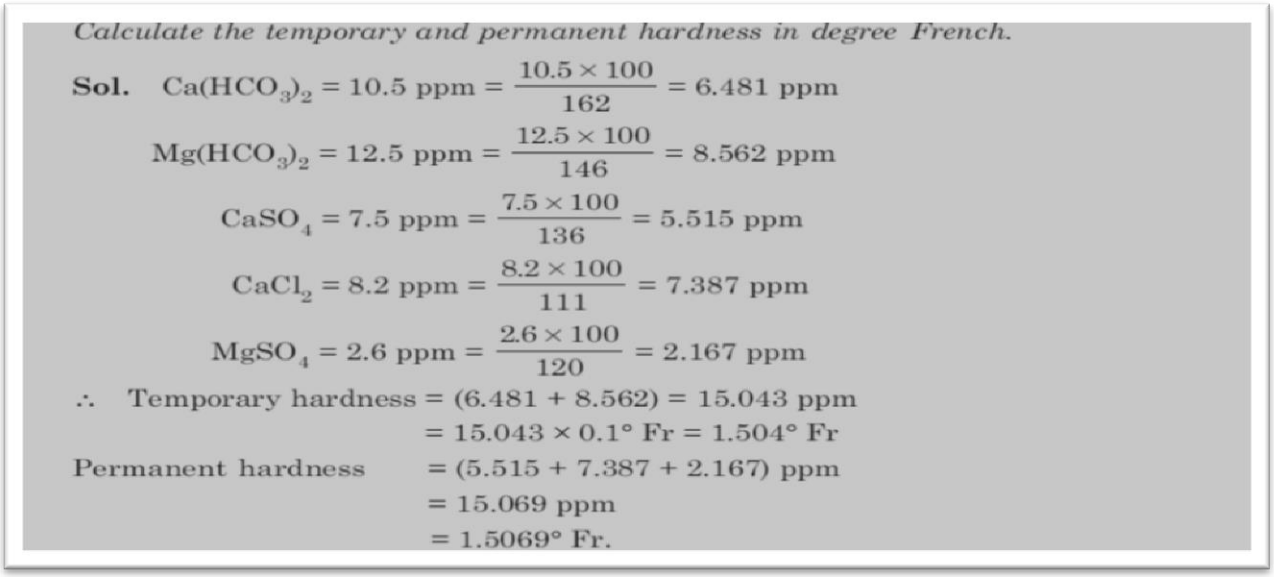


*A sample on water on analysis has been found to contain the following :*

$Ca(HCO_3)_2 = 10.5$ ppm. $Mg(HCO_3)_2 = 12.5$ ppm

$CaSO_4 = 7.5$ ppm $\quad CaCl_2 = 8.2$ ppm $\quad MgSO_4 = 2.6$ ppm.

# Water



*Calculate the temporary and permanent hardness in degree French.*

**Sol.** $Ca(HCO_3)_2 = 10.5 \text{ ppm} = \frac{10.5 \times 100}{162} = 6.481 \text{ ppm}$

$Mg(HCO_3)_2 = 12.5 \text{ ppm} = \frac{12.5 \times 100}{146} = 8.562 \text{ ppm}$

$CaSO_4 = 7.5 \text{ ppm} = \frac{7.5 \times 100}{136} = 5.515 \text{ ppm}$

$CaCl_2 = 8.2 \text{ ppm} = \frac{8.2 \times 100}{111} = 7.387 \text{ ppm}$

$MgSO_4 = 2.6 \text{ ppm} = \frac{2.6 \times 100}{120} = 2.167 \text{ ppm}$

∴ Temporary hardness = (6.481 + 8.562) = 15.043 ppm
= 15.043 × 0.1° Fr = 1.504° Fr

Permanent hardness = (5.515 + 7.387 + 2.167) ppm
= 15.069 ppm
= 1.5069° Fr.

**PROBLEM 3:** A sample of hard water contains the following dissolved salts per litre. $Ca(HCO_3)_2$=16.4mg, $Mg(HCO_3)_2$=14.6mg, $CaCl_2$=111mg, $MgSO_4$=12mg,$CO_2$=44mg, $CaSO_4$=13.6mg.Calculate temporary and permanent hardness of water in ppm and degree of clark?

| salt | Quantity of the salt | M.W | Equivalent to **$CaCO_3$(mg/l)** |
|---|---|---|---|
| **$Ca(HCO_3)_2$** | 16.4 | 162 | $\frac{16.4X100}{162}$ =10.12 |
| **$Mg(HCO_3)_2$** | 14.6 | 146 | $\frac{14.6X100}{146}$ =10 |
| **$CaCl_2$** | 111 | 111 | $\frac{111X100}{111}$ =100 |
| **$MgSO_4$** | 12 | 120 | $\frac{12X100}{120}$ =10 |
| **$CO_2$** | 44 | 44 | $\frac{44X100}{44}$ =100 |
| **$CaSO_4$** | 13.6 | 136 | $\frac{13.6X100}{136}$ =10 |

Temporary hardness= $Ca(HCO_3)_2$+ $Mg(HCO_3)_2$
= 10.12+10=20.123mg/l
= 20.123X0.07=1.408 °Cl

Permanent hardness= $CaCl_2$+ $MgSO_4$+ $CaSO_4$
=100+10+10=120 mg/l
=120X0.07=8.4°Cl

# Water

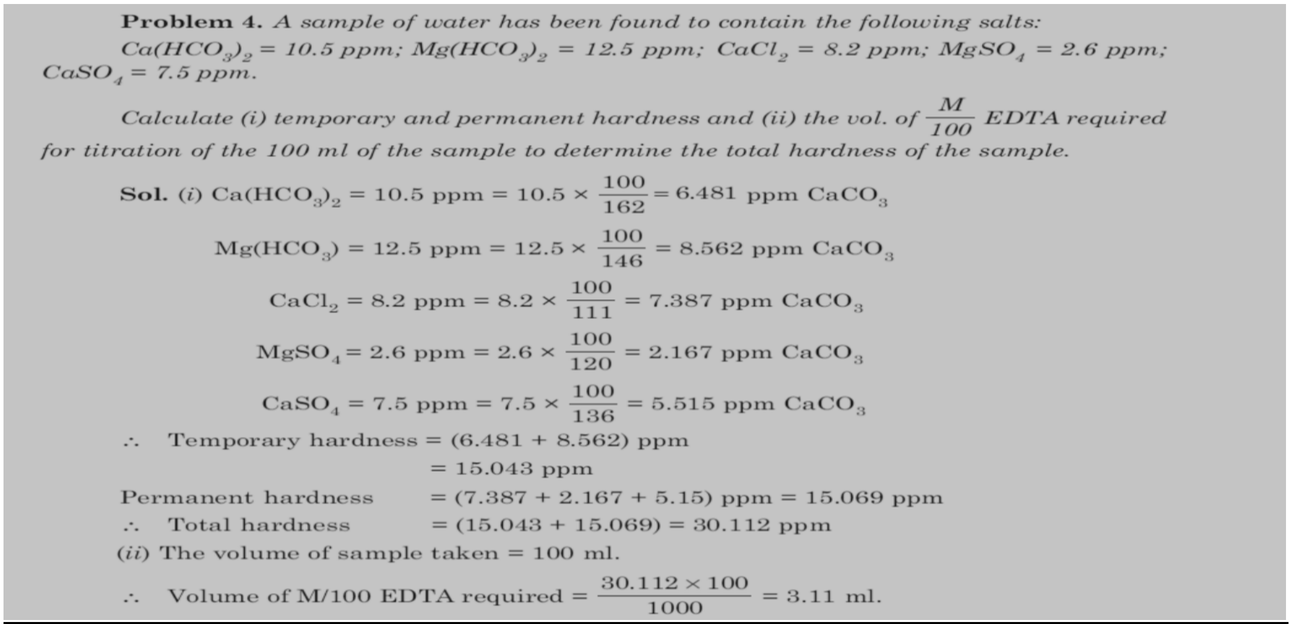
**PROBLEM 4:** A sample of hard water contains the following dissolved salts per unit. $CaCl_2$=111mg, $CaSO_4$=1.36 mg, $Ca(HCO_3)_2$=16.2 mg, $Mg(HCO_3)_2$=14.6 mg, silica=40 mg, turbidity=10 mg. Calculate the total , permanent and temporary hardness of water in ppm, degree of clark and degree of French?

| salt | Quantity of the salt | M.W | Equivalent to **$CaCO_3$(mg/l)** |
|---|---|---|---|
| **$Ca(HCO_3)_2$** | 16.2 | 162 | $\frac{16.2X100}{162}$ =10 |
| **$Mg(HCO_3)_2$** | 14.6 | 146 | $\frac{14.6X100}{146}$ =10 |
| **$CaCl_2$** | 111 | 111 | $\frac{111X100}{111}$ =100 |
| **$CaSO_4$** | 1.36 | 136 | $\frac{1.36X100}{136}$ =1 |

Temporary hardness= $Ca(HCO_3)_2$+ $Mg(HCO_3)_2$
= 10+10=20 mg/l, 20 ppm
= 20X0.07=1.4 °Cl
=20X0.1=2 °Fr

Permanent hardness= $CaCl_2$+$CaSO_4$
=100+1=101 mg/l, 101ppm
=101X0.07=7.07°Cl
=101X0.1=10.1 °Fr

Total hardness=Temporary hardness + Permanent hardness
=20+101=121 mg/l, 121 ppm
=121X0.07=8.47°Cl
=121X0.1=12.1 °Fr



**Problem 4.** *A sample of water has been found to contain the following salts:* *$Ca(HCO_3)_2$ = 10.5 ppm; $Mg(HCO_3)_2$ = 12.5 ppm; $CaCl_2$ = 8.2 ppm; $MgSO_4$ = 2.6 ppm; $CaSO_4$ = 7.5 ppm.*

*Calculate (i) temporary and permanent hardness and (ii) the vol. of $\frac{M}{100}$ EDTA required for titration of the 100 ml of the sample to determine the total hardness of the sample.*

**Sol.** (*i*) $Ca(HCO_3)_2 = 10.5 \text{ ppm} = 10.5 \times \frac{100}{162} = 6.481 \text{ ppm } CaCO_3$

$Mg(HCO_3) = 12.5 \text{ ppm} = 12.5 \times \frac{100}{146} = 8.562 \text{ ppm } CaCO_3$

$CaCl_2 = 8.2 \text{ ppm} = 8.2 \times \frac{100}{111} = 7.387 \text{ ppm } CaCO_3$

$MgSO_4 = 2.6 \text{ ppm} = 2.6 \times \frac{100}{120} = 2.167 \text{ ppm } CaCO_3$

$CaSO_4 = 7.5 \text{ ppm} = 7.5 \times \frac{100}{136} = 5.515 \text{ ppm } CaCO_3$

∴ Temporary hardness = (6.481 + 8.562) ppm
= 15.043 ppm

Permanent hardness = (7.387 + 2.167 + 5.15) ppm = 15.069 ppm

∴ Total hardness = (15.043 + 15.069) = 30.112 ppm

(*ii*) The volume of sample taken = 100 ml.

∴ Volume of M/100 EDTA required = $\frac{30.112 \times 100}{1000}$ = 3.11 ml.

# Water

## BOILER TROUBLES

A boiler is a closed vessel, in which water under pressure is transformed in to steam by heat to generate power. The water should be free from impurities and softened before being used in boilers. When hard water is fed into boiler the following problems arise,

1. Priming and Foaming
2. Caustic embrittlement
3. Boiler corrosion
4. Scale and Sludge

### (1) Priming and Foaming

**Priming:** It may defined as the violent or rapid boiling of water in the boiler which results in carrying out of water droplets pass with steam in in the form of a spray. This process of wet steam formation is called **priming**. Priming in boilers is due to
(1) The presence of suspended and dissolved salts
(2) High level of water in boilers
(3) Improper design of boiler
(4) High velocities of steam in the boiler

Priming can be controlled by: (a) Maintain low water levels in boilers
(b) Filtering water before feed into boilers
(c) Avoid high-velocities of the steam
(d) Proper evaporation and using adequate heating surfaces

**Foaming:** Formation of stable, persistent foam (or) bubbles at the surface of water in the boiler is called foaming. The oil and alkali react with water to form soap, as a result the surface tension of water decreases. Foaming is due to the presence of oil drops, grease and suspended solids.

Foaming can be removed by adding antifoaming agents like polyamide and castor oil and removing oil from boiler water by adding compounds like $NaAlO_2$.

### (2) Caustic embrittlement

This is a type of boiler corrosion, caused by using highly alkaline water. The source of alkali in the boiler is due to presence of residual $Na_2CO_3$ in water by softening process by lime soda process. This undergo hydrolysis at high temperature and pressure to give NaOH.

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

**“**The term caustic embrittlement used for the cracks in boiler water due to the increased concentration of caustic alkali”. Accumulation of NaOH in the walls of the boiler parts becomes brittle, known as caustic embrittlement. Caustic embrittlement can be prevented by:

(a) Using $Na_3PO_4$ as softening reagent instead of $Na_2CO_3$ in external treatment of boiler water. (b) Adding tannins, lignin to boiler water, which blocks the cracks in the boiler walls. (c) Neutralizing alkali with very small quantity of acid.

# Water

## 3. Boiler corrosion

The decay of boiler material by chemical (or) electrochemical attack its environment is called **boiler corrosion**. Main reasons for the boiler corrosion are (1) Dissolved oxygen (2) Dissolved $CO_2$ (3) Acids produced from dissolved salts.

(1) **Removal of Dissolved $O_2$:** Dissolved oxygen in water is mainly responsible for boiler corrosion. At high temperatures, dissolved $O_2$ in water attacks boiler material

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

$$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 2[Fe_2O_3 \cdot 3H_2O] \text{ (rust)}$$

Dissolved oxygen can be removed from water by **chemical** and **mechanical** methods.

**Chemical method:** In this method Sodium sulphite ($Na_2SO_3$), hydrazine ($NH_2NH_2$) are added in small quantity (5-10 ppm) is converted to sodium sulphate and $N_2$, respectively.

$$2Na_2SO_3 + O_2 \longrightarrow 2Na_2SO_4$$

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$$

Hydrazine is found to be an ideal compound for removing dissolved oxygen since the products are water and inert $N_2$ gas. It removes oxygen without increasing the concentration of dissolved salts.

**Mechanical method:** Mechanical de-aeration is another method to degasify is dissolved water.

# Water

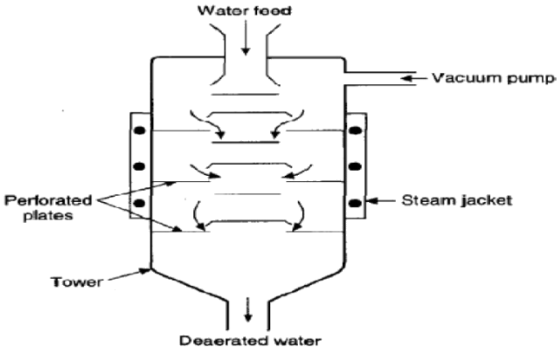


FIGURE 1.2 Mechanical deaeration of water.

In this method, water is allowed to flow down a perforated plate fitted tower. Vacuum is applied to this tower and the sides of the tower are heated. High temperature and low pressure and large exposed area reduce the quantity of dissolved oxygen in water.

**(2) Removal of $CO_2$:** Dissolved $CO_2$ in water produces carbonic acids which is corrosive nature. $CO_2 + H_2O \longrightarrow H_2CO_3$

Carbon dioxide can be removed from water by chemical or mechanical means. In the chemical method $CO_2$ is removed from water by the addition of a calculated quantity of $NH_4OH$

$$2NH_4OH + CO_2 \longrightarrow (NH_4)_2CO_3 + H_2O$$

**(3) Removal of Acids:** Acids produced from salts dissolved in water are also mainly responsible for corrosion of boilers. Certain salts like $MgCI_2$ and $CaCl_2$ on hydrolysis at higher temperatures produce hydrochloric acid which corrodes the boiler.

$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2HCl$$

The liberated acid can produce rust in the following way.

$$Fe + 2HCI \longrightarrow FeCl_2 + H_2$$

$$FeCl_2 + 2H_2O \longrightarrow Fe(OH)_2 + 2HCI$$

$$4Fe(OH)_2 + O_2 + 2H_20 \longrightarrow 2[Fe_2O_3 \cdot 3H_2O] \text{ (rust)}$$

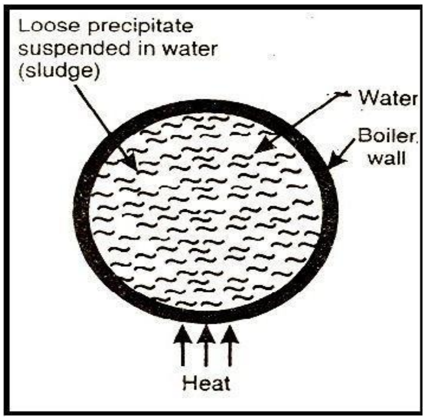
The presence of a small amount of $MgCl_2$ can cause a amount extent of corrosion. Corrosion by acids can be avoided by (1) remove $MgCl_2$from water (2) adding corrosion inhibitors, **sodium silicates, sodium phosphate.**

(4) **Scales and sludge formation:**

In industries, boilers are continuously used for stream generation. When water is continuously converted into steam in boilers, the concentration of dissolved salts in water increases progressively .When the concentration of salts reaches to their saturation point, they are thrown out in the form of precipitation on the inner walls of the boilers. The least soluble one gets precipitate first.

# Water

**Sludge:** A loose, soft and slimy precipitate formed within the boiler is called **slude**. Sludes can be formed by substances which have greater solubility in hot water and less solubility in cold water. Salts like $MgCO_3$, $MgCl_2$, $MgSO_4$ and $CaCl_2$ etc are responsible for slude formation in boilers



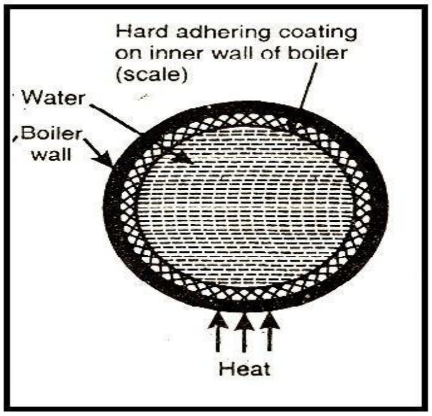
**Disadvantages of sludge formation :**

(1) Sludges are poor conductor of heat, so they tend to waste a portion of heat generated.
(2) If sludges are formed along with scales, then former gets entrapped in the lather and both get deposited as scales.
(3) Excessive sludge formation disturbs the working of the boiler. It settles in the regions of poor water circulation in pipes.

**Prevention of sludge formation:**

(1) By using soft water which is free from salts like $MgCO_3$, $MgCl_2$, $CaCl_2$ and $MgSO_4$ can prevent sludge formation.
(2) By frequently blow – down operation.

**Scale:** On the other hand, if the precipitate is hard and sticky and forms adherent coating on the inner walls of the boiler, it is called **scale**. Scales are formed by substance like Ca $(HCO_3)_2$, $CaSO_4$ & Mg $(OH)_2$.



Scales may be formed inside the boiler due to:

**(1) Decomposition of calcium bicarbonate**

$$Ca(HCO_3)_2 \longrightarrow \underset{\text{Scale}}{CaCO_3} \downarrow + H_2O + CO_2$$

However scale composed chiefly of calcium carbonate is soft and is the main cause of scale formation in low – pressure boilers but in high pressure boilers, $CaCO_3$ is soluble

$$CaCO_3 + H_2O \longrightarrow \underset{\text{Soluble}}{Ca(OH)_2} + CO_2$$

**(ii) Deposition of calcium sulphate :**

The solubility of $CaSO_4$ in water decreases with rise of temperature. Thus, solubility of $CaSO_4$ is 3200 ppm at $15^0C$ and it reduce to 55 ppm at $30^0C$ and 27 ppm at $32^0C$. In other words, $CaSO_4$ is soluble in cold water, but almost completely insoluble in super heated water. Consequently, $CaSO_4$ gets precipitated as hard scale on the boiler. This is the main cause of scales in high – pressure boilers.

**(iii) Hydrolysis of Magnesium salts.**

Dissolved Mg salts undergo hydrolysis forming magnesium hydroxide precipitate, which forms a soft type of scale.

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

(iv) **Presence of Silica ($SiO_2$)**

Silica present in small quantities, deposits as calcium silicate ($CaSiO_3$) and / or Magnesium silicate ($MgSiO_3$), these deposits stick very firmly on the inner side of the boiler surface and are very difficult to remove. One important source of silica in water is the sand filter.

**Disadvantage of scale formation**

**(i) Wastage of Fuel:** Scales have a poor thermal conductivity so the rate of heat transfer from boiler to inside water is greatly reduced. In order to provide a steady supply of heat to water excessive or over – heating is done and this causes increase in fuel consumption.

**(ii) Lowering of boiler safety:** Due to scale formation over heating of boilers is done in order to maintain a steady supply of steam. It makes the boiler material softer and weaker. This causes distortion of boiler tube and also makes the boiler unsafe to bear the pressure of the steam especially in high pressure boilers.

**(iii) Decrease in efficiency:** Deposition of scale in the valves and condensers of the boiler, choke them partially. This results in decrease in efficiency of the boiler.

(iv) **Danger of explosion**: When thick scale cracks due to uneven expansion, the water comes suddenly in contact with over heat portion and large amount of steam is formed instantaneously. This results in development of sudden high pressure which may cause explosion of the boiler.

**Prevention of sludge formation:** Scales can be removed by mechanical and chemical methods. (1) Mechanical methods: They can be removed with a scraper (or) a piece of wood (or) wire brush. They can also be removed by blow down.

(2) Chemical methods: If scales are hard and adhering, they can be removed by dissolving in chemicals.

$CaCO_3$ scales are dissolved in 5-10% HCl

CaSO4 complex is highly soluble in adding EDTA.

# Water

## SOFTENING OF WATER

To minimize boiler troubles, the water must be perfectly soft. So the process of removing the hardness causing salts from water called softening of water. There are two methods are available for softening of water.

1) Internal methods
2) External methods

(1) **<u>Internal treatment methods</u>**: In this method raw water is treated inside the boiler and addition of suitable chemicals to reduce scale and sludges formation. Some important internal treatments are (a) Collodial conditioning (b) Phosphate conditioning (c) Calgon conditioning (d) Carbonate conditioning.

(a) The addition of colloidal substances, like Kerosene, tannin, agar-agar added to low pressure boilers. These substances get adsorbed over the scale forming precipitates and yield non-sticky, loose deposits, which can be easily removed by blow down.

(b) Phosphate conditioning is generally to high pressure boilers. When Sodium phosphate is added to boiler water, it react with Mg and Ca salts forming soft sludges of $Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$ .

$$\mathbf{3CaCl_2 + 2\,Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 6NaCl}$$

$$\mathbf{3MgCl_2 + 2\,Na_3PO_4 \longrightarrow Mg_3(PO_4)_2 + 6NaCl}$$

Sodium phosphate is used when the alkalinity of boiler water PH 9.5-10.5. If the alkalinity of boiler water is too high, $NaH_2PO_4$ (dihydrogen phosphate) is used.

(c) Sodium hexametaphosphate is called CALGON ($Na_2[Na_4(PO_3)_6]$ (or) $(NaPO_3)_6$. It reacts with scale forming $CaSO_4$ and forms a water soluble compound.

$$\mathbf{Na_2\,[Na_4\,(PO_3)_6] \longrightarrow 2Na+ + [Na_4P_6O_{18}]^{-2}}$$

$$\mathbf{2CaSO_4 + [\,Na_4P_6O_{18}]^{-2} \longrightarrow [Ca_2P_6O_{18}]^{-2} + 2Na_2SO_4}$$

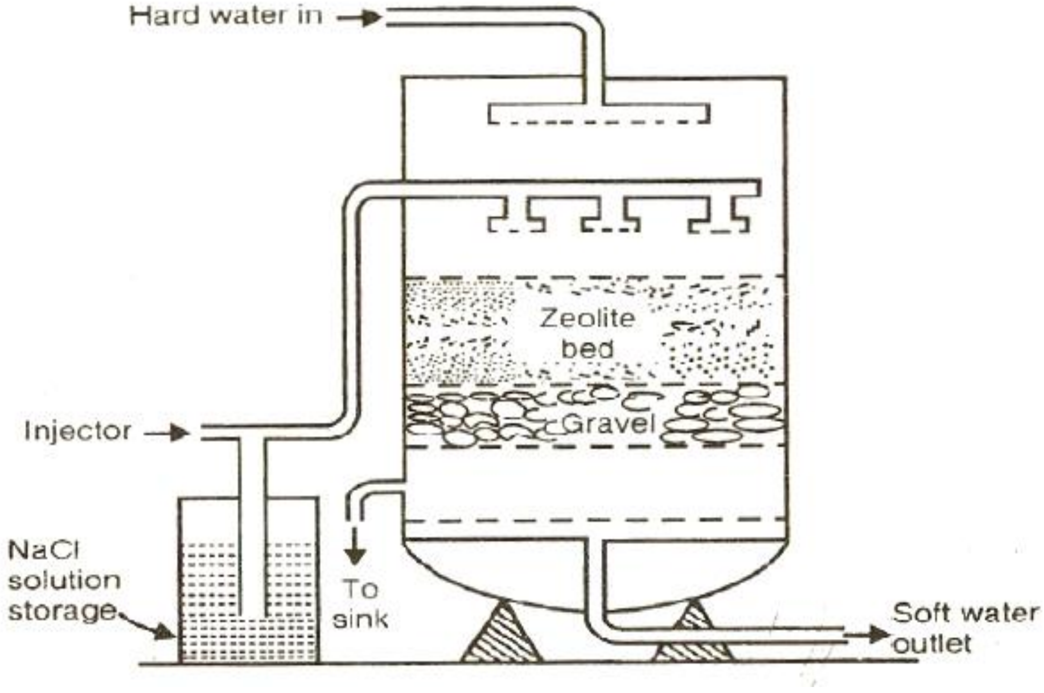
(d) The hard and strong bind scales formed due to $CaSO_4$ are avoided by the addition of $Na_2CO_3$ to boiler water. The $CaSO_4$ is converted to $CaCO_3$, which is loose sludge and it can be removed by blow down operation.

$$\mathbf{CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3 + Na_2SO_4}$$

**(2)** **<u>External treatment methods:</u>** The treatment given to water for the removal of hardness causing salts before into the boiler is called External treatment. Three External methods are: **(a)** Zeolite process (or) Permutit process **(b)** Ion exchange process (or) Deionisation (or) Demineralisation **(c)** Lime-soda process.

# Water

## (a) Zeolite process (or) Permutit process



The chemical composition of Zeolites is hydrated aluminium silicate, represented as $Na_2O$, $Al_2O_3$ $xSiO_2$ y $H_2O$ where x=2-10 and y=2-6. It can be represented as Sodium Zeolite ($Na_2Ze$). Zeolites are capable of exchange reversible its sodium ion for hardness causing $Ca^{+2}$ and $Mg^{+2}$ in water. Hence Zeolites are cation exchangers.

Zeolites are mainly 2 types:

1. **Natural zeolites** are non-porous, eg. Natrolite- **$Na_2O.Al_2O_3.4SiO_2.2H_2O$**.
2. **Synthetic Zeolites** are porous and possess gel structure. Synthetic Zeolites possess higher exchange capacity.

**PROCESS:** The hard water is passed through a Zeolite bed fixed in a cylinder at a specific rate. The hardness causing ions $Ca^{+2}$ and $Mg^{+2}$ are retained by the Zeolite as CaZe and MgZe, respectively.

$$Na_2Ze + Ca(HCO_3)_2 \longrightarrow CaZe + 2NaHCO_3$$
$$Na_2Ze + Mg(HCO_3)_2 \longrightarrow MgZe + 2NaHCO_3$$
$$Na_2Ze + MgCl_2 \longrightarrow MgZe + 2NaCl$$
$$Na_2Ze + CaCl_2 \longrightarrow CaZe + 2NaCl$$
$$Na_2Ze + MgSO_4 \longrightarrow MgZe + Na_2SO_4$$
$$Na_2Ze + CaSO_4 \longrightarrow CaZe + Na_2SO_4$$

**REGENERATION:** After some time the Zeolite bed is completely converted to Calcium and Magnesium Zeolites and no purification of raw water takes place. i.e., the

Zeolite bed got exhausted. At this stage the purification of hard water is stopped and the Zeolite bed is regenerated by treating with 10% brine (NaCl) solution.

$$\mathbf{CaZe + 2\,NaCl \longrightarrow Na_2Ze + CaCl_2}$$
$$\mathbf{MgZe + 2\,NaCl \longrightarrow Na_2Ze + MgCl_2}$$

## Advantages:

**a**. It removes the hardness completely and water of about 10 ppm hardness is produced.
**b**. The equipment used is compact, occupying a small space.
**c**. No impurities are precipitated, so there is no danger of sludge formation in the treated water at a later stage.
**d**. The process automatically adjusts itself for variation in hardness of incoming water.
**e**. It is quite clean
**f**. It requires less time for softening.
**g**. It requires less skill for maintenance as well as operation.

## Disadvantages:

**a.** The treated water contains more sodium salts than in lime-soda process.
**b**. Hard water containing acids destroys the Zeolite bed.
**c**. If suspended particles (turbidity) are present the pores of the Zeolites are blocked and softening is not possible.
**d**. If raw water contains large quantities of coloured ions such as Mn+2 and Fe+2 they must be removed first, because these ions produce magnesium and Ferrous zeolites, which cannot be regenerated.

## (b) Ion exchange process (or) Deionisation (or) Demineralisation

Ion exchange process also known as demineralization or de-ionization process. Ion-Exchange resins are insoluble and cross linked long chain organic polymers with a micro porous structure, and the "functional Groups" attached to the chains are responsible for the ion-exchanging properties.

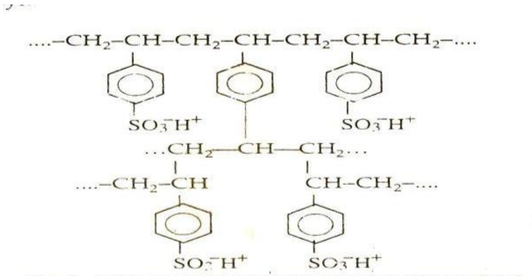
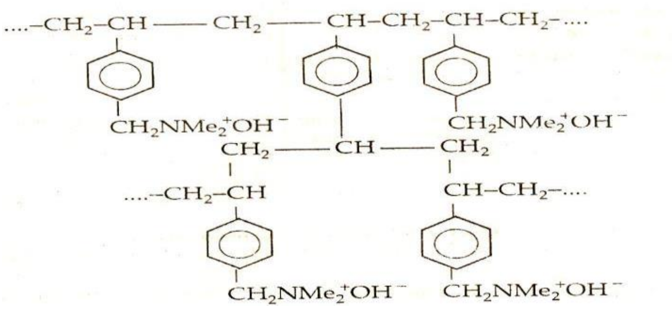


Fig 6. Acidic or cation exchange resin (sulphonate form).



**Ion exchangers are two types**

1. Cation Exchange Resins
2. Anion Exchange Resins

1 **Cation Exchange Resins:** Cation exchangers are capable of exchanging their $H^+$ ions

replaced by cations such as $Mg^{+2}/Ca^{+2}$. The general formula of cation exchangers are RH. These are made by copolymers of **styrene** and **divinyl benzene** containing the functional groups **COOH** (or) **–$SO_3$H**.

2. **Anion Exchange Resins:** Anion exchange resins are **styrene-divinyl benzene** copolymers which contain **amino**, **quaternary ammonium group** an internal part of the resins, which exchange $OH^-$ ion in the dissolved salts. The anion exchangers are represented by the formula R'OH.

**Softening Process:** The hard water is first passed through cation exchange resins, which remove $Ca^{+2}$ and $Mg^{+2}$ ions in the following way.

$$2RH + Ca(HCO_3)_2 \longrightarrow R_2Ca + 2H_2CO_3$$
$$2RH + Mg(HCO_3)_2 \longrightarrow R_2Mg + 2H_2CO_3$$

$$2RH + MgCl_2 \longrightarrow R_2Mg + 2HCl$$
$$2RH + CaCl_2 \longrightarrow R_2Ca + 2HCl$$

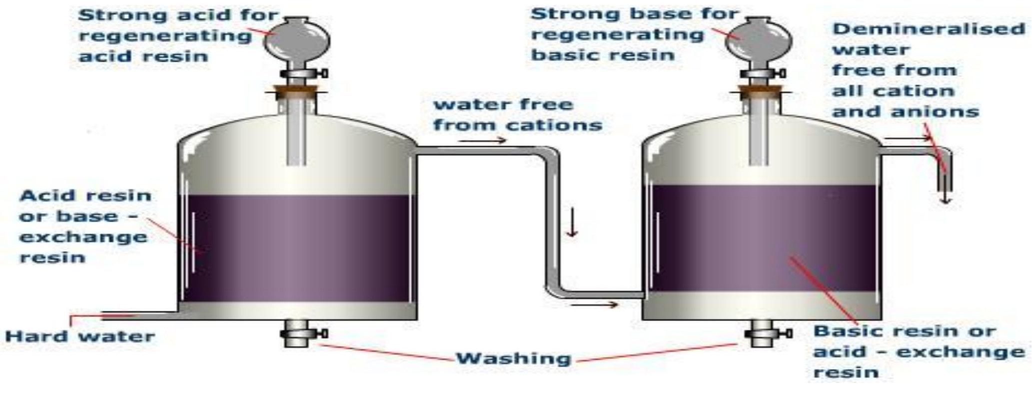
$$2RH + MgSO4 \longrightarrow R_2Mg + H_2SO_4$$
$$2RH + CaSO4 \longrightarrow R_2Ca + H_2SO_4$$

$$2RH + Mg(NO_3)_2 \longrightarrow R_2Mg + 2HNO_3$$
$$2RH + Ca(NO3)_2 \longrightarrow R_2Ca + 2HNO_3$$

The $Mg^{+2}$ and $Ca^{+2}$ are retained by the cation exchangers as CaR and MgR releasing H+ into water. The water coming out of the resin is highly acidic. Then the water is passed through the anion exchange resin, the acids present in water are removed by the exchanger releasing $OH^-$ into water. The $H^+$ and $OH^-$ are combined and produce $H_2O$.

$$R'OH + HCl \longrightarrow R'Cl + H_20$$
$$2\ R'OH + H_2SO_4 \longrightarrow R'_2SO_4 + 2H_20$$
$$2\ R'OH + H_2CO_3 \longrightarrow R'HCO_3 + H_20$$
$$2\ R'OH + HNO_3 \longrightarrow R'NO_3 + H_20$$

Thus the water coming out from exchangers is free from all ions known as deionized (or) demineralized water.



**Regeneration:** After deionization the cation and anion exchangers will be exhausted. Regeneration of cation exchanger is carried out by passing dil. HCl (or) $H_2SO_4$.

$$R_2Ca + 2HCl \longrightarrow 2RH + CaCl_2 \text{ (washings)}$$

$$R_2Ca + H_2SO_4 \longrightarrow 2RH + MgSO_4 \text{ (washings)}$$

Similarly the anion exchanger is treated with dil.NaOH solution.

$$R'Cl + NaOH \longrightarrow R'OH + NaCl \text{ (washings)}$$
$$R_2'SO4 + NaOH \longrightarrow 2R'OH + Na_2SO_4 \text{ (washings)}$$
$$R'NO_3 + NaOH \longrightarrow R'OH + NaNO_3 \text{ (washings)}$$

The washings are discarded into sink. The regenerated ion-exchanger is used for softening.
**Advantages:** (1) Highly acidic (or) alkaline water samples can be purified by this process. (2) The hardness possessed by the deionized water is 2 ppm.
**Disadvantages:** (1) The resins are expensive, the cost of purification is high. (2) The raw water should contain turbidity below 10 ppm, otherwise pores in the resin will be blocked and output of the process is reduced.

## (C) Lime (L)-Soda (S) Process

The basic principle of this process is to chemically convert all the soluble hardness causing impurities into insoluble precipitates which may be removed by settling and filtration.

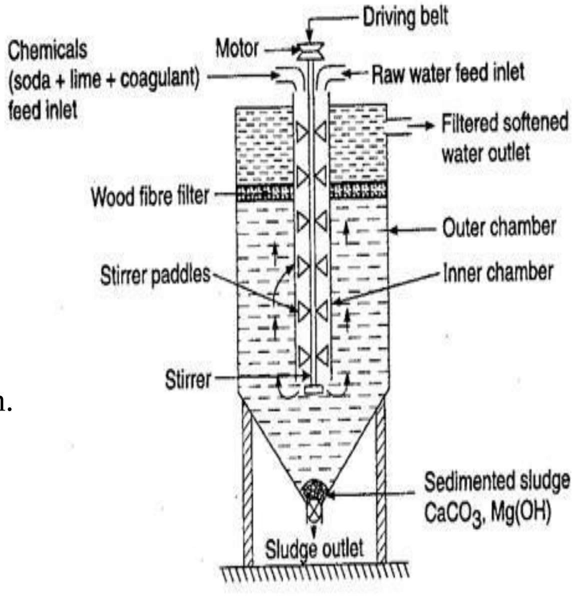
In this process Lime [$Ca(OH)_2$] and Soda [$Na_2CO_3$] are the reagents used to precipitate the dissolved salts of $Ca^{+2}$ and $Mg^{+2}$ as $CaCO_3$ and $Mg(OH)_2$. The precipitates are filtered off.
Lime soda process mainly two types, they are

1. Cold Lime-soda process
2. Hot Lime-soda process.

### 1. Cold Lime-soda process

In this method, water is treated with lime [$Ca(OH)_2$] and Soda [$Na_2CO_3$] at room temperature. Precipitate and filtration cannot be done easily. Hence small amount of alum is added. Sodium aluminate ($NaAlO_2$) can act as a coagulant and help to removal of silica and oil.

Raw water along with calculated amount of chemicals (Lime+ Soda+ Coagulant) are fed from the top into the Chamber and sludge setting at the bottom is drawn off. The water sample contains residual hardness 50-60 ppm.



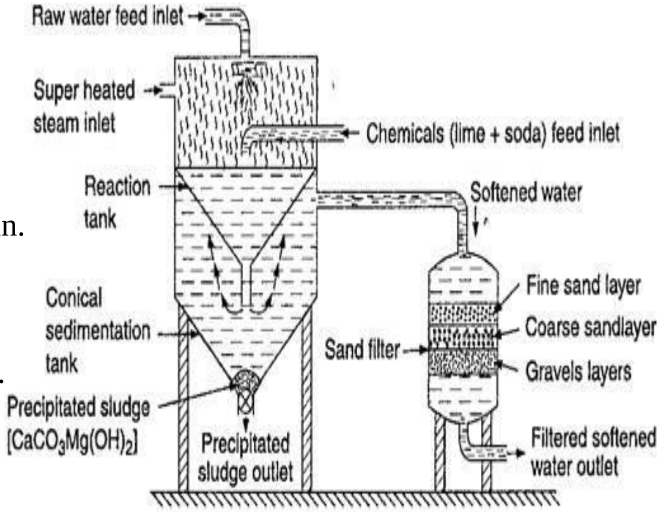
# Water

## 2. Hot Lime-soda process

In this process the raw water is treated with Softening chemicals at 80-150$^{0}$C. At higher Precipitation takes place and coagulant is not Required.

Advantages of hot L-S process:

1. Precipitation is rapid and completes in 15 min.
2. No coagulant is required
3. Bacteria are killed in hot L-S process.
4. The process is economical
5. The residual hardness of water is 15-30 ppm.



Lime reacts with temporary hardness causing salts, magnesium permanent hardness, $CO_2$, acids, bicarbonates, which could be removed by soda.

**Amount of Lime required for softening:**

74/100 [temporary $Ca^{+2}$ hardness+ (2 x temporary $Mg^{+2}$) + permanent $Mg^{+2}$ hardness+ $CO_2$+ ½ HCl+$H_2SO_4$+ ½ $NaHCO_3$+1/2$KHCO_3$+$FeSO_4$ + (3 x $Al_2(SO_4)_3$-1/2 $NaAlO_2$ hardness] all the hardness in terms of CaCO3 equivalent.

**Amount of soda required for softening:**

106/100 [permanent $Ca^{+2}$ hardness + permanent $Mg^{+2}$ hardness+ ½ HCl+$H_2SO_4$- ½ $NaHCO_3$- 1/2$KHCO_3$+ (3 x $Al_2(SO_4)_3$ + $FeSO_4$ hardness] all the hardness in terms of CaCO3 equivalent.

In this process, calculated amount of lime and soda is added to the hard water. Lime

(a) Removal of Dissolved $CO_2$ and $H_2S$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 \downarrow + H_2O$$

(b) Neutralization of free mineral acids

$$Ca(OH)_2 + 2HCl \longrightarrow CaCl_2 + 2H_2O$$

$$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$$

(c) Removal of temporary hardness

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

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

(d) Removal of permanent magnesium hardness

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

$Ca(OH)_2 + MgSO_4 \longrightarrow Mg\ (OH)_2 \downarrow + CaSO_4$

$Ca(OH)_2 + Mg(NO_3)_2 \longrightarrow Mg\ (OH)_2 \downarrow + Ca(NO_3)_2$

(e) Removal of dissolved Iron and Aluminium salts.

$Ca(OH)_2 + FeSO_4 \longrightarrow \underset{\text{Unstable}}{Fe(OH)_2} + CaSO_4$

$2Fe(OH)_2 + H_20 + O_2 \longrightarrow 2Fe(OH)_3$

(f) Removal of bicarbonate salts.

$2NaHCO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + Na_2CO_3 + 2H_2O$

$2KHCO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + K_2CO_3 + 2H_2O$

$NaHCO_3$ present in hard water reacts with soda and produce more sodium carbonate.

(f) Reactions of Soda ($Na_2CO_3$). Soda Remove all the $Ca^{2+}$ permanent hardness

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

$Na_2CO_3 + CaSO_4 \longrightarrow CaCO_3 \downarrow + Na_2SO_4$

$Al_2\ (SO_4)_3 + 3Ca(OH)_2 \longrightarrow 2Al(OH)_3 + 3CaSO_4 + H_2O$

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

$2NaOH + CaCl2 \longrightarrow Ca(OH)_2 + 2NaCl$

$2NaOH = Ca(OH)_2$

NaOH produced reacts with hardness causing salts and produces lime. Hence, its hardness must be subtracted from lime required.

**Advantages of lime-soda process:**

1. It is very economical
2. If this process is combined with sedimentation with coagulation, lesser amounts of coagulants shall be needed.
3. The process increases the pH value of the treated-water; thereby corrosion of the distribution pipes is reduced.
4. Besides the removal of harness, the quantity of minerals in the water is reduced.
5. To certain extent, iron and manganese are also removed from the water.
6. Due to alkaline nature of treated-water, amount of pathogenic bacteria in water is considerably reduced.

**Dis-advantages of lime-soda process:**

1. For efficient and economical softening, careful operation and skilled supervision is required.
2. Disposal of large amounts of sludge or insoluble precipitates poses a problem. However, the sludge may be disposed off in raising low-lying areas of the city.

# Water

| Sl.No | Cold L-S Process | Hot L – S Process |
|---|---|---|
| 1 | It done at room temp ($25^0$ – $30^0$C) | It is done at elevated temp ($90^0$ – $100^0$C) |
| 2 | It is a slow process | It is a rapid process |
| 3 | The use of coagulants is must | Coagulants not needed |
| 4 | Filtration is not easy | Filtration is easy as the viscosity of water becomes low at elevated temperature |
| 5 | Softened water has residual hardness around 60ppm | Softened water has residual hardness of 15-20 ppm |
| 6 | Dissolved gases are not removed | Dissolved gases such as $CO_2$ are removed to some extent |

| LIME-SODA PROCESS | ION-EXCHANGE/RESIN |
|---|---|
| Water treatment plant occupies more area or place. | Water treatment plant occupies less area. |
| Water after treatment has lesser dissolved solids. | Water after treatment free from dissolved solids |
| This method of water treatment plants is not much | This method of water treatment plants is more |
| expensive and material used is cheap. | expensive and material used for softening is expensive. |
| Operation expenses are higher | Operation expenses are higher |
| The cost incurred on softening of water is high. | The cost incurred on softening of water is high |
| It cannot operate in under pressure. | It can even operate in under pressure. |
| It can be used for treating acidic water also. | It can be used for treating acidic and alkaline water also. |
| There is a problem of settling, coagulation and | There is problem of turbidity. |
| removal of sludge. | |
| It is not possible. | This method can be made automatic. |
| In order to meet the changing hardness of incoming | Control test comprises only in checking the |
| water, frequent control and adjustment of reagents is needed. | hardness of treated-water. |
| Residual hardness is low about 15 to 50 ppm | Residual hardness is low about 0 to 2 ppm |
| It is not good for boilers | It is very good for treating water for use in high pressure boilers. |
| Skilled persons required | It required less skill for maintenance as well as operation |

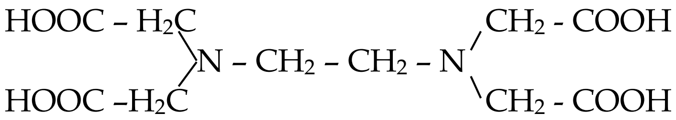
# Water

## Estimation of temporary & permanent hardness of water by EDTA method:

The hardness of water indicates the quality in terms of Calcium and Magnesium expressed in terms of $CaCO_3$. The analysis is done by complexometric titration using standard EDTA and EBT as an indicator.

**Principle:** In this complex metric Titration, the water sample is titrated with standard solution of Di sodium salt of EDTA using EBT indicator.

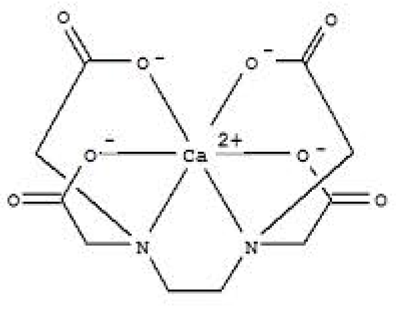
This method give more accurate results than the soap solution method.

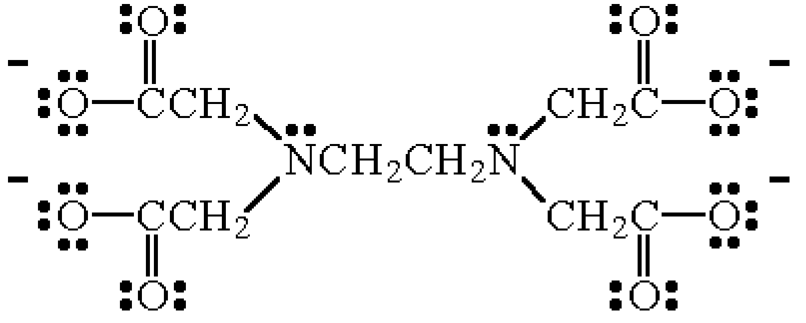


$$\begin{array}{lcl} HOOC-H_2C & & CH_2-COOH \\ & N-CH_2-CH_2-N & \\ HOOC-H_2C & & CH_2-COOH \end{array}$$

Structure of EDTA

Ethylene diamine tetra acetic acid (EDTA) forms complexes with $Ca^{2+}$ and $Mg^{2+}$ as well as with many other metal cations, in aqueous solution. These complexes have the general formula given below





**Reactions involved**: EBT indicator when added to hard water at pH = 10, forms weak complexes with calcium and magnesium present in hard water. It results in the formation of Ca-EBT or Mg-EBT complexes which is wine-red, these are unstable.

# Water

$(Ca^{2+} / Mg^{2+}) + EBT \rightarrow [Ca - EBT] / [Mg - EBT]$
blue wine-red color complex

During titration with EDTA, EDTA extracts metal ions from the above complex to give a colorless and stable complex releasing the free indicator (blue). The color changes from wine-red to blue at the endpoint.

$[Ca - EBT] / [Mg - EBT] + EDTA \rightarrow [Ca - EDTA] / [Mg - EDTA] + EBT$
Wine-red complex colorless complex blue

Various steps involved in this method are…

1. **Preparation of standard hard water:** Dissolve 1g of pure, dry $CaCO_3$ in minimum quantity of dil. HCl and then evaporate the solution to dryness on a water bath. Dissolve the residue in distilled water to make 1 Litre solution. Each mL of this solution thus contains 1mg of $CaCO_3$ equivalent hardness.
 1 mL hard water solution = 1mg of $CaCO_3$ equivalent hardness.

2. **Standardization of EDTA solution:** Rinse and fill the burette with EDTA solution. Pipette out 50 mL of standard hard water in a conical flask. Add 10-15 mL of buffer solution and 4 to5 drops indicator. Titrate with EDTA solution till wine-red colour changes to clear blue. Let volume used by V1 mL.
3. **Titration of Unknown Hard water:** Rinse and fill the burette with EDTA solution. Pipette out 50 mL of unknown sample hard water in a conical flask. Add 10-15 mL of buffer solution and 4 to 5 drops indicator. Titrate with EDTA solution till wine-red colour changes to clear blue. Let volume used be V2 mL.
4. **Titration of Permanent hardness:** Take 100 mL of the water sample in a large beaker. Boil it. Till the volume is reduced to about 50 mL, filter it, makeup the volume to 100 mL with distilled water. Then, titrate 50 mL of boiled water sample just as in Step (2). Let volume used by V3 mL.

**CALCULATION:**

Total hardness of water = $\frac{1000 \times V_2}{V1}$ ppm

Permanent hardness = $\frac{1000 \times V_3}{V_1}$ ppm

Temporary hardness = [Total hardness – Permanent hardness]

Temporary hardness = $\frac{1000 \times (V_2 - V_3)}{V1}$ ppm

# Water

**Impurities in water**: The impurities present in water may be broadly classified as follows. [1] ***Dissolved impurities*****:** The dissolved impurities are mainly the carbonates, bicarbonates, chlorides and sulphates of calcium, magnesium, iron, sodium and potassium. The presence of these salts imparts hardness to water. The dissolved impurities also include dissolved gases like oxygen and carbon

dioxide. [2] ***Suspended impurities*****:** The following are the types of suspended impurities: (a) Inorganic: Clay and sand (b) Organic: Oil globules, vegetable and animal matter. The above suspended impurities impart turbidity, colour and odour to water.

[3] ***Colloidal impurities*****:** They are finely-divided silica and clay, organic waste products, complex protein amino acids, etc.

[4] ***Microorganisms*****:** They are algae, fungi and bacteria

**Potable Water (water for domestic supply): "**Water free from contaminants or water that is safe for human consumption is called potable water". Municipalities have to supply potable water, i.e., It is a water of sufficiently high quality that it can be consumed or used without risk of immediate or long term harm. The following are *characteristics* of *potable water.*

1) Water should be clear, colorless and odorless.
2) Free from pathogenic bacteria and gases like $H_2S$
3) Hardness of water must be 125 ppm.
4) PH at 7-8
5) Terbidity in drinking water should not exceed 25 ppm
6) Free from heavy metals like Pb, As, Cr and Mn.

**Desalination:** The process of removal of dissolved salts (NaCl, KCl) present in water is known as desalination. Water is divided into 3 categories on the basis of salinity.

**(1)** Sea water: The salinity is greater than 35,000 mg/l

**(2)** Brakish water: The salinity is in the range of 1000 -35,000 mg/l.

**(3)** Fresh water: The salinity of water is less than 1000 mg/l.

Brakish water and sea water are not fit for drinking as well as industrial purposes. They can be subjected to desalination to make them suitable for drinking. Important

# Water

desalinations methods are (1) Reverse Osmosis (2) Electrodialysis (3) Distillation

Various stages involved in the purification of water for domestic purposes. Sources of water → Screening → Aeration → Sedimentation → Filtration → Sterilization (or) Disinfection → Storage and Distribution

### Screening

Screening is the process of removing floating materials like wood pieces and leaves from water. Raw water is allowed to pass through a screen having a large number of holes which removes the small and large floating matter.

### ***Sedimentation***

Sedimentation is the process of removing suspended impurities by allowing the water to stand undisturbed for 2-6 hours in big tanks. Due to force of gravity, most of the suspended particles settled down at the bottom and they are removed. Sedimentation removes only 70-75% of the suspended matter.

### Coagulation

Finely-divided silica, clay, etc. do not settle down easily and hence cannot be removed by sedimentation. Most of these are in colloidal form and are negatively charged and hence do not coalesce because of mutual repulsion. Such impurities are removed by coagulation method. Here, certain chemicals like alum and $Al_2(SO_4)_3$ are added to water. When $Al_2(SO_4)_3$ is added to water, it hydrolyzes to form a gelatinous precipitate of $AI(OH)_3$' The gelatinous precipitate of $Al(OH)_3$ settles to the bottom and can be removed easily.

### Filtration

For removing bacteria, colour, taste, odour, fine suspended particles, etc. and to produce clear water, filtration is used. In this process, water is passed through beds of fine sand, coarse sand and other granular material. The porous material used is the filtering medium and the equipment used for filtration is known as filter, e.g. slow sand filter.

A typical slow sand filter is shown in Figure 1.5. It consists of a tank containing thick beds of fine sand (at the top), coarse sand, fine gravel and coarse gravel (at the bottom). When the water passes through the filtering medium, it flows through the various beds slowly due to gravity. The rate of filtration slowly decreases due to the blockage of impurities in the pores of the sand bed. When the rate of flow becomes very slow, filtration is stopped and the bed is cleaned by scraping of a smaller layer of the sand bed (top layer) and replacing it with the clean sand. Bacteria are partly removed by this filtration process.

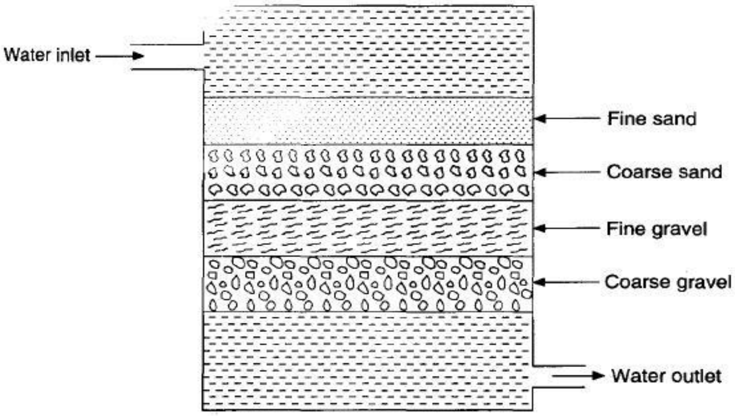


FIGURE 1.5 Slow sand filter.

**Disinfection /Sterilization:**

**Disinfection**: The process of destroying/killing the disease producing Bacteria, microorganisms from the water and making it safe for use, is called disinfection.

**Disinfectants:** The chemicals or substances which are added to water for killing the Bacteria. The disinfection of water can be carried out by following methods:

A) **Boiling**: Water for 10-15 minutes, all the disease-producing bacteria are killed and water becomes safe for use. This method is not possible for the municipal supply of water.

B) **Ozone:** Ozone is a powerful disinfectant and is readily absorbed by water. Ozone is highly unstable and decomposes to give **nascent oxygen** which is capable of destroying the bacteria. $O_3 \longrightarrow O_2 + [O]$. This process is relatively expensive and ozone is unstable and cannot be stored for long time.

C) **UV**: UV light is used as a disinfectant for swimming pool water. No chemical are used and it is safe for skin. In this process, water is exposed to UV rays, which are generated from an electric mercury vapor lamp.

D) **Chloramines**: When added chloramine in water, which generates hypochlorous acid, a powerful disinfectant, that kills bacteria.

$$ClNH_2 + H_2O \longrightarrow HOCl + NH_3$$

HOCl inactivates the enzymes of bacteria and kills. Chloramine is useful for disinfection in swimming pools.

E) **Bleaching powder**: Calculated amount of bleaching powder is added to water and allowed to stand for several hours. Bleaching powder contains 80% chlorine.

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

$$Cl_2 + H_2O \longrightarrow HCI + HOCI$$

$$\text{HOCI + Bacteria} \longrightarrow \text{Bacteria are killed}$$

Disadvantages: 1) Bleaching powder introduces $Ca^{+2}$ hardness in water and adds lime residue. 2) Excess of it gives bad smell and bad taste. 3) Excess chlorine is irritating to mucous membrane.

F) **Chlorine:** Chlorination is the process of purifying the drinking water by producing a powerful Germicide like Hypochlorous acid. When this Chlorine is mixed with water it produces Hypochlorous acid which kills the germs present in water.

$$H_2O + Cl_2 \rightarrow HOCl + HCl$$
$$\text{Bacteria} + HOCl \rightarrow \text{Bacteria are killed}$$

Chlorine is basic (means pH value is more than 7) disinfectant and is much effective over the germs. Hence Chlorine is widely used all over the world as a powerful disinfectant. Chlorinator is an apparatus, which is used to purify the water by chlorination process.

**Advantages**

1. It is effective and economical
2. It requires very little space for storage
3. It is stable and does not deteriorate on keeping
4. It can be used at low as well as high temperatures
5. It introduces no salt impurities in the treated water.
6. It is the most ideal disinfectant.

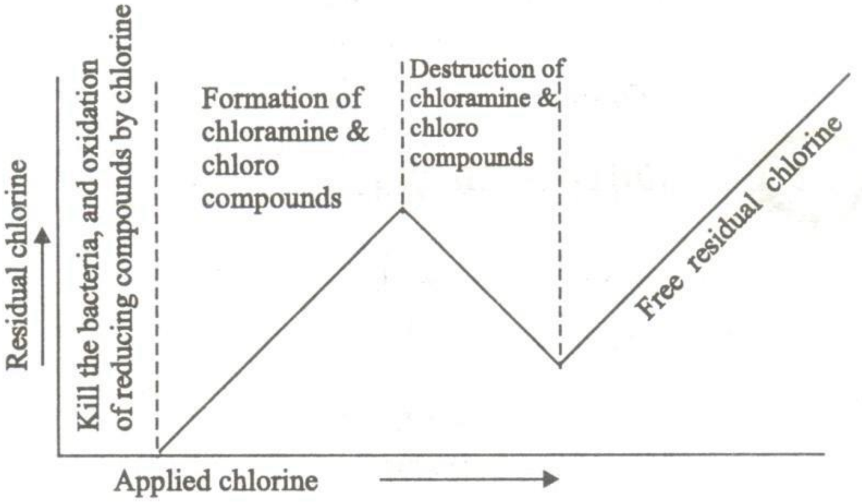
**Disadvantages**

1. Excess chlorine if added, produces unpleasant taste and odour
2. Its excess produces irritation on mucous membrane

**Break-point chlorination (or free-residual chlorination)** involves the addition of sufficient amount of chlorine to oxidize (a) organic matter (b) reducing substances (c) Free ammonia; leaving behind free chlorine which possesses disinfecting action against disease-producing bacteria.

A known volume of sample of water is treated with an increasing amount of chlorine and then analyzed for the remaining chlorine. When a graph is plotted between the amounts of residual chlorine against the added chlorine, a curve is obtained as shown below. The addition of Chlorine at the dip or break is called break point chlorination. This indicates the point at which free chlorine begins to appear and resulting in water free from bad tastes and odor.

# Water



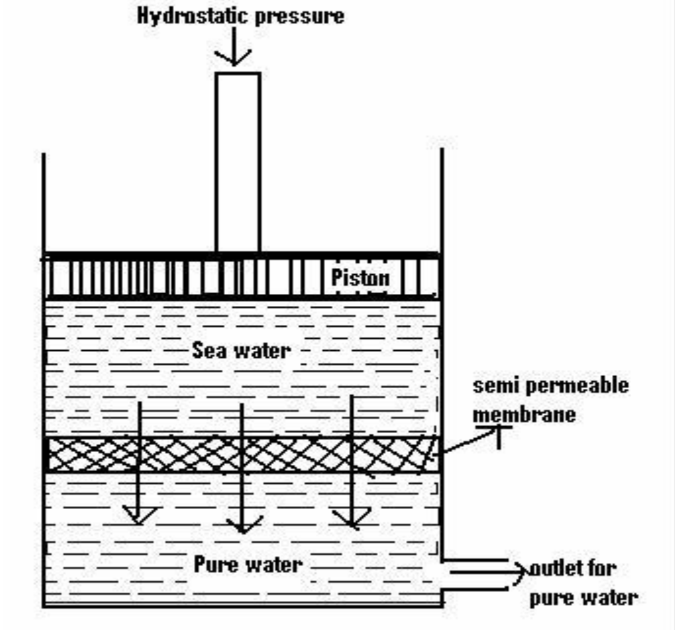
**Desalination:** The process of removing common salt from the water is known as desalination. The water containing dissolved salts with a peculiar salty taste, is called brackish water. Sea water, containing on an average about 3.5% salts, comes under this category. Brackish water is totally unfit for drinking purpose.

Commonly used methods for the desalination of brackish water is:

1. Reverse Osmosis
2. Electrodyalias
3. Distillation

**Reverse Osmosis:** When two solutions of unequal concentrations are separated by a semi permeable membrane, flow of solvent takes place from dilute to concentrated sides, due to osmosis. If, however, a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the solvent flow reverse, ie. Solvent is forced to move from concentrated side to dilute side across the membrane. This is the principle of reverse osmosis. Thus, in reverse osmosis (RO) methods, pure solvent is separated from its contaminants, rather than removing contaminants from the water.

This membrane filtration is also called **'super-filtration' or 'hyper – filtration'**.



Process: in Reverse osmosis process, pressure (15 to 40 kg $cm^{-2}$) is applied to the sea water or impure water to force its pure water out through the semi-permeable membrane, leaving behind the dissolved solids. The principle of reverse osmosis, as applied for treating saline or sea water. The membrane consists of very thin films of cellulose acetate, affixed to either side of a perforated tube. However, mover recently superior membranes made of polymethacrylate and polyamide polymers have come into use.

**Advantages:**

a. Reverse osmosis possesses a distinct advantage of removing ionic as well as non-ionic, colloidal and high molecular weight organic matter.
b. It removes colloidal silica, which is not removed by demineralization.
c. The maintenance cost is almost entirely on the replacement of the semi permeable membrane.
d. The life time of membrane is quite high, about 2 years.
e. The membrane can be replaced within a few minutes, thereby providing nearly uninterrupted water supply.
f. Due to low capital cost, simplicity, low operating cost and high reliability, the reverse osmosis is gaining ground at present for converting sea water into drinking water and for obtaining water for very high pressure boilers.

## Alkalinity of water:

Alkalinity is a measure of the capability of water to absorb $H^+$ ions without significant change of pH. In other words, alkalinity is a measure of the acid buffering capacity of water. The determination of alkalinity of water is necessary for controlling the corrosion, to calculate the amount of lime and soda needed for water softening; in conditioning the boiler feed water, etc. Alkalinity of a sample of water is due to the presence of $OH^-$ (hydroxide ion), $HCO_3^-$ (bicarbonate ion) and $CO_3^{2-}$ (carbonate ion) or the mixture of two ions present in water. The possibility of $OH^-$ and $HCO_3^-$ ions together is not possible since they combine together to form $CO_3^{2-}$ ions.

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

The alkalinity due to different ions can be estimated separately by titration against standard acid solution, using selective indicators like phenolphthalein and methyl orange.

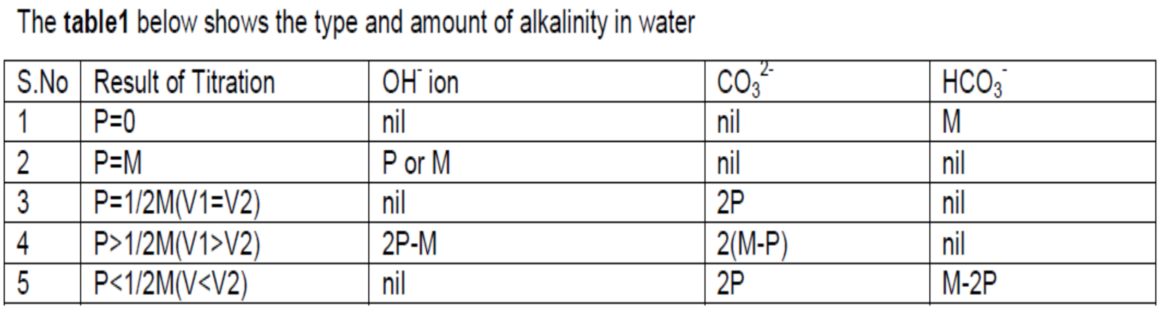
i) $OH^- + H^+ \longrightarrow H_2O$
ii) $CO_3^{2-} + H^+ \longrightarrow HCO_3^-$
iii) $HCO_3^- + H^+ \longrightarrow H_2O + CO_2$

The neutralization reaction up to **phenolphthalein** end point shows the completion of reactions (i) and (ii) ($OH^-$ and $CO_3^{2-}$) and ($CO_3^{2-}$ and $HCO_3^-$) only. The amount of acid used thus corresponds to complete neutralization of $OH^-$ plus half neutralization of $CO_3^{2-}$. This is also called partial alkalinity.

$$P = OH^- + \tfrac{1}{2}\,CO_3^{2-}$$
$$M = OH^- + CO_3^{2-} + HCO_3^-$$

The titration of water sample using methyl **orange** indicator marks the completion of the reactions (i), (ii) and (iii). The amount of acid used after phenolphthalein end point corresponds to one half of normal carbonate and all the bicarbonates. Total amount of acid used represent the total alkalinity due to all ions present in water sample. This is also called total alkalinity.

# Water



The **table1** below shows the type and amount of alkalinity in water

| S.No | Result of Titration | $OH^-$ ion | $CO_3^{2-}$ | $HCO_3^-$ |
|---|---|---|---|---|
| 1 | P=0 | nil | nil | M |
| 2 | P=M | P or M | nil | nil |
| 3 | P=1/2M(V1=V2) | nil | 2P | nil |
| 4 | P>1/2M(V1>V2) | 2P-M | 2(M-P) | nil |
| 5 | P<1/2M(V<V2) | nil | 2P | M-2P |

i) Phenolphthalein alkalinity (P) = 0; that means the volume of acid used till the completion of reaction (i) and (ii) is 0. This can only happen when both $OH^-$ and $CO_3^{2-}$ ions are not present in water. Alkalinity is present due to $HCO_3^-$ ion only which can be determined using methyl orange indicator and called methyl orange alkalinity (M).

ii) P = ½ M; indicates that only $CO_3^{2-}$ ions are present. Using phenolphthalein indicator neutralization reaches up to $HCO_3^-$ but using methyl orange indicator the complete neutralization of $HCO_3^-$ takes place.

iii) P > ½M; implies $OH^-$ ions are also present along with $CO_3^{2-}$ ions. Up to phenolphthalein alkalinity $OH^-$ ions will be neutralized completely, whereas $CO_3^{2-}$ will be neutralized up to $HCO_3^-$ ion. But using methyl orange indicator $HCO_3^-$ will be completely neutralized along with $OH^-$ and $CO_3^{2-}$ .

iv) P < ½ M; indicates that beside $CO_3^{2-}$ ions $HCO_3^-$ ions are also present. The volume of acid required for the neutralization up to phenolphthalein end point correspond half neutralization of $CO_3^{2-}$ (equation ii). Neutralization using methyl orange indicator corresponds to $HCO_3^-$ obtained from $CO_3^{2-}$ and $HCO_3$ – originally present in the water sample.

v) P = M; indicates only $OH^-$ ions are present.

## Specifications for Drinking water: (BIS and WHO standards):

Water is an incredibly important aspect of our daily life. Every day we drink water, cook with water, bath in water and participate in many activities involving water. It is essential for all dimensions of life. The water may contain many harmful constituents, there are no universally recognized and accepted international standard for drinking water.

Many developed and developing countries specify standards to be applied in their own. The physical parameters (temperature and turbidity) of water have significant influence on aquatic life. The chemical parameters (PH, TDS, total alkalinity, total hardness, chlorides, phosphates and nitrates) of water before attempting to study the animals and plants living in it.

**TEMPERATURE:** Temperature measurements are very useful in understanding the trend of physical, chemical and biological activities which are enhanced/ retarded by the variation of temperature. The WHO (1993) did not recommend any definite temperature value for drinking water. A temperature of about 40°C is permissible limit for drinking water (BIS 1991).

# Water

**TURBIDITY:** The acceptable limit of BIS (1991) and recommendation is 10 NTU. The WHO recommendation of turbidity is 5- 25 NTU.

NTU=Nephelometric Turbidity Unit

**PH:** The pH was found ranging between 7.0 and 8.3. pH as such has no adverse effect on health, however a lower value below 4 will produce sour taste; and a higher value above 8.5 an alkaline taste. pH range from 6.5 to 7.5 is most favorable for production in a water body. The WHO and BIS recommendation of pH is 6.5- 8.5. In the current study the pH range is a safe for fish production and drinking water.

**Total dissolved salts (TDS):** The BIS (1991) has set desirable limit of TDS value to be 500 mg/l in potable water. However the permissible limit is 2000 mg/l in the absence of any alternative source in water. According to WHO (1993), the standard permissible limit for TDS is 1000 mg/l. Water at a TDS level of above 500 mg/l is unsuitable for flora and tastes unpleasant to drink.

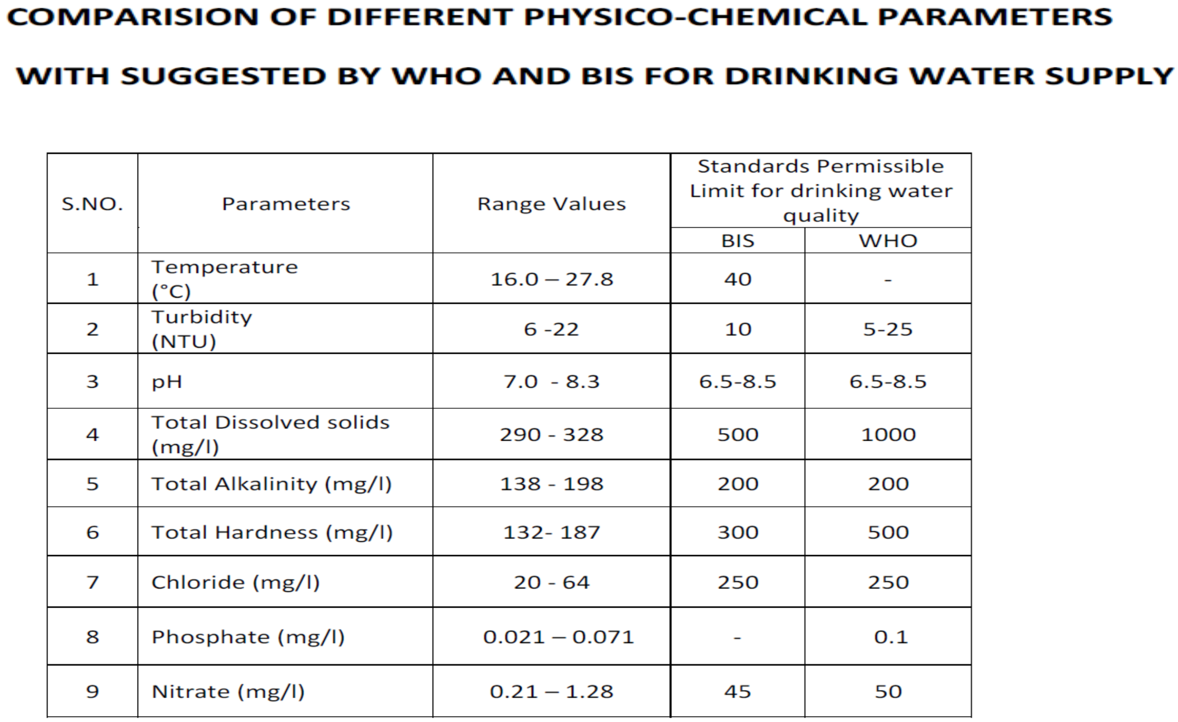
**Alkalinity:** BIS has set the desirable limit of alkalinity for drinking water to be 200 mg/l and the permissible value has been prescribed to be 600 mg/l in the absence of any alternative source; however according to WHO (1993) it is to be 200 mg/l.

**Total hardness:** The standard permissible limit of total hardness value of drinking water set by BIS (1991) is 300 mg/l. According to WHO (1993) its value is 500 mg/l.

**Chlorides:** BIS (1991) have set a desirable limit of chloride in drinking water to be 250 mg/l and permissible value has been prescribed to be 1000 mg/l in the absence of any alternative source. Whereas according to WHO (1993), it is 250 mg/l.

**Phosphates:** There is no BIS standard permissible limit for phosphate for drinking water, while WHO (1993) has fixed it to be 0.1 mg/l. If level becomes too high, plant growth can accelerate resulting in the dense growth of algae and plants in the water body.

**Nitrate:** WHO (1993) has fixed the value of nitrate in drinking water to be 50 mg/l and BIS (1991) has set a desirable limit of nitrate in drinking water to be 45 mg/l and permissible value has been prescribed to be 100 mg/l in the absence of any alternative source.



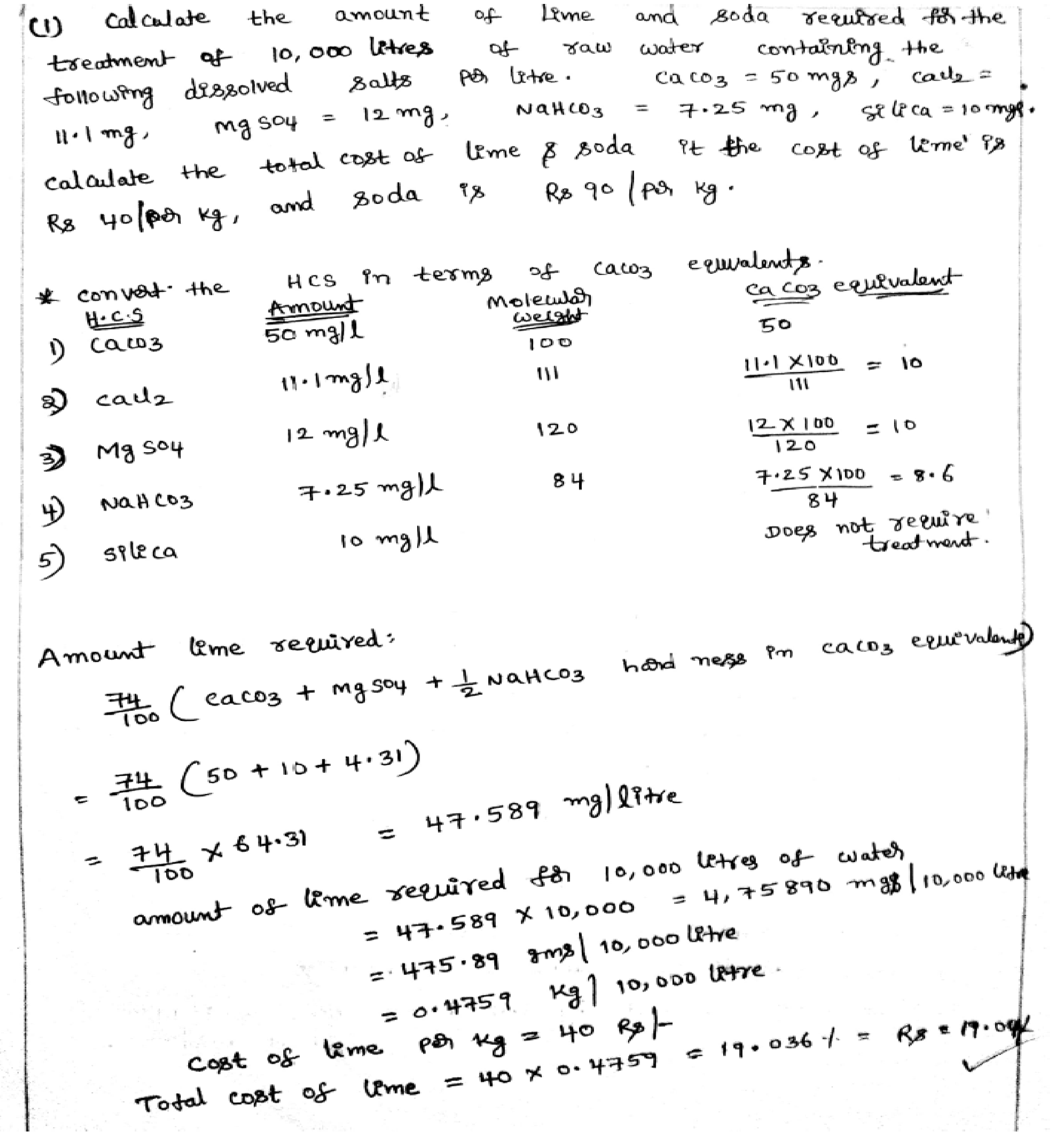
**COMPARISION OF DIFFERENT PHYSICO-CHEMICAL PARAMETERS**

**WITH SUGGESTED BY WHO AND BIS FOR DRINKING WATER SUPPLY**

| S.NO. | Parameters | Range Values | Standards Permissible Limit for drinking water quality | |
|---|---|---|---|---|
| | | | BIS | WHO |
| 1 | Temperature (°C) | 16.0 – 27.8 | 40 | - |
| 2 | Turbidity (NTU) | 6 -22 | 10 | 5-25 |
| 3 | pH | 7.0 - 8.3 | 6.5-8.5 | 6.5-8.5 |
| 4 | Total Dissolved solids (mg/l) | 290 - 328 | 500 | 1000 |
| 5 | Total Alkalinity (mg/l) | 138 - 198 | 200 | 200 |
| 6 | Total Hardness (mg/l) | 132- 187 | 300 | 500 |
| 7 | Chloride (mg/l) | 20 - 64 | 250 | 250 |
| 8 | Phosphate (mg/l) | 0.021 – 0.071 | - | 0.1 |
| 9 | Nitrate (mg/l) | 0.21 – 1.28 | 45 | 50 |

# Water

## PROBLEMS ON LIME-SODA PROCESS



(1) Calculate the amount of lime and soda required for the treatment of 10,000 litres of raw water containing the following dissolved salts per litre. $CaCO_3$ = 50 mgs, $CaCl_2$ = 11.1 mg, $MgSO_4$ = 12 mg, $NaHCO_3$ = 7.25 mg, silica = 10 mgs. Calculate the total cost of lime & soda if the cost of lime is Rs 40/per kg, and soda is Rs 90/per kg.

* convert the HCS in terms of $CaCO_3$ equivalents.

| H.C.S | Amount | Molecular weight | $CaCO_3$ equivalent |
|---|---|---|---|
| 1) $CaCO_3$ | 50 mg/l | 100 | 50 |
| 2) $CaCl_2$ | 11.1 mg/l | 111 | $\frac{11.1 \times 100}{111} = 10$ |
| 3) $MgSO_4$ | 12 mg/l | 120 | $\frac{12 \times 100}{120} = 10$ |
| 4) $NaHCO_3$ | 7.25 mg/l | 84 | $\frac{7.25 \times 100}{84} = 8.6$ |
| 5) silica | 10 mg/l | | Does not require treatment. |

Amount lime required: (hardness in $CaCO_3$ equivalents)

$\frac{74}{100}(CaCO_3 + MgSO_4 + \frac{1}{2}NaHCO_3$

$= \frac{74}{100}(50 + 10 + 4.31)$

$= \frac{74}{100} \times 64.31 = 47.589$ mg/litre

amount of lime required for 10,000 litres of water = 4,75890 mgs/10,000 litre

= 47.589 × 10,000

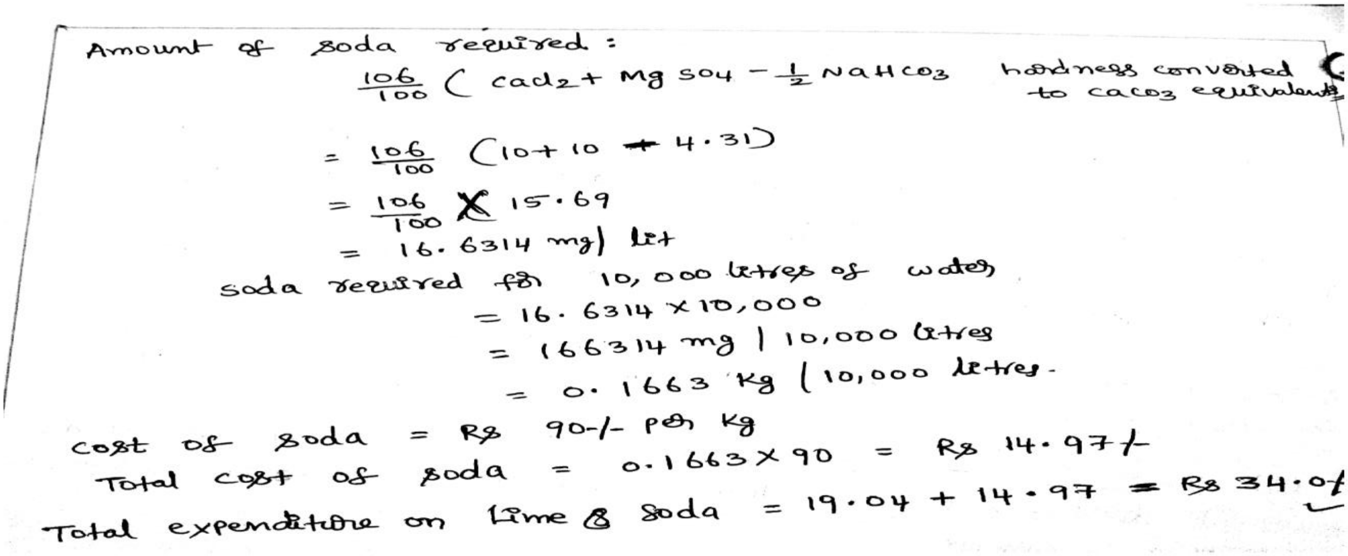
= 475.89 gms/10,000 litre

= 0.4759 kg/10,000 litre.

Cost of lime per kg = 40 Rs/-

Total cost of lime = 40 × 0.4759 = 19.036/- = Rs = 19.0

# Water



Amount of soda required :

$\frac{106}{100}$ ( $CaCl_2 + MgSO_4 - \frac{1}{2} NaHCO_3$ hardness converted (
to $CaCO_3$ equivalents

$= \frac{106}{100}$ (10+10 + 4.31)

$= \frac{106}{100} \times 15.69$

= 16.6314 mg/ lit

soda required for 10,000 litres of water

= 16.6314 × 10,000

= 166314 mg / 10,000 litres

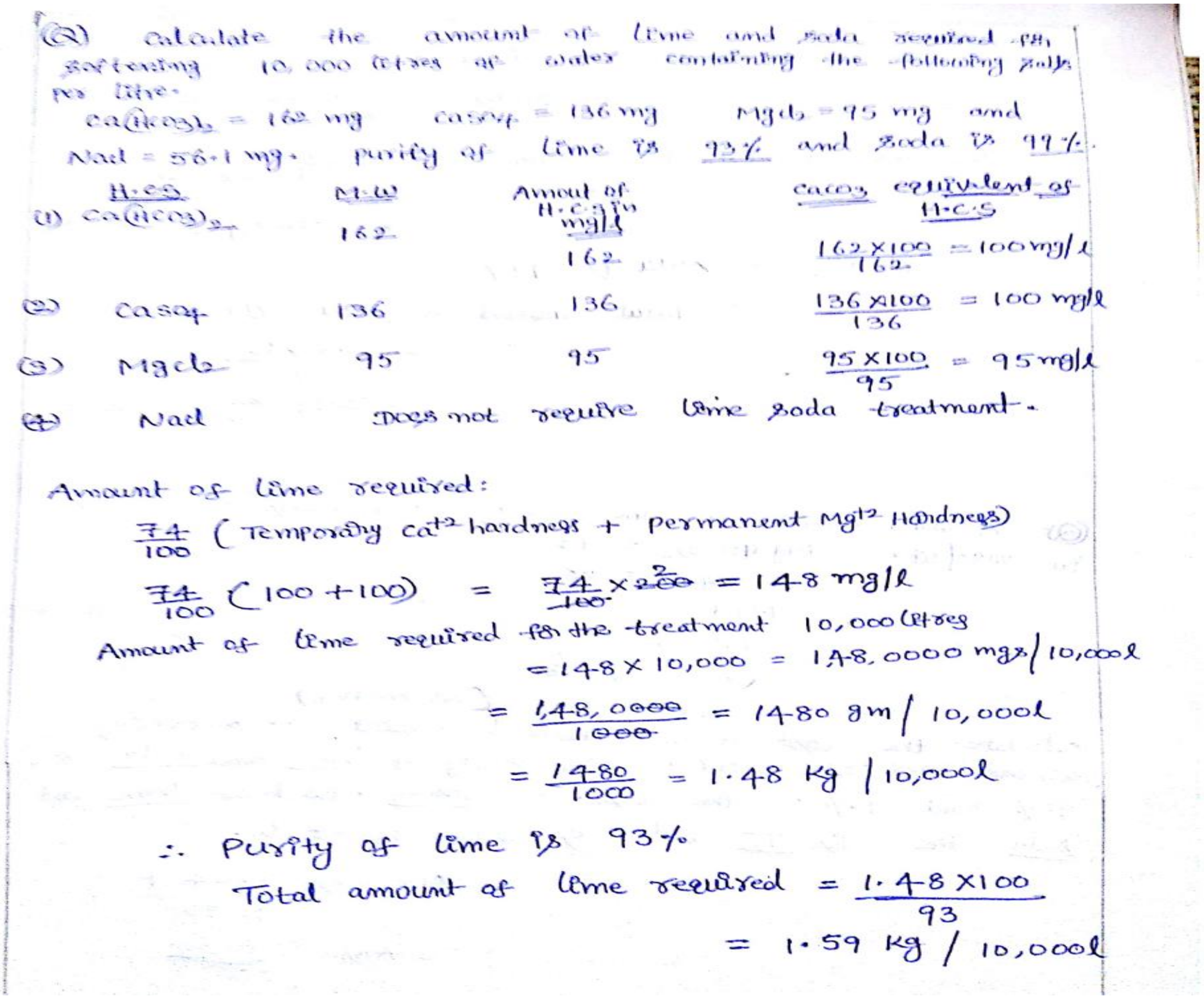
= 0.1663 kg / 10,000 litres.

cost of soda = Rs 90-/- per kg

= 0.1663 × 90 = Rs 14.97/-

Total cost of soda =

Total expenditure on Lime & soda = 19.04 + 14.97 = Rs 34.01 ✓



(Q) Calculate the amount of lime and soda required for softening 10,000 litres of water containing the following salts per litre.

$Ca(HCO_3)_2$ = 162 mg $CaSO_4$ = 136 mg $MgCl_2$ = 95 mg and $NaCl$ = 56.1 mg. purity of lime is 93% and soda is 99%.

| H.C.S | M.W | Amount of H.C.S in mg/l | $CaCO_3$ equivalent of H.C.S |
|---|---|---|---|
| (1) $Ca(HCO_3)_2$ | 162 | 162 | $\frac{162 \times 100}{162} = 100$ mg/l |
| (2) $CaSO_4$ | 136 | 136 | $\frac{136 \times 100}{136} = 100$ mg/l |
| (3) $MgCl_2$ | 95 | 95 | $\frac{95 \times 100}{95} = 95$ mg/l |
| (4) $NaCl$ | Does not require lime soda treatment. | | |

Amount of lime required:

$\frac{74}{100}$ ( Temporary $Ca^{+2}$ hardness + Permanent $Mg^{+2}$ Hardness)

$\frac{74}{100}(100+100) = \frac{74}{\cancel{100}} \times \overset{2}{\cancel{200}} = 148$ mg/l

Amount of lime required for the treatment 10,000 litres

= 148 × 10,000 = 148,0000 mgs / 10,000l

$= \frac{148,0000}{1000} = 1480$ gm / 10,000l

$= \frac{1480}{1000} = 1.48$ kg / 10,000l

∴ Purity of lime is 93%

Total amount of lime required $= \frac{1.48 \times 100}{93}$

= 1.59 kg / 10,000l

# Water

Amount of soda required:

$$= \frac{106}{100}(100+100) = \frac{106}{\cancel{100}} \times \overset{2}{\cancel{200}} = 212 \text{ mg/l}$$

for the treatment of 10,000 lit $= \frac{212 \times 10000}{1000 \times 1000}$

$= 2.12$ Kg / 10,000 lit

purity of soda is 99%.

∴ Total amount of soda required

$$= \frac{2.12 \times 100}{99}$$

$= 2.14$ Kg / 10,000 l

(Q) A water sample gave the following constituents on analysis in mgs/lit.

$Mg(HCO_3)_2 = 73$

$CaSO_4 = 68$

$MgCl_2 = 95$

$MgSO_4 = 12$

$Ca(HCO_3)_2 = 81$

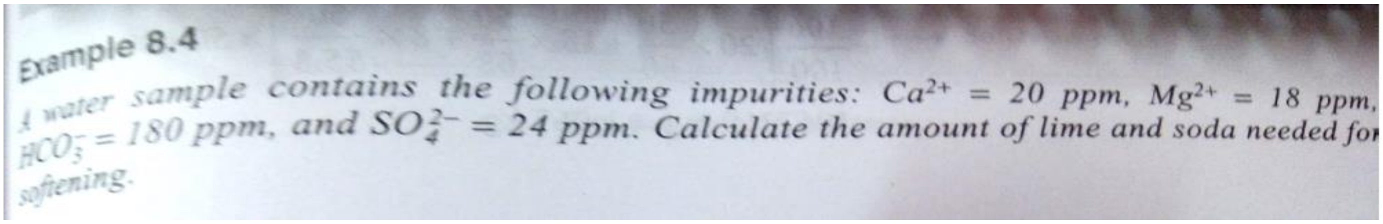
$NaCl = 4.8$ (No hardness)

calculate the cost of the chemicals required for softening 20,000 litres of water. The purity of lime and soda are 95% and 90%. The cost per 100 kg. Each of lime and soda are Rs 75 and Rs 2480 respectively.

Ans: Rs: 3.04 +
93.50

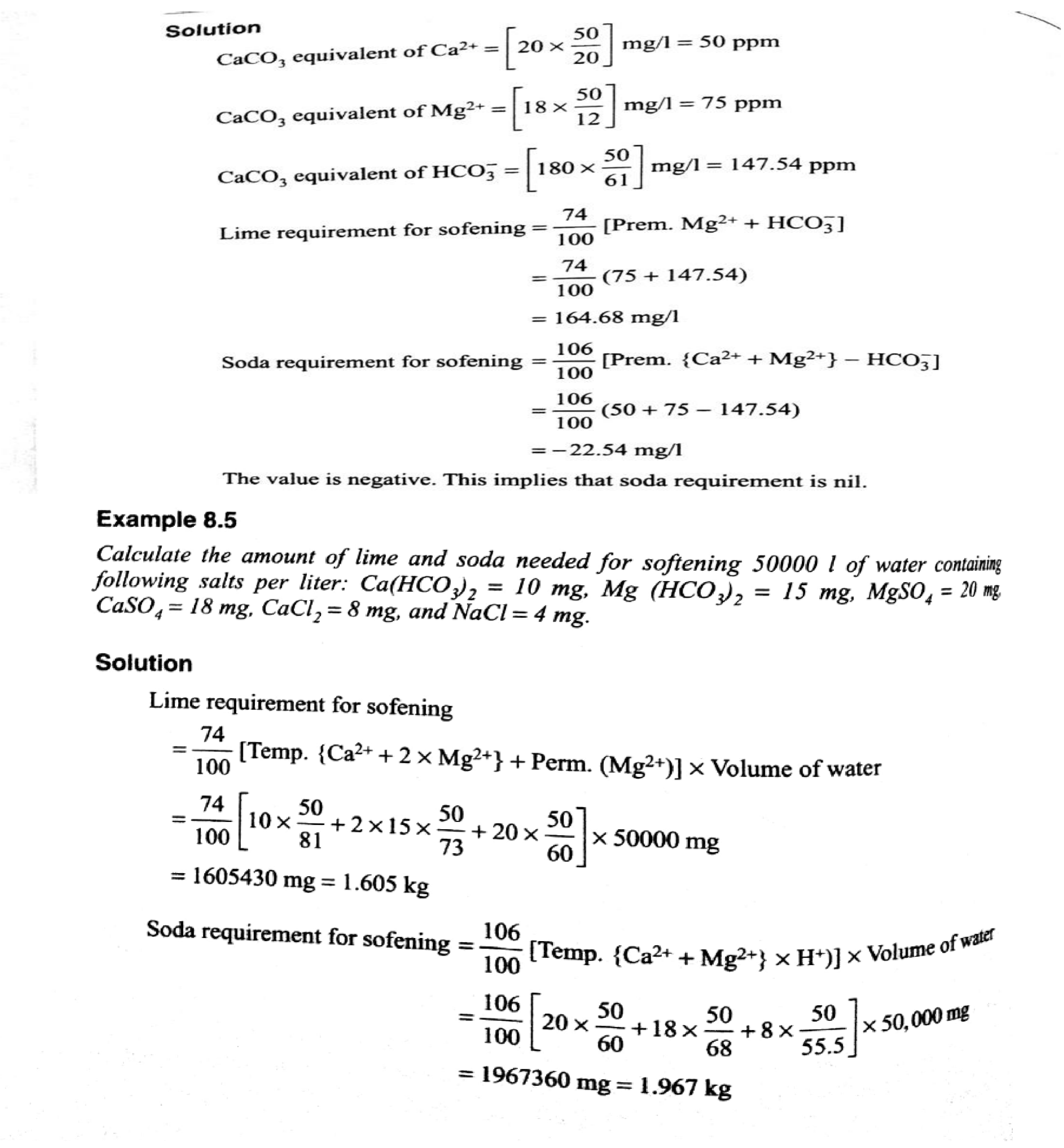
~~Ans~~ = 96.54

# Water



**Example 8.4**

*A water sample contains the following impurities:* $Ca^{2+} = 20$ *ppm,* $Mg^{2+} = 18$ *ppm,* $HCO_3^- = 180$ *ppm, and* $SO_4^{2-} = 24$ *ppm. Calculate the amount of lime and soda needed for softening.*



**Solution**

$$CaCO_3 \text{ equivalent of } Ca^{2+} = \left[20 \times \frac{50}{20}\right] \text{mg/l} = 50 \text{ ppm}$$

$$CaCO_3 \text{ equivalent of } Mg^{2+} = \left[18 \times \frac{50}{12}\right] \text{mg/l} = 75 \text{ ppm}$$

$$CaCO_3 \text{ equivalent of } HCO_3^- = \left[180 \times \frac{50}{61}\right] \text{mg/l} = 147.54 \text{ ppm}$$

$$\text{Lime requirement for sofening} = \frac{74}{100}[\text{Prem. } Mg^{2+} + HCO_3^-]$$

$$= \frac{74}{100}(75 + 147.54)$$

$$= 164.68 \text{ mg/l}$$

$$\text{Soda requirement for sofening} = \frac{106}{100}[\text{Prem. } \{Ca^{2+} + Mg^{2+}\} - HCO_3^-]$$

$$= \frac{106}{100}(50 + 75 - 147.54)$$

$$= -22.54 \text{ mg/l}$$

The value is negative. This implies that soda requirement is nil.

**Example 8.5**

*Calculate the amount of lime and soda needed for softening 50000 l of water containing following salts per liter:* $Ca(HCO_3)_2 = 10$ *mg,* $Mg\ (HCO_3)_2 = 15$ *mg,* $MgSO_4 = 20$ *mg,* $CaSO_4 = 18$ *mg,* $CaCl_2 = 8$ *mg, and* $NaCl = 4$ *mg.*

**Solution**

Lime requirement for sofening

$$= \frac{74}{100}[\text{Temp. } \{Ca^{2+} + 2 \times Mg^{2+}\} + \text{Perm. } (Mg^{2+})] \times \text{Volume of water}$$

$$= \frac{74}{100}\left[10 \times \frac{50}{81} + 2 \times 15 \times \frac{50}{73} + 20 \times \frac{50}{60}\right] \times 50000 \text{ mg}$$

$$= 1605430 \text{ mg} = 1.605 \text{ kg}$$

$$\text{Soda requirement for sofening} = \frac{106}{100}[\text{Temp. } \{Ca^{2+} + Mg^{2+}\} \times H^+)] \times \text{Volume of water}$$

$$= \frac{106}{100}\left[20 \times \frac{50}{60} + 18 \times \frac{50}{68} + 8 \times \frac{50}{55.5}\right] \times 50,000 \text{ mg}$$

$$= 1967360 \text{ mg} = 1.967 \text{ kg}$$

# Water

## Example 8.6

*Calculate the amount of lime and soda needed for softening 50000 l of water with the following analysis using 10 ppm of sodium aluminate as coagulant. Analysis result:* $Ca^{2+} = 100$, $Mg^{2+} = 35$, $CO_2 = 50$, $HCO_3^- = 250$, $H^+ = 2$ *ppm.*

## Solution

$$\text{Lime requirment for sofening (mg/l)} = \frac{74}{100}[Mg^{2+} + CO_2 + H^+ + HCO_3^- - NaAlO_2]$$

$$\text{Soda requirment for sofening (mg/l)} = \frac{106}{100}[Ca^{2+} + Mg^{2+} + H^+ - HCO_3^-]$$

Substitute the values after converting into $CaCO_3$ equivalent as per Example 8.5.

**Problem 3.11 :**

**A sample of water contains the following dissolved salts in mgs/litre. $CaSO_4$ = 6.8, $MgCO_3$ = 8.4, $Al_2(SO_4)_3$ = 34.2, $CO_2$ = 4.4, HCl = 3.65. Calculate the amount of lime and soda required for the treatment of 5000 litres of water. The purity of lime 80% and soda is 90%. 10% of excess chemicals were added.**

**Sol :** Conversion of the amounts of hardness causing salts into $CaCO_3$ equivalents.

| Sl. No. | Hardness causing salt (H.C.S.) | Amount of H.C.S. mg/l | Mol. wt. of H.C.S. | $CaCO_3$ equivalents |
|---|---|---|---|---|
| 1. | $CaSO_4$ | 6.8 | 136 | $\frac{6.8 \times 100}{136} = 5$ |
| 2. | $MgCO_3$ | 8.4 | 84 | $\frac{8.4 \times 100}{84} = 10$ |
| 3. | $Al_2(SO_4)_3$ | 34.2 | 342 | $\frac{34.2 \times 100}{342} = 10$ |
| 4. | $CO_2$ | 4.4 | 44 | $\frac{4.4 \times 100}{44} = 10$ |
| 5. | HCl | 3.65 | 36.5 | $\frac{3.65 \times 100}{36.5} = 10$ |

Amount of lime required $= \frac{74}{100}$ [$(2 \times MgCO_3) + (3 \times Al_2(SO_4)_3) + CO_2 + \frac{1}{2}$ HCl hardness in terms of $CaCO_3$ equivalents]

$$= \frac{74}{100} \times \left((2 \times 10) + (3 \times 10) + 10 + \frac{1}{2} \times 10\right) = \frac{74}{100} \times 65 = 48.1 \text{ mg/}l$$

Lime required for 5,000 litres of water = 48.1 × 5,000

= 240500 mg/5000 lit. = 0.2405 kg/5000 lit.

Purity of lime = 80%.

Out of 100 kgs of raw lime used only 80 kgs is pure lime

? raw lime should be used if 0.2405 kg of pure lime required

The amount of raw lime required $= \frac{0.2405 \times 100}{80} = 0.3006$ kg/5000 lit.

10% excess lime is added.

Total amount of lime along with 10% excess chemicals $= \frac{0.3006 \times 110}{100}$

$= 0.33066$ kg/5000 litre

Amount of soda required

$$= \frac{106}{100}\ (CaSO_4+(3\times Al_2(SO_4)_3)+\frac{1}{2}\ HCl \text{ hardness in } CaCO_3 \text{ equivalents}$$

$$= \frac{106}{100}\ [5+(3\times 10)+5]$$

$$= \frac{106}{100} \times 40 = 42.4 \text{ mg/l.}$$

Lime required for 5000 litres of water = 42.4 × 5000

= 212000 mg/1000 lit = 0.212 kg/5000 li

Purity of soda = 90%

Amount of raw soda to be required $= \frac{0.212 \times 100}{90} = 0.2356$ kg/5000 litre

10% excess soda is added

Total amount of soda along with 10% excess chemicals

$= \frac{0.2356 \times 110}{100} = 0.2591$ kg/5000 litre

**Problem 3.12 :**

Calculate the amount of lime and soda required for softening 10,000 litres of water containing the following salts per litre.

$Ca(HCO_3)_2$ = 162 mgs, $CaSO_4$ = 136 mgs, $MgCl_2$ = 95 mgs and NaCl = 56.1 mgs. Purity of lime is 93% and that of soda is 99%. (BIT Mesra I.B.E. 1993)

**Sol :**

| S.No. | Hardness causing salt (H.C.S.) | Amt. of H.C.S. in mg/l | Mol.wt.of H.C.S. | $CaCO_3$ equivalent of H.C.S. |
|---|---|---|---|---|
| 1. | $Ca(HCO_3)_2$ | 162 | 162 | $\frac{162 \times 100}{162} = 100$ mgs/l |
| 2. | $CaSO_4$ | 136 | 136 | $\frac{136 \times 100}{136} = 100$ mgs/l |
| 3. | $MgCl_2$ | 95 | 95 | $\frac{95 \times 100}{95} = 100$ mgs/l |
| 4. | NaCl | Does not require lime soda treatment | | |

Amt. of lime required = $\frac{74}{100}$ (temporary hardness of $Ca(HCO_3)_2$ + permanent hardness of $MgCl_2$)

$$= \frac{74}{100} \times 200 = 148 \text{ mg}/l.$$

Amount of lime required for the treatment 10,000 litres

$$= 148 \times 10000 = 14,80,000 \text{ mgs}/10000\ l$$

$$= \frac{1480000}{1000} = 1480 \text{ gms}/10000\ l$$

$$= \frac{1480}{1000} = 1.48 \text{ kg}/10000\ l$$

Purity of lime is 93%

Total amount of lime required = $\frac{1.48 \times 100}{93} = 1.59 \text{ kg}/10,000\ l$

Amount of soda required = $\frac{106}{100} \times 200 = 212 \text{ mgs}/l$

for the treatment of 10,000 litres = $\frac{212 \times 10000}{1000 \times 1000} = 2.12 \text{ kg}/10000\ l$

Purity of soda is 99%

Total amount of soda required = $\frac{2.12 \times 100}{99} = 2.14 \text{ kg}/10,000\ l$

**Problem : 3.13**

A water works has to supply 1000 litres of water, that contains $Mg^{2+}$ 36 ppm $HCO_3^- = 18.3$ ppm and $H^+ = 1.5$ ppm. Calculate the amount of lime and soda required

**Sol :**

| S.No. | (H.C.S) | Amt. in ppm | Mol.wt. | $CaCO_3$ equivalents |
|---|---|---|---|---|
| 1. | $Mg^{2+}$ | 36 | 24 | $\frac{36 \times 100}{24} = 150$ ppm |
| 2. | $HCO_3^-$ | 18.3 | 122* | $\frac{18.3 \times 100}{122} = 15$ ppm |
| 3. | $H^+$ | 1.5 | 2* | $\frac{1.5 \times 100}{2} = 75$ ppm |

$$\text{Amount of lime required} = \frac{74}{100}\left[Mg^{2+} + HCO_3^- + H^+\right]$$

$$= \frac{74}{100}(150 + 15 + 75)$$

$$= \frac{74}{100}(240) = 177.6\,\text{mg}/l$$

Lime required for the treatment of 1000 litres of water

$$= \frac{177.6 \times 1000}{1000 \times 1000} = 0.1776\,\text{kg}$$

$$\text{Soda required for the treatment} = \frac{106}{100}\left(Mg^{2+} + H^+ - HCO_3^-\right)$$

$$= \frac{106}{100}(150 + 75 - 15)$$

$$= \frac{106}{100} \times 210 = 222.6\,\text{mg}/l$$

Amount of soda required for the treatment of 1000 litres of water

$$= \frac{222.6 \times 1000}{1000 \times 1000} = 0.2226\,\text{kg}$$

[* Note : $\frac{1}{2}$ $HCO_3^-$ and $\frac{1}{2}$ $H^+$ hardness must be considered. That is why the molecular weights of $HCO_3^-$ and $H^+$ are taken as 122 and 2 instead of 61 and 1 respectively]

**Problem 3.14 :**

**Analysis of water gave the following results : $H_2SO_4$ = 196mg/*l*, $MgSO_4$ = 24mg/*l* $CaSO_4$ = 272mg/*l* and NaCl = 25mg/*l*. Water is to be supplied to the/town of the population one lakh only. The daily consumption of water is 50 litres per head. Calculate the cost of lime and soda required for softening of hardwater for town for the month April 2002, if the cost of lime is Rs. 5.00 per kg and cost of soda is Rs. 8.00 per kg.**

**(MREC 2002)**

**Sol :**

| **S.No.** | **(H.C.S)** | **Amt. in mg/*l*** | **Mol. wt.** | **$CaCO_3$ equivalents** |
|---|---|---|---|---|
| 1. | $H_2SO_4$ | 196 | 98 | $\frac{196 \times 100}{98} = 200$ |
| 2. | $MgSO_4$ | 24 | 120 | $\frac{24 \times 100}{120} = 20$ |
| 3. | Ca~~$Cl_2$~~$SO_4$ | 272 | 136 | $\frac{272 \times 100}{136} = 200$ |
| 4. | NaCl | No treatment with lime & soda required | | |

Amount of lime required = $\frac{74}{100}$ (Hardness of $H_2SO_4$ + $MgSO_4$ in terms of $CaCO_3$ equivalents)

$$= \frac{74}{100} \times 220 = 162.8\,\text{mg}/l$$

Daily consumption of water = 50 *l* per head.
Population of the town = 1,00,000

Lime required for the treatment for the population $= \frac{162.8 \times 50 \times 1,00,000}{1000 \times 1000} = 814\,\text{kg}$

For April 2002 (30 days) total amount of lime required

= 814 × 30 = 24420 kgs.

Given cost of lime = 5/- per kg.

Total cost of lime in Rs. = 24420 × 5 = 1,22,100/-

Amount of soda required $= \frac{106}{100}$ (hardness of $H_2SO_4$ + $MgSO_4$ + $CaSO_4$ in terms of $CaCO_3$ equivalents)

$$= \frac{106}{100}(420) = 445.2\,\text{mg}/l$$

Soda required for the treatment for the population

$$= \frac{445.2 \times 50 \times 1,00,000}{1000 \times 1000} = 2226\,\text{kg.}$$

For April 2002 (30 days) the amount of soda required = 2226 × 30 = 66780 kg

Cost of soda = Rs 8/- per kg.

Total cost of soda = 66780 × 8 = Rs.5,34,240/-

**Problem 3.15 :**

**Calculate the amount of lime and soda required for softening 10,000 litres of water, which was analysed as follows :**

**Analysis of raw water :**

**$Ca^{2+}$ = 380 ppm, Dissolved $CO_2$ = 120 ppm**

**$Mg^{2+}$ = 144 ppm, $FeSO_4 .7H_2O$ = 278 ppm**

**$HCO_3^-$ = 1500 ppm**

**Analysis of treated water**

**$OH^-$ = 34 ppm , $CO_3^{2-}$ = 32ppm.**

**(MREC 2000)**

| S.No. | H.C.S | Amt. (ppm) | At.wt/mol. wt | $CaCO_3$ equivalents |
|---|---|---|---|---|
| **Raw water** | | | | |
| 1. | $Ca^{2+}$ | 380 | 40 | $\frac{380 \times 100}{40} = 950$ |
| 2. | $Mg^{2+}$ | 144 | 24 | $\frac{144 \times 100}{24} = 600$ |

# Water

| S.No. | H.C.S | Amt. (ppm) | At.wt/mol. wt | $CaCO_3$ equivalents |
|---|---|---|---|---|
| **Raw water** | | | | |
| 3. | $HCO_3^-$ | 1500 | 122 | $\frac{1500 \times 100}{122} = 1229.5$ |
| 4. | Dissolved $CO_2$ | 120 | 44 | $\frac{1420 \times 100}{44} = 272.7$ |
| 5. | $FeSO_4.7H_2O$ | 278 | 278 | $\frac{278 \times 100}{278} = 100$ |
| **Treated water** | | | | |
| 6. | $OH^-$ | 34 | 34 | $\frac{34 \times 100}{34} = 100$ |
| 7. | $CO_3^{2-}$ | 32 | 60 | $\frac{32 \times 100}{60} = 53.3$ |

Amount of lime required for raw water = $\frac{74}{100}$ (Hardness of $Mg^{2+}$ + $HCO_3$ + $CO_2$+ $FeSO_4.7H_2O$ converted in terms of $CaCO_3$ equivalents)

$$= \frac{74}{100}(600 + 1229.5 + 272.7 + 100) = 1629.6 \text{ mg/l.}$$

Amt. of lime required for 10,000 litres of raw water

$$= \frac{1629.6 \times 10{,}000}{1000 \times 1000} = 16.296 \text{ kg}/10{,}000\,l$$

Amt. of soda required for raw water = $\frac{106}{100}$ (Hardness of $Ca^{2+}$ + $Mg^{2+}$ + $FeSO_4.7H_2O$ − $HCO_3^-$ in terms of $CaCO_3$ equivalents)

$$= \frac{106}{100}(950 + 600 + 100 - 1229.5)$$

$$= \frac{106}{100} \times 420.5 = 445.73 \text{ mg}/l$$

Amt. of soda required for 10,000 litres of raw water

$$= \frac{445.73 \times 10000}{1000 \times 1000} = 4.4573 \text{kg}/10{,}000\,l$$

Amount of lime required for excess $OH^-$ in treated water

$$= \frac{74}{100} \times 100 = 74 \text{ mg}/l$$

Amount of lime required for excess $OH^-$ in 10,000 $l$ of treated water

$$= \frac{74 \times 10000}{1000 \times 1000} = 7.4 \text{kg}/10{,}000\,l$$

Total amount of lime required for the treatment of raw + treated 10,000 litres of water = 16.296 + 7.4 = 23.696 kg/10,000 $l$.

Amt. of soda required for excess of $OH^-$ and $HCO_3^-$ in treated water

$$= \frac{106}{100}(100 + 53.3) = \frac{106}{100} \times 153.3 = 162.498 \text{ mg}/l$$

Amount of soda required for excess $OH^-$ and $HCO_3^-$ in 10,000 $l$ of treated water

$$= \frac{162.498 \times 10000}{1000 \times 1000} = 1.625 \text{kg}/10{,}000\,l$$

Total amount of soda required for the treatment raw + treated 10,000 $l$ of water = 4.4573 + 1.625 = 6.0823kg/10000 $l$.

**Problems for Practise :**

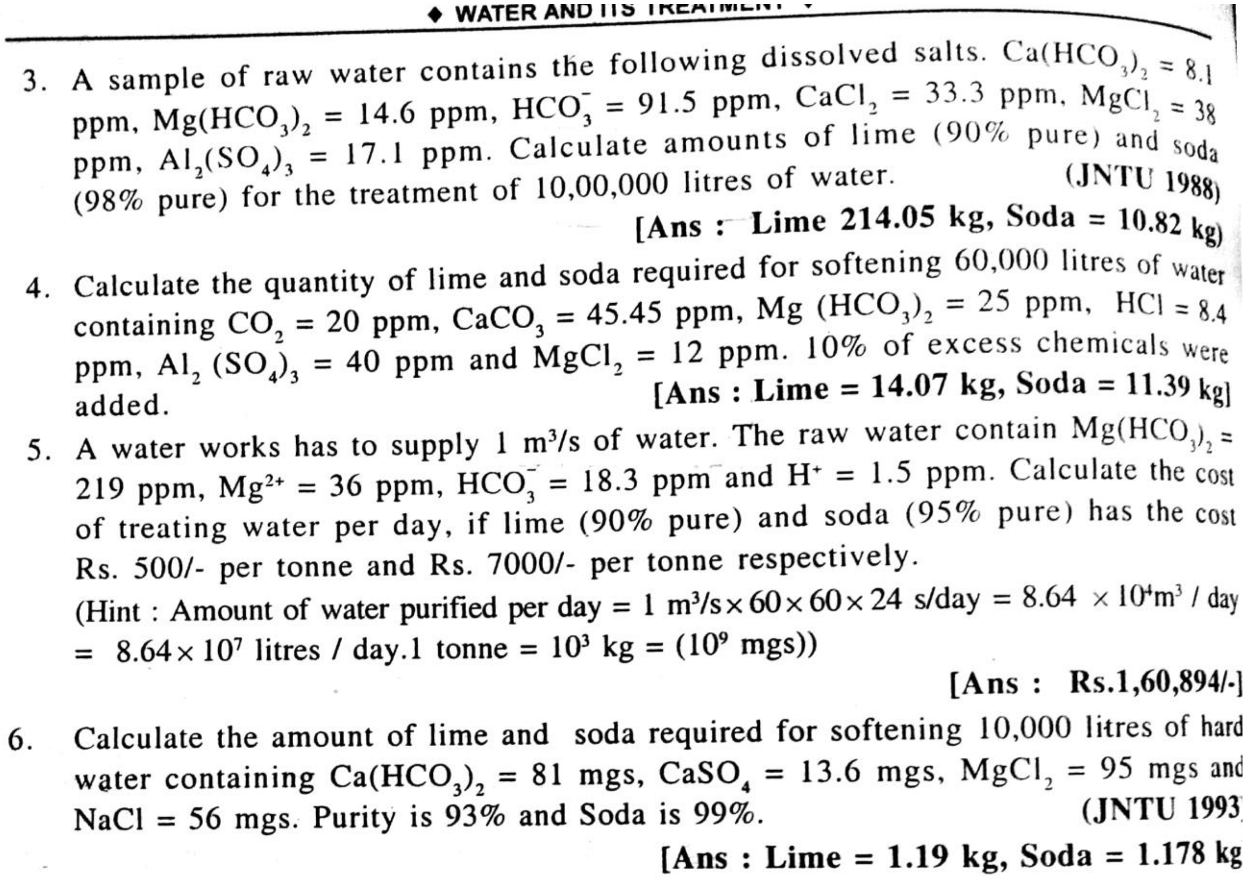
1. A water sample gave the following constituents on analysis in mgs/litre. $Mg(HCO_3)_2$ = 73, $CaSO_4$ = 68, $MgCl_2$ = 95, $MgSO_4$=12, $Ca(HCO_3)_2$ = 81, NaCl = 4.8. Calculate the cost of the chemicals required for softening 20,000 litres of water. The purity of lime and soda are 95% and 90%. The costs per 100 kg. each of lime and soda are Rs. 75 and Rs. 2480 respectively. **(Nagpur IBE 1997)**

   **[Ans : Rs. 3.04 + 93.50 = 96.54/-]**

2. Calculate the amount of lime and soda required to soften 1 million litres of a water sample containing the following dissolved salts (calcium permanent hardness) $Ca^{2+}$ = 20 ppm, $Mg^{2+}$ = 24 ppm, $HCO_3^-$ = 150 ppm, and $CO_2$ = 30 ppm. The purity of lime is 87% and soda is 91%. 10% of excess chemicals were added.

   **[Ans : time = 272.46 kg, Soda = 34.6 kg]**

# Water



3. A sample of raw water contains the following dissolved salts. $Ca(HCO_3)_2 = 8.1$ ppm, $Mg(HCO_3)_2 = 14.6$ ppm, $HCO_3^- = 91.5$ ppm, $CaCl_2 = 33.3$ ppm, $MgCl_2 = 38$ ppm, $Al_2(SO_4)_3 = 17.1$ ppm. Calculate amounts of lime (90% pure) and soda (98% pure) for the treatment of 10,00,000 litres of water. **(JNTU 1988)**

**[Ans : Lime 214.05 kg, Soda = 10.82 kg)**

4. Calculate the quantity of lime and soda required for softening 60,000 litres of water containing $CO_2 = 20$ ppm, $CaCO_3 = 45.45$ ppm, $Mg\ (HCO_3)_2 = 25$ ppm, $HCl = 8.4$ ppm, $Al_2\ (SO_4)_3 = 40$ ppm and $MgCl_2 = 12$ ppm. 10% of excess chemicals were added. **[Ans : Lime = 14.07 kg, Soda = 11.39 kg]**

5. A water works has to supply 1 $m^3/s$ of water. The raw water contain $Mg(HCO_3)_2 = 219$ ppm, $Mg^{2+} = 36$ ppm, $HCO_3^- = 18.3$ ppm and $H^+ = 1.5$ ppm. Calculate the cost of treating water per day, if lime (90% pure) and soda (95% pure) has the cost Rs. 500/- per tonne and Rs. 7000/- per tonne respectively.

   (Hint : Amount of water purified per day = $1\ m^3/s \times 60 \times 60 \times 24$ s/day = $8.64 \times 10^4 m^3$ / day = $8.64 \times 10^7$ litres / day.1 tonne = $10^3$ kg = ($10^9$ mgs))

   **[Ans : Rs.1,60,894/-]**

6. Calculate the amount of lime and soda required for softening 10,000 litres of hard water containing $Ca(HCO_3)_2 = 81$ mgs, $CaSO_4 = 13.6$ mgs, $MgCl_2 = 95$ mgs and NaCl = 56 mgs. Purity is 93% and Soda is 99%. **(JNTU 1993**

**[Ans : Lime = 1.19 kg, Soda = 1.178 kg**

# Module-II

## Molecular structure and Theories of Bonding

# II. Molecular Structure and Theories of Bonding ①

## Molecular orbital theory:

To overcome the limitations of VBT, Hund and Mulliken put forward a new theory to explain formation of covalent bonds known as molecular orbital (MO) theory. MO theory to explain:

(i) the formation of chemical bond

(ii) relative bond strengths

(iii) Paramagnetic (or) diamagnetic nature, etc of molecules.

## Salient features of MO theory are:

(i) The atomic orbitals (with same energy (or) nearly same energy and appropriate symmetry under linear combination) of the combing atoms overlap to form new orbitals, called molecular orbitals (M.O). As a result of this, the atomic orbitals lose their individual identity.

(ii) The number of molecular orbitals formed is equal to the number of atomic orbitals participating in linear combination.

(iii) The molecular orbital formed by addition (constructive) (when atomic orbitals remain in phase) overlap of atomic orbitals is called "Bonding molecular orbital". Such an orbital possesses less energy than the combining atomic orbitals.

(iv) The molecular orbital formed by substraction (destructive) (when atomic orbitals remain in different phase) overlap of atomic orbitals is called "Anti bonding molecular orbital". Such an orbital possesses more energy than the combining atomic orbitals.

(v) unlike atomic orbitals, molecular orbital is polycentric region in space, defined by its size and shape. Thus, in a molecular orbital, electrons are revolving in the field of more than one nucleus.

(vi) The shapes of molecular orbitals depend on the shapes of atomic orbitals from which they are generated.

(vii) Filling of molecular orbitals follows the same rules used for filling of atomic orbitals.

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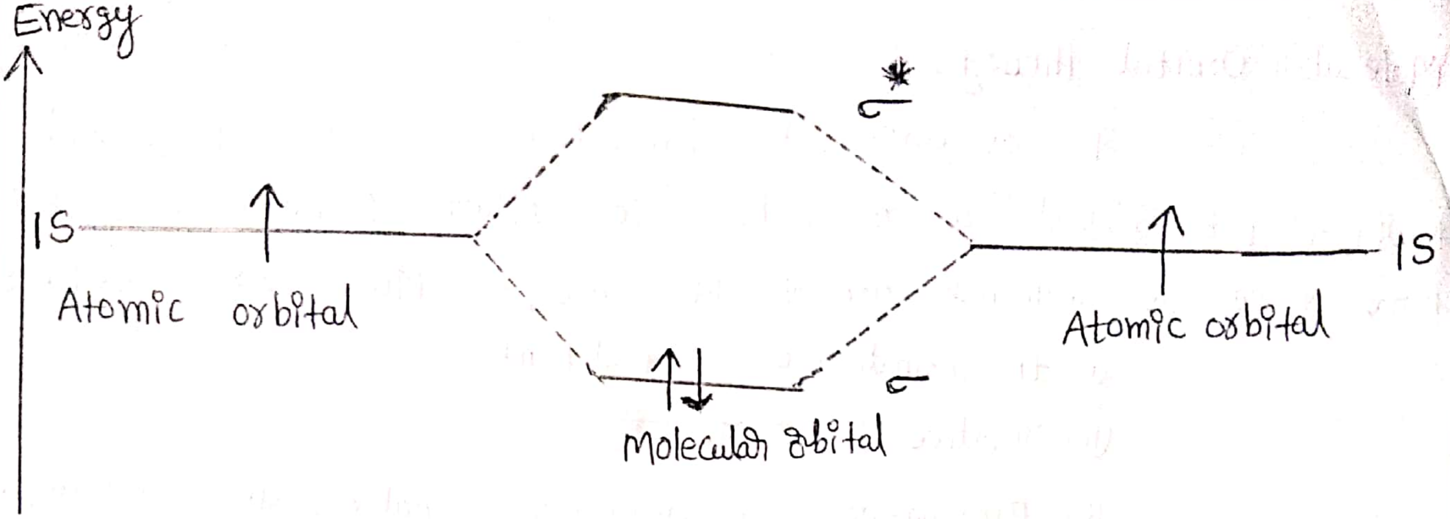
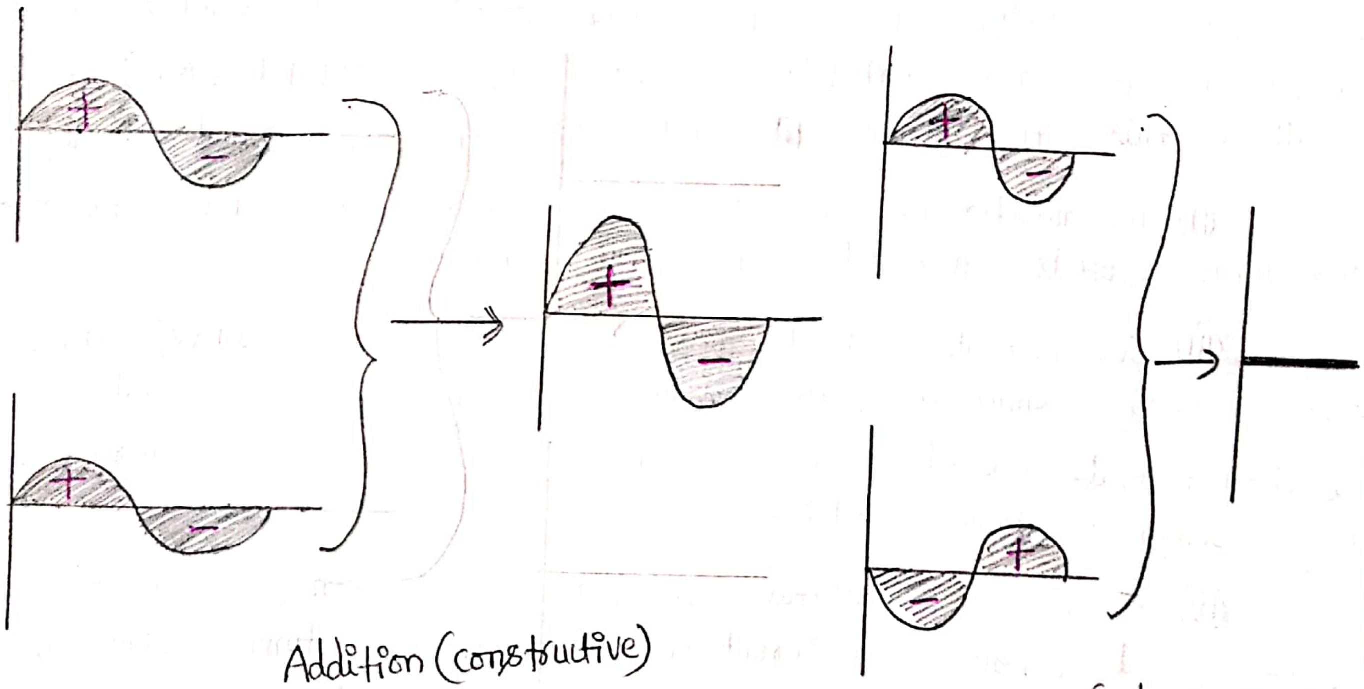


## Linear Combination of Atomic orbitals (LCAO) :



Addition (constructive)

Substraction (destructive)

According to wave mechanics the atomic orbitals canbe expressed by wave functions ($\psi$'s), which represent by the amplitude of electron waves. Their values canbe calculated from the solutions of Schrodinger's wave equation. However, it is difficult to solve the above exactly for many electron systems. Therefore, an approximate method known as Linear combination of atomic orbitals (LCAO) has been adapted.

According to this method, the molecular orbitals are formed by the Linear combination (addition (constructive) or substraction (destructive) of atomic orbitals of the constituent atoms of the molecule.

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Let us consider this method to simplest homonuclear diatomic molecule, hydrogen which consists of two hydrogen atoms represented by HA and HB. The atomic orbitals of these atoms are represented by the wave functions $\psi_A$ and $\psi_B$. When these atoms approach each other come two possibilities.

(i) Molecular orbital is formed by the addition of wave functions atomic orbitals. It can be represented by

$$\psi_{(MO)} = \psi_A + \psi_B \text{ — (constructive interaction)}$$

The M.O formed is called "Bonding molecular orbital". It lowers the energy than that constituent overlapping atomic orbitals. The difference in energy between combining atomic orbitals and the bond molecular orbital formed, is called stabilization energy. Thus, bonding M.O stabilizes the molecule.

**Characteristics of bonding molecular orbital:**

(i) It possesses lower energy than that of the combining the atomic orbitals.

(ii) It possesses high electron-density in the region between the two nuclei

(iii) It imparts stability to the molecule.

(iv) Every electron in it makes contribution to the attraction of two combining atoms.

(v) It is only formed, when the lobes of the combining atomic orbitals possess same sign.

(ii) Molecular orbital is formed by the substraction of wave functions of atomic orbitals. It can be represented by

$$\psi^{*}_{(MO)} = \psi_A - \psi_B \text{ — (destructive interaction)}$$

The M.O formed is called anti-bonding molecular orbital. This type of M.O corresponds to higher energy state. The difference in energy between the anti-bonding molecular orbital and the combining atomic orbitals, is called destabilization energy. Thus, antibonding M.O destabilizes the molecule.

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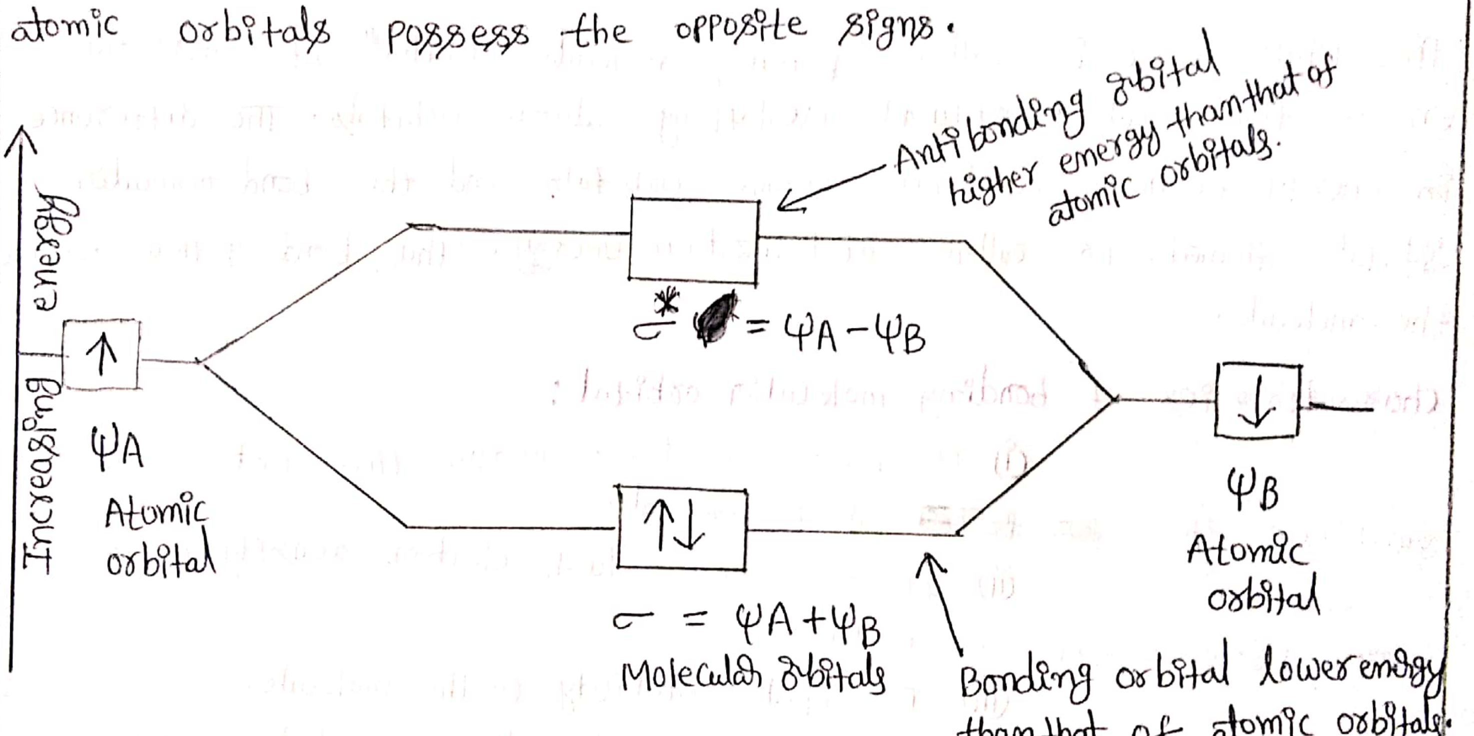
## Characteristics of anti-bonding molecular orbital:

(i) It possesses higher energy than that of the combinin atomic orbitals. (ii) It possesses low-electron density in the region between the two nuclei.

(iii) It imparts instability to the molecule

(iv) Every electron in it makes contribution to the repulsion of two combining atoms.

(v) It is formed, when the lobes of the combining atomic orbitals possess the opposite signs.



Anti bonding orbital higher energy than that of atomic orbitals.

Bonding orbital lower energy than that of atomic orbitals.

Formation of bonding (σ) and antibonding (σ*) molecular orbitals by the linear combination of atomic orbitals $\psi_A$ and $\psi_B$ centered on two atoms A and B respectively.

## Significance of bonding and anti-bonding molecular orbital:

The probability density in bonding and anti-bonding molecular orbitals, the bonding molecular orbital formation ($\psi^2$) greater than that of antibonding molecular orbital ($\psi^{*2}$) formation. This is because we known that probability is gives by the square of amplitude (ψ), therefore

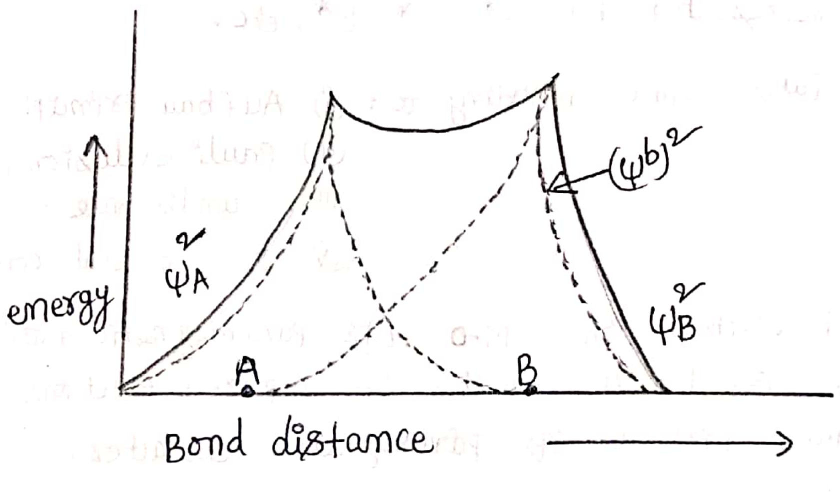
$$\psi^2_{(M\cdot O)} = (\psi_A + \psi_B)^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B$$

$$\psi^{*2}_{(M\cdot O)} = (\psi_A - \psi_B)^2 = \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B$$

Taking squares of the bonding MO wave function ($\psi^b$), we get

$$(\psi^b)^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B$$

The terms $\psi_A^2$ and $\psi_B^2$ indicate electronic charge densities of wave functions $\psi_A$ and $\psi_B$ belonging to isolated atoms A and B, respectively. $(\psi^b)^2$ is the electronic charge density of the wave function $\psi^b$, i.e, the bonding M.O. Thus, the more is the value of $(\psi^b)^2$, the more is the charge density between the two combining nuclei. Again from the equation is also evident that $(\psi^b)^2 > \psi_A^2 + \psi_B^2$ by a term, $2\psi_A\psi_B$. This term $2\psi_A\psi_B$ results from the overlap of AO's and is called overlap integral. Larger is the overlap integral more is the charge density between the nuclei and stable bond is formed. The plot of electron charge density as a function of inter-nuclear distance for bonding M.O is shown below.

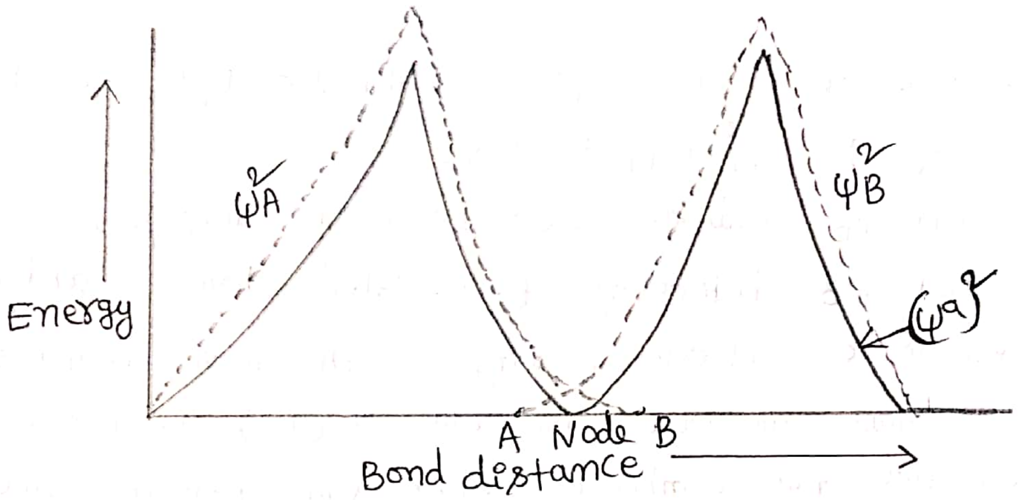


∴ Again, taking square of the antibonding M.O wave function ($\psi^a$) we get

$$(\psi^a)^2 = \psi_A^2 + \psi_B^2 - 2\psi_B\psi_A$$

It is evident from the above equation that $(\psi^b)^2 < \psi_A^2 + \psi_B^2$ by a term $2\psi_A\psi_B$. Thus, in anti-bonding M.O, there is less charge density between the nuclei. It is, therefore, the energy of the anti-bonding m.o. is more than the sum of the energies of the two interacting atoms A and B. The plot of electron charge density is shown below.

The charge density touches the axis at midpoint between the nuclei. This mid point is called a node and at this point the electron charge density is zero.



(a) M.O. gives the electron probability distribution around a group of nuclei just as an A.O gives the electron probability distribution around the nucleus.

(b) The shape of the M.O formed depends on the type of the combining atomic orbitals.

(c) The bonding M.O are represented by $\sigma$, $\pi$, $\delta$ etc; whereas antibonding M.O are represented by $\sigma^*$, $\pi^*$, $\delta^*$, etc.

(d) The filling of M.O takes place according to: (i) Aufbau principle
(ii) Pauli exclusion principle
(iii) Hund's rule
(iv) If a molecule contains one (or) more unpaired electrons in it M.O, it is paramagnetic nature, otherwise diamagnetic. Greater the number of unpaired electrons in M.O's of a substance, high is its paramagnetic character.

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## Conditions for the formation of molecular orbitals :

Any two atomic orbitals on combination donot form molecular orbitals. In fact, there are certain limitations to the combination of atomic orbitals. They are :

(1) The energies of combining atomic orbitals should of similar (or) nearly the same magnitude.

This means that 1S orbital can combine with another 1S orbital but not with the 2S orbital, because the energy of 2S orbital appreciably higher than that of 1S orbital. This is true only for homonuclear diatomic molecules.

(2) The combining atomic orbitals must be overlap to the maximum extent.

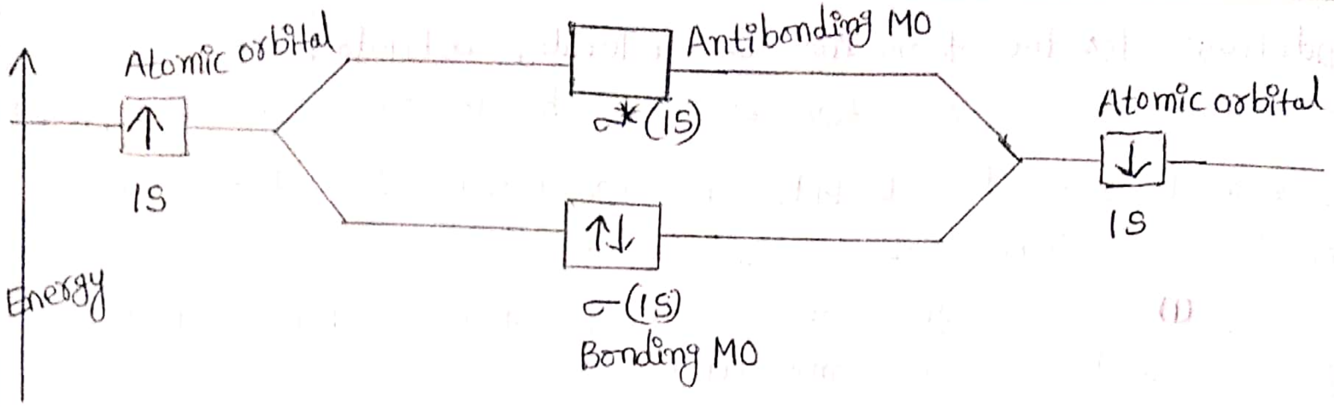
Greater the extent of overlap, the greater will be the electron-density between the nuclei of a molecular orbital.

(3) The combining atomic orbitals must have the same symmetry about the molecular axis.

By convention z-axis is taken as the molecular axis. It is important to note that atomic orbitals having same (or) nearly the same energy will not combine it they donot have the same symmetry. For example, 2Pz orbital of one of atom can combine with 2Pz orbital of another atom but not with 2Px (or) 2Py orbitals because of their different symmetries.

## Formation of M.O's :

**From S-atomic orbitals :** when two 1S orbitals combine two new molecular orbitals are formed. one of these pertains to the bonding molecular orbital with lower energy while the other corresponds to higher energy as compared to both the atomic orbitals concerned in the process. Thus we find that the number of molecular orbitals formed from atomic orbitals is equal to the number of atomic orbitals responsible for their formation and are shown below.



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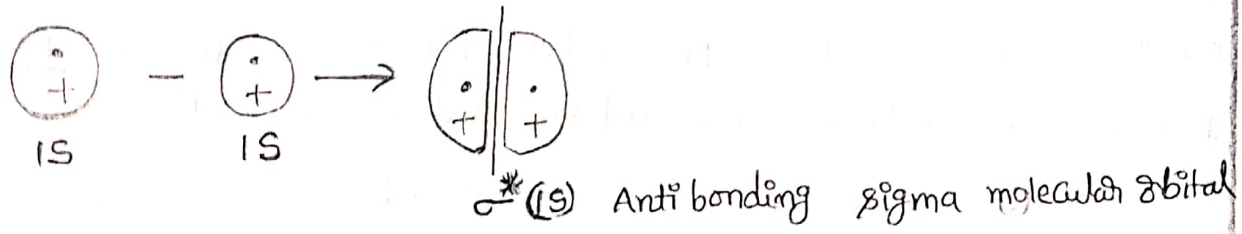
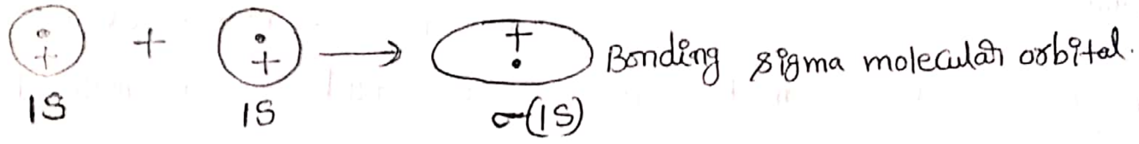
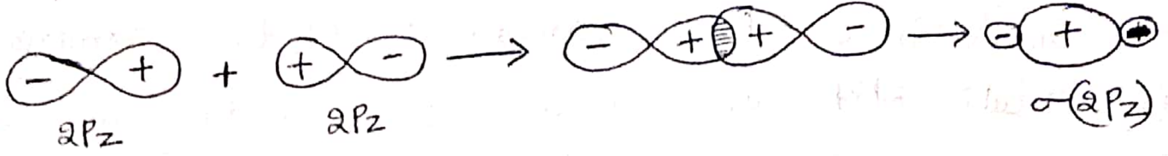


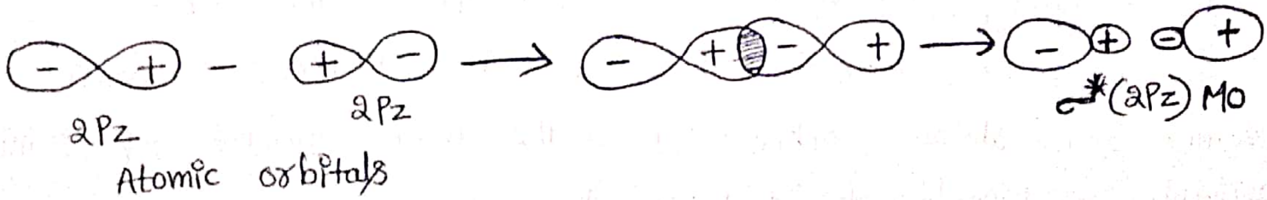


## Molecular orbitals from p-atomic orbitals:

Combination of p-orbitals is slightly complicated. There being three types of 2p-orbitals namely $2p_x$, $2p_y$ and $2p_z$ directed along the cartesian coordinates $x$, $y$ and $z$, respectively. By convention we assume that z-axis is the intermolecular axis.

**(i) Combination of $2p_z$ atomic orbitals:** The linear combination of two $2p_z$ orbitals on two atoms approach each other along the internuclear axis, they combine by the addition of electrons wave. This results in the formation of bonding $\sigma(2p_z)$ orbital while combination in substraction of electron waves gives rise to $\sigma^*(2p_z)$. It is representes as follows.





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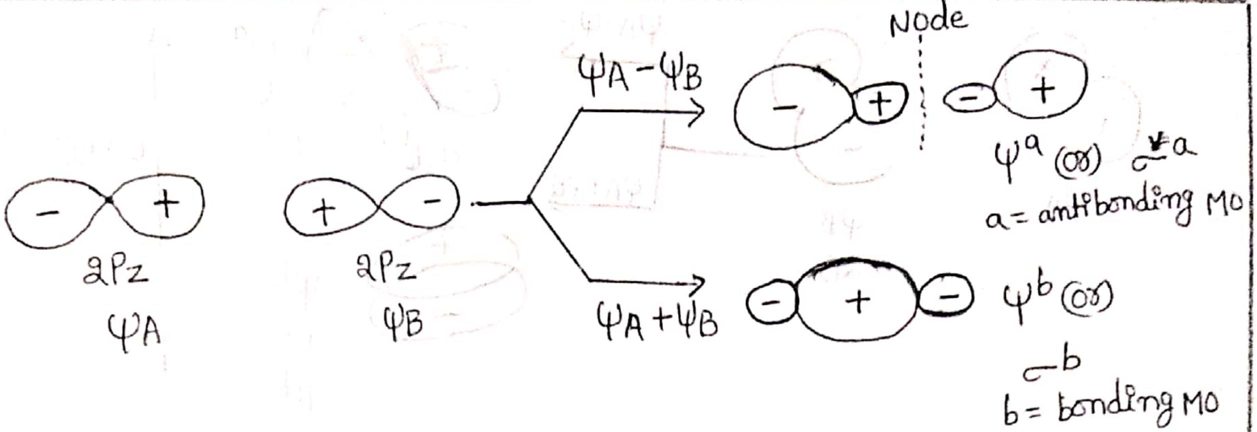
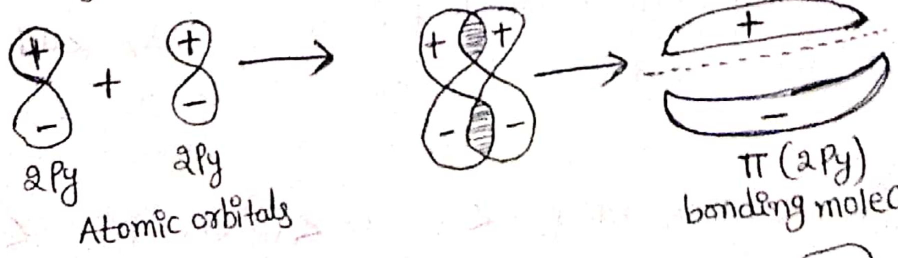


Molecular orbitals formed from 2Pz orbitals

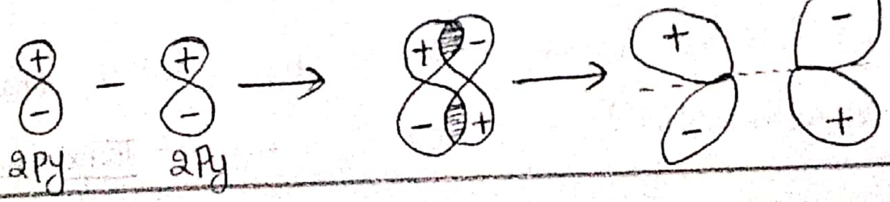
**(ii) Combination of 2Py and 2Px atomic orbitals:**

when two 2Py and 2Px orbitals on two atoms are approaching in a manner that their axes are mutually parallel, they interact to give rise to the formation of molecular orbitals that are not symmetrical about the internuclear axis and are called molecular orbitals represented by $\pi(2Py)$ (or) $\pi(2Px)$ bonding orbitals. These $\pi(2Py)$ and $\pi(2Px)$ bonding MO's have zero electron density on the plane that contains the nuclear axis (nodal plane), while the electron density is concentrated in two regions above and below the nodal plane.

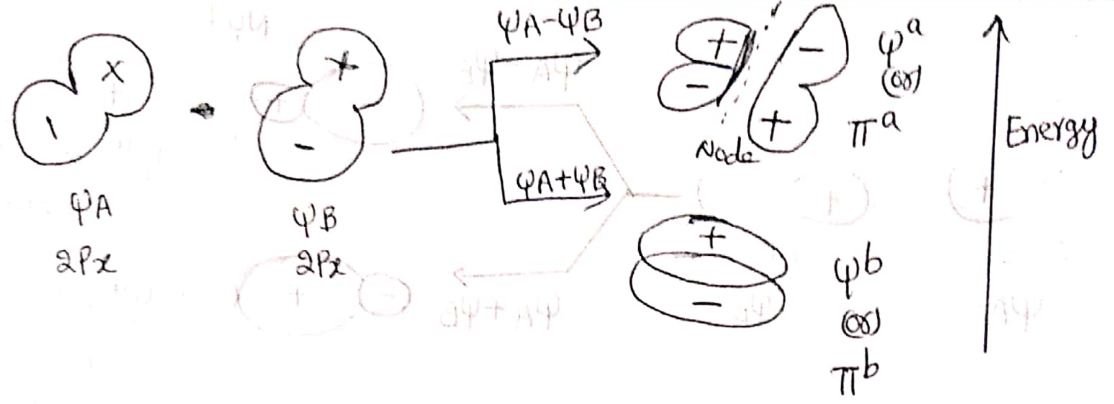
The $\pi^*(2Py)$ and $\pi^*(2Px)$ anti-bonding MO's have higher energy than their corresponding molecular and atomic orbitals. Since 2Py and 2Px atomic orbitals on an atom are degenerate (are of equal energy), the $\pi$ molecular orbitals arising out of them will also be degenerate i.e; $\pi(2Py)$ and $\pi(2Px)$ bonding molecular orbitals possess equal energy and the same situation prevails in antibonding molecular orbitals $\pi^*(2Py)$ and $\pi^*(2Px)$.



$\pi(2Py)$
bonding molecular orbital



$\pi^*(2Py)$
antibonding molecular orbital



Molecular orbitals formed from 2Px and 2Py orbitals

## Energy level diagram for Molecular orbitals :

We have seen that 1S atomic orbitals on two atoms form two molecular orbitals designated as $\sigma 1S$ and $\sigma^* 1S$. In the same manner, the 2S and 2P atomic orbitals (eight atomic orbitals on two atoms) give rise to the following eight molecular orbitals.

Antibonding MO's: $\sigma^*(1S)$, $\sigma^*(2S)$, $\sigma^*(2Pz)$, $\pi^*(2Py)$, $\pi^*(2Px)$
Bonding MO's : $\sigma(1S)$, $\sigma(2S)$, $\sigma(2Pz)$, $\pi(2Py)$, $\pi(2Px)$

The energy levels of these molecular orbitals have been determined experimentally from spectroscopic data for homonuclear diatomic molecules of second row elements of periodic table.

The increasing order of energies of various molecular orbitals for $O_2$ and $F_2$ is given below.

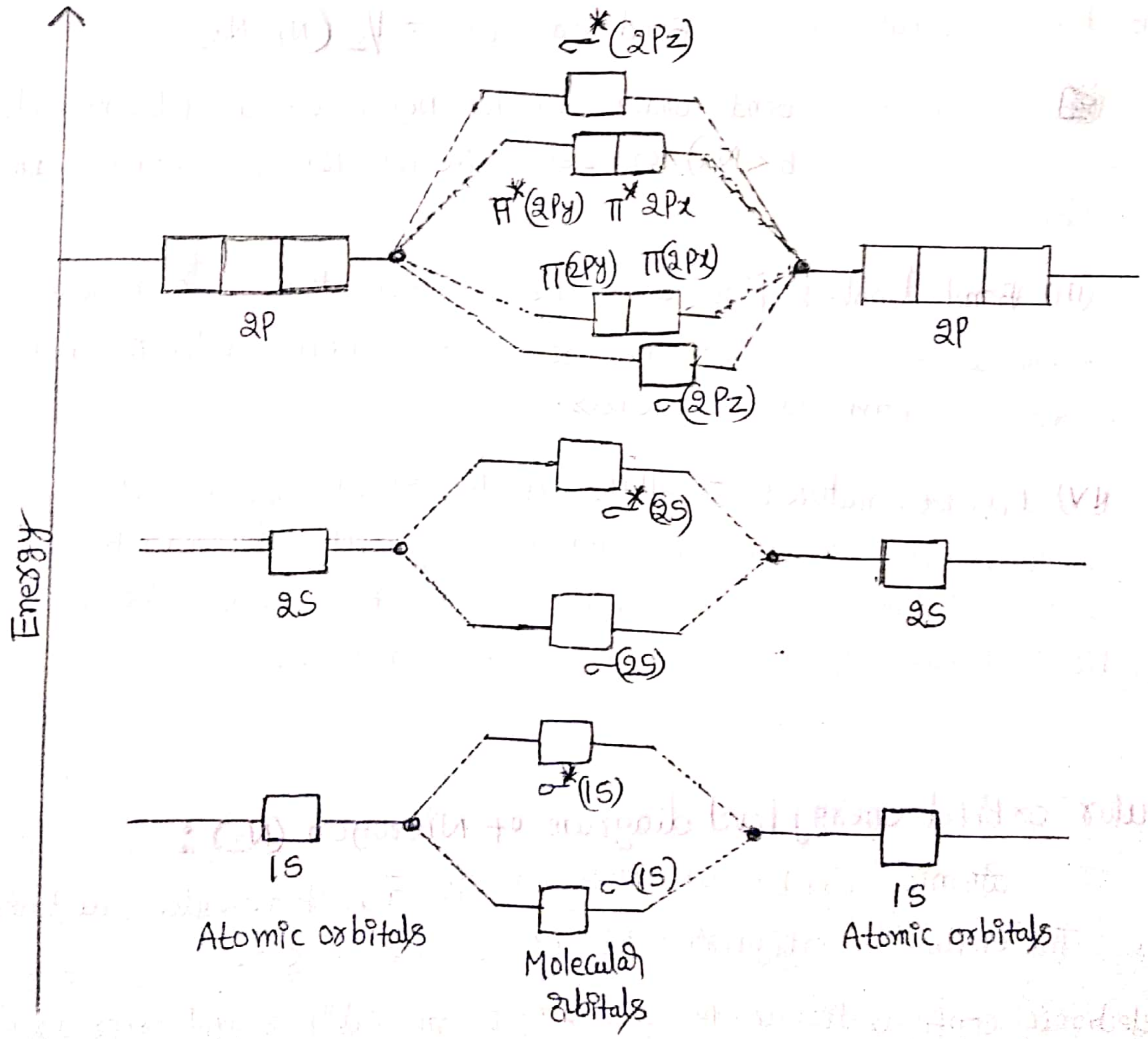
$$\sigma 1S < \sigma^* 1S < \sigma 2S < \sigma^* 2S < \sigma 2Pz < (\pi 2Px = \pi 2Py) < (\pi^* 2Px = \pi^* 2Py) < \sigma^* 2Pz$$

However, this sequence of energy levels of molecular orbitals is not correct for the remaining molecules $Li_2$, $Be_2$, $B_2$, $C_2$, $N_2$. For instance, it has been observed experimentally that for molecules such as $B_2$, $C_2$, $N_2$ etc. the increasing order of energies of various molecular orbital is

$$\sigma 1S < \sigma^* 1S < \sigma 2S < \sigma^* 2S < (\pi 2Px = \pi 2Py) < \sigma 2Pz < (\pi^* 2Px = \pi^* 2Py) < \sigma^* 2Pz$$

The important characteristics feature of this order is that the energy of $\sigma 2Pz$ molecular orbital is higher than that of $\pi 2Px$ and π 2Py molecular orbitals.

For diatomic molecules obtained from atom having more than one electronic shell, the inner shells do not appreiably affect the bonding and may be omitted. Such inner electrons are called <u>non-bonding</u> electrons. Electronic structures of simple molecules can be worked out by feeding in the molecular orbitals in the order of increasing energy. Here also <u>Aufbau</u> principle feeding electrons in the increasing order of energy of orbitals repeat it self. This order shown is figure.



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## Electronic configuration and molecular behaviour:

The distribution of electrons among various molecular orbitals is called electronic configuration of the molecule. From the electronic configuration of the molecule, it is possible to get important information about the molecule as discussed below.

i) **Stability of molecule:** If Nb is the number of electrons occupying orbitals and Na the number occupying the anti-bonding orbitals, the (a) the molecule is stable if Nb is greater than Nb, and (b) the molecule is unstable if Nb is less than Na.

ii) **Bond order:** Bond order (B.O) is defined as one half the difference between the number of electrons present in the bonding and anti-bonding orbitals i.e; Bond order (B.O) = $\frac{1}{2}(N_b - N_a)$

A positive bond order (i.e $N_b > N_a$) means a stable molecule while a negative (i.e $N_b < N_a$) (or) zero (i.e $N_b = N_a$) bond order means an unstable molecule.

iii) **Bond-length:** Bond order between two atoms in a molecule may be taken as an approximate measure of the bond length. The bond length decreases as bond order increases.

iv) **Magnetic nature:** If all the molecular orbitals in a molecule are doubly occupied, the substance is diamagnetic (repelled by magnetic field). However if one (or) more molecular orbitals are singly occupied it is paramagnetic (attracted by magnetic field). Eg. $O_2$ molecule.

## Molecular orbital energy level diagram of Nitrogen ($N_2$):

The atomic number of Nitrogen is 7, Homonuclear, diatomic molecule. The electronic configuration of N is $1s^2 2s^2 2p^3$.

The electronic configuration of $N_2$ according to molecular orbital approach is

$(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\pi 2p_x)^2, (\pi 2p_y)^2, (\sigma 2p_z)^2.$

Total number of electrons N + N = 7 + 7 = 14

Number of electrons in bonding molecular orbitals $(N_b) = 10$

Number of electrons in anti-bonding molecular orbitals $(N_a) = 4$

Total number of electrons $= 14$

$$\text{Bond order} = \frac{1}{2}[N_b - N_a]$$

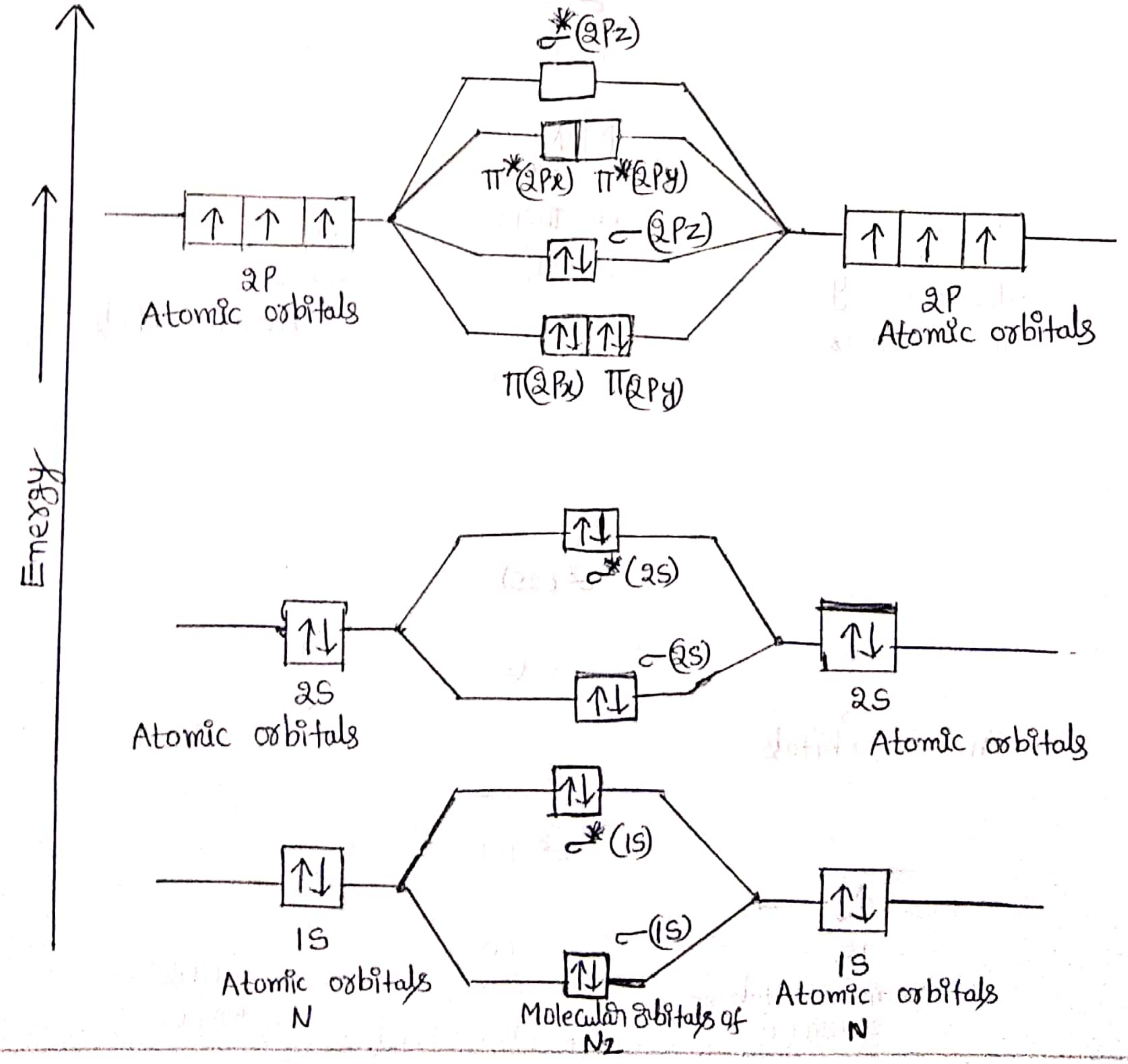
$$= \frac{1}{2}[10-4]$$

$$= \frac{1}{2} \times 6 = 3.0$$

Nature of bonding = Triple bonding, the two N atoms are bonded with three covalent bonds. i.e., a triple bond.

High value of bond order shows that $N_2$ contains highest bond dissociation energy.

**Magnetic nature:** $N_2$ is diamagnetic, since all electrons in bonding as well as anti-bonding MO. are paired and it has no unpaired electrons.



presence of $N_2$ paired electrons (all paired electrons) shows that $N_2$ is dia magnetic. The bond length is inversely proportional to the bond order.

## Molecular orbital Energy level diagram of $O_2$:

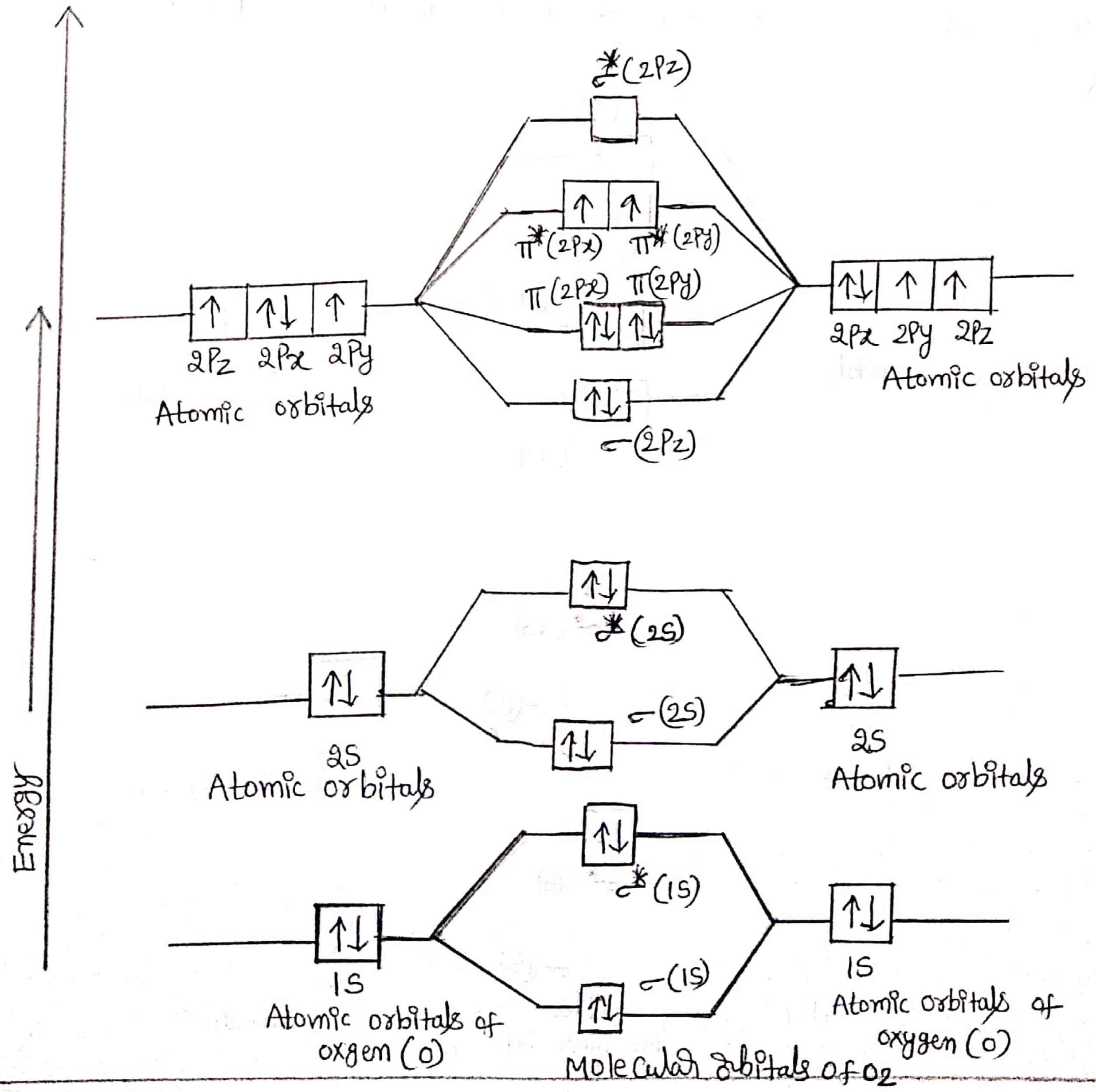
Oxygen molecule is homonuclear, diatomic molecule with following configuration. Atomic number of oxygen (O) = 8

The electronic configuration is $= 1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$

The electronic configuration of $O_2$ according to molecular orbitals is given as follows.

$\sigma(1s)^2, \sigma^*(1s)^2, \sigma(2s)^2, \sigma^*(2s)^2, \overset{\sigma(2p_z),}{\pi(2p_x)^2}, \pi(2p_y)^2, \pi^*(2p_x)^1, \pi^*(2p_y)^1, \sigma^*(2p_z)$

The molecular orbital energy diagram of $O_2$ is given as follows.



Number of Bonding electrons (Nb) = 10

Number of anti-bonding electrons (Na) = 6

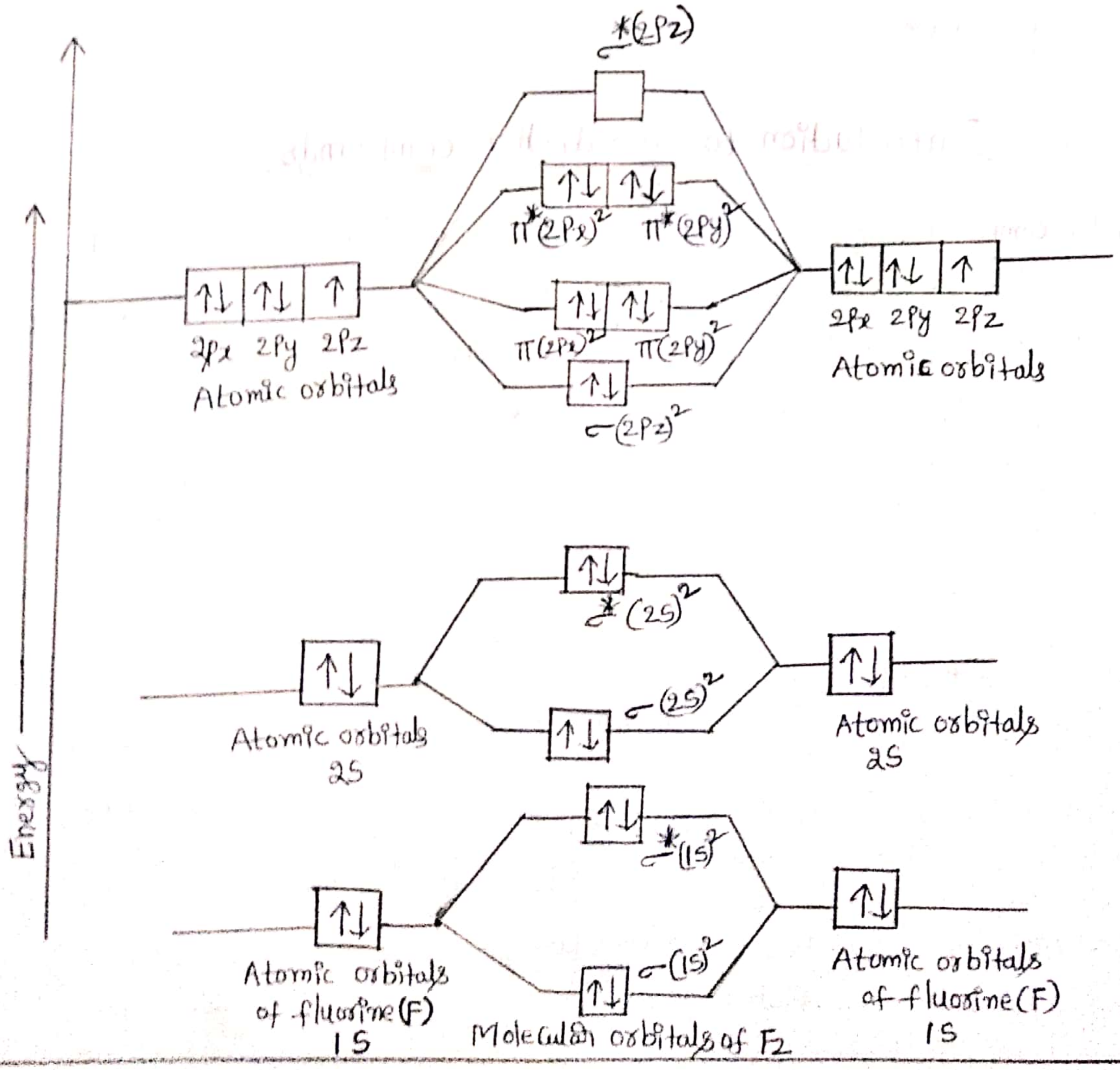
$$\text{Bond order} = \frac{1}{2}[Nb - Na]$$

$$= \frac{1}{2}[10 - 6]$$

$$= \frac{1}{2} \times 4 = 2.0$$

The bond order 2 justifies the presence of a double bond in $O_2$ molecule. The presence of two unpaired electrons show that oxygen molecule is paramagnetic, because it contains two unpaired electrons in $\pi^*(2Px)$ and $\pi^*(2Py)$ molecular orbital.

## Molecular energy diagram of Fluorine ($F_2$):



The electronic configuration of fluorine molecule is $= 1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$

Atomic number of fluorine $= 9\ (1s^2 2s^2 2p^5)$

The electronic configuration of fluorine molecule orbitals is

$(\sigma 1s)^2, (\sigma^* 1s)^2, (\sigma 2s)^2, (\sigma^* 2s)^2, (\sigma 2p_z)^2, (\pi 2p_x)^2 = (\pi 2p_y)^2, (\pi^* 2p_x^2 = \pi^* 2p_y^2), (\sigma^* 2p_z)$

Number of electrons in bonding molecular orbitals $(N_b) = 10$

Number of electrons in anti-bonding molecular orbitals $(N_a) = 8$

$$\text{Bond order} = \frac{1}{2}[N_b - N_a]$$
$$= \frac{1}{2}[10-8]$$
$$= \frac{1}{2} \times 2 = 1.0$$

The molecule ($F_2$) is very stable. The presence of all paired electrons in both bonding and anti-bonding molecular orbitals shows that fluorine molecule is diamagnetic.

## Introduction to coordination compounds

**Addition compounds:** The compounds obtained upon evaporation of solutions containing two (or) more simple compounds in molecular proportions are known as addition (or) molecular compounds, for example

$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$ (Potash alum)

$(NH_4)_2SO_4 + FeSO_4 + 6H_2O \longrightarrow (NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O$ (Mohr's salt)

] double salts

$CuSO_4 + 4NH_3 \longrightarrow CuSO_4 \cdot 4NH_3$ (Tetraammine copper sulfate)

$Fe(CN)_2 + 4KCN \longrightarrow Fe(CN)_2 \cdot 4KCN$ (Potassium ferrocyanide)

] Coordination compounds

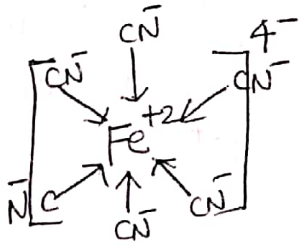
The addition compounds can be classified into two types on the basis of their behaviour in solution phase.

**Double salts:** The addition compounds which are stable in solid state but dissociate to provide all of their constituent ions upon dissolution in water (or) any other polar solvents are known as double salts. Therefore, such a salt behave similar to simple salts in solution. For example, potash alum upon dissolution in water provides $K^+$, $Al^{+3}$, $SO_4^{-2}$ ions.

**Coordination compounds:** The addition compounds which do not provide all of their constituent ions in solution are known as coordination (or) complex compounds. In such compounds, some of the constituent ions lose their identity. For example, potassium ferrocyanide upon dissolution in water provides only $K^+$ and $[Fe(CN)_6]^{4-}$. Here $Fe^{+2}$ and $C\bar{N}$ ions lose their identities and a complex ion $[Fe(CN)_6]^{4-}$ is formed instead.

## Termenologies :

**Ligand:** The moleacules (or) ions which remain directly attached to the central metal in a complex compound through coordinate linkages are known as ligands. The atom of the ligand which actually donates the electron pair for coordination is known as donor (or) coordination atoms. For example, in ferrocyanide ion, $C\bar{N}$ ions are ligands and "C" is the coordinating atom.



Ligands are classified usually on the basis of their number of donor sites into the following two categories.

(1) Monodentate ligands: such a ligand carries only one donor site.

For example, $\ddot{N}H_3$, $ph_3\ddot{P}$, $H_2\ddot{O}:$, $C_5H_3\ddot{N}$, $\bar{F}$, $N\overset{\ominus}{H_2}$ etc

(2) polydentate ligands: such a ligand carries more than one donor sites

For example: EDTA, oxalate etc.

**Co-ordination number:**

Co-ordination number of the central metal atom/ion is the number of donor sites of the ligands which remain attached to it through coordinate linkage. For example, $[Fe(CN)_6]^{4-}$: coordination number is 6; $[Cu(en)_2]^{+2}$: coordination number is 4; $[Co(NH_3)_5Cl]^{4+}Br_2$: coordination number is 6. coordination number of some common transition metals are given in the following table.

| Metal ion | coordination number | Metal ion | coordination number |
|---|---|---|---|
| $Fe^{+2}$ | 6 | $Au^{+}$ | 2,4 |
| $Co^{+2}$ | 4,6 | $Al^{+3}$ | 4,6 |
| $Ni^{+2}$ | 4,6 | $Cr^{+3}$ | 6 |
| $Cu^{+2}$ | 4,6 | $Fe^{+3}$ | 6 |
| $Zn^{+2}$ | 4 | $Co^{+3}$ | 6 |
| $Pt^{+2}$ | 4 | $Au^{+3}$ | 4 |
| $Cu^{+}$ | 2,4 | $Pt^{+4}$ | 6 |
| $Ag^{+}$ | 2 | | |

**Coordination Sphere:** The central metal atom/ion along with the ligands attached to it are placed within square brackets and is known as inner sphere (or) coordination sphere. The portion outside the square brakets is known as ionization (or) outersphere. The species in the inner sphere are non ionizable, whereas those in the outer sphere are ionizable.

$$\underbrace{[Co(NH_3)_5Cl]}_{\text{inner sphere}}\ \underbrace{Br_2}_{\text{outer sphere}} \longrightarrow [Co(NH_3)_5Cl]^{2+} + 2Br^-$$

**Spectrochemical series:** An arrangement of ligands according to their ability to increase magnitude (Δ) for a given metal center is called spectrochemical series.

Weak – $I^-$, $Br^-$, $SCN^-$, $Cl^-$, $N^{3-}$, $F^-$, $H_2NCONH_2$, $OH^-$, $OX^{-2}$, $O^{-2}$, $H_2O$, $NCS^-$, Py, $NH_3$, en, bpy, phen, $NO_2^-$, $CH^{3-}$, $C_6H_5^-$, $CN^-$, CO – Strong

A ligand that produces a large Δ is a strong-field (or low spin) ligand.

A ligand that produces a small Δ is a weak-field (or high spin) ligand.

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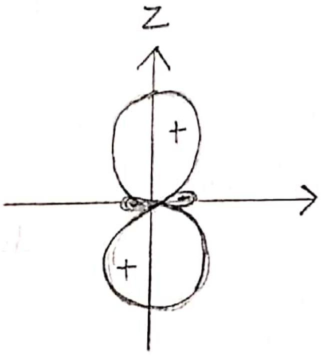
# Grouping of d-orbitals into two sets:

Based on the orientation of the lobes with respect to coordinates, five d-orbitals have been grouped as follows:

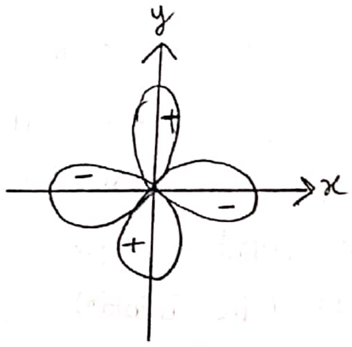
**(i) eg set of orbitals:** This group has the orbitals which have their lobes along the axes and hence are called axial orbitals. Quite obviously these are $d_{x^2y^2}$ and $d_{z^2}$ orbitals. Group theory calls these eg orbitals in which "e" refers to doubly degenerate set.

**(ii) t2g set of orbitals:** This group includes the orbitals whose lobes lie between the axes and are called non-axial orbitals. Quite obviously these are $d_{xy}$, $d_{yz}$ and $d_{zx}$ orbitals. Group theory calls these t2g orbitals, in which "t" refers to triply degenerate set.

eg set:

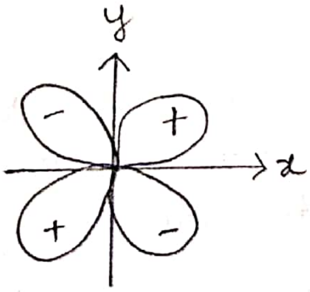


$3d_{z^2}$

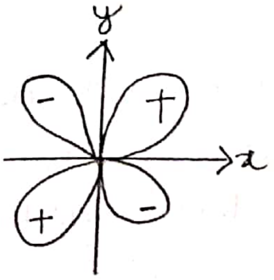


$3d_{x^2-y^2}$

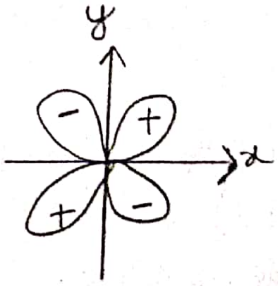
t2g set:



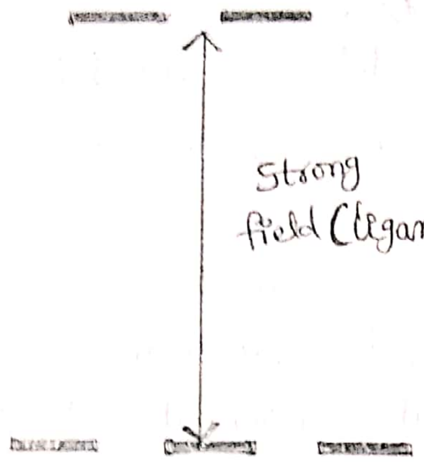
$3d_{xy}$

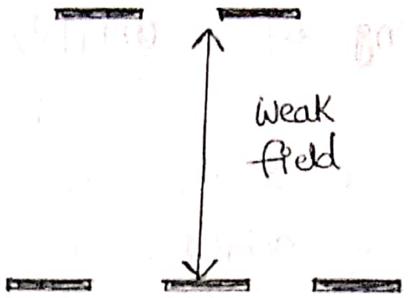


$3d_{xz}$



$3d_{yz}$





The $CN^-$ ligands has maximum splitting power whereas the ligands $I^{\ominus}$ has least splitting power.

**Salient features of crystal field theory (CFT):** This theory was developed by Brethe and Van Vleck. The salient features of this theory are as follows.

(i) The central metal cation is surrounded by ligands, which contain one or more lone pair of electrons.

(ii) The ligands are treated as point charges.

(iii) The ionic ligands (eg: $F^-$, $Cl^-$, $CN^-$ etc) are regarded as negative point charges, while neutral ligands (eg: $H_2O$, $NH_3$ etc) are regarded as dipoles (i.e dipolar). In metal complexes, the negative end of the neutral ligand is oriented towards the central metal cation.

(iv) There is no interaction between metal orbitals and ligand orbitals.

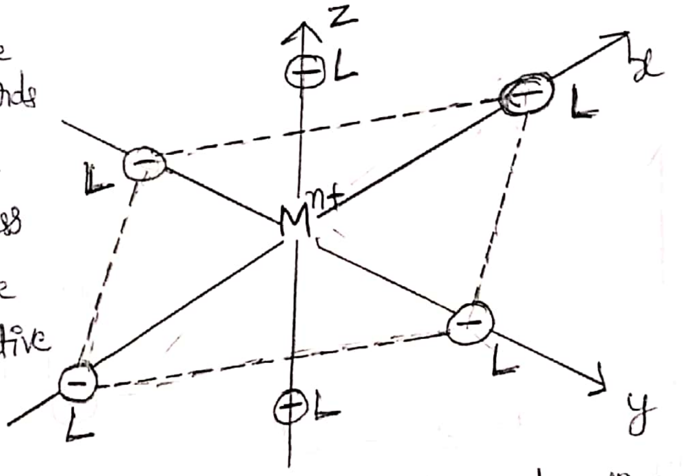
(v) The bonding between the metal cation and ligand is purely electrostatic (or) coulombic attraction between anion (positively charged) and negatively charged anion (or) negative end of neutral dipole molecule.

(vi) All the d-orbitals on the metal have the same energy (i.e degenerate) in the free atom. However, when a complex is formed, the ligand destroy the degeneracy of these orbitals, i.e. the orbitals now have the different energies.

# Crystal field splitting of d-orbitals in octahedral complexes :

In case of free metal ion all the five d-orbitals are degenerate, i.e; these have the same energy. Now let us consider an octahedral complex $[ML_6]^{n+}$ in which the central metal cation, $M^{n+}$ is placed at the centre of the octahedron and its surrounded by six ligands which reside at the corners of the octahedron as shown in fig.

(i) The ligands on each of the three axes are allowed to approach towards the metal cation, $M^{n+}$ from both the ends of the axes. In this process the electrons in d-orbitals of the metal cation are repelled by negative point charge (or) by the negative end of the dipole of the ligands.

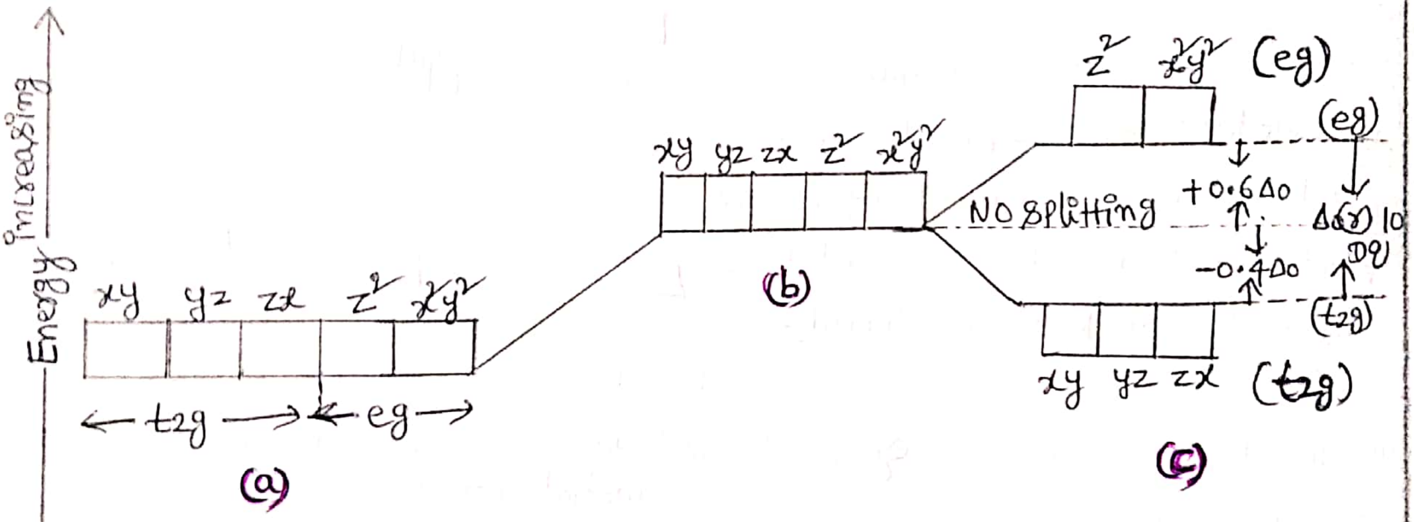


Position of the central metal cation, $M^{n+}$ and six ligands, L's in an octahedral complex.

(ii) The lobes of the two eg orbitals (i.e $d_{z^2}$ and $d_{x^2-y^2}$), lie directly in the path of the approaching ligands, the electrons in these orbitals experience greater force of repulsion than those in three $t_{2g}$ orbitals ($d_{xy}$, $d_{yz}$ and $d_{zx}$), whose lobes are directed in space between the path of the approaching ligands. So the energy of eg orbitals is increased while that $t_{2g}$ orbitals is decreased. (greater is the repulsion, greater is increase the energy).

So under the influence of approaching ligands the five d-orbitals which were split into two levels. (i) $t_{2g}$ level, which is triply degenerate and is of lower energy and (ii) $e_g$ level, which is doubly degenerate and is of higher energy. The separation of five d-orbitals of the metal ion into 2 sets having different energies is called crystal field splitting (or) energy level splitting.

This energy difference arises because of the electrostatic field exerted by the ligands on $t_{2g}$ and $e_g$ sets of orbitals of the central metal cation is called crystal field stabilization energy. It is denoted by $\Delta_o$ (or) 10 Dq. Thus, we find that $t_{2g}$ set loses an energy equal to $0.4\Delta_o$ $(= 4Dq)$, while $e_g$ set gains an energy equal to $0.6\Delta_o$ $(= 6Dq)$. The loss and gain in energies of $t_{2g}$ and $e_g$ orbitals is shown by negative and positive signs, respectively.



(a) five degenerate d-orbitals of free metal cation which are free from any ligand field. (b) Hypothetical degenerate d-orbitals at a higher energy level under spherically ligand field. (c) Splitting of d-orbitals is under influence of approaching ligands in-to $t_{2g}$ and $e_g$ sets.

**Distribution of d-electrons in $t_{2g}$ and $e_g$ orbitals in octahedral complexes :** The distribution of d-electrons in $t_{2g}$ and $e_g$ orbitals takes place on the basis of the nature of the ligands. i.e. whether the ligands are weak (or) strong.

(i) **when the ligands are weak :** under the influence of weak ligands the energy difference, $\Delta_o$ between $t_{2g}$ and $e_g$ sets is relatively small and hence all the five d-orbitals of these two sets may be supposed to be degenerate, i.e. in the presence of weak ligands all the d-orbitals have the same energy and consequently the distribution of d-electrons in $t_{2g}$ and $e_g$ sets takes place according to Hund's rule, which states that electrons will pairup only when each of the five-d-orbitals is at least singly filled.

(ii) **when the ligands are strong :** In octahedral complexes containing strong ligands, distribution of d-electrons in $t_{2g}$ and $e_g$ sets does not obey Hund's rule. Thus in stronger field the first six electrons numbered as 1-6 will go $t_{2g}$-set and the remaining four electrons numbered as 7-10 enter $e_g$-set.

| $d^n$ ions | Stronger field (low-spin complexes) | | | Weak field (high-spin complexes) | | |
|---|---|---|---|---|---|---|
| | $t_{2g}$ $e_g$ configuration | n | S | $t_{2g}$ $e_g$ configuration | n | S |
| $d^1$ | $t_{2g}^{1}$ $e_g^{0}$ | 1 | ½ | $t_{2g}^{1}$ $e_g^{0}$ | 1 | ½ |
| $d^2$ | $t_{2g}^{2}$ $e_g^{0}$ | 2 | 1 | $t_{2g}^{2}$ $e_g^{0}$ | 2 | 1 |
| $d^3$ | $t_{2g}^{3}$ $e_g^{0}$ | 3 | 3/2 | $t_{2g}^{3}$ $e_g^{0}$ | 3 | 3/2 |
| $d^4$ | $t_{2g}^{4}$ $e_g^{0}$ | 2 | 1 | $t_{2g}^{3}$ $e_g^{1}$ | 4 | 2 |
| $d^5$ | $t_{2g}^{5}$ $e_g^{0}$ | 1 | ½ | $t_{2g}^{3}$ $e_g^{2}$ | 5 | 5/2 |
| $d^6$ | $t_{2g}^{6}$ $e_g^{0}$ | 0 | 0 | $t_{2g}^{4}$ $e_g^{2}$ | 4 | 2 |
| $d^7$ | $t_{2g}^{6}$ $e_g^{1}$ | 1 | ½ | $t_{2g}^{5}$ $e_g^{2}$ | 3 | 3/2 |
| $d^8$ | $t_{2g}^{6}$ $e_g^{2}$ | 2 | 1 | $t_{2g}^{6}$ $e_g^{2}$ | 2 | 1 |
| $d^9$ | $t_{2g}^{6}$ $e_g^{3}$ | 1 | ½ | $t_{2g}^{6}$ $e_g^{3}$ | 1 | ½ |
| $d^{10}$ | $t_{2g}^{6}$ $e_g^{4}$ | 0 | 0 | $t_{2g}^{6}$ $e_g^{4}$ | 0 | 0 |

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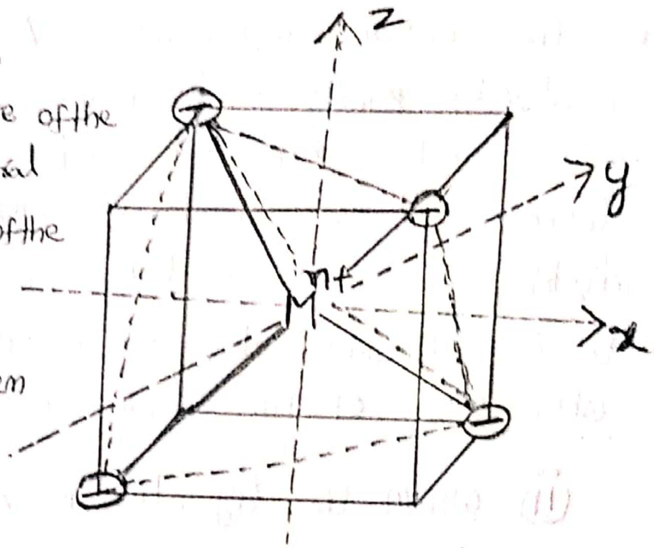
n = No. of unpaired electrons

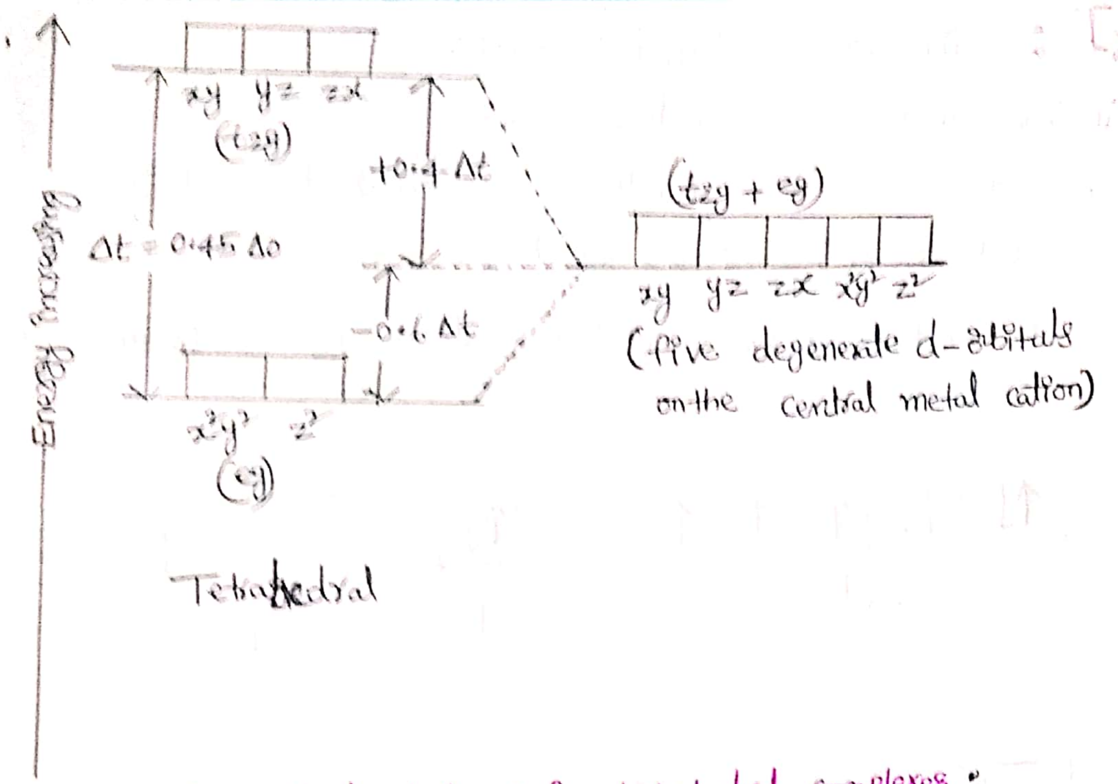
S = Resultant spin = $\frac{1}{2} \times n$

## Crystal field splitting of d-orbitals in Tetrahedral complexes:

A tetrahedron placed in a cube. The centre of the cube is the centre of the tetrahedron at which is placed central metallic cation $M^{n+}$. Four corners of the cube are the four corners of the tetrahedron at which are placed the four negative ligands which have been shown by circles with negative signs.



In order to understand the splitting of d-orbitals in tetrahedral complexes it is convienient to picture a tetrahedron placed inside a cube. The four negative ligands placed at the four corners of the tetrahedron are located at the four corners of the cube. Thus, these four ligands are lying between the three axes viz: x, y and z axes. The lobes of $t_{2g}$ orbitals ($d_{xy}$, $d_{yz}$ and $d_{zx}$) are lying between the axes, i.e are lying directly in the path of the ligands, these orbitals will experience greater force of repulsion from the ligands than those of eg orbitals ($d_{z^2}$ and $d_{x^2y^2}$) whose lobes are lying along the axes, i.e are lying in space between the ligands. Thus the energy of $t_{2g}$ orbitals will be increased while that of eg orbitals will be decreased. Consequently the d-orbitals are again split into two sets as shown below. The order of energy of $t_{2g}$ and eg sets is the reverse of that seen in octahedral complexes. The energy difference between $t_{2g}$ and eg sets for tetrahedral complex is represented as $\Delta t$.



Tetrahedral

## Distribution of d-electrons in tetrahedral complexes :

| $d^n$ configuration | Weak field (HS-complexes) | | | Strong field (LS-complexes) | | |
|---|---|---|---|---|---|---|
| | $t_{2g}$ $e_g$ configuration | n | S | $t_{2g}$ $e_g$ configuration | n | S |
| $d^1$ | $t_{2g}^0\ e_g^1$ | 1 | ½ | $t_{2g}^0\ e_g^1$ | 1 | ½ |
| $d^2$ | $t_{2g}^0\ e_g^2$ | 2 | 1 | $t_{2g}^0\ e_g^2$ | 2 | 1 |
| $d^3$ | $t_{2g}^1\ e_g^2$ | 3 | 3/2 | $t_{2g}^0\ e_g^3$ | 1 | ½ |
| $d^4$ | $t_{2g}^2\ e_g^2$ | 4 | 2 | $t_{2g}^0\ e_g^4$ | 0 | 0 |
| $d^5$ | $t_{2g}^3\ e_g^2$ | 5 | 5/2 | $t_{2g}^1\ e_g^4$ | 1 | ½ |
| $d^6$ | $t_{2g}^3\ e_g^3$ | 4 | 2 | $t_{2g}^2\ e_g^4$ | 2 | 1 |
| $d^7$ | $t_{2g}^3\ e_g^4$ | 3 | 3/2 | $t_{2g}^3\ e_g^4$ | 3 | 3/2 |
| $d^8$ | $t_{2g}^4\ e_g^4$ | 2 | 1 | $t_{2g}^4\ e_g^4$ | 2 | 1 |
| $d^9$ | $t_{2g}^5\ e_g^4$ | 1 | ½ | $t_{2g}^5\ e_g^4$ | 1 | ½ |
| $d^{10}$ | $t_{2g}^6\ e_g^4$ | 0 | 0 | $t_{2g}^6\ e_g^4$ | 0 | 0 |

n = number of unpaired electrons

$S = n \times \frac{1}{2}$

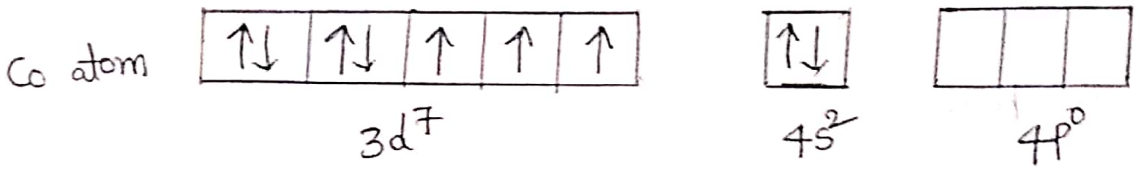
CFT is helpful in determining the number of unpaired electrons in a given HS (high spin) - and LS (Low spin) - tetrahedral and octahedral complexes, and consequently with the help of "spin only" - formula. $\mu = \sqrt{n(n+2)}$ BM.

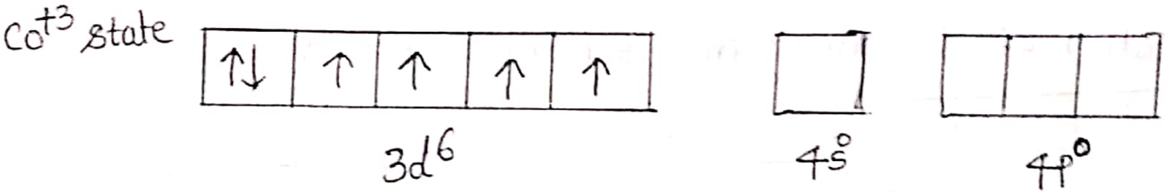
$[Co(CN)_6]^{3-}$ : This is a octahedral complex

Atomic number of cobalt is = 27

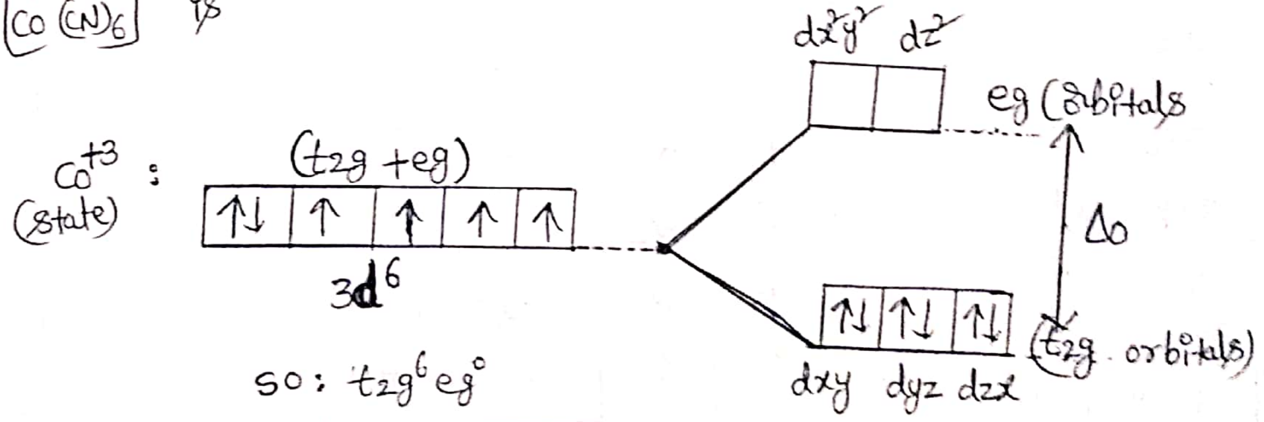
The electronic configuration of cobalt in ground state = $3d^7 4s^2$
$(1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7)$

In this complex cobalt is in oxidation state = +3 on formation of Co(III).





In the presence of $CN^-$, which is a strong-field ligand, the 3d electrons show tendency to pair up. So the splitting pattern of $[Co(CN)_6]^{3-}$ is



so: $t_{2g}^6 e_g^0$

spin-only formula = $\mu = \sqrt{n(n+2)}$ BM

$\mu$ = Magnetic moment
n = number of unpaired electrons

So in $[Co(CN)_6]^{3-}$ number of unpaired electrons = 0

S = $\mu = 0$ BM

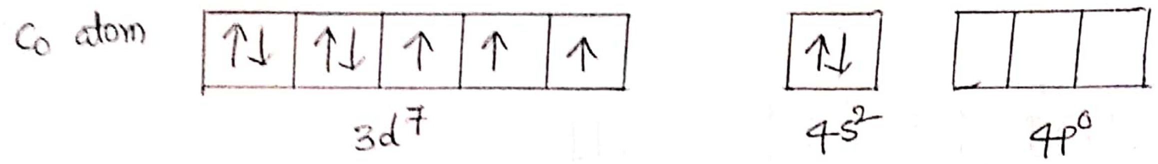
So $[Co(CN)_6]^{3-}$ has no magnetic property.

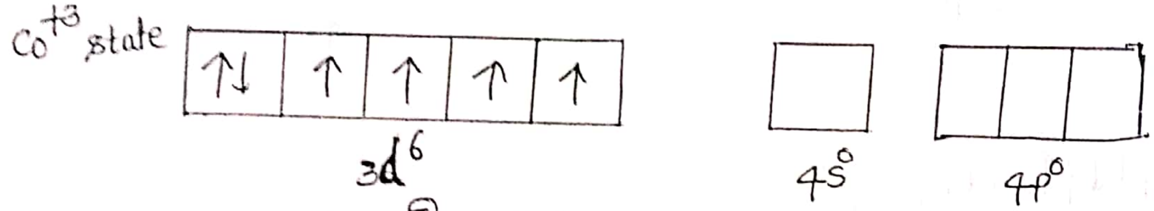
$[CoF_6]^{3-}$ : This is a octahedral complex

Atomic number of cobalt = 27

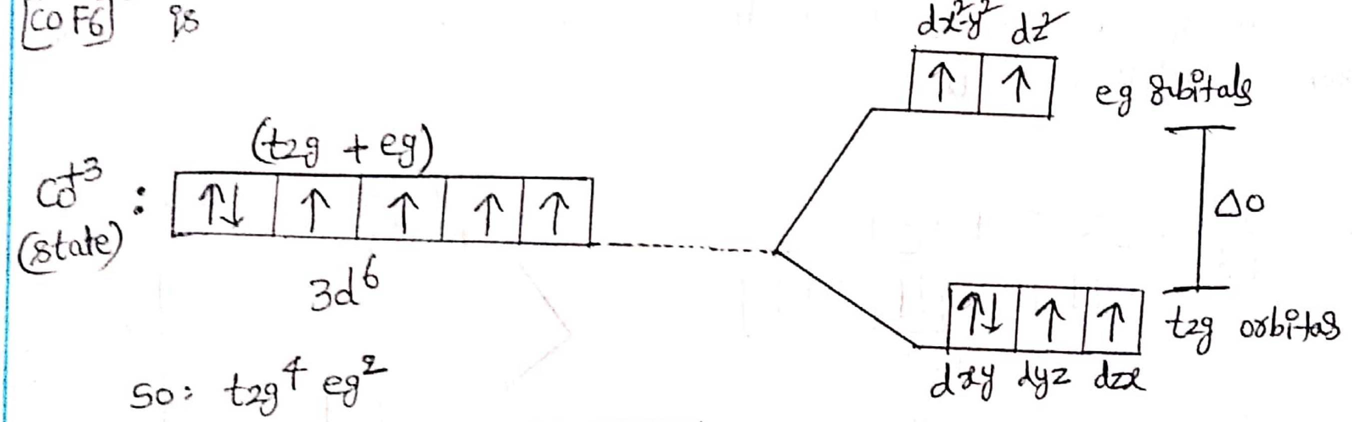
The electronic configuration of cobalt in ground state $= 3d^7 4s^2$
$(1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2)$

In this complex Cobalt is in oxidation state = +3 on formation of Co(III).





In the presence of $F^{\ominus}$, which is a weak-field ligand, the 3d electrons do not show only tendency to pair up. So the splitting pattern of $[CoF_6]^{3-}$ is



So: $t_{2g}^4\ e_g^2$

Spin only formula $= \mu = \sqrt{n(n+2)}$ BM

$\mu$ = Magnetic moment

$n$ = number of unpaired electrons

So in $[CoF_6]^{3-}$ unpaired ~~paired~~ electrons = 4

$\therefore \mu = \sqrt{n(n+2)}$

$\mu = \sqrt{4(4+2)}$

$\mu = \sqrt{24}$

$\mu = 4.89$ BM

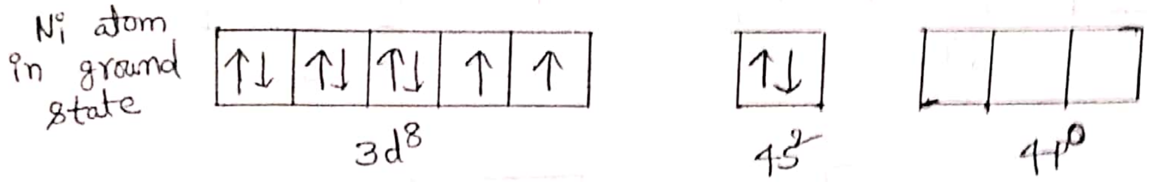
$[CoF_6]^{-3}$ has exhibiting magnetic property.

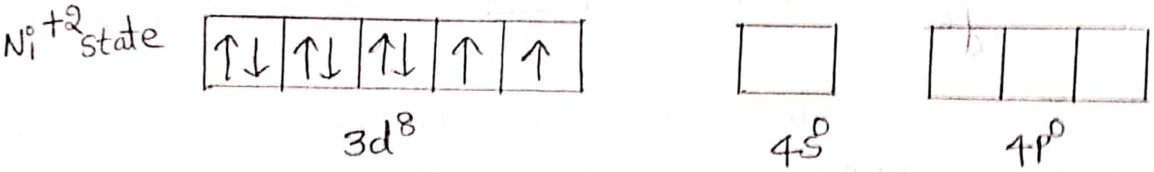
$[NiCl_4]^{2-}$ : This is a tetrahedral complex

Atomic number of Nickel is = 28

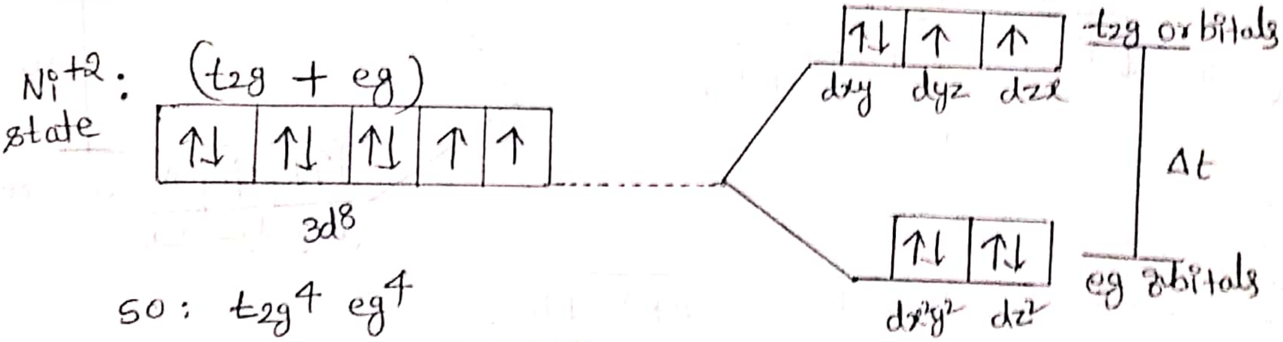
The electronic configuration of Nickel in ground state = $3d^8 4s^2$
$(1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8)$

In this complex Nickel is in oxidation = +2, so on formation of Ni (II) complex.





In the presence of $Cl^-$, which is weak-field legand, it does not have the tendency to pair up the electrons in the 3d level. so the splitting pattern of $[NiCl_4]^{-2}$ is



So : $t_{2g}^4\ eg^4$

spin only formula = $\mu = \sqrt{n(n+2)}$ BM

$\mu$ = Magnetic moment

n = number of unpaired electrons

So in $[NiCl_4]^{2-}$ : $\mu = \sqrt{n(n+2)}$

$\mu = \sqrt{2(2+2)}$

$\mu = \sqrt{8}$

$\mu$ = 2.82 BM

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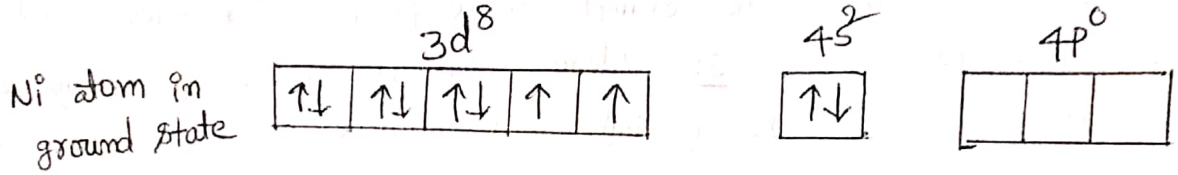
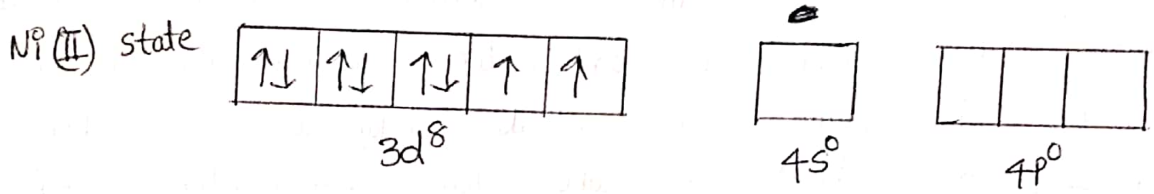
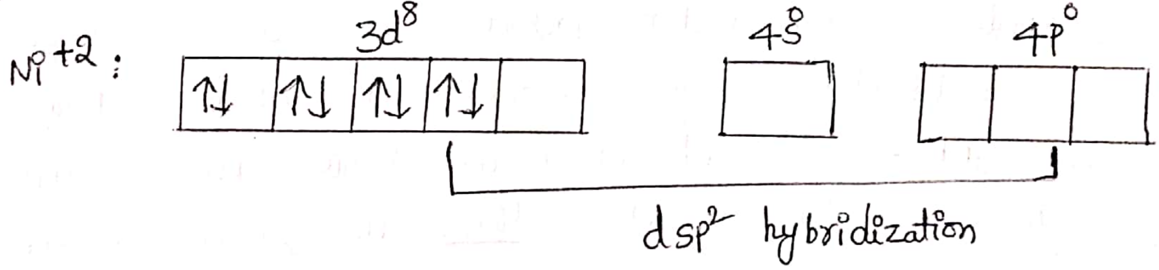
$[Ni(CN)_4]^{-2}$: This is a Tetrahedral complex. In this case again Ni is in (+2) oxidation state. The electronic configuration of Ni atom is $3d^8 4s^2$ ($1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^8$) in ground state which changes to $3d^8 4s^0$ on the formation of Ni(II) with the loss of two electrons.





Since $CN^{\ominus}$ is a very strong field ligand, it has the tendency to pair up electrons in the 3d level so as to set up space for its own electrons to be accommodated. Now, the configuration changes as shown



Thus, empty 3d-orbitals, 4s and two 4p orbitals hybridize to form four equivalent $dsp^2$ orbitals. The four lone pairs from cyanide ligands occupy these orbitals to form square planar and diamagnetic complex.

$[Ni(CN)_4]^{2-}$ in this complex unpaired electrons = 0 so spin only formula

$$\mu = \sqrt{n(n+2)}$$

$$\mu = 0$$

# BAND Structure of solids :

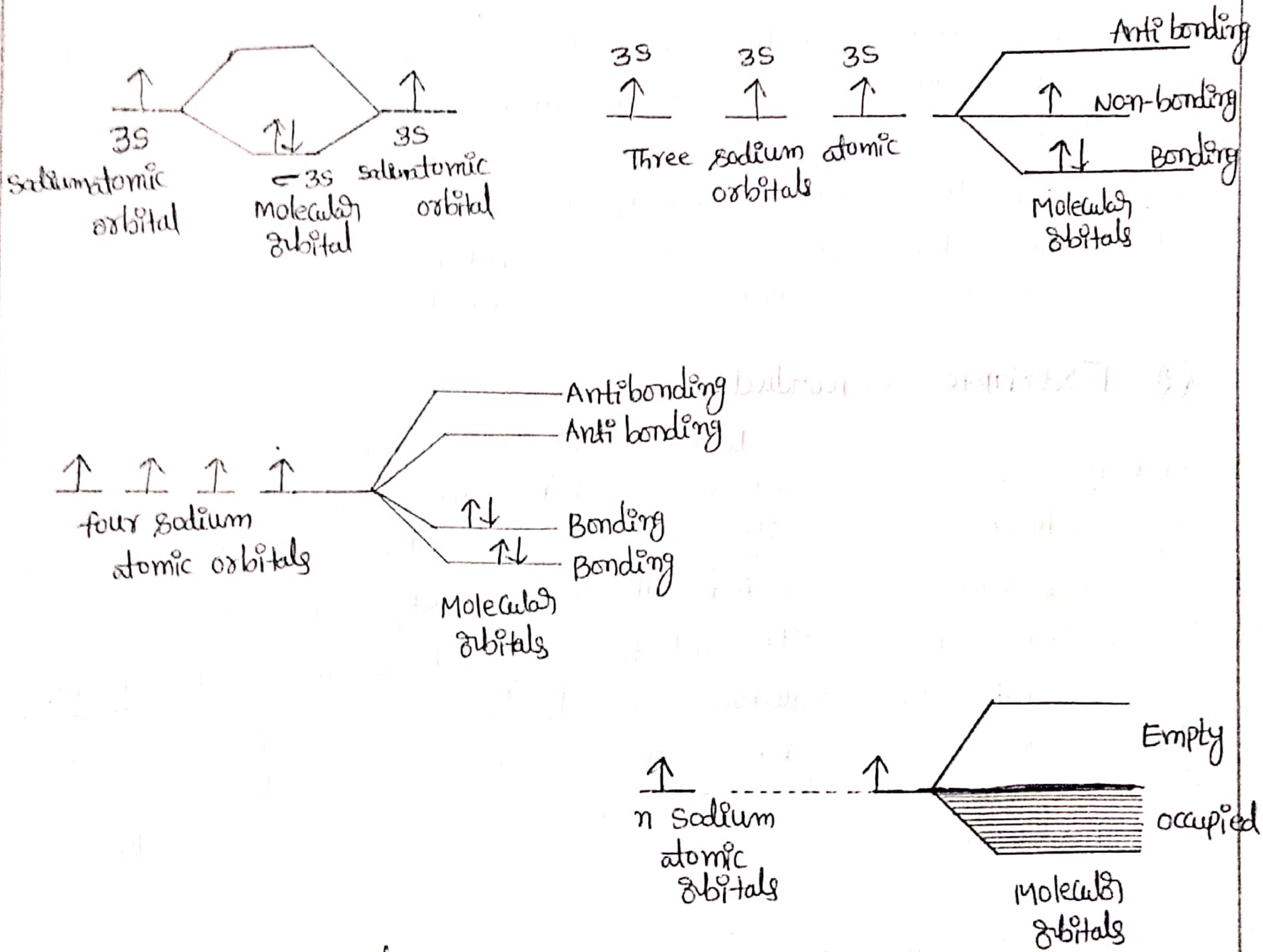
The molecular orbital theory of metals is known as band model. Since the smallest perceptible piece of metal would contain about $10^{20}$ atoms. A large number of molecular orbital are formed from a large number of atomic orbitals.

Let us consider the example of a piece of sodium metal. Each sodium atom has single 3s valence electron. When two atoms are closer together, the atomic orbitals will combine to form two molecular orbitals, $\underline{3\sigma^{s}}$ and $\underline{3\sigma^{s*}}$. The two electrons will occupy the bonding molecular orbital, while the antibonding orbital will remain empty. Similarly for three atoms, three molecular orbitals are formed - bonding, non-bonding and antibonding. When four sodium atoms combine, we get two $\underline{3\sigma^{s}}$ orbitals and $\underline{3\sigma^{s*}}$ orbitals. The quantum mechanical considerations do not permit these orbitals to be degenerate but they are closely placed, being almost similar in energy. The concept can be extended to $\underline{n}$ number of sodium atoms present in a piece of sodium metal. In this multi-atom system, the number of molecular orbital states will be equal to the number (n) of the atomic orbitals combining. Since the number of molecular orbitals is <u>large</u>, the spacing between them <u>decreases</u> to become almost neglegible and we get a "<u>band of continuous energy levels</u>". These molecular orbitals extend in all three dimensions over all the atoms in the metal piece. The energy levels known as bands. The molecular orbital theory is known as <u>Band model</u>.

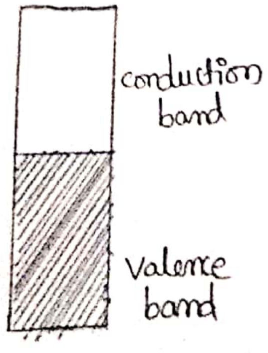
The molecular orbital which contains the pair of electrons is called <u>valence orbitals</u> and the <u>band</u> formed it is called <u>valence band</u>. The molecular orbital which is higher energy level is vacant and it is called <u>conducting orbitals</u>, which is formed by the <u>band</u> is called <u>conducting band</u>. Now the fermi <u>energy</u> gap between the valence band and conducting band plays an important role. If the <u>fermi gap</u> is more the material becomes <u>insulator</u>, if the <u>fermi</u> energy gap is <u>least</u>

the material becomes conductor because when the electron in valence band are exposed to heat, light, energy, they absorb the energy and excited to higher energy level. when fermi energy gap is more, the electrons can not be excited to the conducting band, and the material becomes insulator.

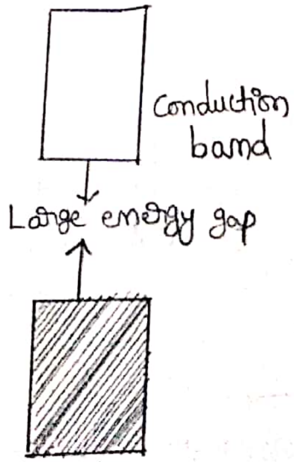
If the fermi energy gap is in between a conductor and insulator, then that material becomes semiconductor.



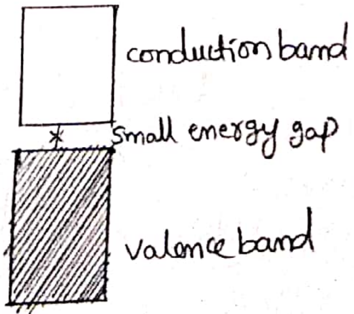
MO diagram for 2, 3, and n sodium atoms



Conductors



Insulators



semiconductors

# Role of doping in band structures :

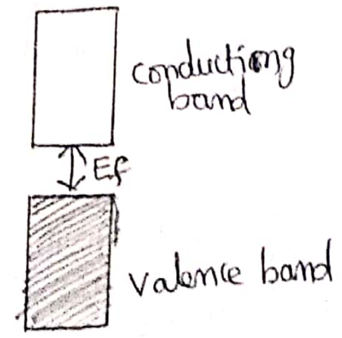
**Types of semiconductors :** semiconductors are of two types (1) Intrinsic semiconductors
(2) Extrinsic semiconductors

## (1) Intrinsic semiconductors :

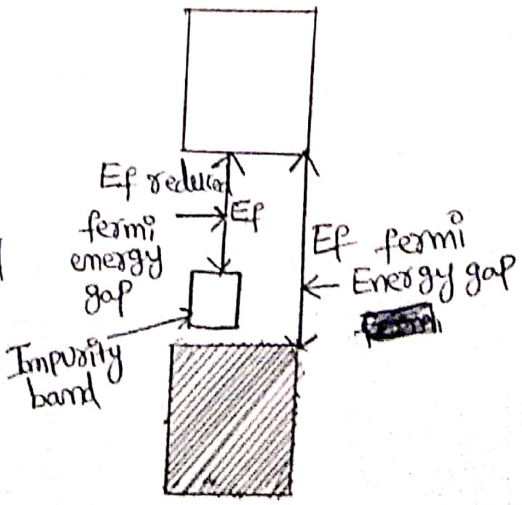
If the fermi energy gap is small between the valence band and conducting band, the electron from valence band is exited to conducting band, it is called intrinsic semiconductor both the hole left in valence band and the excited electron to the conduction band contribute towards conductivity. As the temperature rises, the number of electrons promoted to the conduction band increases contributing to the increase in conductivity of semiconductor.

## (2) Extrinsic semiconductors :

If the fermi energy gap is more, where the electrons cannot be excited to conduction band, conductance can be improved by introducing an impurity into the semiconducting material which is called doping. Doping can be carried out by introducing an electron deficient (or) electron rich impurity into the material which produces p-type and n-type semiconductors respectively. The impurity forms an impurity band called donor band between valence band and conducting band of the material, whereby the fermi energy gap is reduced and conduction takes place.



Intrinsic semi conductor



Extrinsic semiconductor

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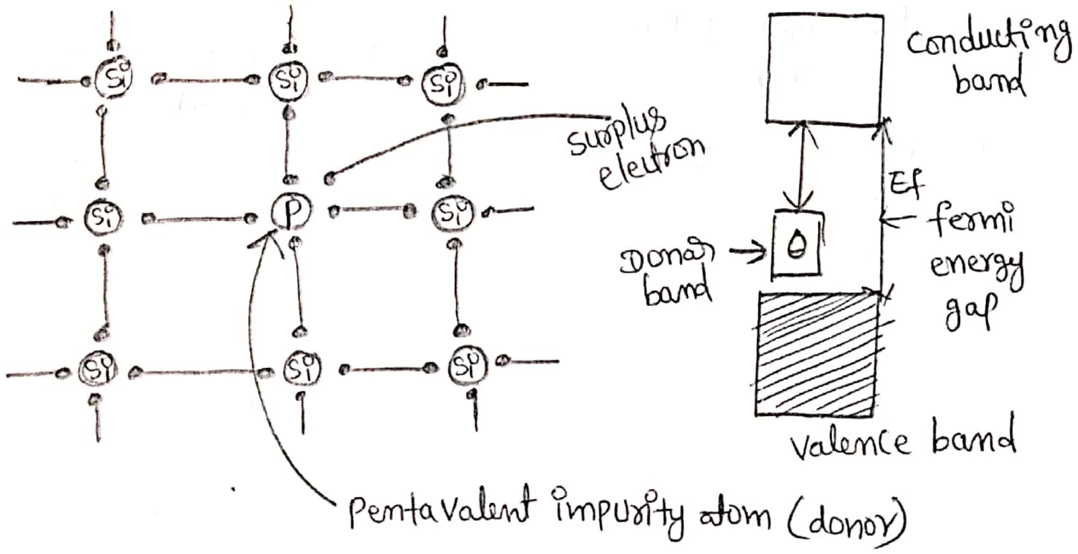
## n - Type semiconductor :

n- type semiconductors were produced by doping Si (or) Ge with pentavalent impurity atoms like P, As etc. A minute amount of Si (or) Ge atoms are replaced by P (or) Ge atoms are replaced by P with five electrons in it's outer shell. only four electrons from covalent bonds with Si (or) Ge and the fifth electron is localized at absolute zero. At the normal temperature some of the fifth electrons of impurity are promoted to conduction band, causing conduction. Since the conductivity of such semiconductors are due to negative electrons, there are called n-type semiconductors.



## P- Type semiconductor:

By introducing a trivalent impurity atom like, B, Al, Ga. into Si (or) Ge the replacement of these Si (or) Ge atoms by impurity produces an incomplete bond in the structure producing a positive hole. The positive holes are localized around trivalent impurity atom at low temperatures (or) absolute zero. At normal temperatures the valence electrons on the adjacent Si (or) Ge atom may gain sufficient energy to move into the hole, thus creating a new hole on the Si (or) Ge. By a series of hops, the positive hole can migrate across the crystall, thus current is carried out by the migration of positive centres.

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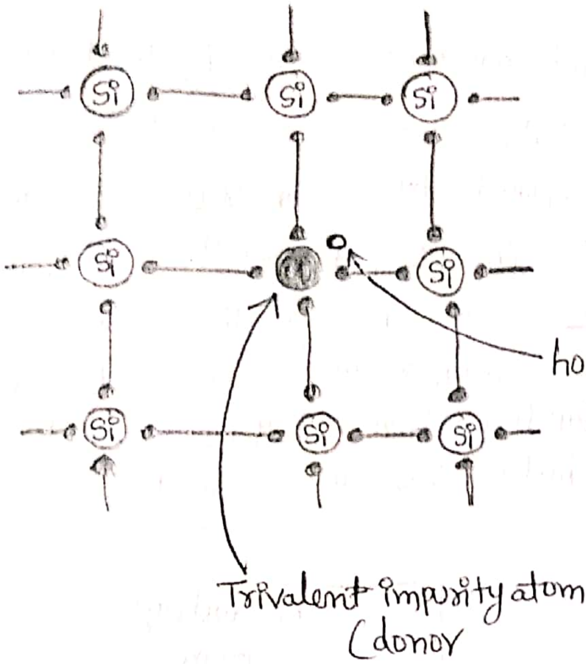
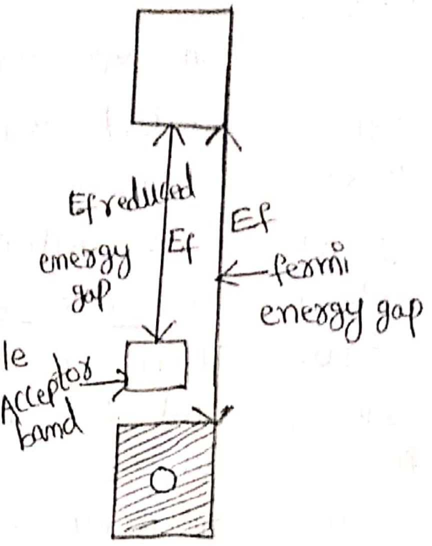


Positive hole on Si crystal lattice



A mobile hole in the band of semiconductor

# Module-III

## Electrochemistry and Corrosion

# MODULE-III

# ELECTRO CHEMISTRY AND CORROSION

## Q.1. Define Specific, Equivalent and Molecular conductance and their units?

**Specific conductance:** The resistance offered by a conductor to the passage of electricity through it is directly proportional to length (l) and inversely proportional to the area of cross section (a). The resistance R

$$R \;\alpha l/a$$
$$R = \rho\ l/a$$
$\rho$= specific resistance
$$R = \rho l/a$$
$$\rho = Ra/l$$
Units: Resistance = R = Ohm

Where $\rho$ (rho) is a constant known as "specific resistance".

Specific conductance (Kv) is the reciprocal of specific resistance. Kv= $1/\rho$

Kv=l/Ra

Specific conductance is expressed in reciprocal $Ohm^{-1}Cm^{-1}$(or) $SCm^{-1}$S= siemens

**Equivalent conductance:** "If one gram equivalent weight of an electrolyte is dissolved in "V" ml of the solvent, the conductivity of all ions produced at the dilution V is known as equivalent conductance, which is denoted by **$\lambda$v".**

The equivalent conductance is equal to the product of specific conductance (Kv) and the volume (V). **$\lambda$v**=Kv X V V=1000/C or 1000/normality

**$\lambda$v** = l/Ra X Kv

**$\lambda$v** = l/Ra X 1000/N

**$\lambda$v=Ohm$^{-1}$ cm$^2$ equiv-1 (or) S cm$^2$ equiv$^{-1}$**

**Molecular conductance:** "If one gram molecular weight of an electrolyte is dissolved in "V" ml of the solvent, the conductivity of all ions produced at the dilution V is known as equivalent conductance, which is denoted by **$\mu$v".**

**$\mu$v**=Kv X V V=1000/C or 1000/molarity

**$\lambda$v** = l/Ra X Kv

**$\lambda$v** = l/Ra X 1000/Moles

**$\lambda$v=Ohm$^{-1}$ cm$^2$ mol$^{-1}$ (or) S cm$^2$ mol$^{-1}$**

**Cell constant (x)**

It is a constant, characteristic of the cell in which the electrolytic is taken and its value depends on the distance between the electrodes and area of cross section of the electrodes

$$\text{Cell Constant} = \frac{\text{Distance between the electrodes}}{\text{Area of cross section of each electrodes}}$$

$$x = \frac{l}{a}$$

**(1)** The equivalent conductance of 0.005 N NaOHsolution is 240 mho $cm^2$ $equi^{-1}$. What is the specific conductance and resistance the electrodes are 1 cm apart and each have a surface area of $1cm^2$.

$$V = \frac{1000}{C}$$

$\lambda v = Kv \times V$

$$240 = Kv \times \frac{1000}{0.005}$$

$$Kv = \frac{240 \times 0.005}{1000}$$

$Kv = 1.2 \times 10^{-3}$ $ohm^{-1}$ $cm^{-1}$

Specific conductance of 0.005 N NaOH is= 0.0012 $ohm^{-1}$ $cm^{-1}$

Kv = l/Ra        l=1 cm and a = 1 cm2

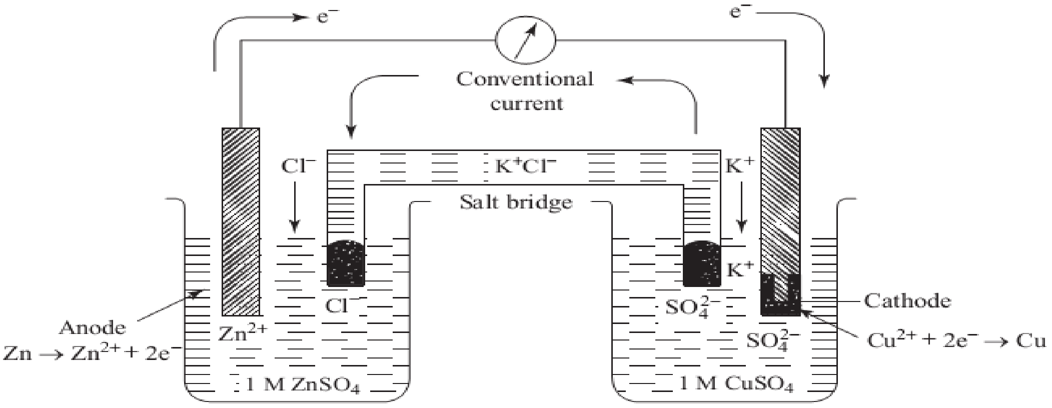
R= 1/Kv

R=1/0.0012

R=833.3 ohm

## Q.2. Write a short note on galvanic cell and cell potential.

**Galvanic Cell:** An electrochemical cell is a device for converting chemical energy into electrical is called galvanic cell. A galvanic cell is made of two half cells. One is oxidation or anodic half cell and the other one is reduction or cathodic half cell.
Daniel cell is an example of galvanic cell having zinc and copper electrodes. The first half cell consists of zinc electrode dipped in ZnSO4 solution and the second half cell is made of copper electrode dipped in copper sulphate solution. Both half cells are connected externally by metallic conductor (connecting wire) and internally by a bent glass tube having saturated solution of a strong electrolyte (KCl) called salt bridge. It acts as a bridge between the two half cells.



The chemical reaction that takes place in a galvanic cell is the redox reaction. One electrode acts as anode in which oxidation takes place and the other acts as the cathode in which reduction takes place. In electrochemical cells anode has negative polarity and cathode has positive polarity.

## Representation of Galvanic cell:

A zinc or a copper galvanic cell can be represented as

$$Zn/ZnSO4 \,||\, CuSO4/Cu$$

The double bar shows a salt bridge, i.e. electrolyte–electrolyte junction. The chemical reactions taking place at both electrodes may be written as follows:

At anode: Oxidation takes place with the liberation of two electrons.

$$Zn \rightarrow Zn^{+2} + 2e^{-} \text{ (oxidation)}$$

At cathode: Reduction occurs and cuprous ion is reduced to metallic copper.

$$Cu^{+2} + 2e^{-} \rightarrow Cu \text{ (reduction)}$$

The overall reaction is

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

- The electrode showing oxidation reaction is anode and the other electrode where reduction occurs is cathode. As per IUPAC convention, the anode is always represented on the left and the cathode always represented on the right side of the cell.

- As the connection is complete, the flow of electrons will be externally from anode to cathode and internally from cathode to anode through the salt bridge. The flow of current is due to the difference in electrode potentials of both the electrodes. The potential difference in the cell is called the EMF and is measured in volts. It can be measured by the potentiometer. The flow of current becomes slow after using the electrodes for a long time because of the polarization of the electrodes.

Salt bridge: Salt bridge is a U-shaped tube containing concentrated solution of an inert electrolyte such as KCl, $KNO_3$, and $K_2SO_4$ or a paste of inert electrolyte (whose ions do not take part in redox reaction and do not react with the electrolyte) in agar–agar medium or gelatin.

Functions of salt bridge:

- Salt bridge helps to complete the circuit by allowing the ions to flow from one solution to the other without mixing the two solutions.
- It helps to maintain electrical neutrality of the solution in the two half cells.

## Cell Potential:

The potential difference between the two electrodes in a galvanic cell is called a cell potential or emf of the cell. It is measured in volts. The difference of potential, which causes flow of electrons from the electrode of higher potential to the electrode of lower potential, is called electromotive force (EMF). The emf of galvanic cell is calculated from the reduction half-cell potentials using the following relation.

$$\mathbf{E(cell) = E(right) - E(left)}$$

emf of the cell = Potential of the half cell on the right hand side (Cathode) - Potential of the half cell on the left hand side (Anode)

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

OR

$$E(cell) = E(right) - E(left)$$

Where E(cell) = e.m.f of cell
E(right) = reduction potential of right hand side electrode
E (left) = reduction potential of left hand side electrode

The difference in potentials of the two half – cells of a cell arises due to the flow of electrons from anode to cathode and flow of current from cathode to anode.

## Q.3. what is Single Electrode potential and how to measure single electrode potential?

Potential difference is developed between the metal (electrode) ions from metal to the solution (electrolyte solution) (or) from solution to the metal is called Single Electrode potential. The tendency of an electrode to lose electrons is a direct measure of its tendency to get oxidized: and this tendency is called, oxidation potential, similarly, the tendency of an electrode to gain electrons is a direct measure of its tendency to get reduced and this tendency is known as reduction potential.

It is quite obvious that the value of reduction potential negative of its oxidation potential and vice versa. Thus, the oxidation potential of an electrode is - x volt, then its reduction potential will have a value of + x volt.

(1) Calculate the e.m.f. of the following reaction at 25 $^0$C.

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

$E^0_{Zn}$(oxi)=0.763 volts
$E^0_{Cu}$(oxi)=-0.337 volts

E(cell) = E(right) – E(left)
=0.337-(-0.763)
=0.337+0.763
E(cell) =1.1 volts.

### Measurement of Single Electrode potential:

Single electrode potential cannot be directly measured. The single electrode potential of a half cell depends on

1. Concentration of the ions in the solution
2. Tendency to form ions
3. Temperature

The single electrode potential is conveniently measured by combining the half cell with a standard electrode or reference electrode and measuring the total EMF of a cell

**E(cell) = E(right) – E(left)**

If the standard cell acts as Anode the equation becomes

$$\mathbf{E(cell) = E(right) – E^0}$$

If the standard cell acts as Cathode the equation becomes

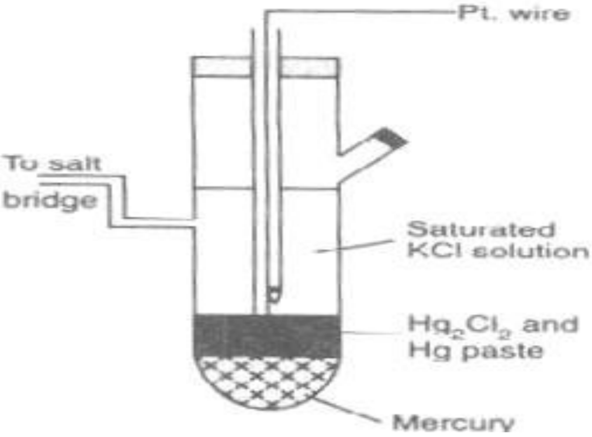
$$\mathbf{E(cell) = E^0 – E(left)}$$

Where $\mathbf{E^0}$ = Standard electrode potential

**Standard electrode potential**: The potential exhibited by a single electrode at unit concentration of the concerned metal ion or non-metal ion solution at 25° C is called **standard electrode potential**. This is expressed by ‘$E^0$’

## Q.4. Explain the construction and working of Calomel Electrode and mention its advantages.

The second type of reference electrode employed for measuring the single electrode potential is Calomel electrode. Calomel electrode is particularly very simple to construct, free from surface sensitivity and accurate to use even in a very normal laboratory. It consists of a glass tube having side tube on each side. High purity of mercury is placed at the bottom of the tube and connected to the circuit by a platinum wire, sealed in a glass tube. The surface of mercury is covered with a paste of mercurous chloride ($Hg_2Cl_2$) (commercially known as calomel) and mercury in KCl solution. KCl solution is used as electrolyte. The electrode is represented as Hg, $Hg_2Cl_2$/KCl. The standard electrode potential of this electrode at $25^0$C is



0.1M KCl | $Hg_2Cl_2$(s) | Hg, $E^0$=0.3338 V
1.0M KCl | $Hg_2Cl_2$ (s) | Hg, $E^0$= 0.2800 V
Saturated KCl | $Hg_2Cl_2$ (s) | Hg, $E^0$= 0.2422V
The corresponding electrode reaction is;

$$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$$

Measurement of single electrode potential of Zn using saturated calomel electrode.

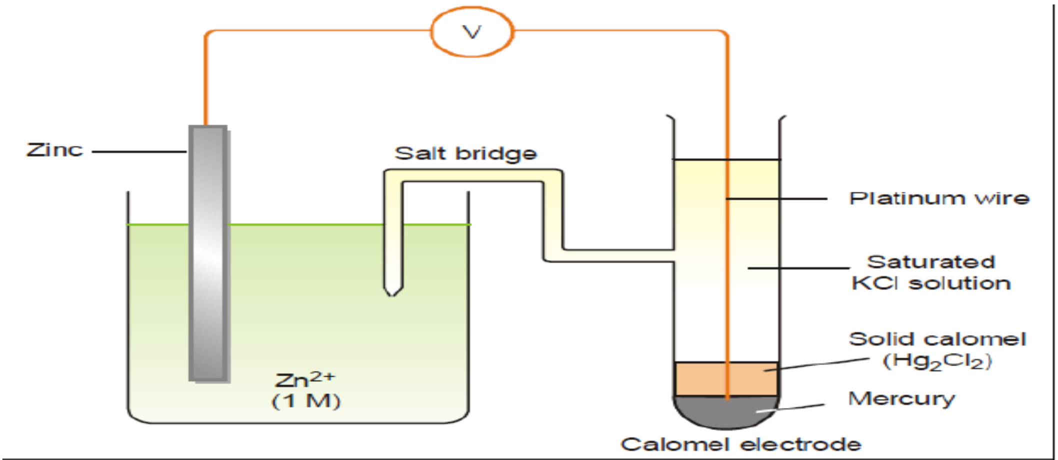


Fig. 10: The calomel electrode coupled determine its emf with zinc electrode to

To measure the electrode potential of Zn, a cell is made by combining the saturated calomel electrode with Zn electrode, the potential to determine. The reduction potential of Zn electrode is less than $E^0$ of calomel electrode (0.2422 v), the calomel electrode will act as cathode and Zn electrode act as anode. The following cell reaction will occur in the above cell.

At anode: $Zn \rightarrow Zn^{+2} + 2e^{-}$ (oxidation)
At cathode: $\underline{Hg2Cl2+2e- \longrightarrow 2Hg +2Cl-}$
Cell reaction: $Zn+Hg2Cl2 \longrightarrow ZnCl2+2Hg$ e.m.f=1.0052 volts
The electrode potential is calculated from the e.m.f of the cell as follows.

$$E(cell) = E(right) – E(left)$$
$$E(cell) = E^0(calomel) – E(left)$$
$$E(cell) = E^0(calomel) – E(Zn)$$
$$E(Zn) = E^0(calomel) – Ecell$$
$$= 0.2422-1.0052$$
$$=-0.763 \text{ volts}$$

The reduction potential of Zn electrode is = - 0.763 volts

### Q. 5. Write Nernst equation? Explain its terms and its applications.

Nernst equation is a thermodynamic equation which relates the change in free energy ($\Delta G$) and cell potential with concentration, $M^{n+}$

The decrease in free energy in the reversible reaction will produce electrical energy i.e.
$-\Delta G = nFE$ and
$\Delta G^0 = -nFE^0$-------------Eq-(1)

Where E = Electrode potential
$E^0$ = Standard electrode potential
F = Faraday (96,500 coulombs)

Consider the following redox reaction
$M^{n+}{}_{+}ne^{-} \leftrightarrow M$

For such a redox reversible reaction, the free energy change (D G) and its equilibrium constant (K) arerelated as;
$\Delta G = \Delta G^0 + RT \ln [Product]/ [Reactant]$-------------Eq- (2)
Where $\Delta G^0$ = standard free energy change
The above equation is known as Van't Hoff Isotherm.

Comparing equation 1 & 2
$-nFE = -nFE^0 + RT \ln[M]/[M^{n+]}$
$= -nFE^0 + RT \ln 1/[M^{n+]}$
Where, concentration of the metal is unity or
$-nEF = -nFE^0 - RT \ln [M^{n+]}$
Dividing the equation by –nF
$E= E^0 + RT/nF\ln [M^{n+]}$

$E= E^0 + 2.303RT/nF \log [M^{n+]}$ R= 8.314J/K/mole, T= 298 K $(25\ ^{0C})$

**$E = E^0 + 0.0591/n \log [M^{n+}]$**----------------Eq-(3)

This equation-3 is known as "Nernst Equation" for reduction electrode potential.
For oxidation potential **$E = E^0 - 0.0591/n \log [M^{n+}]$**

## Applications of Nernst Equation

1. It can be used to study the effect of electrolyte concentration on electrode potential.
2. It can be used for the calculation of the potential of a cell under non-standard conditions.
3. Determination of unknown concentration of one of the ionic species in a cell is possible with the help of Nernst equation, provided $E_{cell}$ and concentration of other ionic species are known.
4. The pH of a solution can be calculated from the measurement of EMF and Nernst equation.
5. It can be also be used for finding the valency of an ion or the number of electrons involved in the electrode reaction.

**(1)** What is the potential of a lead electrode that is in contact with a solution of 0.015 M $Pb^{+2}$ions. Standard electrode potential (E0) for Pb $\longrightarrow Pb^{+2} + 2e^-$ is 0.13 volts

The Nernst equation for oxidation potential of Pb is $E = E^0 - 0.0591/n \log [Pb^{+2}]$
$E=E^0-0.05991/2 \log [0.015]$
$E=0.13-0.05991/2 \log [0.015]$
$E=0.13-0.02955 \log [-1.824]$
$E= 0.13+0.0539$
Oxidation potential of Pb electrode is E=0.184 volts

**(2)** Calculate the reduction potential of Cu+2/Cu=0.5M at $25^0$C.$E^0$ of Cu+2/Cu=0.337 volts.

Concentration of [Cu+2]=0.5M
$E^0$ Cu+2/Cu=0.337
n=2
The Nernst equation for reduction potential of Cu+2 is
$E= E^0 +0.0591/n \log [Cu^{+2}]$
$E= 0.337+0.0591/2 \log [0.5]$
$E =0.3337+0.02955[-0.3010]$
$E =0.337-0.0089$
E=0.328 volts

Reduction potential of Cu =0.328 volts

**(3)** Find the Oxidation potential of $Zn/Zn^{+2}$=0.2M electrode at $25^0$C. Standard oxidation potential of $Zn/Zn^{+2}$ is 0.763 volts.

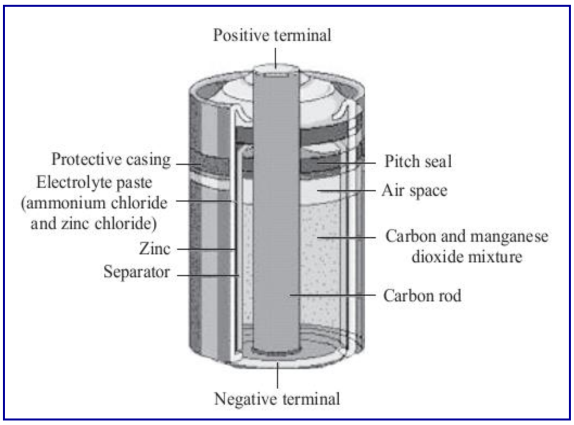
Concentration of $[Zn^{+2}]$=0.2M
$E^0$ $Zn/Zn^{+2}$ =0.763 volts
The Nernst equation for reduction potential of Zn is
$E= E^0 -0.0591/n \log [Zn^{+2}]$
$E= 0.763-0.0591/2 \log [0.2]$
$E =0.763-0.02955[-0.69897]$
$E =0.763+0.02065$
Oxidation potential of Zn E =0.78365 volts

## Q. 6. Explain the primary batteries with suitable example.

**Primary batteries or Primary Cell:** These batteries can convert chemical energy in to electrical energy. These are also called non-rechargeable batteries.Eg.,Voltaic cells, Leclanche cell, and lithium primary cell.

### Dry cell or Leclanche cell or Zn-$MnO_2$ cell:

Dry cell is one important primary cell. The cell contains a cylindrical Zinc container that acts as an Anode. A graphite rod placed in the centre of the cell and acts as a cathode. The space between the anode and cathode is packed with the paste of $NH_4Cl$, $ZnCl_2$ and the graphite rod is surrounded by powdered $MnO_2$ and carbon as shown in figure. This cell is called Dry cell because of the absence of any liquid phase, even the electrolyte consists of $NH_4Cl$, $ZnCl_2$and $MnO_2$to which starch is added to make a thick paste which prevents leakage. The graphite rod is fitted with a metal cap and the cylinder is sealed at the top with a pitch.



Anode: Zinc container

Cathode: Graphite rod

Electrolyte: $NH_4Cl+ZnCl_2+MnO_2$

At anode: $Zn \rightarrow Zn^{2+} + 2e-$ (oxidation)

At cathode: $\underline{2MnO_2+H_2O+2e- \rightarrow Mn_2O_3+2OH^-\ \text{(reduction)}}$

The net cell reaction is $Zn+2MnO_2+H_2O \longrightarrow Zn^{2+}+Mn_2O_3+2OH^-$

The resulting OH-ions react with $NH_4Cl$ to produce $NH_3$, which is not liberated as gas but immediately combines with $Zn^{2+}$ and $Cl^-$ ions to form a complex $[Zn(NH_3)_2Cl_2]$ (diamminedichloro zinc).

$$2NH_4Cl + 2OH^- \longrightarrow 2NH_3+2Cl^-+2H_2O$$

$$Zn^{2+}+2NH_3+2Cl^- \longrightarrow [Zn(NH_3)_2Cl_2]$$

The obtained zinc complex is disrupts the current flow. The cell exhibits a potential of nearly 1.5 volts. When the reactants have been completed (or) converted in to products, no electricity is produced and the cell becomes dead, and cannot be used after that.

**Advantages:**

1) These cells have voltage ranging from 1.25v to 1.50v.

2) Primary cells are used in the torches, radios, transistors, hearing aids, pacemakers, watches etc.
3) Price is low.

**Disadvantages:**

This cell does not have a long life, because the acidic $NH_4Cl$ corrodes the container even when the cell is not in use.

### Q. 7. Describe the construction and working of lead-acid battery along with reactions involved during discharging and charging.

These batteries are rechargeable. A good secondary cell undergoes a number of **discharging** and **charging** cycles. In these cells both "voltaic cell" and "electrolytic reaction" takes place. When operating voltaic cell, it supplies electrical energy and it becomes "run down", when being charged the cell operates as an electrolytic cell.

**Examples**

1. Lead-acid battery
2. Nickel–cadmium battery
3. Lithium-ion cell battery

1. **Lead-acid batteries:** Lead-acid battery consists of **Pb** anode and lead dioxide ($Pbo_2$) cathode. A number of Pb plates (-Ve) are connected in parallel and $Pbo_2$ (+Ve) plates are also connected in parallel. The plates are separated by one insulators like strips of wood, rubber or glass fibre and entire combination was immersed in dil $H_2SO_4$ (38%), which is worked as an electrolyte.

**Anode:** Sponge metallic Lead (Pb)
**Cathode:** Lead-dioxide ($PbO_2$)
**Electrolyte:** 5M $H_2SO_4$ (38%)
**EMF:** 2V

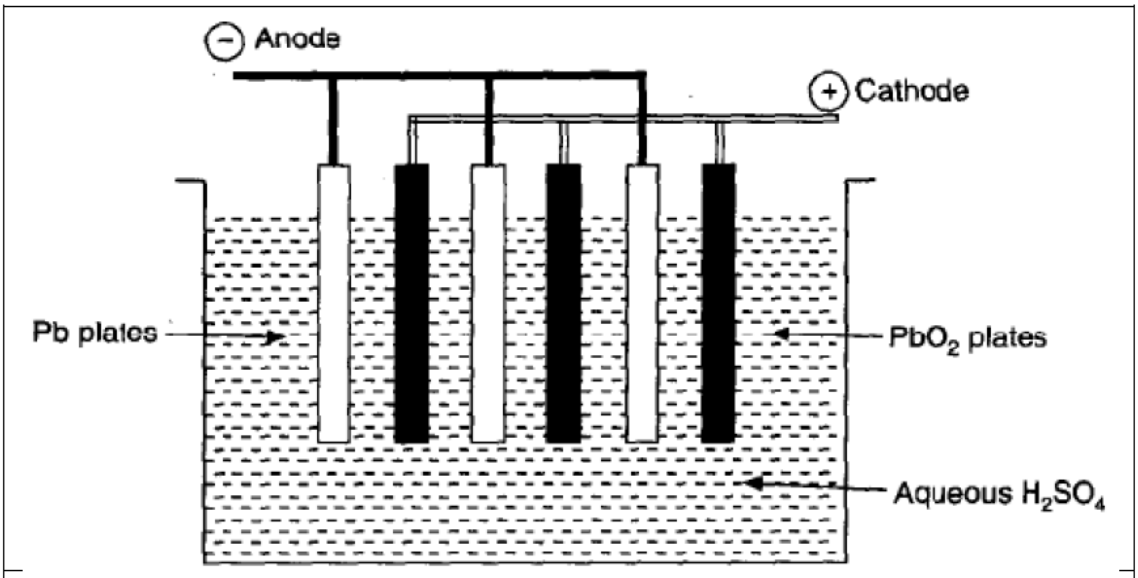


Figure 2: Lead-acid storage cell

**Discharging:** When the battery is in use (discharging) the reactions at the electrodes are as follows.

At anode: $Pb + SO_4^{2-} \rightarrow PbSO_4 + 2e^-$ (0.356V)

At cathode: $PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$ (1.658V)

The overall reaction is: $Pb(s) + PbO_2(s) + 2H_2SO_4 \rightarrow 2PbSO_4 + 2H_2O$ (2.041 V)

During discharging of battery, $H_2SO_4$ (d=1.84 g/cm$^3$) is consumed for the oxidation of Pb, and as a hence the density of $H_2SO_4$ falls. When it is falls below 1.20g/cm$^3$, the battery needs recharging. In discharging, the cell acts as a voltaic cell.

**Charging:** In recharging, the cell operates like an electrolytic cell and an external EMF greater than 2V is passed, the electrode reactions are the reverse of those that occur during discharge.

$$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$$

$$PbSO_4 + 2H_2O \rightarrow PbO_2 + SO_4^{2-} + 4H^+ + 2e^-$$

The overall reaction is

$$2PbSO_4 + 2H_2O \rightarrow Pb(s) + PbO_2(s) + 2H_2SO_4$$

During this process, lead (Pb) is deposited at the cathode and $PbO_2$ is deposited at the anode and $H_2SO_4$ is regenerated. A 12 volts Lead-acid battery is generally used, which consists of six cells.

**Applications:** Automobiles and construction equipment, standby/backup systems. Used mainly for engine batteries, these cells represent over half of all battery sales. Some advantages are their low cost, long life cycle, and ability to withstand mistreatment. They also perform well in high and low temperatures.

**Advantages**

- These cells have a low cycle life, a quick self discharge, and low energy densities. However, with a nominal voltage of 2V and power densities of up 600 W/kg, the lead-acid cell is an adequate, if not perfect, design for car batteries.
- Rechargeable, portable constant potential at low cost.

**Disadvantages**

- Use of $H_2SO_4$ is dangerous its usage is fragile.

**Q. 7. Describe the construction and working of Ni-Cd battery along with reactions involved during discharging and charging.**

**Nickel-Cadmium (Nicad) Cells:** It is a rechargeable secondary cell. It consists of a Cadmium (Cd) as the anode and Nickel oxyhydroxide (NiO(OH) acts as cathode. KOH is used as an electrolyte. The cell reaction during discharging and charging are as follows.

**Anode:** Cadmium
**Cathode**: Nickel oxy-hydroxide (NiO(OH))
**Electrolyte**: Aqueous potassium hydroxide (KOH)
**EMF**: 1.4V

**Discharging:**

At anode: $Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$ (during discharging)

At cathode: $2NiO(OH) + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2OH^-$(during discharging)

Net reaction: $Cd + 2NiO(OH) + 2H_2O \rightarrow 2Ni(OH)_2 + Cd(OH)_2$

**Charging:** $Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$ (during charging)

$2Ni(OH)_2 + 2OH^- \rightarrow 2NiO(OH) + 2H_2O + 2e^-$ (during charging)

---

The overall reaction : $Cd(OH)_2 + 2Ni(OH)_2 \rightarrow 2H_2O + Cd + 2NiO(OH) + 2H_2O$

**Applications:** Calculators, digital cameras, pagers, laptops, tape recorders, flashlights, medical devices (defibrillators), electrical vehicles, space applications

**Advantages**

- Good performance in high-discharge and low-temperature applications.
- They also have long shelf and use life.
- Small size
- High rate of charge/discharge capacity
- Higher energy efficiency

**Disadvantages** are that they cost more than the lead –acid battery and have lower power densities. Possibly it's most well-known limitation is a memory effect, where the cell retains the characteristics of the previous cycle. This term refers to a temporary loss of cell capacity, which occurs when a cell is recharged without being fully discharged. This can cause cadmium hydroxide to passive the electrode, or the battery to wear out.

## Q. 8. What are fuel cells? Explain the construction and working of $H_2$-$O_2$ fuel cell and its applications.

A fuel cell is an electrochemical cell which converts chemical energy contained in readily available fuel oxidant system into electrical energy.

**Principle:** The basic principle of the fuel cell is same as that of an electrochemical cell. The fuel cell operates like a galvanic cell. The only difference is that the fuel and the oxidant are stored outside the cell. Fuel and oxidant are supplied continuously and separately to the electrodes at which they undergo redox reactions. Fuel cells are capable of supplying current as long as reactants are replenished.

$$\text{Fuel} + \text{Oxidant} \rightarrow \text{OxidationProducts} + \text{Electricity}$$

Examples: (1) $H_2$– $O_2$fuel cell

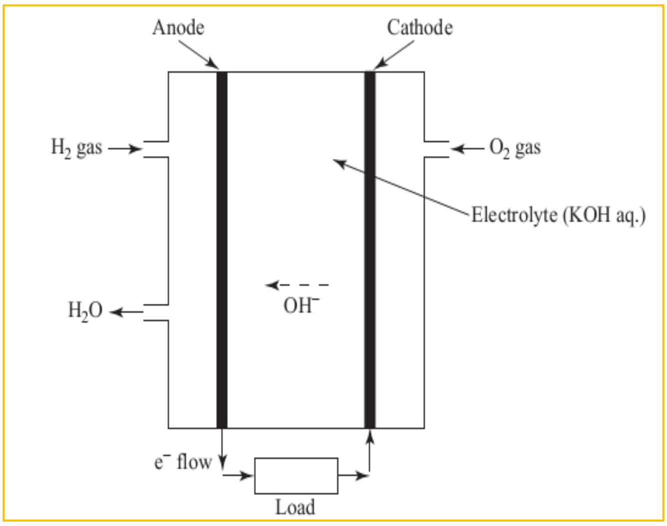
(2) Propane – $O_2$fuel cell

(3) $CH_3OH$ – $O_2$fuel cell

**Hydrogen-oxygen fuel cell**:

The best example of fuel cell is Hydrogen-oxygen fuel and in which hydrogen gas is used as a fuel and oxygen as oxidant. A schematic diagram of $H_2$-$O_2$ fuel cell is shown below;

The cell consists of a two inert porous electrodes (made of graphite impregnated with finely divided platinum or Nickel) and an



electrolyte 2.5% KOH solution. The hydrogen gas fuel is continuously supplied at the anode and oxygen gas is supplied at the cathode. As hydrogen gas diffuses through the anode, it is adsorbed on the electrode surface and reacts with hydroxyl ions to form water. At the cathode oxygen diffusing through the electrode is adsorbed and reduced to hydroxyl ions. These electrode reactions are summarized below;

At the anode: $2H_2 \rightarrow 4H^+ + 4e^-$

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

------------------------------

$2H_2 + 4OH^- \rightarrow 4H_2O + 4e^-$

------------------------------

At the cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

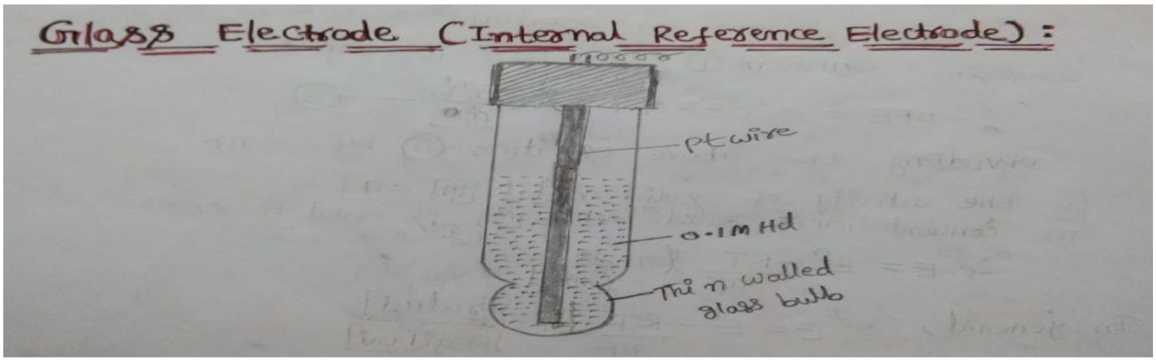
The net cell reaction is, $2H_2 + O_2 \rightarrow 2H_2O$

The product discharged is $H_2O$ and standard e.m.f of the cell is $E^0 = 1.23$ volts. A number of such fuel cells are connected together in series to make a fuel battery.

**Advantages of Fuel Cells:**

- No emission of toxic gases and chemical wastes are in safe limits.
- They have less weight, so these cells are preferred for space crafts and the product of $H_2O$ is a valuable water source for astronauts.
- The reactants and products are environment friendly and only we have to bother about disposal of cell material.
- High efficiency (75-85%) of energy conversion from chemical energy to electrical energy. So offer an excellent use of our renewable energy resources.
- No noise pollution like in generators and low thermal pollution.
- Low maintenance costs, fuel transportation costs, cell parts are modular and exchangeable.
- The fuels and electrolyte materials are available in plenty and inexhaustible unlike fossil fuels.
- Unlike acid cells used in automotives the fuel cells are far less corrosive.
- Unlike nuclear energy, fuel cell energy is economical and safe.

## Q. 9. Explain the construction, working of glass electrode and the determination of pH using glass electrode.



Glass electrode is widely used for pH measurements by combining with calomel electrode. The glass electrode is made of a special glass, with the composition $Na_2O$ (22%), CaO (6%) and $SiO_2$ (72%). The glass electrode consists of thin-walled glass bulb and relatively low melting point and high electrical conductivity. Glass electrode containing a Pt wire in a 0.01 M HCl. The glass electrode is represented as

**Pt, 0.1M HCl/Glass**

HCl in the bulb furnishes a constant $H^+$ ion concentration. Glass electrode is used as the “internal reference electrode”. When glass electrode is immersed in another solution determined for pH values especially coloured solutions containing oxidizing (or) reducing agents. The glass membrane of the glass electrode undergoes an ion exchange reaction between the $Na^+$ ions of glass and $H^+$ ions in solution. The potential difference varies with the $H^+$ ion concentration and its e.m.f is given by the expression.

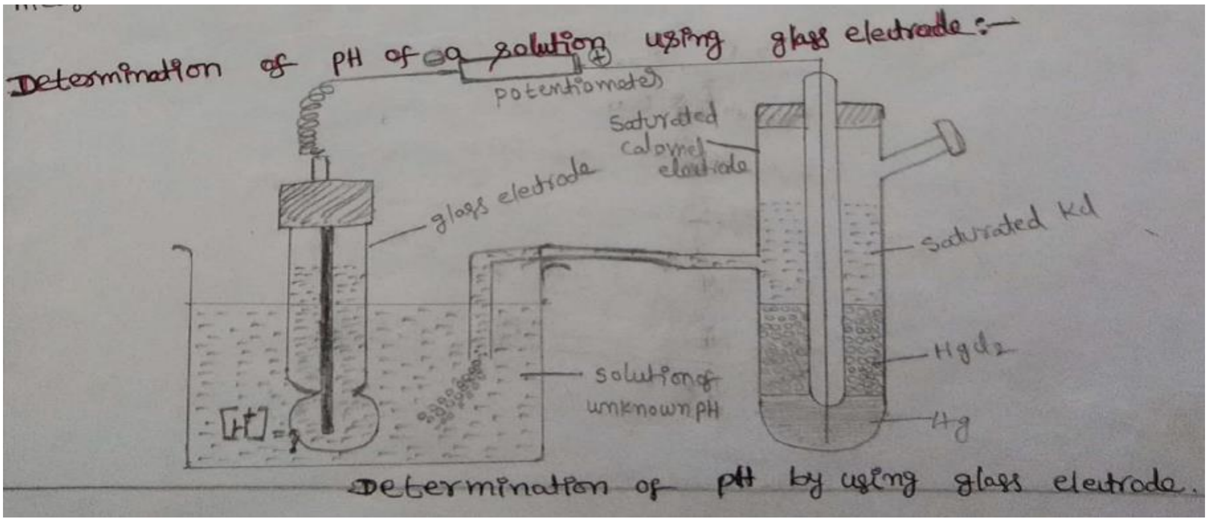
$$\text{Glass membrane}^- — Na^+ + H^+ \rightleftharpoons \text{Glass membrane}^- — H^+ + Na^+$$

$$E_G = E^0G - 0.0592 \log [H]^+$$

(or)

$$E_G = E^0G + 0.0592\ pH \qquad \text{so} \quad [-\log H^+ = pH]$$

From the equation it is clear that the pH of a solution is a direct measure of e.m.f of a glass electrode.


Determination of pH of aq solution using glass electrode :-

Determination of pH by using glass electrode.

The glass electrode is placed in the solution under test and is coupled with saturated calomel electrode as shown in the figure above.

The e.m.f of the cell reaction is measured. From the e.m.f , the pH of the solution is calculated as follows.

$$E_{cell} = E_{(Right)} - E_{(Left)}$$

$$E_{cell} = E_{(calomel)} - E_{(glass\ electrode)}$$

$$E_{cell} = E_{(calomel)} - E(E^0G + 0.0592\ pH)$$

$$pH = \frac{E(Calomel) - E^0G - E_{cell}}{0.0592}$$

Where $E^0G$ is a constant, which is determined by using a solution of known pH.

Advantages: (a) It can be easily constructed and readily used

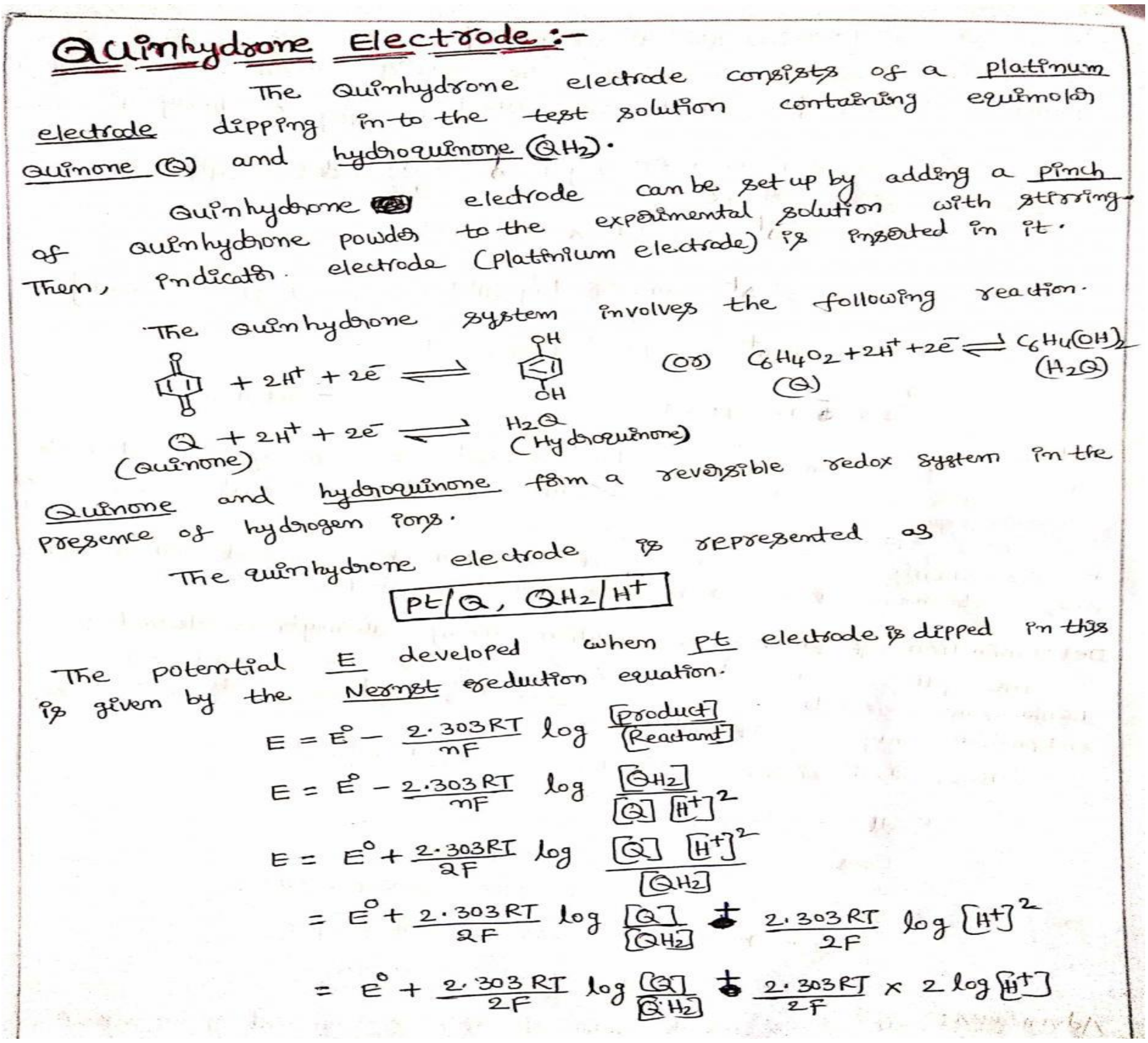
(b) The results are accurate

(c) Equilibrium is rapidly achieved.

(d) Glass electrode is easy to operate.

Disadvantages: (a) The resistance is quite high, special electronic potentiometers are required for measurements. (b) The glass electrode can be used in solutions only pH range of 0 to 10. However, above the pH 12 (high alkalinity), cations of the solution affect the glass and make it the electrode useless.

Q10. Explain the construction and working principle of Quinhydrone electrode and to determination of PH of solution by using quinhydrone electrode.



## Quinhydrone Electrode :-

The Quinhydrone electrode consists of a platinum electrode dipping in-to the test solution containing equimolar quinone (Q) and hydroquinone ($QH_2$).

Quinhydrone electrode can be set up by adding a pinch of quinhydrone powder to the experimental solution with stirring. Then, indicator electrode (Platinium electrode) is inserted in it.

The quinhydrone system involves the following reaction.

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

(or) $C_6H_4O_2 + 2H^+ + 2e^- \rightleftharpoons C_6H_4(OH)_2$

(Q) ($H_2Q$)

$$\underset{\text{(Quinone)}}{Q} + 2H^+ + 2e^- \rightleftharpoons \underset{\text{(Hydroquinone)}}{H_2Q}$$

Quinone and hydroquinone form a reversible redox system in the presence of hydrogen ions.

The quinhydrone electrode is represented as

$$\boxed{Pt/Q,\ QH_2/H^+}$$

The potential E developed when Pt electrode is dipped in this is given by the Nernst reduction equation.

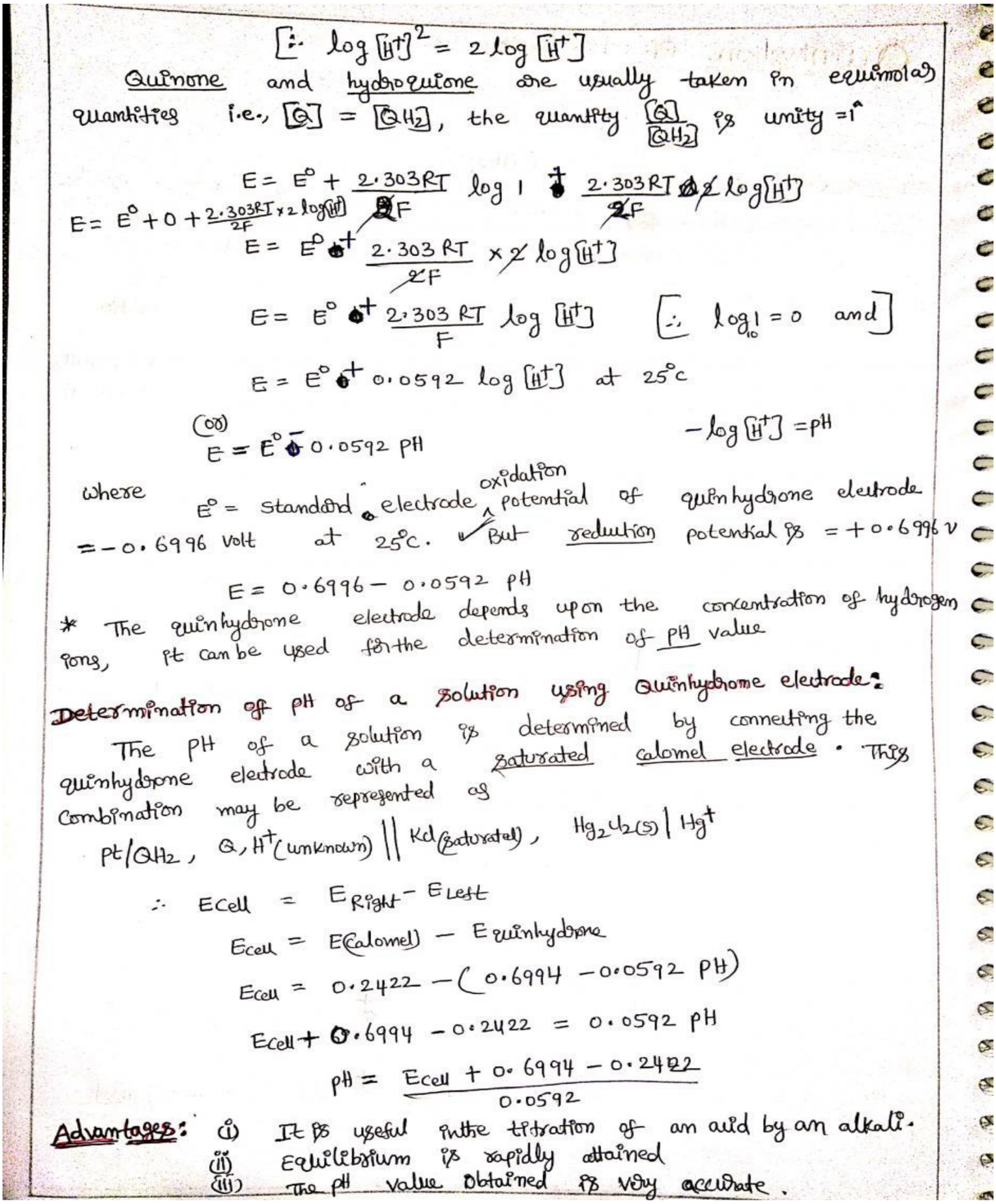
$$E = E^0 - \frac{2.303RT}{nF} \log \frac{[\text{product}]}{[\text{Reactant}]}$$

$$E = E^0 - \frac{2.303RT}{nF} \log \frac{[QH_2]}{[Q][H^+]^2}$$

$$E = E^0 + \frac{2.303RT}{2F} \log \frac{[Q][H^+]^2}{[QH_2]}$$

$$= E^0 + \frac{2.303RT}{2F} \log \frac{[Q]}{[QH_2]} + \frac{2.303RT}{2F} \log [H^+]^2$$

$$= E^0 + \frac{2.303RT}{2F} \log \frac{[Q]}{[QH_2]} + \frac{2.303RT}{2F} \times 2 \log [H^+]$$



$$\left[\therefore \log[H^+]^2 = 2\log[H^+]\right]$$

Quinone and hydroquinone are usually taken in equimolar quantities i.e., $[Q] = [QH_2]$, the quantity $\frac{[Q]}{[QH_2]}$ is unity $= 1$

$$E = E^\circ + \frac{2.303RT}{\cancel{2}F}\log 1 + \frac{2.303RT}{\cancel{2}F}\cancel{2}\log[H^+]$$

$$E = E^\circ + 0 + \frac{2.303RT}{2F}\times 2\log[H^+]$$

$$E = E^\circ + \frac{2.303\,RT}{\cancel{2}F}\times\cancel{2}\log[H^+]$$

$$E = E^\circ + \frac{2.303\,RT}{F}\log[H^+] \qquad \left[\therefore \log_{10} 1 = 0 \text{ and}\right]$$

$$E = E^\circ + 0.0592\log[H^+] \text{ at } 25^\circ c$$

(or)

$$E = E^\circ - 0.0592\text{ pH} \qquad -\log[H^+] = \text{pH}$$

where $E^\circ$ = standard electrode oxidation potential of quinhydrone electrode $= -0.6996$ volt at 25°C. But reduction potential is $= +0.6996\,V$

$$E = 0.6996 - 0.0592\text{ pH}$$

* The quinhydrone electrode depends upon the concentration of hydrogen ions, it can be used for the determination of pH value

**Determination of pH of a solution using Quinhydrone electrode:**

The pH of a solution is determined by connecting the quinhydrone electrode with a saturated calomel electrode. This combination may be represented as

$$Pt/QH_2,\ Q, H^+(\text{unknown}) \,||\, KCl(\text{saturated}),\ Hg_2Cl_2(s)\,|\,Hg^+$$

$$\therefore E_{Cell} = E_{Right} - E_{Left}$$

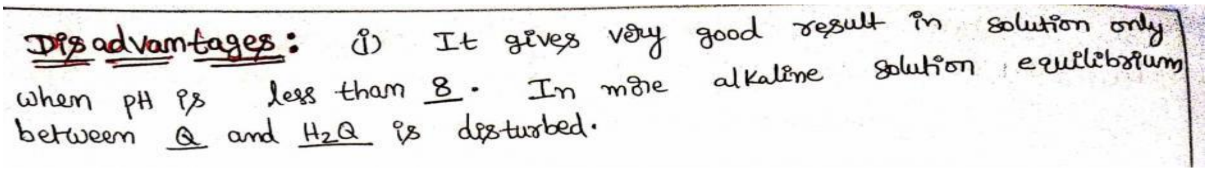
$$E_{cell} = E(\text{Calomel}) - E_{\text{quinhydrone}}$$

$$E_{cell} = 0.2422 - (0.6994 - 0.0592\text{ pH})$$

$$E_{cell} + 0.6994 - 0.2422 = 0.0592\text{ pH}$$

$$\text{pH} = \frac{E_{cell} + 0.6994 - 0.2422}{0.0592}$$

**Advantages:**
(i) It is useful in the titration of an acid by an alkali.
(ii) Equilibrium is rapidly attained
(iii) The pH value obtained is very accurate.



**Disadvantages:** (i) It gives very good result in solution only when pH is less than 8. In more alkaline solution equilibrium between Q and $H_2Q$ is disturbed.

Q11. Explain the electrochemical series and its applications.

## Electrochemical series :—

When the metals are arranged in the order of increasing reduction potentials (or) decreasing oxidation potentials with respect to one molar solutions of in series is called electrochemical series. In this series, hydrogen is situated in the middle having zero electrode potential. Any metal above hydrogen will displace hydrogen from dilute acid solution. For Eg: Na reacts with water to liberate hydrogen because the E° of $Na^+/Na$ (−2.714 V) is less than E° of $H^+/H_2$ (zero). Any metal below the hydrogen in the series will be reduced by hydrogen.

* The higher a metal is in the series, is to be oxidised easily hence they undergo corrosion easily.

Standard oxidation potentials at 25°c

| Electrode | Halfcell reaction | E° volts | |
|---|---|---|---|
| $Li/Li^+$ | $Li \rightarrow Li^+ + e^-$ | +3.045 | Active anodic |
| $K/K^+$ | $K \rightarrow K^+ + e^-$ | +2.925 | |
| $Ca/Ca^{+2}$ | $Ca \rightarrow Ca^{+2} + 2e^-$ | +2.87 | |
| $Na/Na^+$ | $Na \rightarrow Na^+ + e^-$ | +2.714 | |
| $Mg/Mg^{+2}$ | $Mg \rightarrow Mg^{+2} + 2e^-$ | +2.37 | |
| $Zn/Zn^{+2}$ | $Zn \rightarrow Zn^{+2} + 2e^-$ | +0.763 | |
| $Fe/Fe^{+2}$ | $Fe \rightarrow Fe^{+2} + 2e^-$ | +0.440 | |
| $Cd/Cd^{+2}$ | $Cd \rightarrow Cd^{+2} + 2e^-$ | +0.403 | |
| $Pb/Pb^{+2}$ | $Pb \rightarrow Pb^{+2} + 2e^-$ | +0.126 | |
| $Pt/H_{2(g)(1atm)}/H^+_{(1M)}$ | $H_{2(1atm)} \rightarrow 2H^+ + 2e^-$ | 0.000 | |
| $Cu/Cu^{+2}$ | $Cu \rightarrow Cu^{2+} + 2e^-$ | −0.337 | Noble Cathode |
| $Ag/Ag^{+1}$ | $Ag \rightarrow Ag^{+1} + e^-$ | −0.799 | |
| $Pt/Cl^{-1}/Cl^{2+}$ | $2Cl^- \rightarrow Cl_2 + 2e^-$ | −1.36 | |
| $Au/Au^{+3}$ | $Au \rightarrow Au^{+3} + 3e^-$ | −1.50 | |

The higher a metal is in the series, the greater tendency to be oxidised. The metals high up in the series are strong reducing agents, and their ions are stable whereas those near the bottom of the series are inactive, and their ions are easily reduced to metals.

**Applications of electrochemical series:** (1) The relative corrosion tendencies of the metals and alloys. (2) Relative ease of oxidation (or) reduction of metals. (3) Replacement tendency to metals. (4) calculating the equilibrium constant as given below

$$E^\circ = \frac{RT}{nF} \ln K_{(eq)}$$

$$E^\circ = \frac{2.303\,RT}{nF} \log_{10} K_{(eq)}$$

$$\log_{10} K_{(eq)} = \frac{nFE^\circ}{2.303\,RT}$$

$$\log_{10} K_{(eq)} = \frac{nE^\circ}{0.0591} \text{ at } 25^\circ c$$

⑤ Predicting spontaneity of redox reactions.

# CORROSION

## Types of corrosion (Theories of corrosion):

The corrosion process proceeds in two types (1) **chemical (Dry corrosion)** and (2) **electrochemical (wet corrosion)** attack of environment.

### Q.1. EXPLAIN THE MECHANISM OF CHEMICAL CORROSION (DRY CORROSION).

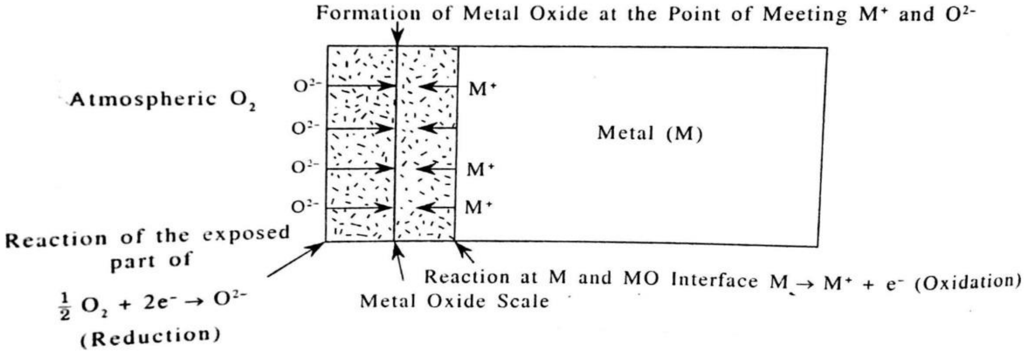
This type of corrosion occurs mainly through the direct chemical action of environment/atmospheric gases such as oxygen, halogen, hydrogen sulphides, Sulphur dioxide, nitrogen or anhydrous inorganic liquids.
There are three main types of chemical corrosion: (a) oxidation corrosion
(b) corrosion by other gases
(c) liquid metal corrosin

### a. Oxidation corrosion:

"Direct action of oxygen at high or low temperatures on metals in the **absence of moisture** is called oxidation corrosion". Metals such as Ag, Au, and Pt are not oxidised as they are noble metals.

$$\begin{array}{l} 2\,M \longrightarrow 2\,M^{+} + 2\,e^{-} \text{ (Loss of electron: Oxidation)} \\ O_2 + 2\,e^{-} \longrightarrow 2\,O^{2-} \text{ (Gain of electron: Reduction)} \\ \hline 2\,M + O_2 \longrightarrow 2\,M^{+} + 2O^{2-} \longrightarrow 2MO\text{(metal oxide layer)} \\ \hline \end{array}$$

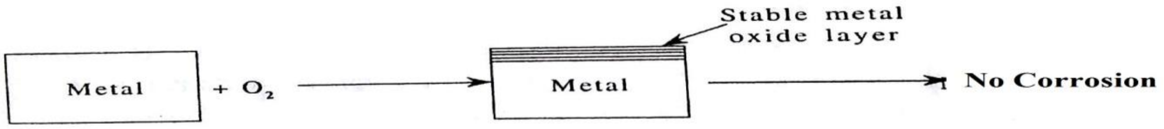
**Mechanism**: The oxidation of the metal occurs at the surface first, resulting the formation of metal oxide scale, which restricts further oxidation.
Further oxidation to continue, either the metal must diffuse outwards through the scale to the surface or the oxygen must diffuse inwards through the scale to the underlying metal. Of the two types of diffusions, the diffusion of the metal is rapid because the size of the metal ion is smaller than oxygen ion, hence higher mobility to metal ion.



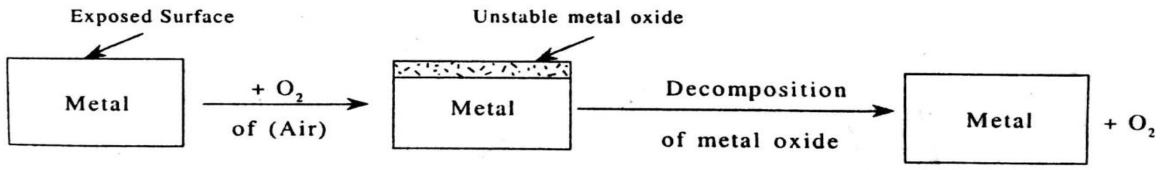
Nature of the oxide formed plays an important part in oxidation corrosion process. The following types of films are there:

1. **Stable metal oxide**: If the formed metal oxide is stable, it prevents further corrosion due to tightly bind to the metal surface is impermeable to the further attacking of oxygen. Fe (iron) corrodes

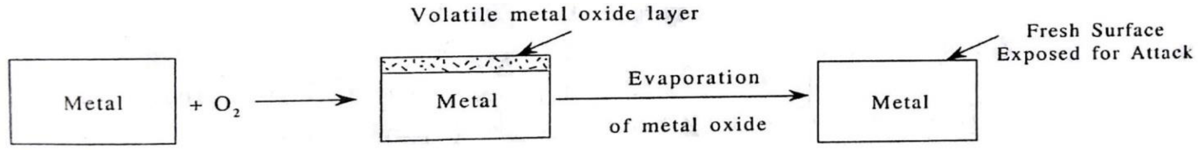
faster than Al (aluminium) because Al forms tightly adhering protective $Al_2O_3$ film on the Al metal surface.



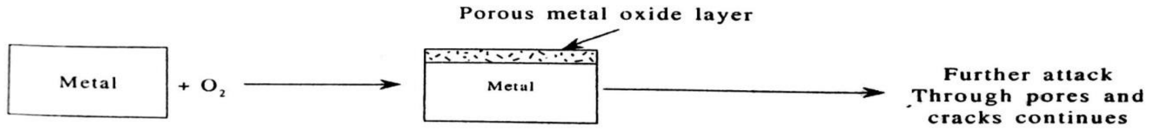
**2. Unstable metal oxide**: The oxide layer formed decomposes back into the metal and oxygen. Consequently, oxidation corrosion is not possible in such a case. Thus, Ag, Au, and Pt do not undergo oxidation corrosion.



**3. Volatile oxide layer:** The oxide layer formed evaporates as soon as it is formed, leaving the underlying metal surface exposed for further attack. This causes rapid and continuous corrosion, leading to excessive corrosion. Ex: Molybdenum oxide ($MoO_3$) is volatile.



4. **Porous oxide layer**: If the formed metal oxide layer is porous, it allows further corrosion. A porous layer of metal oxide contains cracks, gaps etc. provides access to oxygen to reach the underlying surface of the metal. Eg. Alkaline earth metals and alkaline metals.



***Pilling Bedworth rule***: According to Pilling-Bedworth rule, a metal which possess high specific volume ratio does not undergo further corrosion (or) prevent further corrosion.

$$\text{Specific volume ration}=\frac{\text{Volume of metal oxide}}{\text{Volume of metal}}$$

If the volume of the metal oxide layer is at least as great as the volume of metal, which is formed non-porous and protective layer by tightly adhering to the base metal.

Specific volume ratio is more the rate of corrosion is less. For example, the specific volume ratios of W, Cr and Ni are 3.6, 2.0 and 1.6 respectively. Hence, the rate of corrosion is least in Tungsten (W).

**2. Corrosion by other gases:**

The gases like $SO_2$, $CO_2$, $Cl_2$, $H_2S$ and $F_2$ are causes for chemical corrosion and these corrosion mainly depends on the reactivity the gas. Eg: $Cl_2$ attacke the metal (Sn) forming volatile $SnCl_4$ and Ag metal produces adherent ,non porous oxide film (AgCl).

### 3. Liquid metal corrosion:

The corrosion reaction involves either dissolution of a solid metal by a liquid metal or internal penetration of the liquid metal into the solid metal. Both these modes of corrosion cause weakening of the solid metal. Eg: Liquid metal mercury dissolves most metals by forming amalgums, there by corroding them.

## Q. 2. EXPLAIN THE MECHANISM OF ELECTROCHEMICAL CORROSION (WET CORROSION) TAKING IRON (Fe) AS AN EXAMPLE.

Wet or electrochemical corrosion takes place under wet or moist conditions through the formation of short circuited electrochemical cells. According to this theory, there is formation of galvanic cell on the surface of metal. Some of the metal surface act as anode and rest act as cathode. The chemical in the environment and humidity acts as an electrolyte. Oxidation takes place at anode and it results in corrosion, while reduction takes place at cathode.
Electrochemical corrosion involves flow of electron-current between the anodic and cathodic areas. The anodic reaction involves in dissolution of metal as corresponding metallic ions with the liberation of free electrons.

At anodic area*:* $M \longrightarrow M^{n+} + n\,e^-$ (Oxidation)
On the other hand, the cathodic reaction either $H^+$ ,$O_2$, $H_2O$ consumes the electrons generating from anode to produce non-metallic ions like $OH^-$ or $O^{2-}$ either by evolution of hydrogen or absorption of oxygen, depending on the nature of corrosive environment.
Wet corrosion takes place by the following ways.

### a) Evolution of hydrogen at cathode:

This type of corrosion occurs usually in acidic environments. The Rusting of iron takes place in acidic medium. Considering metal like Fe the anodic reaction is dissolution of iron as ferrous ions with the liberation of electrons.

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

These electrons flow through the metal, from anode to cathode, where $H^+$ ions are eliminated as hydrogen gas.

$$2H^+ + 2\,e^- \longrightarrow H_2 \text{ (Reduction)}$$

The net overall reaction is: $Fe + 2H^+ \longrightarrow Fe^{2+} + H_2$

In Hydrogen Evolution type of corrosion the anodes are usually large and the cathodes are small areas.

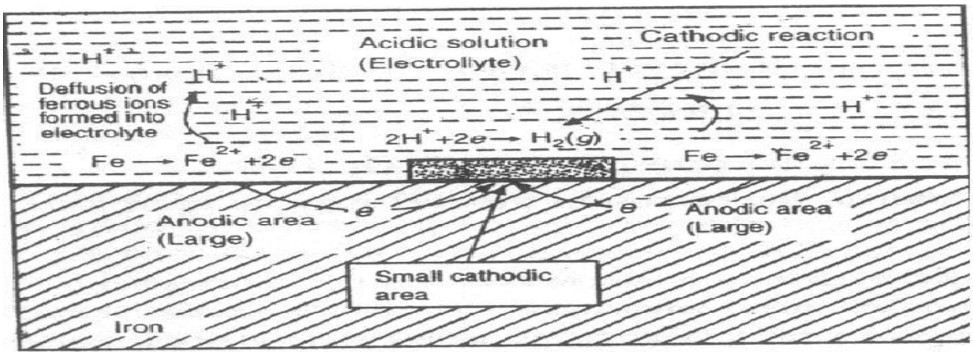
In Neutral medium at the cathode formation of OH- takes place along with the liberation of hydrogen gas.

$$2H_2O + 2e^- \longrightarrow 2\,OH^- + H_2 \text{ (Reduction)}$$

The $Fe^{2+}$ and $OH^-$ diffuse towards each other through the conducting medium forming the corrosion product rust in between the cathodic and anodic areas.

$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2 \text{ (Ferrous Hydroxide)}$$

$$4\,Fe(OH)_2 + O_2 + 2H_2O \longrightarrow \underset{\text{Ferric Hydroxide}}{4\,Fe(OH)_3} \longrightarrow \underset{\text{Hydrated ferrous oxide}}{2(\,Fe_2O_3.\ 3H_2O)\ \text{rust}}$$



In this case, metals react with acidic and neutral conditions to release $H_2$ gas. All metals above hydrogen in electrochemical series can show this type of corrosion.

**b) Absorption of oxygen at cathode**: This type of corrosion takes place in neutral and basic medium in the presence of oxygen. The oxide of iron covers the surface of the iron. The small scratch on the surface creates small anodic area and rest of the surface acts as cathodic area.

The following chemical reactions occur at anode and cathode.

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

The liberated electrons flow from anodic to cathodic areas, through iron metal, where electrons are intercepted by the dissolved oxygen as:

$$O_2 + H_2O + 2e^- \longrightarrow 4OH^- \text{ (Reduction)}$$

The $Fe^{2+}$ ion at anode and $OH^-$ ions at cathode diffuse and when they meet, ferrous hydroxide is precipitated.

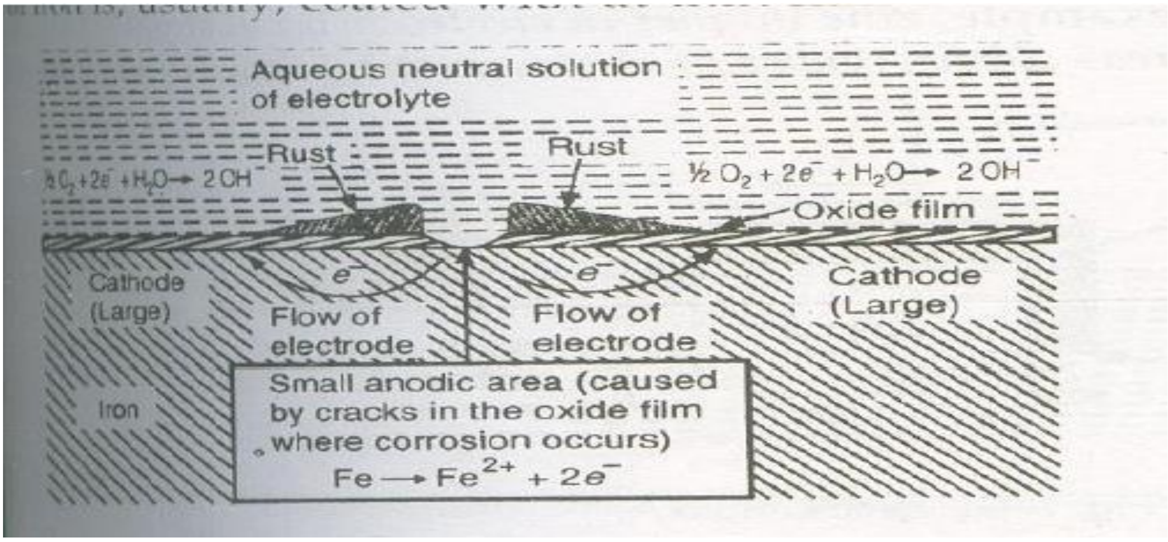
$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$$

If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide.

$$4\,Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3 \longrightarrow 2(Fe_2O_3.3H_2O)$$

This product is called yellow rust, actually corresponds to $2(Fe_2O_3.\ 3H_2O)$

If the supply of oxygen is limited the corrosion product may be even black anhydrous magnetite, $Fe_3O_4$.

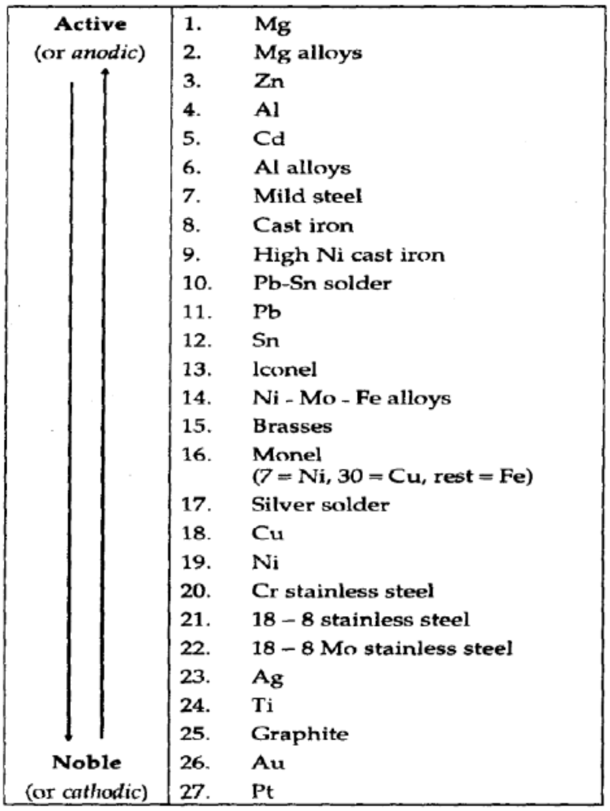


## Q. 3. Explain the Factors influencing rate of corrosion.

Since corrosion is a process of destruction of metal surface by its environment, the two factors that govern the corrosion process are:
(i) Nature of Metal and (ii) Nature of Environment.

### 1.Nature of the metal:

(i)**Position in galvanic series**:
When the oxidation potentials are arranged in the decreasing order of activity in a series of metals called as galvanic series.



| | | |
|---|---|---|
| **Active** | 1. | Mg |
| (or *anodic*) | 2. | Mg alloys |
| | 3. | Zn |
| | 4. | Al |
| | 5. | Cd |
| | 6. | Al alloys |
| | 7. | Mild steel |
| | 8. | Cast iron |
| | 9. | High Ni cast iron |
| | 10. | Pb-Sn solder |
| | 11. | Pb |
| | 12. | Sn |
| | 13. | Iconel |
| | 14. | Ni - Mo - Fe alloys |
| | 15. | Brasses |
| | 16. | Monel<br>(7 = Ni, 30 = Cu, rest = Fe) |
| | 17. | Silver solder |
| | 18. | Cu |
| | 19. | Ni |
| | 20. | Cr stainless steel |
| | 21. | 18 – 8 stainless steel |
| | 22. | 18 – 8 Mo stainless steel |
| | 23. | Ag |
| | 24. | Ti |
| | 25. | Graphite |
| **Noble** | 26. | Au |
| (or *cathodic*) | 27. | Pt |

In the galvanic series series, a metal high in the series is more anodic and undergoes corrosion faster than the metal below it. For example, **Li** corrodes faster than **Mg**; **Zn** corrodes faster than **Fe**; **Fe** corrodes faster than **Sn**; **Cu** corrodes faster than **Ag** and so on. Also more difference in the position of galvanic series will cause faster corrosion at anodic metal.

(ii) **Relative areas of the anodic and cathodic parts:** When two dissimilar metals (or) alloys are in contact, the corrosion of the anodic part is directly proportional to the areas of the cathodic and anodic parts. Smaller the area of anode compared to cathode will lead to faster corrosion of anode. Because the larger cathodic area demands more electrons, which will be fulfilled by fast corrosion at anode (oxidation).

$$\text{Corrosion } \alpha \ \frac{\text{Area of cathode}}{\text{Area of anode}}$$

(iii) **Purity of metal: Impurities in a metal**: Pure metal resists corrosion, while impurities in a metal form a local galvanic cell (metal as anode and impurity as cathode) and result in the corrosion of metal.

Purity less: more corrosion
Purity more: corrosion less

(iv) **Physical state of metal**: The rate of corrosion is influenced by physical state of the metal .The smaller the grain-size of the metal or alloy, the greater will be its solubility and hence, greater will be its corrosion.

More stress: more corrosion
Less stress: less corrosion

(v) **Nature of surface film**: The ratio of the volumes of the metal oxide to the metal is known as a "specific volume ratio." Greater the specific volume ratio, lesser is the oxidation corrosion rate. According to Pilling- Bedworth rule the volume of oxide film is greater than metal from which metal oxide formed, then the film is protective.

(vi) **Solubility and volatility of corrosion products**: In both the cases, the corrosion will be faster. $MoO_3$, $SnCl_4$ are volatile, so faster is corrosion of **Sn** in $Cl_2$ atmosphere. In case of soluble corrosion product by water and metal surface will be exposed to further corrosion.

**2. Nature of the environment:** The role of environment in the corrosion of a metal is very important. Environmental parameters like temperature, humidity, PH etc. play important role.

(i) **Temperature and humidity**: The rate of diffusion increase by rise in temperature, hence the rate of corrosion is also increased. But higher temperature reduces the concentration of $O_2$ and hence corrosion is reduced. In humidity gases like CO2, SO2, NOx are dissolved which form electrolytes. It will cause galvanic corrosion.

(ii) **Influence of pH**: PH value means concentration of $H^+$ (acidic nature). In acidic medium (less than 7), corrosion is faster. In basic medium, some metal such as Pb, Zn, Al, etc. form complexes and hence they corrode.

Eg: Zn corrodes minimum at $P^H$ 11, but at higher $P^H$ (more than 11) it corrodes faster. At $P^H$ 5.5, Al corrodes minimum.

(iii) **Nature of ions present in vicinity**: $Cu^{+2}$ ions present in the vicinity (medium) of Fe, accelerate corrosion, while silicates present in the medium resist corrosion.

(iv) **Conductance of corroding medium**: Due to presence of salts and water in earth, it is of conducting nature. More conductance leads to more stray current and hence fast corrosion. Dry sandy soil is less conducting and hence less corrosion, while mineralised clay soil is more conducting hence more corrosion occurs.

(v) **Oxygen concentration**: Oxygen is one of the important element responsible for corrosion. The % of $O_2$ in atmosphere increases, the rate of corrosion also increases due to formation of Oxygen concentration cell on the surface of metal (iron rod half dipped in water corrodes due to this effect).

Anode $Fe \longrightarrow Fe^{2+} + 2e^-$ (Oxidation)
Cathode $\frac{1}{2} O_2 + H_2O + 2e^- \longrightarrow 2OH^-$

---

$Fe + \frac{1}{2} O_2 + H_2O \longrightarrow Fe^{2+} + 2OH^-$

$$Fe^{2+} + 2OH^{-} \longrightarrow Fe(OH)_2$$

If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide.

$$4\,Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4\,Fe(OH)_3 \longrightarrow 2(Fe_2O_3.3H_2O)$$

This product is called yellow rust, actually corresponds to 2( $Fe_2O_3$. $3H_2O$)

(vi) **Polarisation of the electrode:** More the polarisation at electrodes, less current passed and hence less corrosion.

(vii) **Flow of process stream:** The velocity of the diffusion of ions in the medium increases, the rate of corrosion increases.

## CORROSION CONTROL METHODS:

The following some of the important corrosion control methods are described:

- ✓ Cathodic Protection
- ✓ Protective coatings or metallic coatings
- ✓ Using Pure metal & alloys
- ✓ Modifying the Environment
- ✓ Use of Inhibitors
- ✓ Proper Designing
- ✓

## Q. 4. Explain the Cathodic protection:

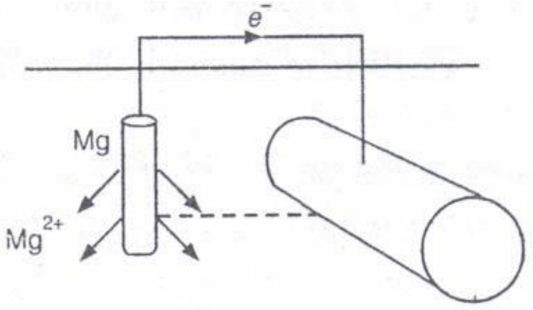
"The principle involved in this method is that the metal is forced to behave like cathode, thereby preventing corrosion". There are two types of cathodic protection.

(a) Sacrificial anodic protection

(b) Impressed current cathodic protection

**(a) Sacrificial anodic protection**: In this method of protection, the metallic structure to be protected called "base metal" is connected to more anodic metal through a wire, so that all the corrosion is concentrated at the more anodic metal. As the more anodic metal is sacrificed in the process of saving base metal from corrosion. Hence, it is known as *sacrificial anod*e.
Metals commonly used as sacrificial anodes are Zn, Al,Mg.

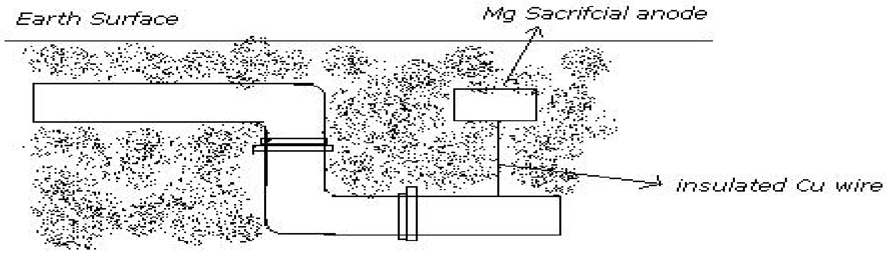
Zn (or) Mg metals are more positive than Fe and, hence in electrochemical it will act as an anode and the Fe will act as cathode. According to the principle of galvanic cell, anode that undergo corrosion and saving cathode from corrosion. Thus, Mg sacrifies itself for saving the Fe.



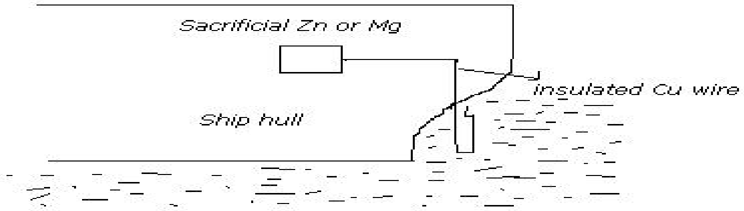
In cathodic protection, an anode of a more strongly reducing metal is sacrificed to maintain the integrity of the protected object (*e.g.* a pipeline, bridge, ship hull or boat).

*Applications:* Important applications of this technique are

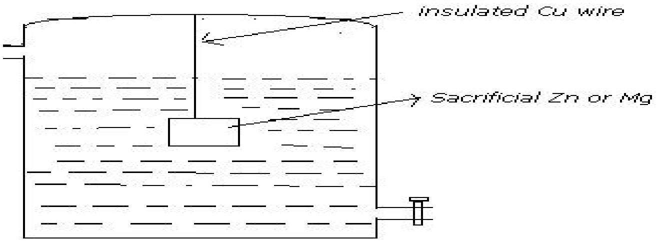
a. Protection of underground cables and pipelines from soil corrosion



b. Protection of ships and boat hulls from marine corrosion. Sheets of Mg or Zn are hung around the ship hull, these sheets being anodic to corrosion so these sheets get corroded, when consumed completely, these are replaced by fresh one.



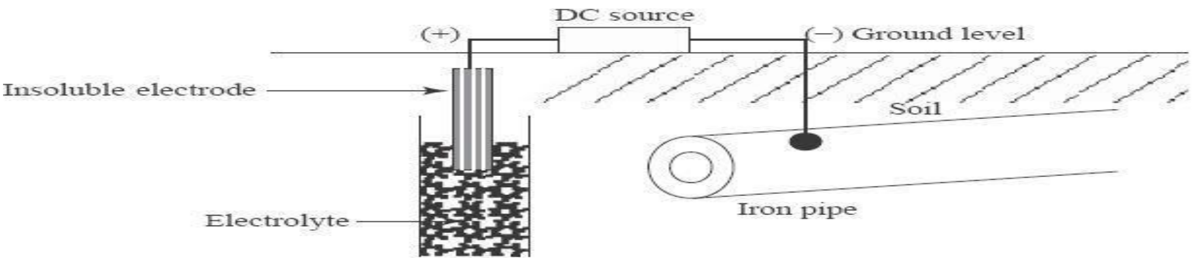
c. The formation of rusty water is prevented by the insertion of Mg sheets or rods into domestic water boilers or tanks.



**Advantages:** (1) It is a simple method (2) It has low maintainance and installation cost (3) It does not required external power

**Disadvantages**: (1) Some times more than one anode is required (2) Current out put is less (3) It does not work properly in high corrosive environment (4) The sacrificial anode must be replaced periodically, when it is consumed.

## (b) Impressed current cathodic protection:



In this method the metal to be protected (the metal is exposed to soil (or) other electrolyte) is made anode by connecting to an external battery. The battery contains an inert graphite anode, which is buried in a back fill to maintain electric contact. A known quantity of direct current is passed through the electrolyte, when the applied current is equal to the current, the corrosion of the metal stops.

Impressed current cathodic protection is given to (i) water tanks (ii) transmission line towers (iii) buried pipe lines and (iv) marine pipes.

### Q. 5. Explain the protective coatings (or) metallic coatings.

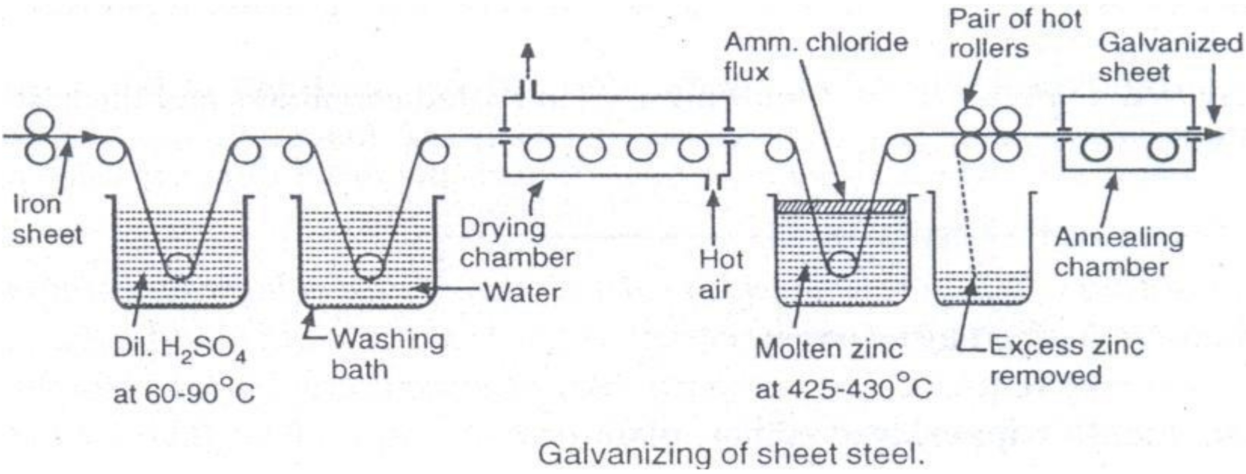
Protective coatings act as a barrier between the coated surface and its environment. Some of the methods used for imparting coating of one metal over another. Metallic coating are applied by

(1) Hot dipping
(2) Electroplating (Cu)
(3) Electrolessplating (Ni)
(4) Paints
(5) Metal Cladding
(6) Cementation

**(1) Hot dipping:** It is one of the common methods for applying metallic coatings on the surface of base metal. In this method, molten metals such as Zn (m.p.=419$^o$C), Sn (m.p.=232$^o$C) Pb, Al, etc., having low melting points than the coated metals such as on iron (Fe), steel and copper (Cu) which have relatively higher melting points.

**Galvanizing:** "The process of coating Fe (iron) with Zn (zinc) is known as galvanization". The method of coating iron (Fe) or any base metal with Tin (Sn) is called Tinning.

The base metal iron or steel sheet is cleaned by acid pickling method with dil.$H_2SO_4$ for 15-20 minutes at 60-90 $^o$C. The sheet is then washed well and dried. It is dipped in a bath of molten zinc maintained at 425-435 $^o$C. The surface of the bath is kept covered with ammonium chloride ($NH_4Cl$) flux to prevent oxide formation. The sheet is taken out and excess Zn is removed by passing it between a pair of hot rollers. Then the sheet is subjected to annealing process at cooled slowly.



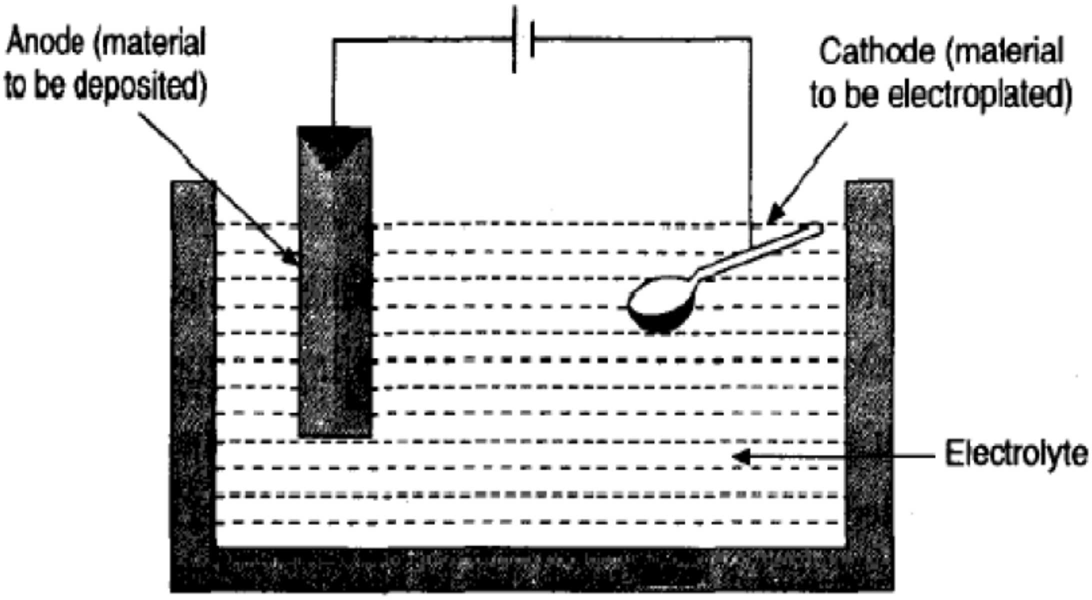
Galvanizing of sheet steel.

Applications: It is mostly used to protect iron used for roofing sheets, wires, pipes, nails, bolts, screws, buckets and tubes.
Galvanizing utensils cannot be used for preparing and storing food stuffs especially acidic in nature, because zinc dissolves to form highly toxic or poisonous compounds.

**(2) Electroplating (or) Electrodeposition:** "The process of depositing the coating metal on the surface of base metal/non metal by electrolysis is called electroplating".

It is an electrochemical process in which a base metal is coated by Zn, Ag, Cr, Au, Sn etc. to protect it from corrosion and also to make it shine and decorative. The base metal is made cathode, dipped in a suitable electrolyte, and the metal to be deposited is made anode (or) an inert material good electrical conductivity material is also used as an anode. A direct current (DC) is passed through the electrolytic solution.

The article to be electroplated to solvent cleaning by trichloroethylene to remove oil, grease etc., Then it is subjected to acid pickling with dil. HCl (or) dil. $H_2SO_4$ to remove any oxides etc., The cleaned article is made cathode of the electrolytic cell and electrodes were dipped in the salt solution of the coating metal, which acts as an electrolyte. When direct current is passed, the coating metal ions migrate to the cathode and deposit on the base metal article in the form of a thin layer.



For eg: electroplating of copper on iron articles, the following are maintained.

At anode: $M \longrightarrow M^{n+} + ne^-$ (dissolution of metal)

At cathode: $M^{n+} + ne^- \longrightarrow M$(deposition on substance)

1. Electrolytic bath solution: copper sulphate
2. Temperature maintained: 40-70 $^0$C
3. Current density: 20-30 mA/cm$^2$
4. Cathode: base metal

If inert electrode used as anode copper sulphate to replenish it.

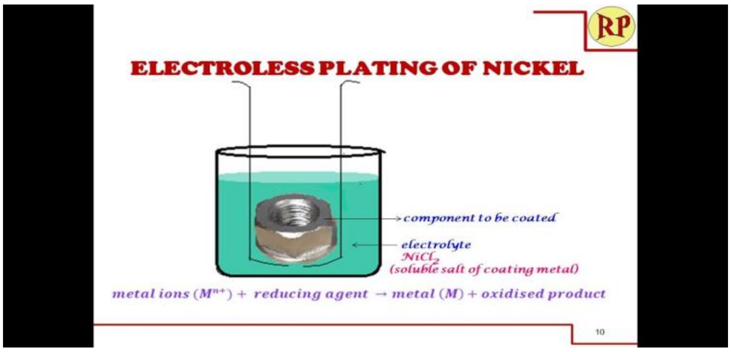
**Application:** Electroplating is a most important and frequently used technique in industries to produce metallic coatings. Both metals and non metals can be electroplated. In metals the electroplating increase resistance to corrosion, chemical attack, hardness, wear resistance and surface properties. In non metals electroplating increases strength and decorates the surface of non metals like plastics, wood, glass etc.

**(3) Electrolessplating (Ni):** In this method of depositing a metal from its salt solution on a catalytically active surface by a suitable reducing agent without using electrical energy is called electroless plating.

$$M^{n+} + \text{Reducing agent} \rightarrow M + \text{oxidized product.}$$

The reducing agent supplies electrons for the reduction of metal ions to metal. The metal gets deposited on the surface of the base metal there by producing a uniform thin coating. Eg: Ni, Co, Cu and some precious metals can be deposited by electroless plating.

The base object, a plastic material like acrylonitrile butadiene styrene (ABS) can be coated with nickel. The base metal surface is activated by stannous chloride ($SnCl_2$) followed by palladium chloride ($PdCl_2$) to get a layer of palladium and the surface is dried. The base metal is dipped in a solution of $NiCl_2$ (nickel chloride), sodium hypophosphite (reducing agent), sodium acetate buffer, sodium succinate (complexing agent) PH of the bath maintained is 4.5 and temperature is 93 $^0$C.The following reactions takes place and nickel get plated electrolessly on the surface of the base object.



ELECTROLESS PLATING OF NICKEL

metal ions ($M^{n+}$) + reducing agent → metal (M) + oxidised product

$$Ni^{+2} + H_2PO^{2-} + H_2O \longrightarrow Ni + H_2PO^{3-} + 2H^{+}$$

Applications: (i) They are used in electronic industry for fabricating printed circuits and diodes. (ii) ABS plastic coated objects are used for decorative applications automotives, electronics etc.

## Q. Explain the Types of Corrosions.

**Galvanic Corrosion:** When two dissimilar metals (eg., zinc and copper) are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. In this process, the more active metal (with more negative electrode potential) acts as a anode while the less active metal (with less negative electrode potential) acts as cathode. In the above example, zinc (higher in electrochemical series) forms the anode and is attacked and gets dissolved; whereas copper (lower in electrochemical series or more noble)acts as cathode.

**Mechanism:** In acidic solution, the corrosion occurs by the hydrogen evolution process; while in neutral or slightly alkaline solution, oxygen absorption occurs. The electron-current flows from the anode metal, zinc to the cathode metal, copper.

**At anode: $Zn \rightarrow Zn^{2+} + 2e^-$ (Oxidation) corrosion**

**At cathode: $Cu^{2+} + 2e \longrightarrow Cu$ [Reduction] unaffected**

Thus it is evident that the corrosion occurs at the anode metal; while the cathodic part is protected from the attack.

Prevention of galvanic corrosion: (i) coupling of metals close to the clectrochemical series (ii) fixing insulating material between two metals (iii) using larger anodic metal and smaller cathodic metal.

**Waterline corrosion:** It has been observed in the case of an iron tank containing water, that the portion of iron tank just below the water level undergoes corrosion. It is due to the difference in oxygen concentration. Corroding portion is poor in oxygen and acts as anode.

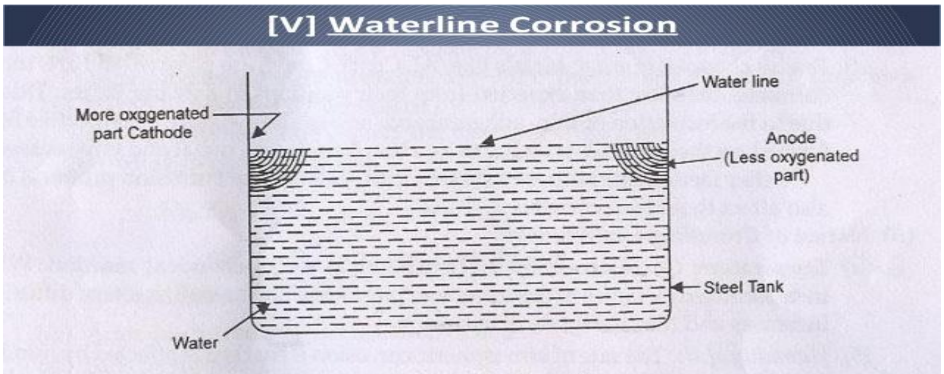


Fig. 5.13 Water line Corrosion

A distinct brown line is formed just below the water line due to the deposition of rust.
The reactions may be represented as follows:

## Cell reactions:

**At anode : $M \rightarrow M^{n+} + ne^-$ (Oxidation of metal M)**

**At cathode : $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (Reduction of oxygen)**

Other example: Ships which remain partially immersed in sea water for a long time undergo water line corrosion.

# Module-IV

## Stereochemistry, Reaction mechanism & synthesis of drug molecules and NMR spectroscopy

# IV Stereochemistry & NMR Spectroscopy

Stereochemistry, a sub discipline of chemistry, that deals with the relative spatial arrangement of atoms that form the structure of molecules and their manipulation. Stereochemistry is a part of chemistry which deals with structure in three dimensions ("stereo" means three dimensional). One aspect of stereochemistry is stereoisomerism.

"Isomers are different compounds, having same molecular formula but different properties (physical, chemical, or both) are known as isomers, and the phenomenon is known as isomerism".

**Types of isomerism:** Isomerism is of two types.

(a) Structural isomerism (or) constitutional isomerism

(b) Stereoisomerism (or) Spatial isomerism.

## (a) Structural isomerism (or) constitutional isomerism:

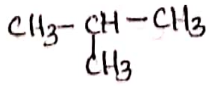
The compounds having same molecular formula but possess different structural arrangement of atoms. This difference may be due to in the nature of carbon chain (chain isomerism) or due to the position of the substituent (position isomerism) or due to the difference in the nature of the functional group (functional isomerism).

**(1) chain isomerism:** It arises due to the different in the nature of carbon chain.

Example:

(1) n-butane ($C_4H_{10}$) $CH_3-CH_2-CH_2-CH_3$

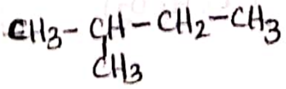
Isobutane ($C_4H_{10}$)



$CH_3-\underset{\displaystyle CH_3}{CH}-CH_3$

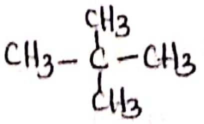
(2) n-Pentane ($C_5H_{12}$) $CH_3-CH_2-CH_2-CH_2-CH_3$

Iso pentane ($C_5H_{12}$)



$CH_3-\underset{\displaystyle CH_3}{CH}-CH_2-CH_3$

Neo-pentane ($C_5H_{12}$)



$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3$

This type of isomerism is due to the difference in the nature of the carbon chain (i.e straight (or) branched) which forms the nucleus of the molecule. $C_4H_{10}$ and $C_5H_{12}$ can exist in 2 and 3 isomeric forms, respectively.

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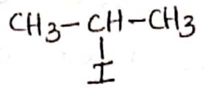
**(ii) position isomerism:** It is arises due to the diffence in the position of the substituent atom (or) group (or) an unsaturated linkage in the carbon chain.

Examples: (1) N-propyl iodide ($C_3H_7I$) $CH_3-CH_2-CH_2-I$

Isopropyl iodide ($C_3H_7I$)

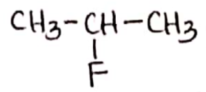

$CH_3-\underset{I}{CH}-CH_3$

(2) 1-butene ($C_4H_8$) $CH_2=CH-CH-CH_3$

2-butene ($C_4H_8$) $CH_3-CH=CH-CH_3$

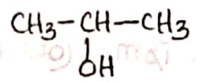
(3) Fluoropropane ($C_3H_7F$) $CH_3-CH_2-CH_2-F$

2-fluoropropane ($C_3H_7F$)


$CH_3-\underset{F}{CH}-CH_3$

(4) N-propyl alcohol ($C_3H_8O$) $CH_3-CH_2-CH_2-OH$

Isopropyl alcoho ($C_3H_8O$)


$CH_3-\underset{OH}{CH}-CH_3$

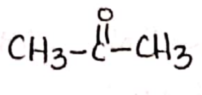
**(iii) Functional isomerism:** compounds having same molecular formula but possess different functional groups.

Examples: (1) Ethyl alcohol ($C_2H_6O$) $CH_3-CH_2-OH$ (alcoholic group)

Dimethyl ether ($C_2H_6O$) $CH_3-O-CH_3$ (ether group)

(2) propanaldehyde ($C_3H_6O$) $CH_3-CH_2-CHO$ (aldehyde group)

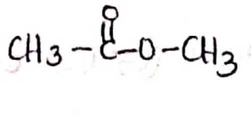
Acetone ($C_3H_6O$)


$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ (Ketone group)

Allyl alcohol ($C_3H_6O$) $CH_2=CH-CH_2-OH$ (alcohol)

(3) proppionic acid ($C_3H_6O_2$) $CH_3-CH_2-COOH$ (acid group)

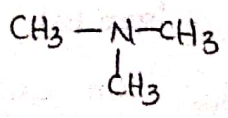
Methyl acetate ($C_3H_6O_2$)


$CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3$ (ester group)

(4) N-propyl amine ($C_3H_9N$) $CH_3-CH_2-CH_2-NH_2$ ($1^\circ$ amine)

Methyl ethyl amine ($C_3H_9N$) $CH_3-NH-CH_2-CH_3$ ($2^\circ$ amine)

Trimethyl amine ($C_3H_9N$)


$CH_3-\underset{CH_3}{\underset{|}{N}}-CH_3$ ($3^\circ$ amine)

This type of isomerism is due to difference in the nature of functional group present in the isomers.

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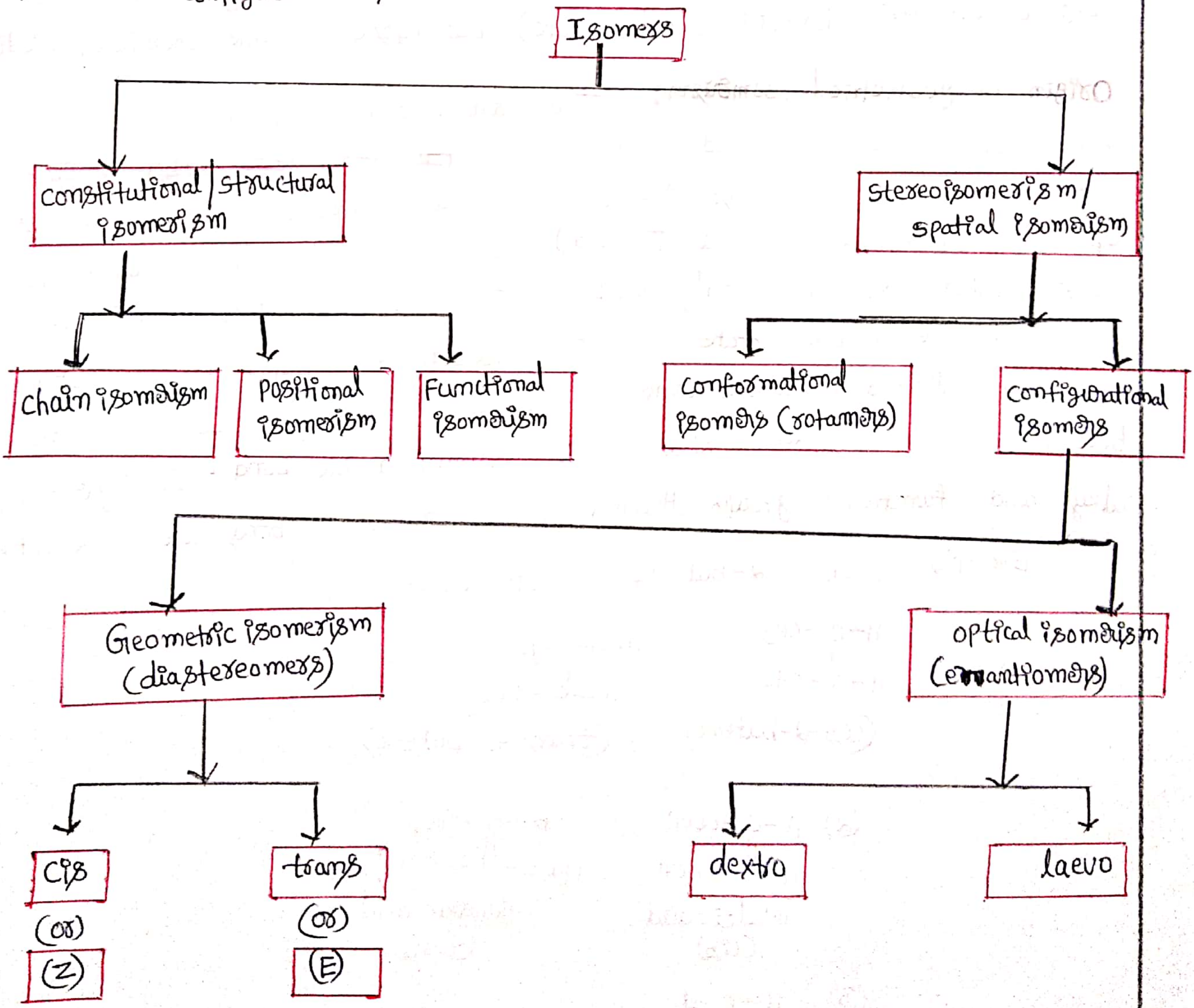
## (b) Stereoisomerism (or) Spatial isomerism: [Stereo = space, Meros = Parts]

The streoisomers (or) spatial isomers are the compounds of identical structure but differ in spatial arrangement of atoms. Stereoisomers are roughly divided into two classes.
ⓘ conformational stereomers
ⓘⓘ configurational isomers.

**ⓘ conformational stereomers:** The stereoisomers which interconvert easily at room temperature through rotations about single bonds are known as conformational isomers.

**ⓘⓘ configurational isomers:** The stereo isomers which are non-super imposable mirror images of each other and are non-interconvertible by rotation around single bonds are known as "configurational isomers" and the phenomenon is known "configurational isomerism".



Configurational isomers can be interconverted only by breaking and making of the bonds. These are of two types.

(a) Geometrical isomers (Diastereomers)

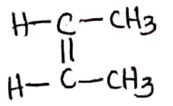
(b) Enantiomers (optical isomer)

**(a) Geometrical isomerism:** A type of isomerism due to the different geometrical arrangement of two different groups about the carbon-carbon double bond is called geometrical isomerism (or) cis-trans isomerism. When similar groups are attached to the same side of molecule, it is called the cis (or syn) isomer, while in trans (or anti) isomer similar groups lie on the opposite side.

Geometrical isomers differ in their physical properties (such as M.P, B.P, density, solubility etc.) but possess same chemical properties.

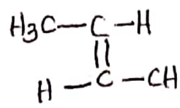
**Origin of geometrical isomerism:** Two carbon atoms joined by a single bond can be freely rotated around it. ~~But when two carbon atoms~~. But when two carbon atoms are joined by a double bond (which consists of a sigma-bond and a π-bond), the free rotation about around the carbon-carbon axis is hardly possible. The two carbon atoms in olefinic compounds are in the state of $sp^2$ hybridization. In this way, the atoms (or) groups attached to carbon atoms in compounds containing $C=C$ double bond become fixed up in space. Now alkenes contain double bond. If hydrogen, alkyl and functional groups attached to carbon-carbon bonds are different.

Examples: (1) 2-butene $CH_3-CH=CH-CH_3$



$$\begin{array}{c} H-C-CH_3 \\ \| \\ H-C-CH_3 \end{array}$$

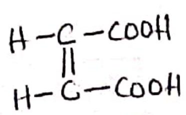
(cis-2-butene)



$$\begin{array}{c} H_3C-C-H \\ \| \\ H-C-CH_3 \end{array}$$

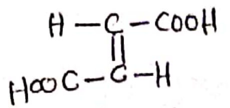
(trans-2-butene)

(2)



$$\begin{array}{c} H-C-COOH \\ \| \\ H-C-COOH \end{array}$$

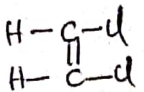
Maleic acid (cis)



$$\begin{array}{c} H-C-COOH \\ \| \\ HOOC-C-H \end{array}$$

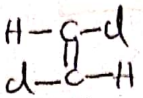
fumaric acid (trans)

(3)



$$\begin{array}{c} H-C-Cl \\ \| \\ H-C-Cl \end{array}$$

cis-1,2-dichloroethylene



$$\begin{array}{c} H-C-Cl \\ \| \\ Cl-C-H \end{array}$$

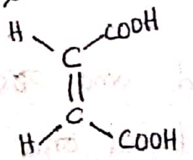
Trans-1,2-dichloroethylene

**Conditions for geometrical isomerism:** (1) The molecule must contain a double bond (2) Each of two carbon atoms of double bond must remain attached to different substituent.

**Characteristics of Diastereomers:** (i) They exhibit similar, but somewhat different chemical properties (ii) Their rates of reaction are different. (iii) The physical properties (Eg: melting point, boiling point, density, solubility, refractive index etc) are different. (iv) They can be separated by fractional distillation, fractional crystallization and chromatography. The relative physical constants of cis and trans isomers are mentioned in the following table.

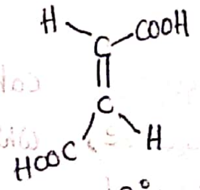
| Physical constants | cis | trans |
|---|---|---|
| Melting point | Lower | Higher |
| Boiling point | Higher | Lower |
| Solubility | Higher | Lower |
| Density | Higher | Lower |
| Dipolemoment | Higher | Lower |
| Refractive index | Higher | Lower |
| Heat of combustion | Higher | Lower |
| | | |

* Eg: Cis isomers have higher dipole moments than trans isomers which may have zero dipole moments. For example, the dipole moment of cis-maleic acid is quite high while that of fumaric acid is zero because dipole moments of C–COOH bonds cancel out the effects of each other as these are in opposite directions.



$\mu = 7.22D$

Maleic acid (cis)



Fumaric acid (trans)

$\mu = 0D$

Similarly in 1,2-dichloroethene, the dipole moment of C–Cl bond is cancelled out in the trans isomer.

$\mu = 1.85D$

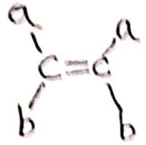
(cis)

$\mu = 0D$

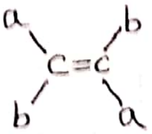
(trans)

**Nomenclature :**

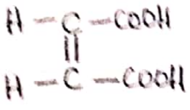
(a) **cis-trans system:** The isomer having the same groups on the same side of the double bond is known as cis-form, whereas the one in which same group remain on the opposite side of the double bond is known as trans-form.



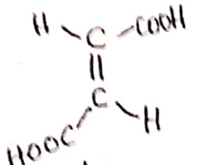
cis



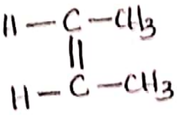
trans



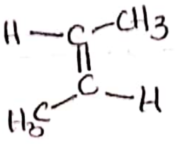
cis
Maleic acid



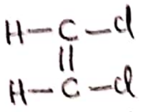
trans
fumaric acid



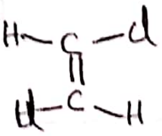
cis-2-butene



trans-2-butene.

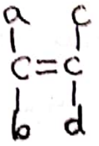


cis-1,2-dichloro ethylene



trans-1,2-dichloro ethylene

(b) **E-Z System:** If four different atoms (or) groups are attached to the carbon atoms of a double bond, then <u>cis</u> and <u>trans</u> designations cannot be employed

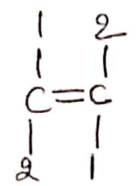


In such cases, cahn, Ingold and prelog developed <u>E and Z</u> system of nomenclature, which is based on a priority system. In this system, the two atoms/groups attached to each carbon atom of the doubly bond carbons are put in order of precedence based on sequence rules.

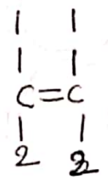
(i) The symbol "E" (from German word Entgegen = across (or) opposite) is assigned to the isomers in which the atoms/

groups of higher precedence are on the opposite side.

(ii) The symbol "z" (from german word zusammen = together) is assigned to the isomer in which the atoms/groups of higher precedence are on the same side. Thus



E-isomer



z-isomer

1 signifies higher precedence
2 signifies lower precedence

**Sequence rules:** (1) Higher the atomic number, higher is the priority assigned to the atom. For example

precedence order : $I > Br > Cl > H$

Atomic number : 53 35 17 1

(2) In case of groups, the precedence order is decided on the basis of atomic number of first atom of the group. For example

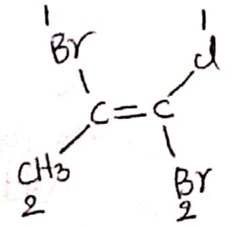
precedence order : $-Cl > -SO_3H > -OH > -NHCH_3 > -COOH$

Atomic number of first atom : 17 16 8 7 6

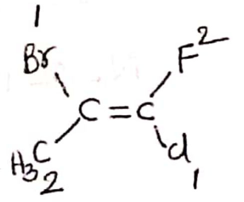
(3) If the precedence order of groups cannot be settled on the basis of atomic number of first atom, then second atom (or) the subsequent groups are considered. For example

precedence order : $-COOH > -CH_2-CH_3 > -CH_3$

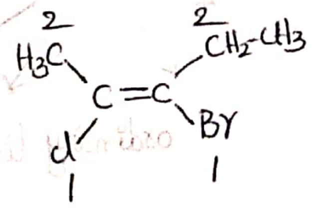
Atomic number of second atom : 8 6 1



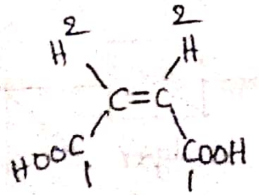
(Z)-isomer



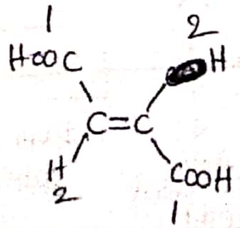
(E)-isomer



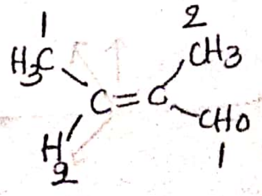
Z-isomer



(Z)-isomer



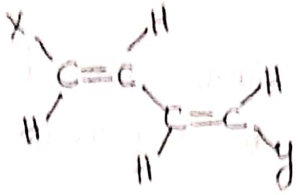
(E)-isomer



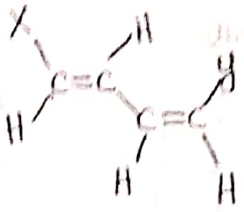
(E)-isomer

## Geometrical isomerism in compounds with more than one double bond:

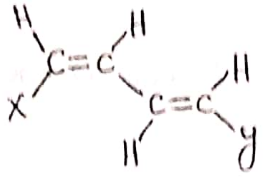
(1) When a compound contains "n" number of dissimilarly substituted double bonds, then the number of geometrical isomers is $2^n$.



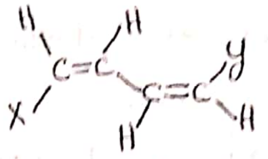
trans-trans



trans-cis



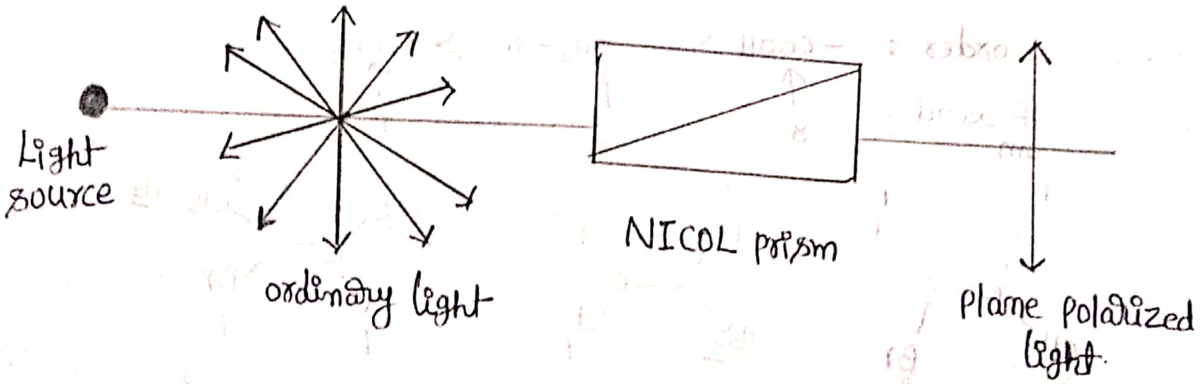
cis-trans

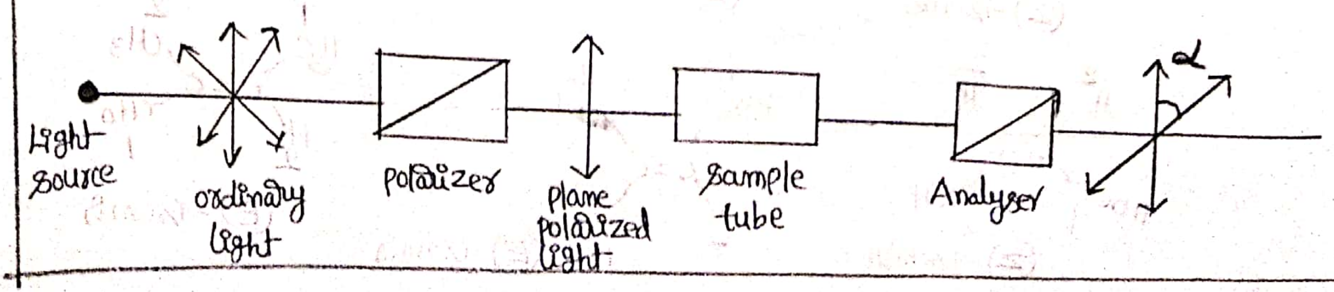


cis-cis

## Optical activity (optical isomerism):

**Plane polarized light:** Ordinary light consists of waves vibrating in all planes perpendicular to in the propagation. When such a light is allowed to pass through NICOL prism, its vibrations in all planes are cut off except one plane. This light having wave motion in one plane only, is called plane polarized light and the plane perpendicular to the plane of vibration, is called the plane of polarization.





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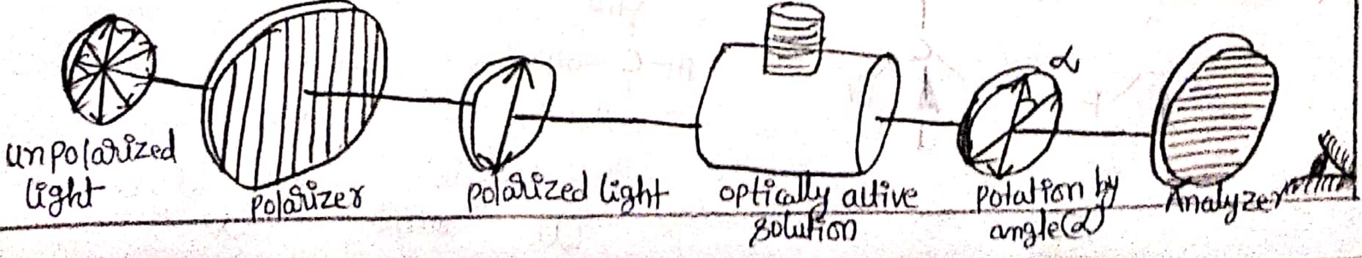
**Optical activity:** The phenomenon by virtue of which certain substances exhibit remarkable ability to plane polarized light is known as optical activity and the substances possessing this property, are said to be "optically active" (or chiral). Substances which rotate the plane polarized light in clockwise direction are known as dextrorotatory, indicated by "d" (or) "+ve" (latin: dextro means right) and those which rotate the plane of polarized light in anticlockwise direction are known as levorotatory, indicated by "l" (or) "-ve" form (Latin: leavopus means left).

A mixture of these two varieties in equal proportions will be optically inactive and it is called "racemic form".

**Polarimeter:**

The instrument for studying interaction between plane-polarized light and chiral molecules is known as a polarimeter. (Fig) Intially, a beam of unpolarized light is passed through a polariod sheet, called polarizer, then through a sample tube. By rotating the analyzer, another polariod sheet, minimal light transmission can be achieved. Next the sample tube is filled with a solution containing an optically active compound. As the plane-polarized light passes through the sample tube this time, its plane of polarization is rotated either to be right (or) to the left by certain amount depending on whether the optical isomer is in the "d" (or) "l"-form. This rotation can be measured readily by turning the analyser in the appropriate in the appropriate direction, untill minimal light transmission is again achieved. The angle of rotation in degrees, $\alpha$, depends not only on the nature of the molecules, but also on the concentration of the solution and the length of sample tube.



**Specific rotation:** optically activity is reported in terms of specific rotation, which is characteristics of a particular compound. It is defined as the rotation in degrees observed when a plane polarized in passes through 1 dm of solution having concentration of 1 gm/ml at a specified temperature and wavelength. This is usually expressed as

$$[\alpha]_D^t = \frac{\alpha(obs)}{lc}$$

where D is the D-line of sodium having wavelength 589.3
t is the temperature (°C)
l is the length of polarimeter tube,
C is the concentration of solution (g/ml).

The specific rotation of pure liquid is given by $[\alpha]_D^t = \frac{\alpha(obs)}{ld}$

If the substance is in solution form then: $[\alpha]_D^t = \frac{\alpha}{lc}$

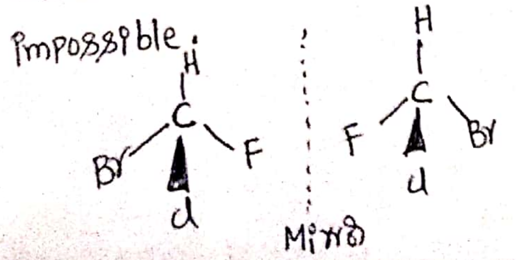
The extent of rotation $[\alpha]$ of the plane of polarization depends on

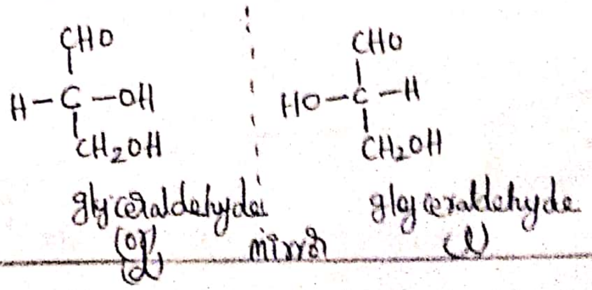
(i) nature of substance
(ii) its temperature
(iii) length "l" through which light passes
(iv) density "d" of the substance and
(v) wavelength of the light employed.

**Requirement of optical activity: (or) cause of optical activity:**

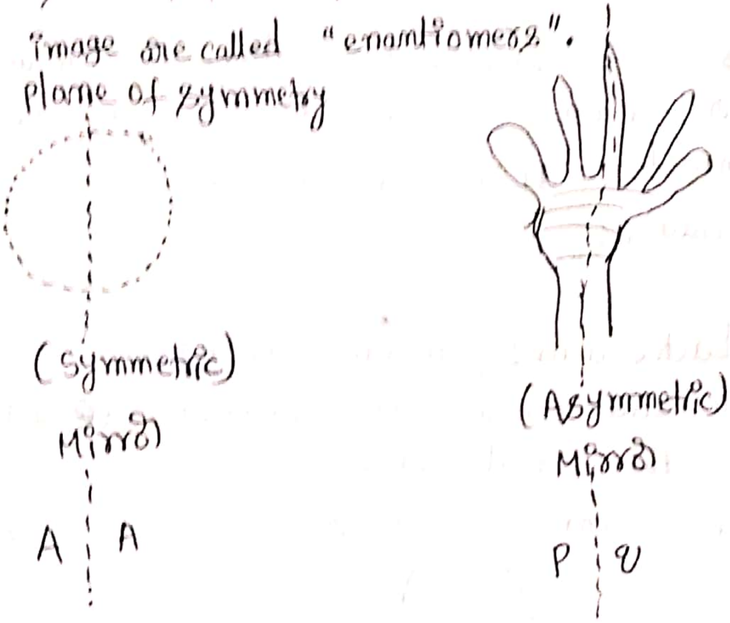
Compound possessing identical molecular and structural formulae and identical physical and chemical properties, but differing only optical activity (i.e; their action on plane polarized light) are called optical isomers (or) enantiomers and the phenomenon is called optical isomerism (or) enantiomerism.

Example: Fluoro chlorobromo methane, CH F Cl Br, contains an assymetric central carbon atom; and it exists in two optical active forms, which are related to each other as mirror images and the the two are non-super impossible:





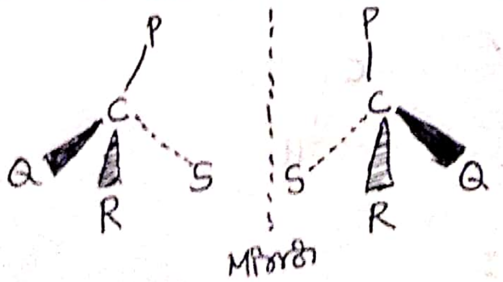
**Cause of optical activity:** The only factor responsible for the optical activity (or rotation of the plane of polarized light) is Molecular Assymetry. A plane which bisects the object into super-impossible mirror image halves, is called the plane of symmetry. "An object which has no plane of symmetry is asymmetric (or) chiral". Thus the reflection of an asymmetric object in a mirror is not super-impossible on the object. Asymmetric object and its mirror image are called "enantiomers".



Symmetric and assymetric object

From the above discussion, it is clear that for an organic compound to show optical activity, it should be (i) have an assymmetric (or) chiral carbon atom and
(ii) not have a plane of symmetry.

**Asymmetric (or) chiral carbon atom:** A carbon atom bonded to four different atoms (or) groups, is called "asymmetric carbon atom". Thus, if a molecule has an asymmetric carbon atom, it is no longer super impossible on its mirror image and will, therefore, exhibit optical activity.



**Plane of symmetry:** If a molecule can be divided by an imaginary plane in which a way that points on one side of plane form a mirror

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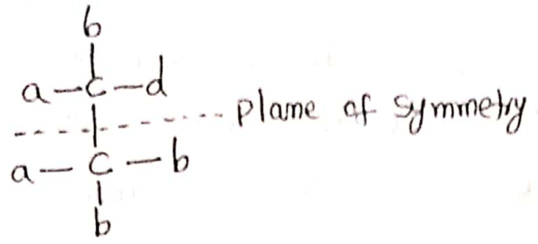
image of those on its otherside, then the compound is said to possess a "plane of symmetry" and hence, is "optically inactive".

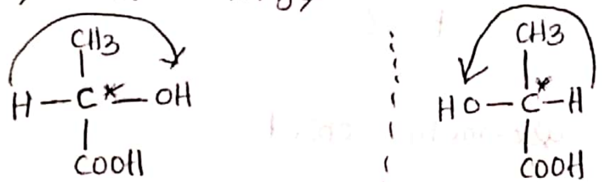
For example: the compound



**Centre of symmetry :** This is an imaginary point in a molecule from which, when equal lengths are drawn on both sides, then they meet exactly at similar points in the molecule. If a compound has a centre of symmetry, it is "optically inactive".

## Optical isomerism of Lactic acid: [$CH_3\overset{*}{C}H\,OH\cdot COOH$]

Lactic acid contains an asymmetric central carbon atom, and it exists in two optical active forms, which are related to each other as mirror images and the two are non-superimpossable.

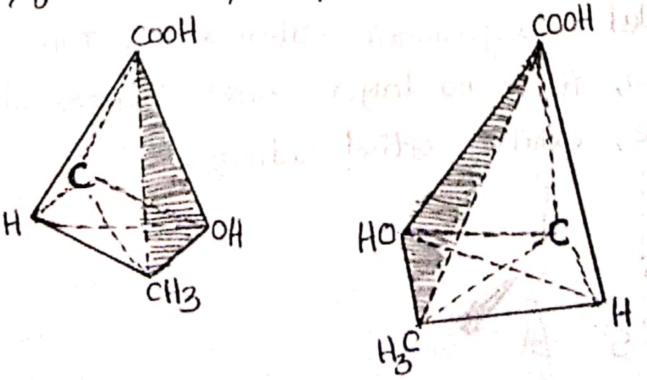


(+) (or) d – lactic acid

(–) (or) L-lactic acid

Mirror

A third form called racemic mixture is obtained, when equimolar quantities of d- and l- enantiomers are mixed. Such a mixture is optically inactive as a result of the cancellation of the equal and opposite rotations of two isomers. The symbol ± is used to denote a racemic mixture.



## Optical isomerism of Tartaric acid :

Tartaric acid has two asymmetric carbon atoms, each linked to the four different groups, i.e; –OH, –H, –COOH and –CH(OH) COOH.

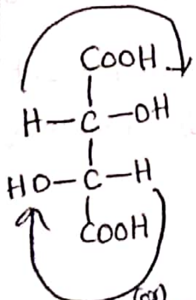
The spatial arrangements of various groups in tartaric acid can be represented in four ways, correspondingly, tartaric acid can exists in four different forms given below.

(i) Dextro tartaric acid is on which rotates the plane polarization of light to the right. This rotation due to upper half is strengthened by one due to lower half.

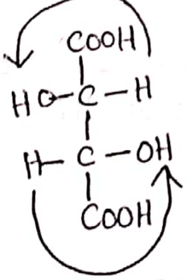
(ii) Levo-tartaric acid is a mirror image of the above and rotates the plane of polarization of the light to the left.

(iii) Racemic tartaric acid is a 50-50 mixture of the above two varieties and is hence, inactive. It can be resolved into the active constituents, viz; dextro and levo-varietie. It is therefore, inactive by external compensation.

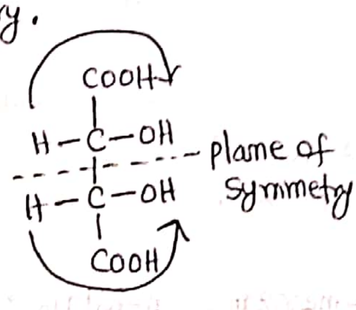
(iv) Meso-tartaric acid is the inactive variety as the rotation of upper-half is compensated by the rotation due to the lower-half (being in opposite direction). It cannot be resolved into active constituents. It is, therefore, inactive by internal compensation. unlike dextro- and levo-varieties, it has a plane of symmetry.



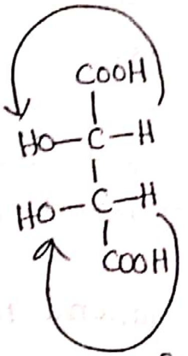
Dextro (or) (+)



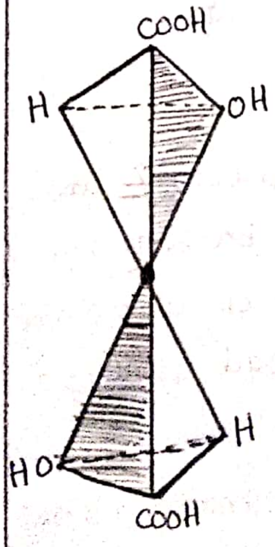
Leavo (or) (−)



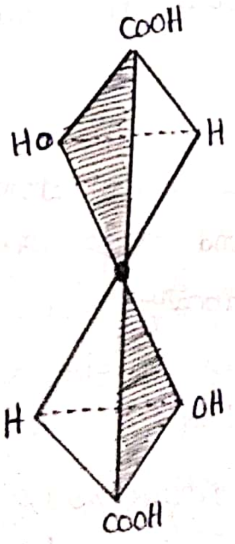
Meso



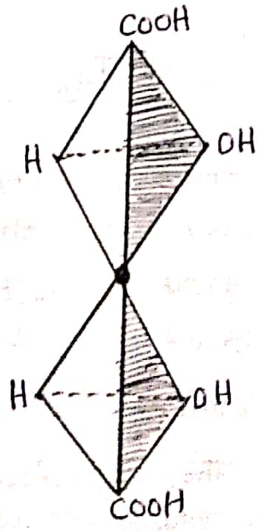
Racemic



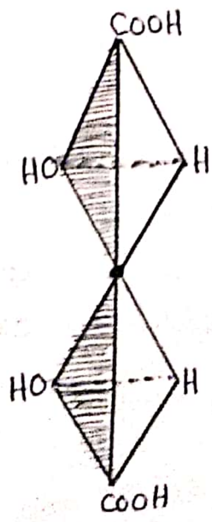
Dextro (or) (+)



Leavo (or) (−)



Meso



Racemic

**Characteristics of enantiomers:** (1) They have identical physical properties such as melting points, boiling points, densities and refractive indices.

(2) They have identical chemical properties except their behaviour toward optically active compounds.

(3) Eantiomers have different biological properties.

(4) They differ in their action toward plane polarized light. They rotate the plane polarized light to the same extent but in opposite directions.

(5) They cannot be separated by methods such as fractional crystallization and fractional destillation, chromatography.

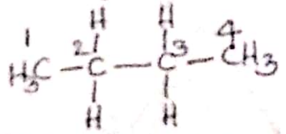
## Conformational isomerism:

Conformational isomerism refers to any one of the infinite number of spatial arrangements of the atoms of a molecule that can arise from rotation about a single bond. The term should not be confused with configuration isomerisms, which are spatial arrangements of the atoms of a molecule that can be changed only by breaking and making of bonds.

The stereoisomers which are non-super impossible but are easily inter convertible by rotation about the single bond are known as conformational isomerism.

### Conformational isomerism of n-butane:

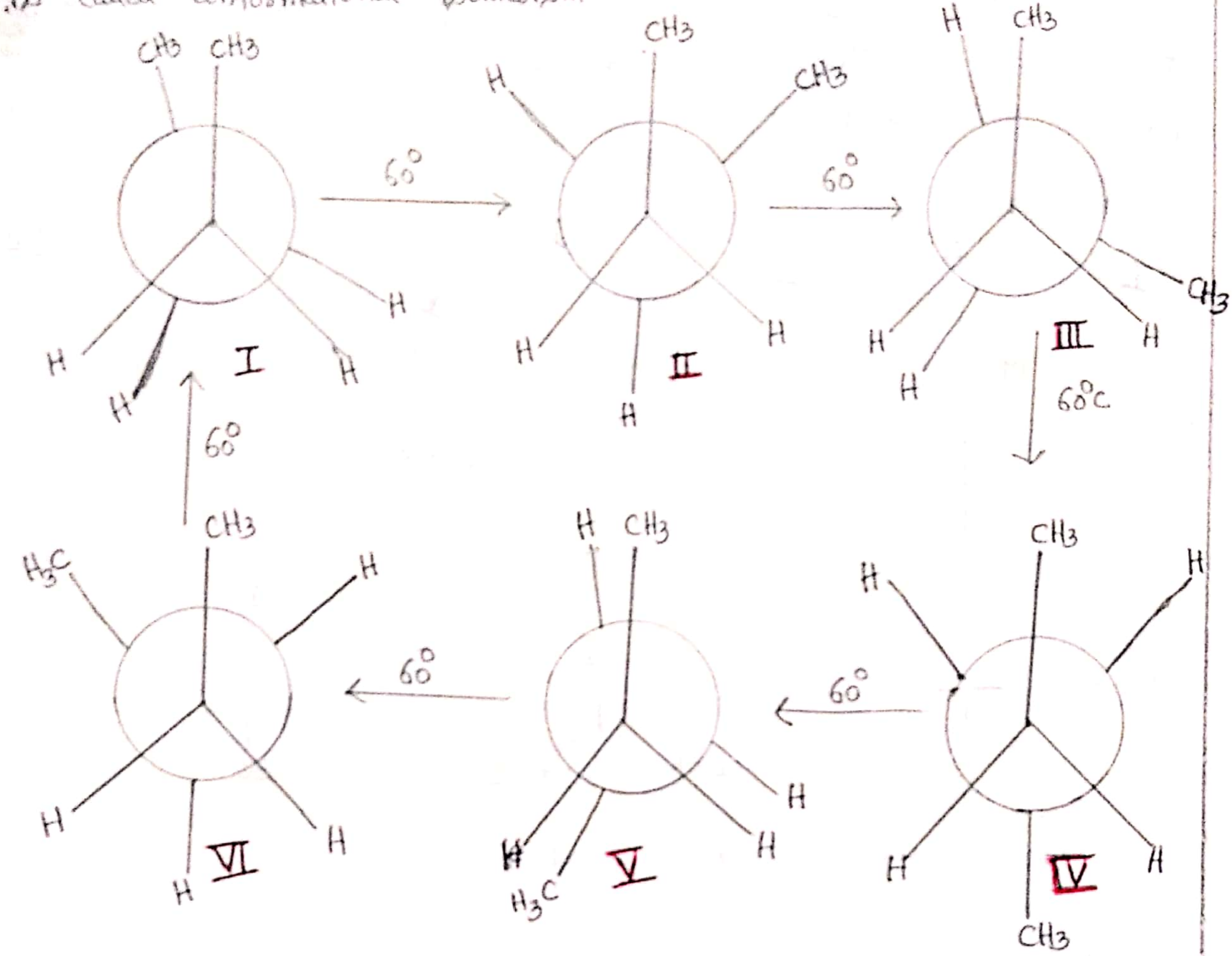
The sigma bond joining the carbon atoms 2 and 3 of butane, is cylindrically symmetrical about the nuclear axis.



$$H_3\overset{1}{C}-\overset{2}{C}H_2-\overset{3}{C}H_2-\overset{4}{C}H_3$$

This in-turn permits the free rotation of carbon atoms number 2 and 3 with respect to each other along their bond axis without breaking the bond. If one $CH_3-CH_2-$ group is kept stationary and other $CH_3-CH_2-$ group is allowed to rotate through 360° in six steps (60° each time), then following six conformations of n-butane are obtained.

These different arrangements of groups in space that results from the free rotation about C2 – C3 bond are called conformations (or) conformational isomers of n-butane and this phenomenon is called conformational isomerism.



The conformation I in which two methyl groups are very much close is called fully eclipsed, and the conformation IV in which they are farthest apart is called fully staggered (or) anti-form. conformation III and V are known as partially eclipsed, whereas II and VI are called partially staggered (or) gauche (or) skew. In the case of n-butane one fully eclipsed conformation and two partially staggered conformations are observed. one fully staggered (or) anti conformation and two gauche (or) skew confirmations are present. II and VI conformations are mirror images of each other.

In case of fully staggered (IV) form 4 $CH_3-H$ and 2 H-H interactions. In fully eclipsed form greater steric effects are acting, i.e; 6 interactions are possible. In gauche conformation 1 $CH_3-CH_3$, 2-$CH_3-H$, 3-H-H interactions are present.

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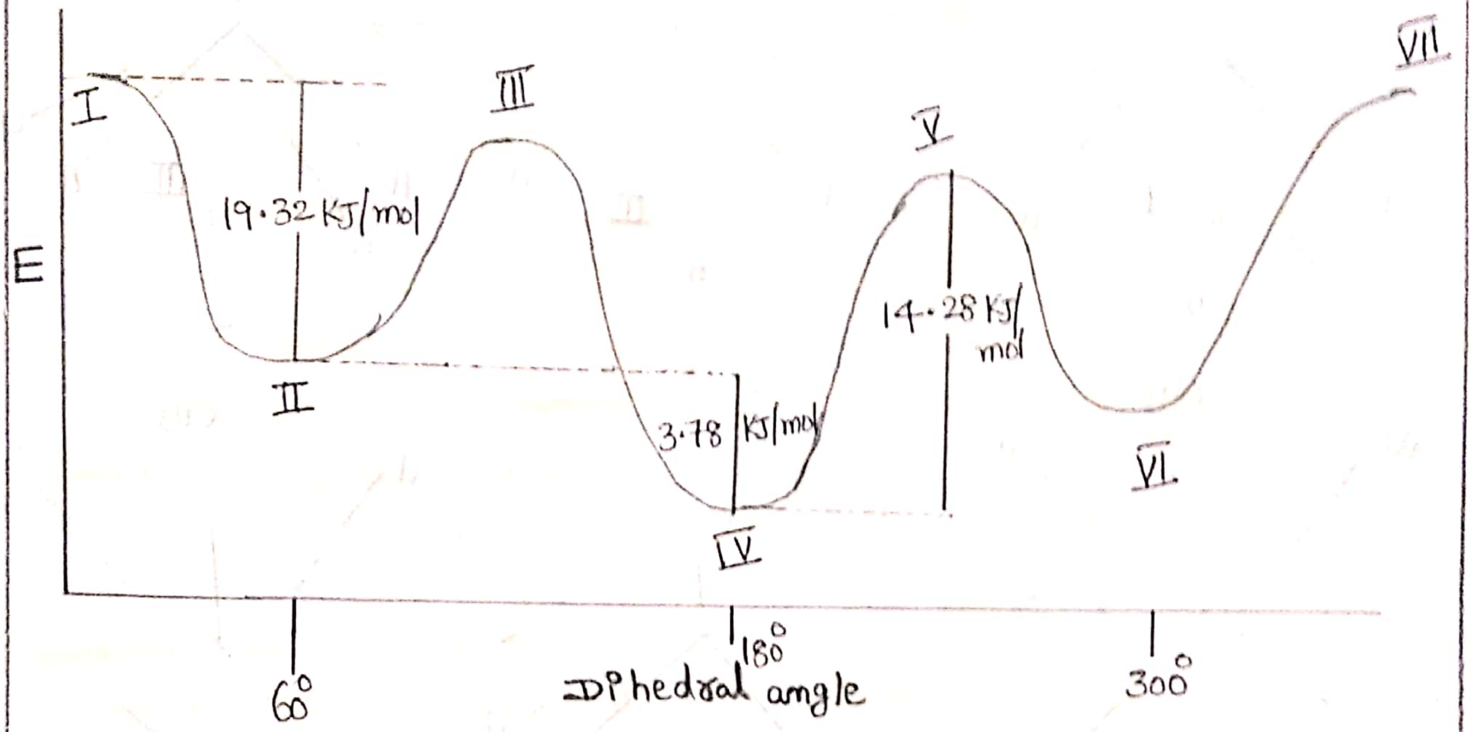
The magnitude of interaction is $CH_3-CH_3 > CH_3-H > H-H$. The relative stabilities of all these conformations are shown in the potential energy diagram.

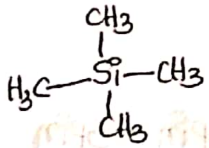


potential energy diagram of n-butane

**(a) CHEMICAL SHIFT:** The number of signals in an NMR spectrum tells the number of the sets of equivalent protons in a molecule. The position of the signals in the spectrum helps to know the nature of protons.

If the resonance frequency of all protons in a molecule were the same, then the NMR spectrum would show only one peak for the compound. The induced field opposing the applied field. The field felt by the proton, is dismissed and the proton is said to be "sheilded". The induced field reinforces the applied field, the proton feels a higher field strength and thus, such a proton is said to be "deshielded". "Shielding shifts" the absorption "upfield" and "deshielding shifts" the absorption "down field".

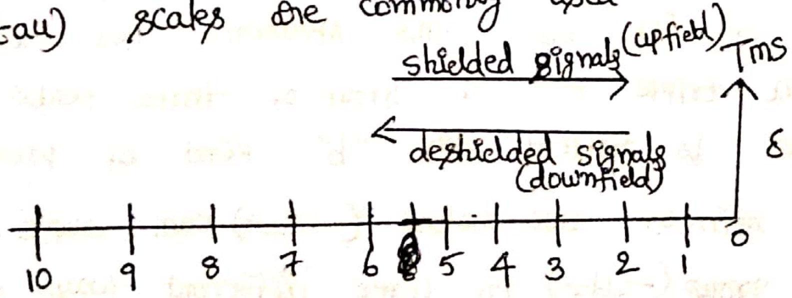
"Such shifts in the positions of NMR absorptions which arise due to the shielding (or) deshielding of protons by the electrons are called "chemical shifts". (δ). For measuring chemical shifts of various protons in a molecule, the signal for tetramethyl silane (TMS) is taken as a reference, due to

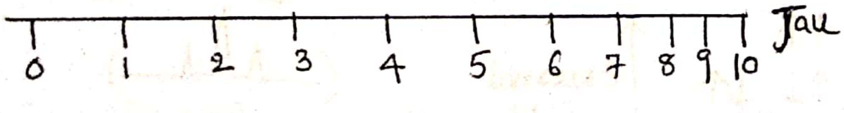


ⓘ the low electronegativity of Silicon

ⓘⓘ the shielding of equivalent protons in TMS is greater than most of the organic compounds.

protons with the same chemical shifts are called equivalent protons. Non-equivalent protons are have different chemical shifts. δ (delta) (or) τ (tau) scales are commonly used.





The values of δ for a substance with respect to TMS can be obtained by measuring

$$\nu_S - \nu_{TMS}$$

where $\nu_S$ = Resonance frequency of the sample

$\nu_{TMS}$ = " " " TMS

$$\delta = \frac{\nu_{sample} - \nu_{reference}}{\text{operating frequency in megacycles}}$$

$$\delta = \frac{\Delta\nu}{\text{operating frequency in megacycles}}$$

The value of $\underline{\delta}$ is expressed in parts per million (ppm). most chemical shifts have $\underline{\delta}$ values between $\underline{0}$ and $\underline{10}$.

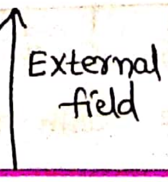
| Type of protons | chemical shift in ppm |
|---|---|
| $CH_4$ | 0.23 |
| $CH_3-I$ | 2.16 |
| $CH_3-Br$ | 2.68 |
| $CH_3-Cl$ | 3.25 |
| $CH_3-F$ | 4.26 |

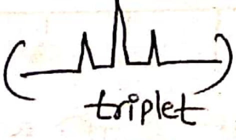
**③ Spin - Spin splitting (spin-spin coupling) :** "The splitting of signal lines in the spectrum into two (or) more components is called spin - spin splitting".

Consider a molecule of $\overset{a}{CH_3}-\overset{b}{CH_2}-Br$ (ethyl bromide). This molecule has two kinds of protons in it and thus, two signals are excepted in its own NMR spectrum. For "a" kind of protons ($CH_3$), a triple i.e: a group of three peaks is observed and a quartet is noticed for "b" kind of protons ($CH_2$).

The spin of two protons ($-CH_2-$) can couple with the adjacent methyl group ($-CH_3-$) in three different ways relative to the external field. The three different ways of allignment are:

(i) ↑↑
(ii) ↑↓ ↓↑
(iii) ↓↓





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Thus, a triplet of peaks results with the intensity ratio of 1:2:1. Similarly, the spin of three protons ($-CH_3$) can couple with the adjacent methylene group ($-CH_2-$) in four different ways. Thus, quartet of peaks results with an intensity ratio of 1:3:3:1.


quartet

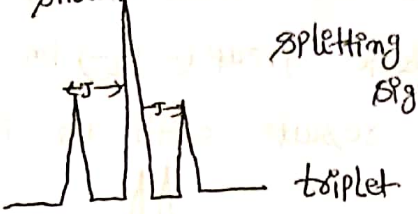
(i) ↑↑↑ 1
(ii) ↑↑↓ ↑↓↑ ↓↑↑ 3
(iii) ↓↓↑ ↓↑↓ ↑↓↓ 3
(iv) ↓↓↓ 1

* The multiplicity of the signal for any group of equivalent protons is clearly related to the number of protons of the adjacent atoms, As a simple rule the multiplicity of a given group is (n+1), where n is the number of protons of the adjacent atoms. Accordingly n-propyl iodide ($CH_3-CH_2-CH_2-I$) has three different types of protons. The NMR spectrum of 3H (triplet) (1:2:1), 2H (sextet) (1:5:10:10:5:1) and 2H (triplet) (1:2:1).

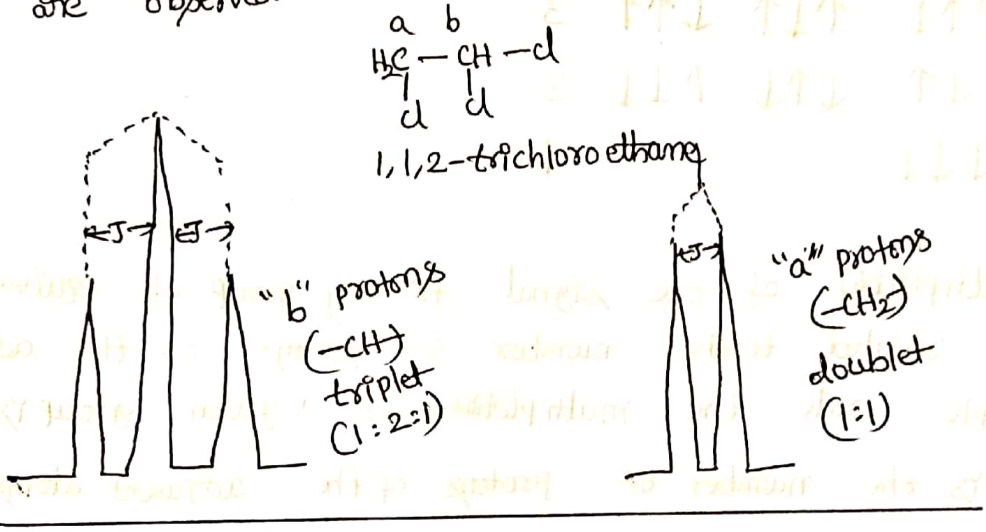
## (Q) Coupling constant (J):

"The distance between the centres of the two adjacent peaks in a multiplet is usually constant and is called the coupling constant". The value of the coupling constant is independant of the external field. It is measured in Hertz (Hz) (or) in cps (Cycles per second). It is denoted by the letter J. The value of "J" generally lies between 0 and 20 Hz.

Now let us consider a compound $>\overset{b}{C}H-\overset{a}{C}H_2-$. In this compound two signals are expected in the NMR spectrum. The influence of two equivalent protons "a" the signal for proton "b" will appear as a triplet. The distance between any two adjacent peaks in a multiplet will be exactly the same. The triplet formed due to spin-spin coupling is shown.

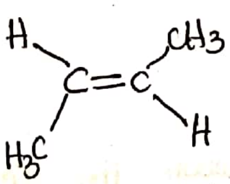


coupling constant in the NMR spectrum of 1,1,2-trichloro ethane two multiplets are observed.

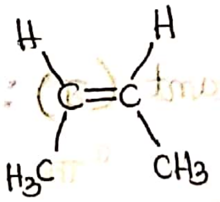


1,1,2-trichloro ethane

coupling constant in 2-butene:



trans-2-butene



cis-2-butene

J = trans = 11-18 Hz

J = cis = 6-10 Hz

# Module : V : Reaction Mechanism and synthesis of drugs

## (Q)-1: Explain homo & heterolytic cleavage with suitable example.

The breaking of a covalent bond between two atoms can take place mainly in two alternate ways, viz., homolytic and heterolytic fissions depending upon the relative electronegatives of the two central atoms.

**Homolytic fission (or) homolysis:** In homolytic bond fission, one electron of the bonding pair goes with each of the departing atom resulting in (to) two electrically neutral fragments (or) atoms known as "free radicals".

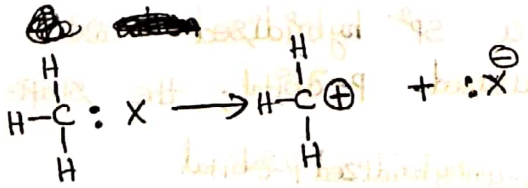
Eg:

$$H_3C : X \longrightarrow H_3C\cdot + \cdot X$$

Homolytic fission takes place when the two atoms are usually of similar electronegativity. Free radical reactions are catalysed by light, peroxides ( $H_2O_2$, benzoyl peroxide) and high temperature, these are said to be the free radical producing agents.

**Heterolytic fission (or) heterolysis:** In this type of fission the electron pair forming the covalent bond goes a single atom and thus electrically charged fragments (ions) are formed. The heterolytic fission of the covalent bond can occur in two ways. Heterolytic fission takes place when the two atoms are usually of different electronegativities.

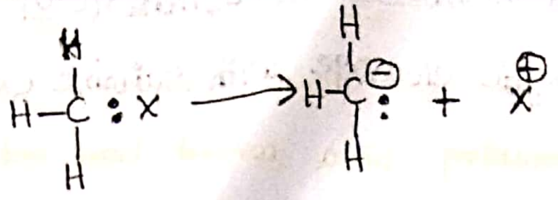
(i)



$$H_3C : X \longrightarrow H_3C^{\oplus} + :X^{\ominus}$$

Such organic species has only six paired of electrons and a positive at its carbon centre is known as "carbonium ion". carbonium ions are generally symbolized as $R^{\oplus}$.

(ii) when the electron pair between "c" and "x" the organic group and the substituent "x" is devoid of its bonding electron and thus gets positive while the organic group is negatively charged.



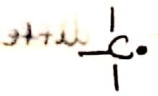
$$H-\overset{H}{\underset{H}{C}}:X \longrightarrow H-\overset{H}{\underset{H}{C}}\overset{\ominus}{:} + \overset{\oplus}{X}$$

Such organic species which has eight paired electrons and a negative charge on one of its carbon centre known as "carbanion". carbanions are generally symbolized as $R^{\ominus}$.

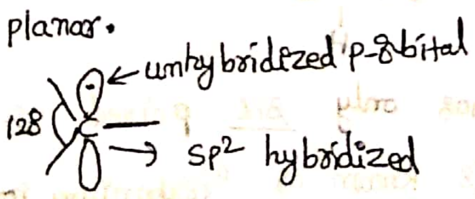
**Q. 2. what are reaction intermediates? Explain their formation and stability with examples.**

Reaction intermediates are generally short-lived and highly reactive species and they react with reagent to form the products. Several intermediates during analysis of organic reactions. They are
(i) Free radicals
(ii) carbocations
(iii) carbanions

**(i) Free radicals:** Free radicals may be defined as an odd electron neutral species which the resides on a carbon atom. These are formed by the homolysis of covalent bonds.



A free radical may have a $sp^2$ hybridised carbon in which the odd electron remains in the unused p-orbital; the shape of this type of free radical will be planar.



**Stability:** Alkyl free radicals are classified into primary (1°), secondary (2°) and tertiary (3°) depending on nature of "c" atom that carries the odd electron. The stability of carbon (alkyl) free radicals is not influenced by inductive effect because they have no charge. However, they are stabilised by hyperconjugation (non-bond resonance). This explains stability of alkyl free radicals which

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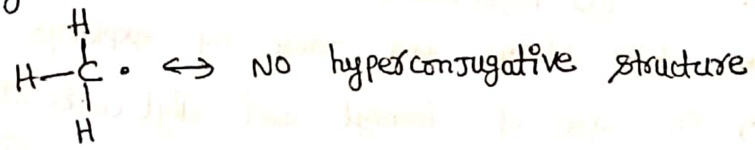
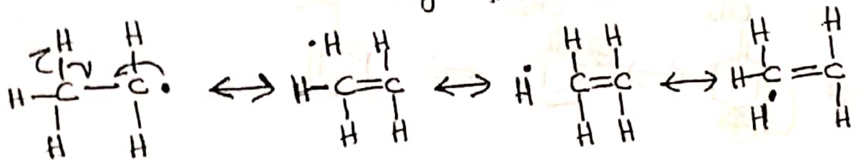
follows the order 3°>2°>1°>methyl. More the number of possible hyperconjugative structures more is delocalization of odd electron and therefore more is the stability. In case of 3°, nine hyperconjugative structures are possible, while in 2° and 1°; six and three structures are possible, respectively, as shown below. This explains the order of stability.

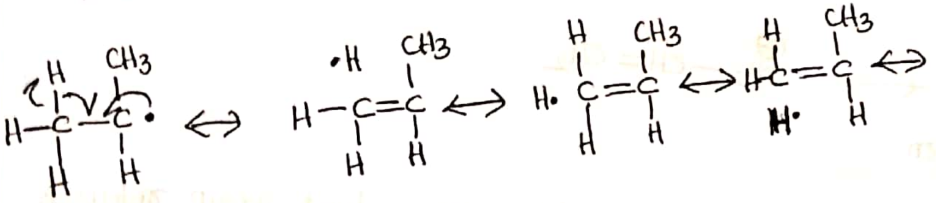


Methyl free radical



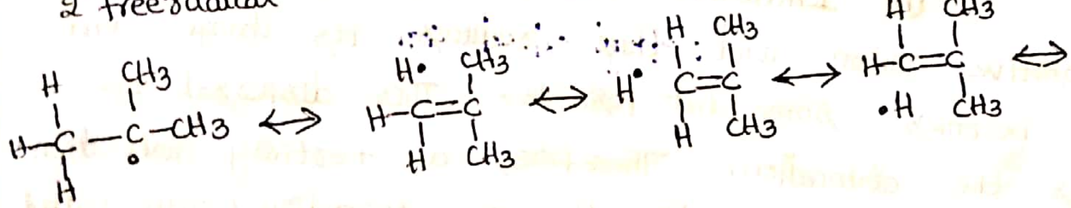
(Hyperconjugative structures of ethyl radical 1°)

1° free radical



Three more structures.

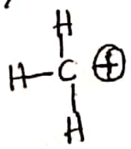
2° free radical



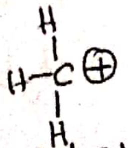
↔ Six more structures

## (ii) Carbocations (Carbonium ions):

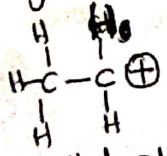
Carbocation is positively charged species containing a carbon atom having an incomplete octet, i.e., only six electrons in three covalent bonds. These are formed by hetereolysis of covalent bonds.



Carbocations are classified as 1°, 2° and 3° depending upon the nature of the carbon atom bearing the positive charge.

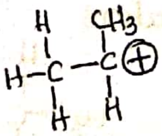


methyl carbocation



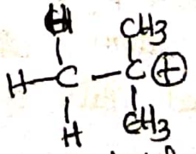
Ethyl carbocation

1°



isopropyl carbocation

2°



t-butyl carbocation

3°

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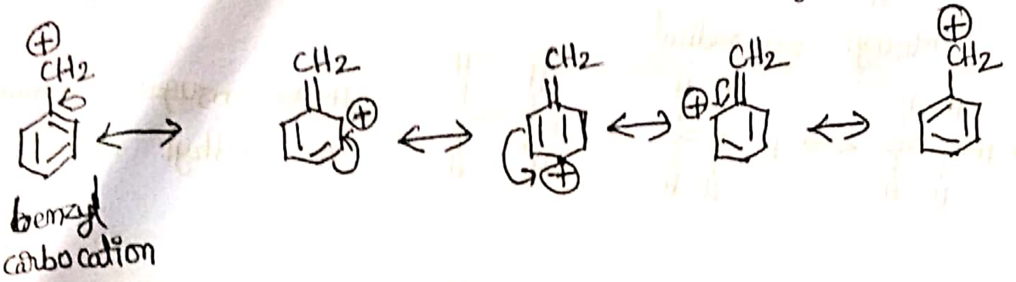
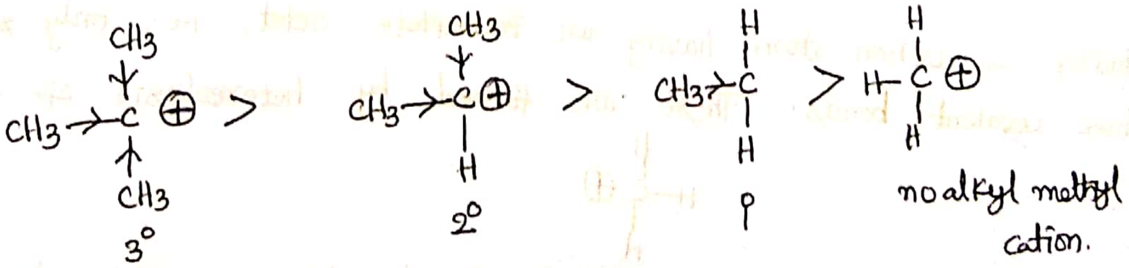
The carbon atom in carbocation is $sp^2$ hybridized and the system is planar at the cationic "c" center and bond angle of 120°.

**Stability:** The stability of carbocation can be explained by either through resonance effect and Inductive effect (electron pushing effect). (a) Resonance effect: Resonance also helps in delocalizing the +ve charge and there by explains the stability of carbocations, e.g.; in case of benzyl and allyl carbocations.

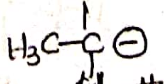


Allyl carbocation

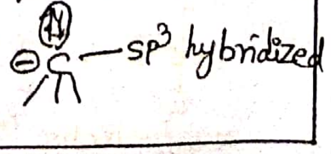
(b) Inductive effect: The alkyl group releases electrons to positive carbon and thus reduces its charge and in turn itself becomes some what positive. This dispersal of charge stabilizes the carbocation. Therefore, a tertiary carbocation (with 3 alkyl groups) is more stable than a secondary (with 2 alkyl groups) which in turn is more stable than a primary (with 1 alkyl group); methyl cation (with no alkyl group) is the least stable. (II)



**(iii) carbanions:** carbanions are negatively charged species containing a carbon atom with six electrons in three bonds and in addition an unshared pair of electrons.

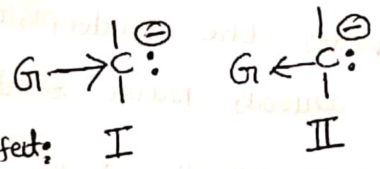


ethyl anion.

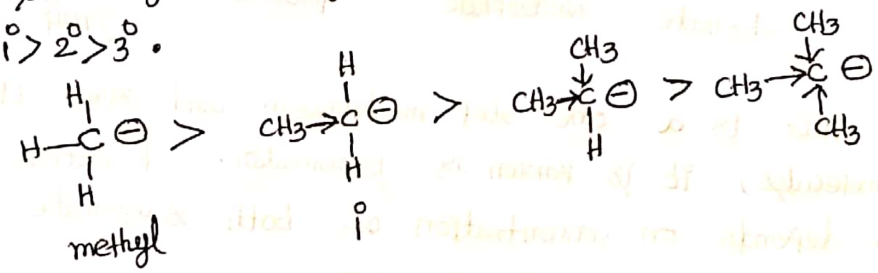


The carbon atom that carries the negative charge is $sp^3$ hybridized. carbanions are classified as 1°, 2° and 3° depending upon the nature of the carbon atom bearing the negative charge.

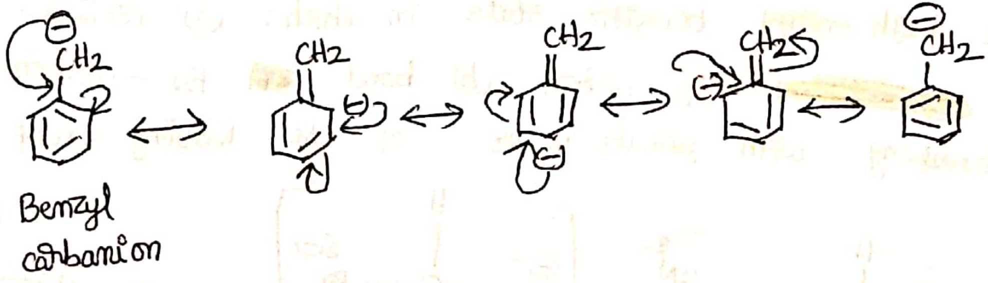
**Stability:** The stability of carbanions mainly responsible for the dispersal of the charge are "Inductive effect" and "resonance". The electron-releasing substituents tend to intensity the charge at the electron rich carbon (I) and thereby making it less stable. Electron withdrawing groups tends to decrease the negative charge density on the electron-rich carbon (II) and hence stabilize it.



Inductive effect:
(a) The stability of alkyl carbanions which follows the order.
methyl > 1° > 2° > 3°.



(b) Resonance: Resonance also helps in decolalizing the -ve charge and there by explains stability of carbanions.



Electrophiles: These are electron seeking (or) loving species
(a) positive electrophiles : $H^+$, $Br^+$, $NO_2^+$
(b) Neutral electrophiles : $BF_3$, $AlCl_3$, $ZnCl_2$, $SO_3$

Nucleophiles : These are electron sufficient species.
(a) Negative nucleophiles : $\overset{\ominus}{X}$, $\overset{\ominus}{OH}$, $\overset{\ominus}{NH_2}$, $\overset{\ominus}{CN}$
(b) Neutral nucleophiles : $H_2O$, $NH_3$, $ROH$, $RNH_2$.

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**(Q) 3. Define substitution reactions and explain the mechanism of $S_N^1$ and $S_N^2$ reactions with suitable example.**

Those substitution reactions which involve the attack of a nucleophile are known as nucleophilic substitution reactions. These are usually written as SN ("S" stands for substitution and "N" for Nucleophilic) and are more common in aliphatic compounds. Hydrolysis of alkyl halides by aqueous KOH is a common example of nucleophilic substitution.

**① Bimolecular nucleophilic substitution ($S_N^2$) mechanism:**

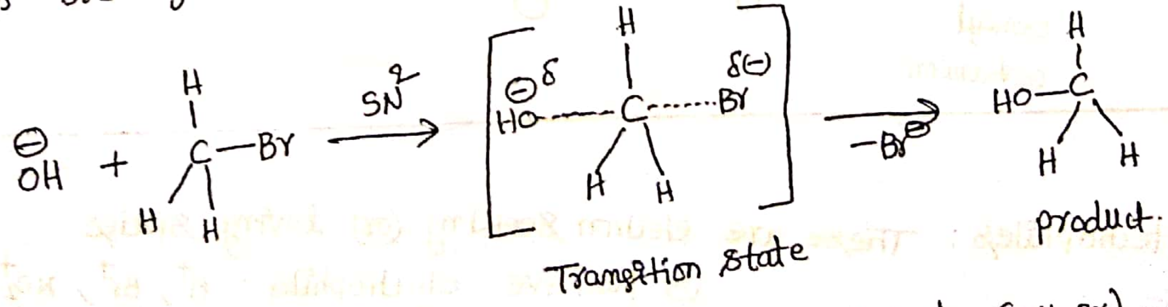
Let us consider the nucleophilic substitution reaction of a methyl bromide in aqueous NaOH solution.

$$\underset{\text{Substrate}}{CH_3Br} + \underset{\text{Nucleophile}}{\overset{\ominus}{OH}} \longrightarrow \underset{\text{product}}{CH_3OH} + \underset{\text{Leaving group}}{\overset{\ominus}{Br}}$$

Mechanism: This is a one-step mechanism and since this step involves two molecules, it is known as bimolecular. Kinetics data reveals that the rate depends on concentration of both substrate and nucleophile.

$$\text{Rate} \propto [CH_3Br]\,[\overset{\ominus}{OH}]$$

In this attacking nucleophile $\overset{\ominus}{OH}$, attacks at carbon in $CH_3Br$, forming a high energy transition state in which: (a) formation of bond between OH–carbon (b) bond Br–carbon is in process breaking with simultaneous of the leaving group, $\overset{\ominus}{Br}$:



In this reaction, the molar concentrations of substrate ($CH_3Br$) and Nucleophile ($\overset{\ominus}{OH}$) are changed and hence, the reaction is of 2nd order (or bimolecular) called $S_N^2$ reaction. In $S_N^2$ reaction, the nucleophile attacks a C-atom from the side opposite to that of leaving group.

In transition state (T.S) both nucleophile ($OH^\ominus$) and leaving group ($Br^\ominus$) carry partial negative charges. "C" is $sp^2$ hybridized in this state. The energy required to break the "C–Br" bond is compensated by the energy released during making of the "C–OH" bond.

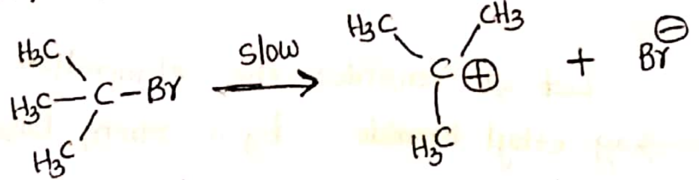
## (ii) Unimolecular nucleophilic substitution ($SN^1$) mechanism:

Let us consider the nucleophilic substitution reaction of a t-butyl bromide in aqueous NaOH solution.

$$\underset{\text{substrate}}{(CH_3)_3-C-Br} + \underset{\text{Nucleophile}}{\overset{\ominus}{O}H} \longrightarrow (CH_3)_3-C-OH + Br^\ominus$$

This is a two-steps mechanism. (a) The first step is slow and it is rate determining step, old bond break and (b) The second step is the attack of a nucleophile ($\overset{\ominus}{OH}$) on the carbonium ion and it is a fast step, new bonds are formed.

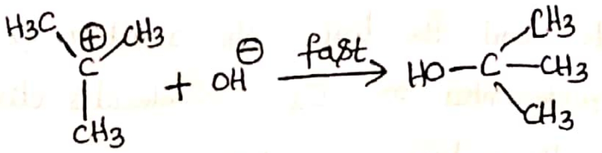
Step-I :



t-bututyl bromide

Intermediate carbocation

Step-II :



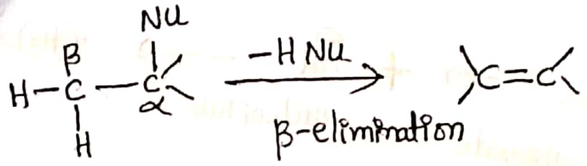
tertiary butyl alcohol

The rate-determing step is first step and this step does not involve the attacking nucleophile. The molar concentration of one reactant ($(CH_3)_3-C-Br$) is only changed, so the overall reaction is of first order, because the time taken by the reaction depends mainly on step-I. such reactions are $SN^1$ reaction (which means substitution, nucleophilic and unimolecular).

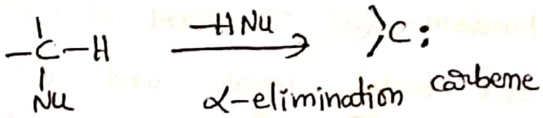
**(Q). 4. What are elimination reactions? Explain $E_1$ and $E_2$ reactions with suitable examples.**

Elimination reactions are identified as the reverse of addition reactions. Such reactions are broadly classified as β-(or) 1,2- elimination and α- elimination. The first one involves loss of two atoms (or) groups from vicinal "c" atoms, resulting in the formation of a double bond (or) triple bond. In the second step, both the atoms are removed from the same carbon atom. This is known as α- elimination reactions.

(Most common)



(Nu – Nucleophile)

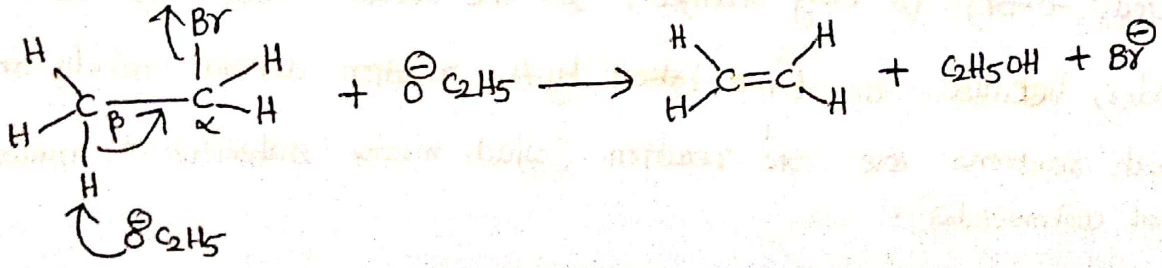


These reactions may proceed either by bimolecular ($E_2$) (or) by unimolecular ($E_1$) mechanism.

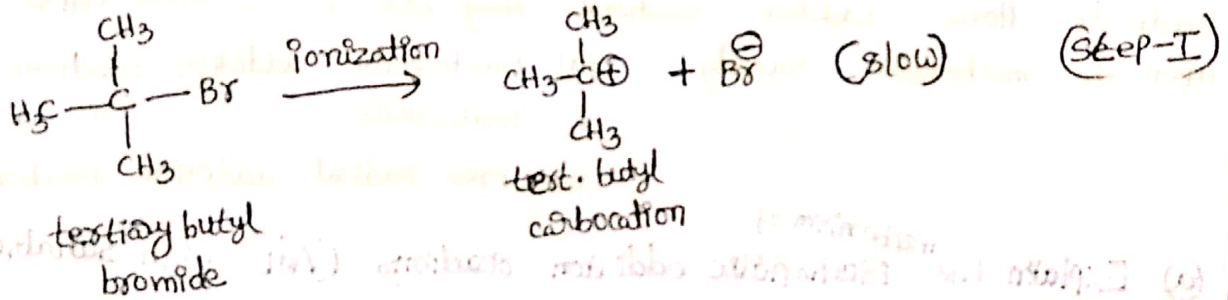
**(i) $E_2$ mechanism:** Let us consider the elimination reaction of a primary alkyl halide, say ethyl bromide by a strong base sodium ethoxide.

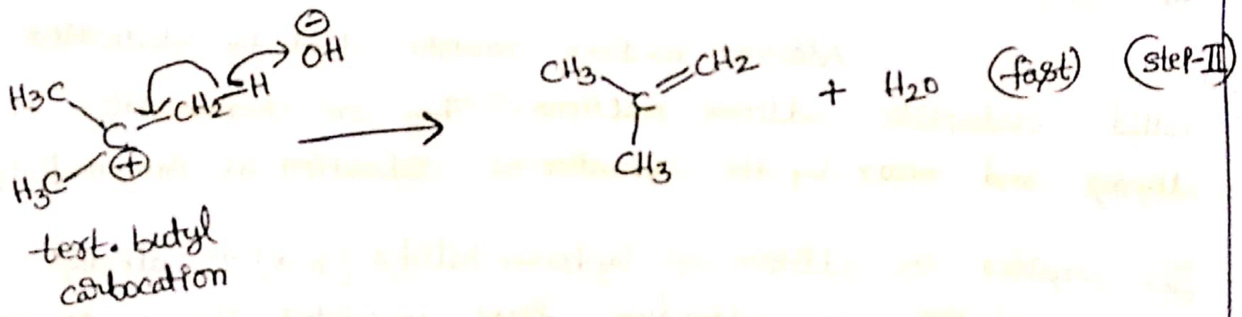
$$\underset{\text{(substrate)}}{CH_3-CH_2-Br} + \underset{\text{(base)}}{C_2H_5ONa} \rightarrow \underset{\text{Product}}{CH_2=CH_2} + C_2H_5OH + Br^{\ominus}$$

The rate of an elimination reactions depend upon the concentration of the substrate and the base, the reaction is said to be of second order and is represented as $E_2$ (bimolecular elimination). The common example of $E_2$ elimination reaction is the dehydrohalogenation of primary halides to form alkenes. Here the abstraction of the proton (by alkali) from the β- carbon atom and the expulsion of the halide ion from the α- carbon occurs simultaneously.



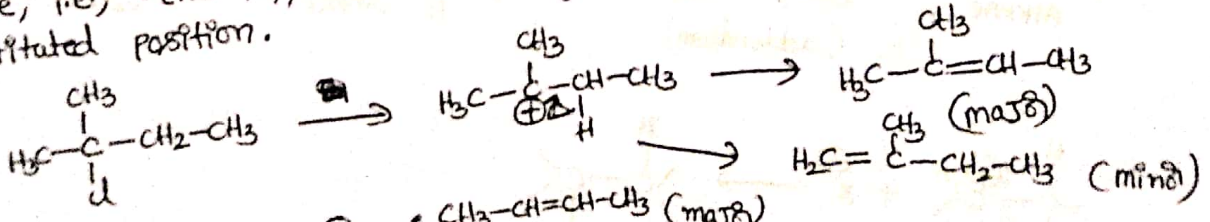
**(ii) E₁ mechanism :** The rate of an elimination reaction depends only on the concentration of the substrate, the reaction is said to be of first order and designated as $E_1$ (unimolecular elimination). $E_1$ reactions are also two step processes. The common example of $E_1$ reaction is dehydrohalogenation of t-alkyl halides. In the first step, under the influence of solvation, the nucleophile goes away along with the bonding electrons to form a carbocation. This is the rate determining step and slow. Subsequently, the carbocation loses a proton to solvent (or) some other proton acceptor.

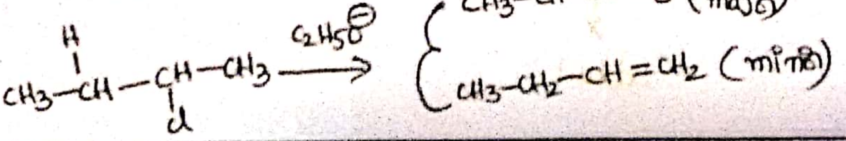




*** orientation :** The elimination reactions of unsymmetrical substrates usually yield a mixture of all posible products.

(i) Saytzeff rule: It states that substrates capable of forming double bond in either side of the chain prefer to yield most substituted alkene, i.e, the loss of the β-hydrogen occurs preferably from the substituted position.

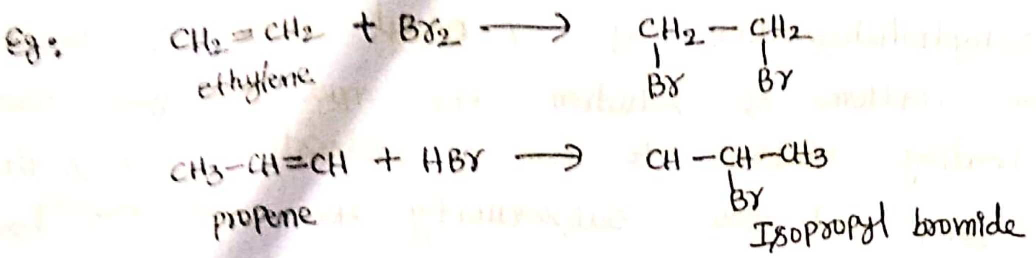




**Q) 5. What are addition reactions? Explain the addition reactions with examples and mechanisms.**

Reactions in which atoms (or) groups of atoms are added to a molecule are known as addition reactions. Addition reaction occurs in compounds containing double (or) triple bonds.

Eg:



$CH_2=CH_2 + Br_2 \longrightarrow CH_2(Br)-CH_2(Br)$

ethylene

$CH_3-CH=CH + HBr \longrightarrow CH-CH(Br)-CH_3$

propene — Isopropyl bromide

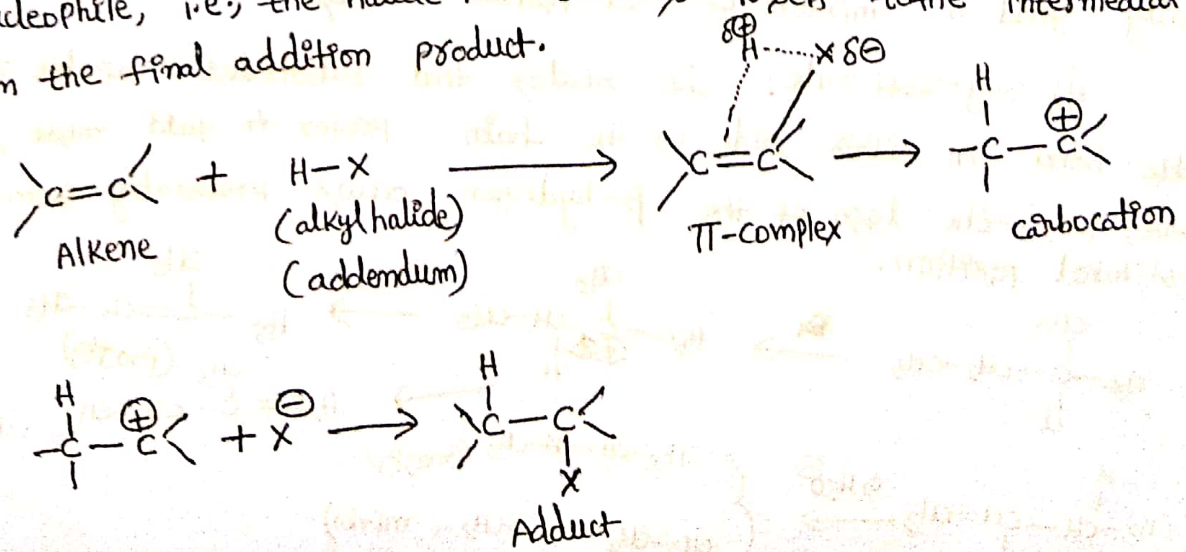
Addition reactions may be initiated by electrophiles, nucleophiles (or) free radicals. Hence addition reactions may also be of three types depending upon the mechanism, namely

(a) Electrophilic addition reactions (AdE)
(b) Nucleophilic " " " (AdN)
(c) Free radical addition reactions.

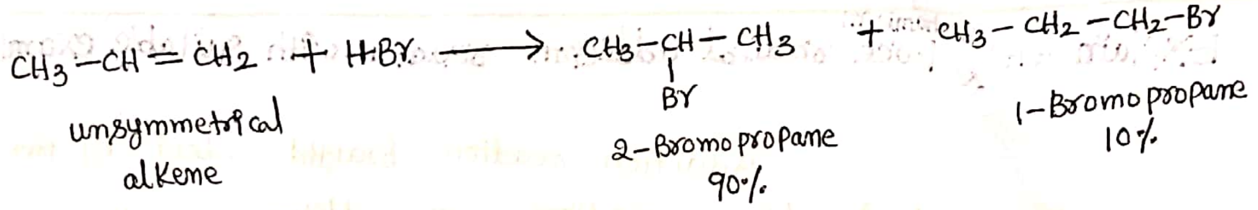
**Q) Explain the mechanism of Electrophilic addition reactions (AdE) with suitable example:**

Addition reactions brought about by electrophiles are called electrophilic addition reactions. They are characteristics of alkenes, alkynes and occur by the formation of carbocation as intermediates.

Eg:- consider the addition of hydrogen halides (H–X) to alkenes: In this addition reaction, the addendum first associates itself to electron-rich π-center to form a π-complex. The π-complex subsequently gets transferred into the intermediate carbocation. In the next step, the nucleophile, i.e., the halide ion attaches itself to the intermediate to form the final addition product.

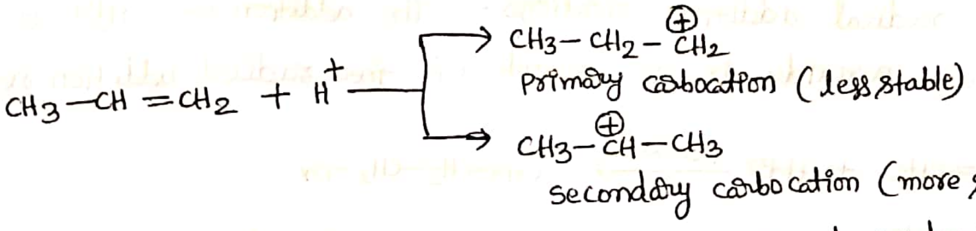


Electrophilic addition to asymmetrical alkenes takes place in accordance to the "Markownikoff's" rule. According to this rule, during addition across unsymmetrical double bond, the negative part of the attacking reagent attaches it self to the carbon atom carrying lesser number of hydrogen atoms, while positive part goes to the carbon atom with more number of hydrogen atoms.



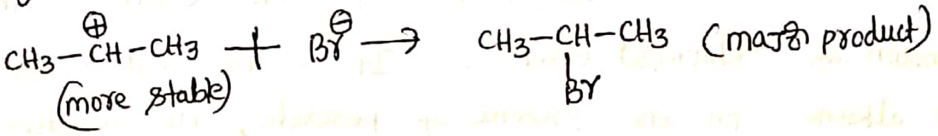
$$CH_3-CH=CH_2 + HBr \longrightarrow \underset{\text{2-Bromopropane 90\%}}{CH_3-\underset{Br}{CH}-CH_3} + \underset{\text{1-Bromopropane 10\%}}{CH_3-CH_2-CH_2-Br}$$

unsymmetrical alkene



$$CH_3-CH=CH_2 + H^+ \longrightarrow \begin{cases} CH_3-CH_2-\overset{\oplus}{C}H_2 & \text{primary carbocation (less stable)} \\ CH_3-\overset{\oplus}{C}H-CH_3 & \text{secondary carbocation (more stable)} \end{cases}$$

As the $2^\circ$ carbocation is more stable, it is formed predominantly and the latter adds the negative ion to form the major product.

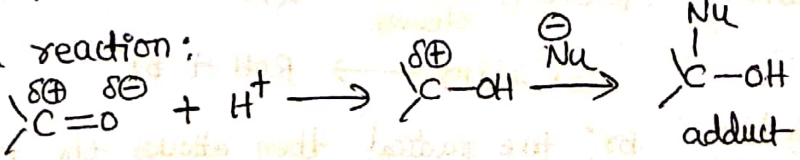


$$\underset{\text{(more stable)}}{CH_3-\overset{\oplus}{C}H-CH_3} + Br^\ominus \rightarrow CH_3-\underset{Br}{CH}-CH_3 \text{ (major product)}$$

**(b) Explain the Mechanism of Nucleophilic addition reactions with suitable example:**

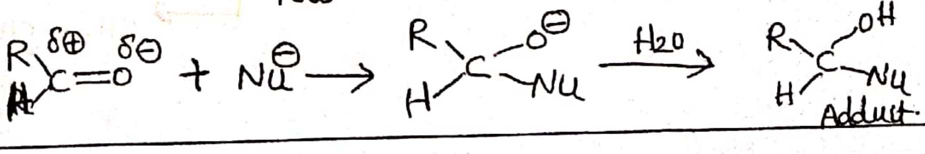
Addition reactions which are brought about by nucleophiles are called nucleophilic addition reactions. common examples of compounds undergoing nucleophilic addition reactions are aldehydes, Ketones etc. In aldehydes and Ketones, the π electrons are pulled towards oxygen (as it is more electronegative than carbon) making the carbonyl carbon electron-deficient and the carbonyl oxygen electron-rich. The reaction can be catalysed by an acid (or) by a base.

acid-catalysed reaction:

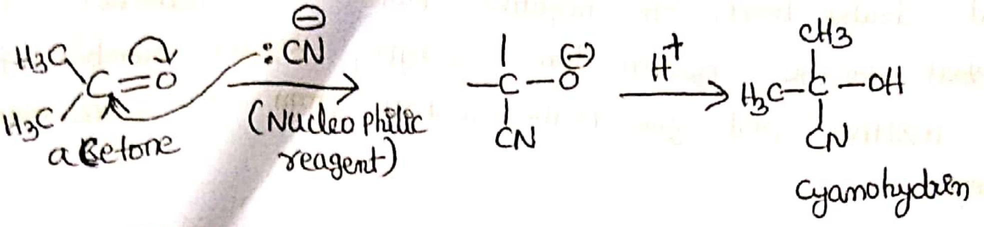


Base-catalysed reaction:

$$Nu-H + OH^\ominus \longrightarrow Nu^\ominus + H_2O$$



Eg:- Mechanism can be explained by considering the addition of HCN to a Ketone to form cyanohydrin.



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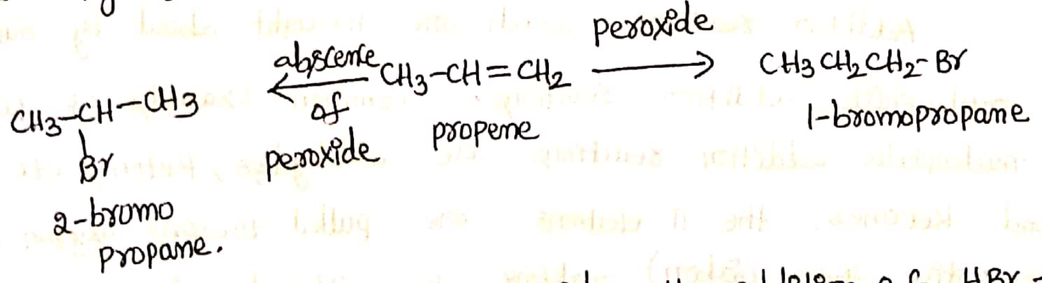
(C) Explain the Mechanism Free radical addition reaction with suitable example:

Addition reaction brought about by free radicals are called free radical addition reactions. The addition of HBr to alkene in the presence of peroxide is an example of free radical addition reaction.

$$CH_3-CH=CH_2 + H-Br \xrightarrow{peroxide} CH_3-CH_2-CH_2-Br$$

The free radical addition of HBr to an unsymmetrical alkene in the presence of peroxide occurs contrary to the Markownikoff's rule and is known as the Anti-Markownikoff's addition (or) peroxide effect. This phenomenon is also known as "Kharasch effect". It states that in case of addition of HBr to alkene in the presence of peroxide, the negative part of the attacking reagent (Br) will be attack the carbon atom carrying larger number of hydrogen atoms.

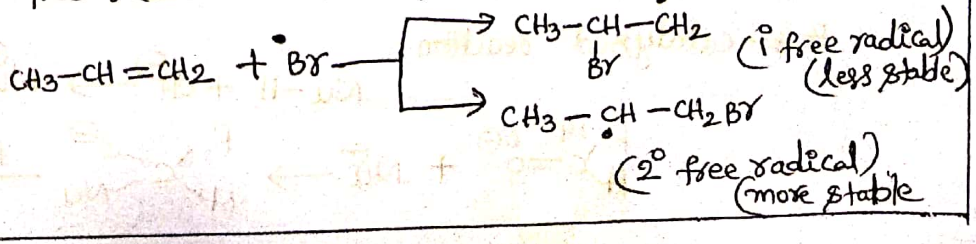


Mechanism: In the presence of peroxide, the addition of HBr to olefins takes place by free radical mechanism.

(i) Initiation : $R-O-O-R \xrightarrow[cleavage]{homolytic} 2RO^\bullet$ (R is generally $C_6H_5CO$)

$$RO^\bullet + HBr \longrightarrow ROH + Br^\bullet$$

(ii) propagation : $Br^\bullet$ free radical then attacks the propene to form 1° and 2° free radicals.



Since 2° free radical is more stable than 1° free radical, hence the final product is obtained from the secondary free radical.

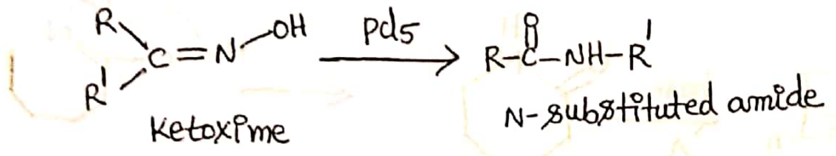
$$CH_3-\dot{C}H-CH_2Br + HBr \longrightarrow CH_3-CH_2-CH_2Br + \dot{Br}$$

(iii) Termination:

$$\dot{Br} + \dot{Br} \longrightarrow Br_2$$

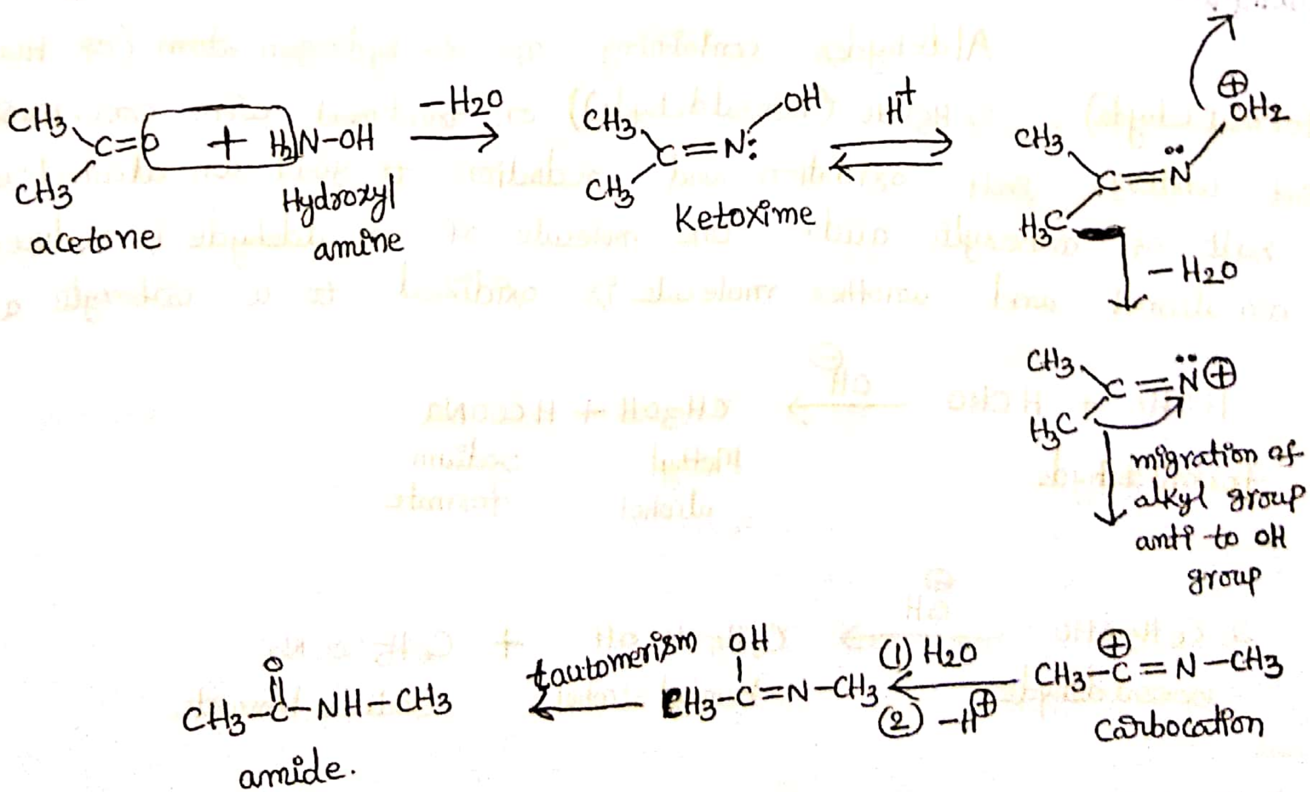
## Q. 6. Explain the mechanism of Beckmann rearrangement suitable example.

It is the conversion of Ketoximes (aliphatic, aromatic, diaryl, alicyclic, heterocyclic) to amides (or) N-substituted amides by intermolecular rearrangement with Lewis acids like $H_2SO_4$, $PCl_5$, $P_2O_5$, $SOCl_2$ etc.



Mechanism: (i) conversion of –OH group to a better leaving group.

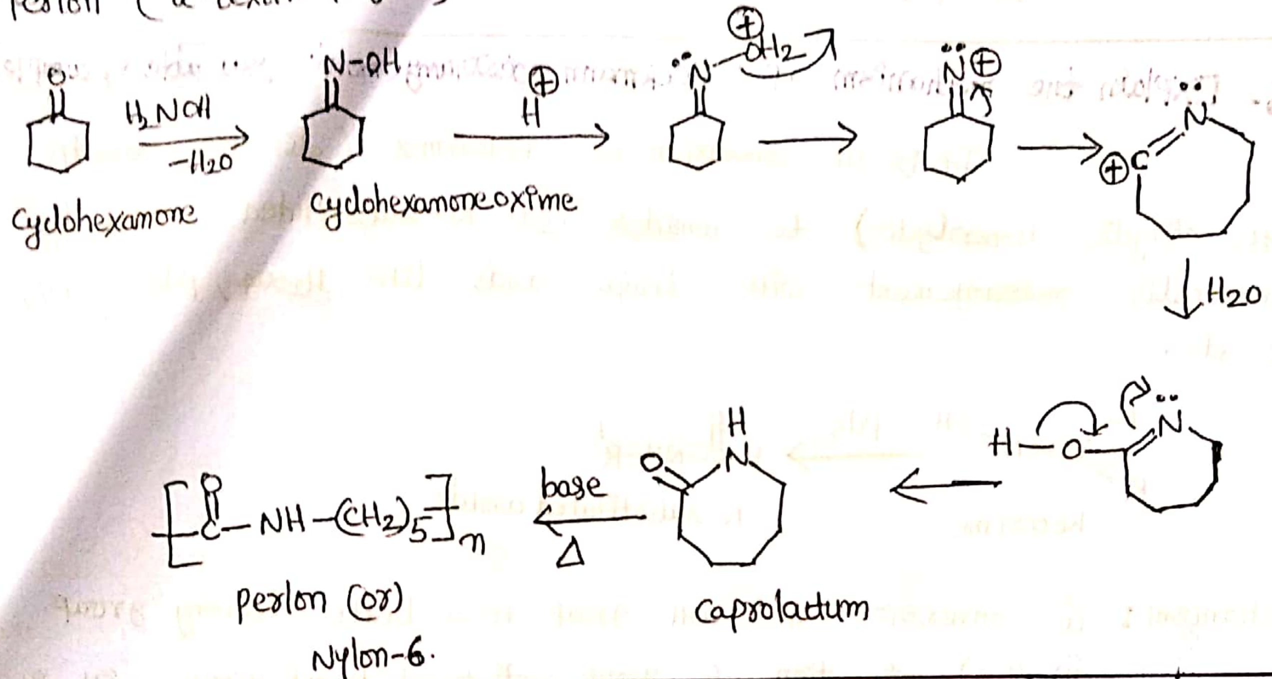
(ii) (1,2)- migration of group anti to hydroxyl group with its bonding electron pair from carbon to nitrogen.



The rearrangement is highly stereospecific in which the group anti to OH group.

**Q) 7. Write the synthesis of Nylon-6 apply beckmann rearrangement.**

The reaction is utilized for ring expansion. An important example is the conversion of cyclohexanone oxime into Caprolactum, which has considerable synthetic importance in manufacture of perlon (a textile polymer).



**Q) 8. Explain the mechanism of Cannizaros reaction with suitable example.**

Aldehydes containing no α- hydrogen atom (eg HCHO, (formaldehyde), $C_6H_5CHO$ (benzaldehyde)) on treatment with conc. NaOH/KOH undergo self oxidation and reduction to yield an alcohol and a salt of carboxylic acid. one molecule of an aldehyde is reduced to an alcohol and another molecule is oxidized to a carboxylic acid.

$$HCHO + HCHO \xrightarrow{OH^{\ominus}} CH_3OH + HCOONa$$

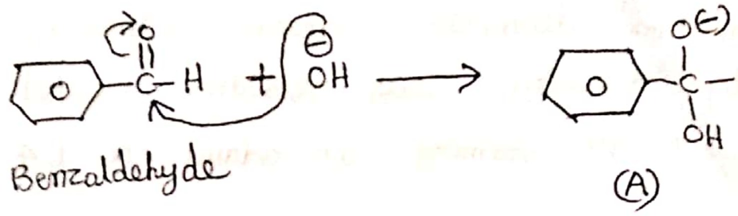
formaldehyde — Methyl alcohol — Sodium formate

$$2\,C_6H_5CHO \xrightarrow{\overset{\ominus}{O}H} C_6H_5CH_2OH + C_6H_5COONa$$

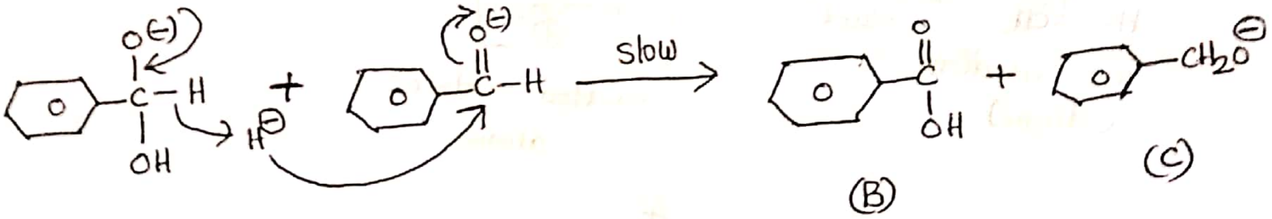
Benzaldehyde — benzyl alcohol — sodium benzoate

Mechanism: Following three steps are involved:

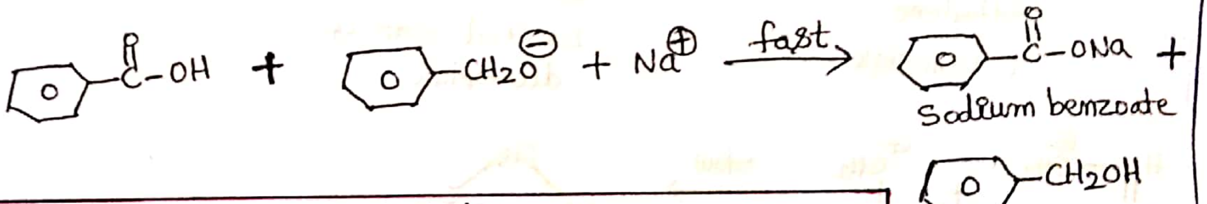
Step-I : Attack of $\overset{\ominus}{OH}$ ions (of NaOH/KOH) on the carbonyl carbon atom



Step-III : Transfer of hydride ion ($\overset{\ominus}{H}$) to another molecule of aldehyde.

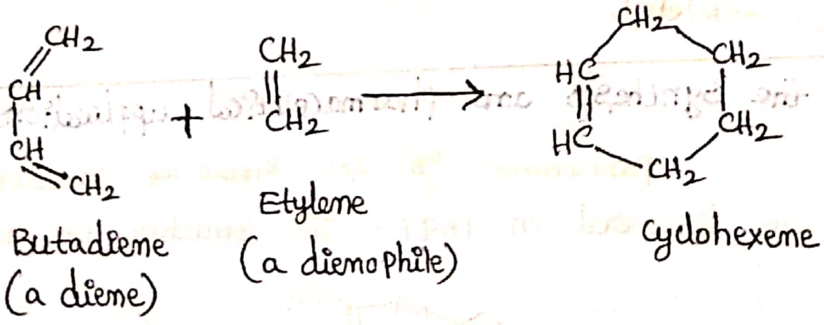


Step-III : Acid-base reaction between (B) and (C)



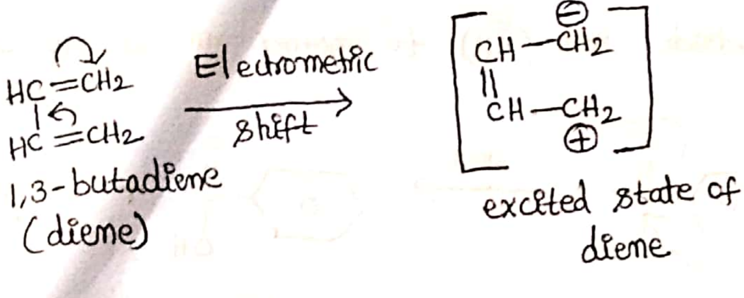
Q 9. Explain the Diel's-Alder reaction mechanism with suitable example.

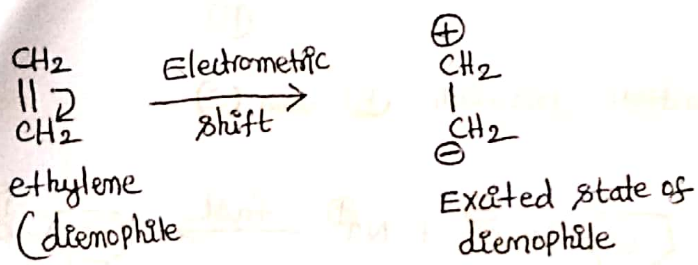
Diels-alder reaction consists in addition of a conjugated diene to an unsaturated molecule called a dienophile, resulting in the formation of a six membered ring. The example is the reaction between butadiene and ethylene.

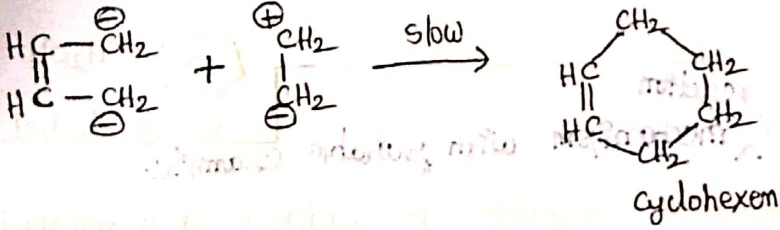


Diels alder reaction belongs to speial class of reactions called pericyclic reactions, which are characterised by the making and breaking of two (or) more bonds in a single concerted step through cyclic transition states. These reactions are known as cycloaddition reactions. The above example involves addition between a 4π electron system (diene) and 2π electron system (dienophile), it is known as [4+2] cycloaddition.

Mechanism: Both diene and dienophile underogo electrometric shifts simultaneously, thereby producing their respective excited state. Then, these excited states condense forming an adduct in 1,4-positions of the diene.







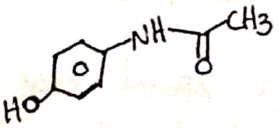
The rate of the above reaction is promoted by the presence of:

(i) Electron-donating group in the diene (like-$CH_3$ group).

(ii) Electron-withdrawing groups on the dienophile (or) the alkene (like $-CHO$, $-COOR$, $-NO_2$, $-CN$) etc).

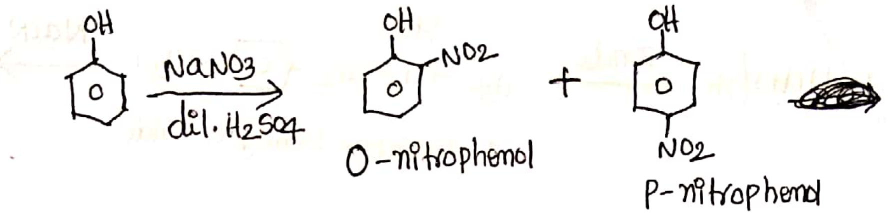
**(Q). 10. Write the synthesis and pharmaceutical applications of paracetamol.**

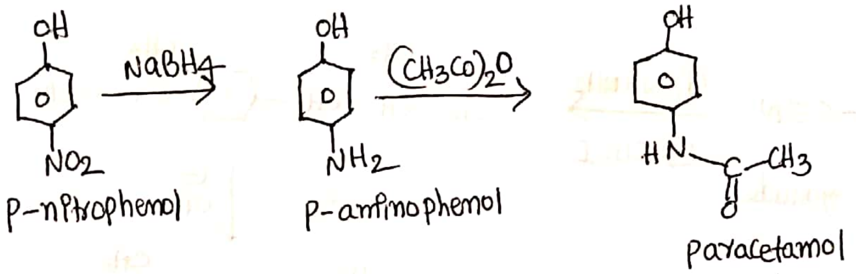
Paracetamol is also known as "acetaminophen" is a medicine and was discovered in 1877. The structure of paracetamol is given below.



It is prepared by the nitration of phenol with sodium nitrite, which gives two isomers of ortho nitro phenol and para nitrophenol. The ortho isomer is removed by steam distillation and the para isomer is reduced to amine inthe presence of sodium borohydride ($NaBH_4$) to give p-aminophenol.

Finally the amine is acetylated with acetic anhydride to produce acetaminophen widely known as paracetamol.





Applications: (i) paracetamol is used for reducing fever in people of all ages under the trade names Tylenol, paradol etc.

(ii) paracetamol is used for the relief of mild to moderate pain. (iii) It has analgesic properties. paracetamol can relieve arthrites i.e., pain of the hip, hand (or) knee.

(iv) paracetamol is recommended with caffeine as one of the several first line therapies for treatment of tension of migrane headache. (v) paracetamol is used for controlling dental pain arising due to dental procedures.

(vi) Although it causes lesser gastrointestinal side effects as compared to aspirin, but overdose of paracetamol causes damage to lever.

## (Q)-11. Write the synthesis and pharmaceutical applications of Ibuprofen.

Ibuprofen, 2-(4-isobutyl phenol) propionic acid, can be synthesized by various method. To the synthesize of ibuprofen consists of the chloromethylation of iso-butyl benzene, giving 4-iso-butyl benzylchloride. This product is reacted with sodium cyanide (NaCN), making 4-iso-butyl benzyl cyanide, which is alkylated in the presence of sodium amide by methyl iodide into 2-(4-isobutyl benzyl) propionitrile.

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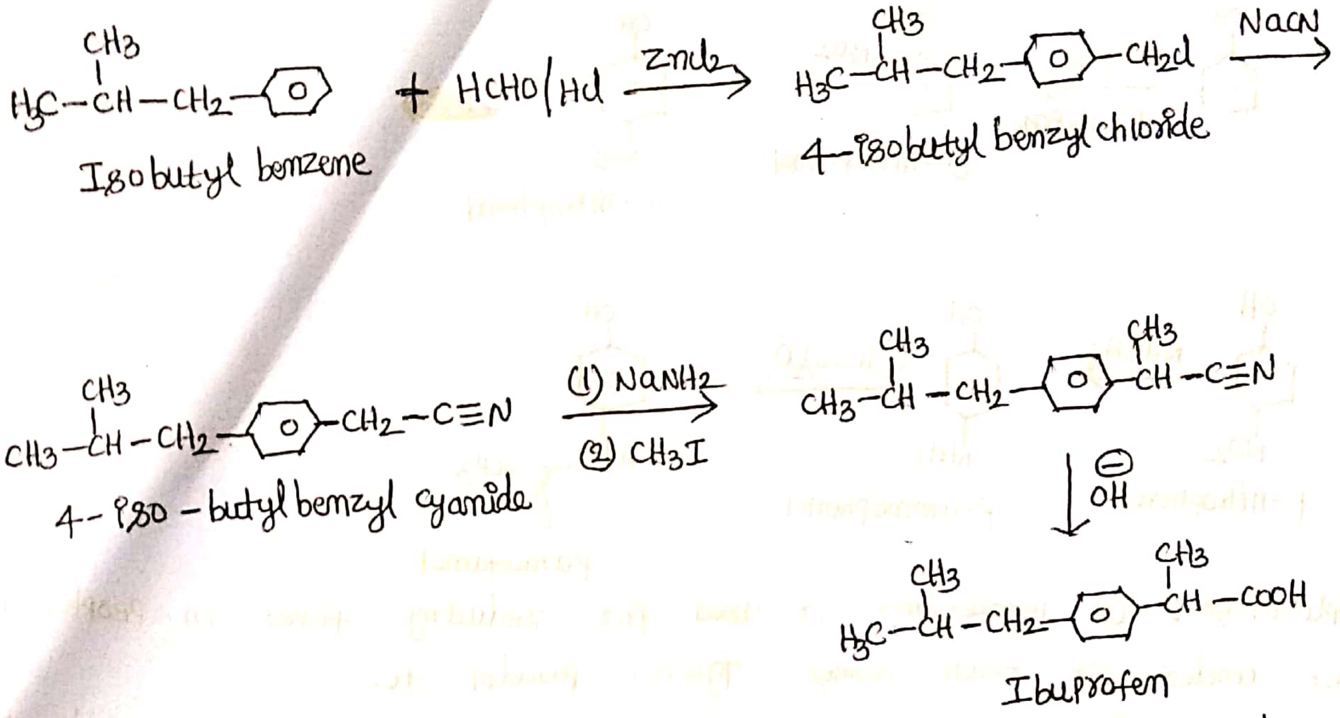
Hydrolysis of the resulting product in the presence of a base produces ibuprofen.



**Applications :** (i) Ibuprofen exhibits analgesic, fever reducing and antiinfammatory action. (ii) It is used in treating rheumatoid arthritis, in various forms of articular and non aticular diseases (iii) It is used for pain relieving from inflammatory peripheral nerve system (iv) It is used for head aches and toothaches.

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# NMR Spectroscopy

Concepts and theory :

"Nuclear magnetic resonance spectroscopy (NMR) is an absorption spectroscopy in which certain magnetic nuclei under the influence of a static external magnetic field are subjected to a second oscillating electromagnetic field in the form of radiofrequency radiation which induces the nucleus to resonate."

NMR spectroscopy is the study of NMR phenomenon to examine the physical and chemical properties of a molecule.

Many atomic nuclei have mechanical spin and angular momentum which is described in terms of "nuclear spin quantum nuber "I". It has values of 0, ½, 1, 3/2 and so on (I=0 denotes no spin). For the nuclei to be magnetic, they should have either odd number of protons (or) odd number of neutrons (or) both. only the nuclei that have spin quantum number greater than zero can exhibit phenomenon (Eg: $^{1}H$, $^{11}B$, $^{13}C$, $^{14}N$, $^{15}N$, $^{17}O$, $^{19}F$, $^{31}P$, etc).

The spin quantum number I determines the number of quantum mechanical states an isolated nucleus may assume in external uniform magnetic field, in accordance with the formula $(2I+1)$. Hence the nucleus of $^{1}H$ has the spin quantum number $I = 1/2$ and has allowed spin states $(2 \times \frac{1}{2} + 1 = 2)$ for its nucleus which are $-1/2$ and $+1/2$. In the absence of applied magnetic field, the energy of all the spin states of a nucleus are equivalent (degenerate).

| Element | $^{1}_{1}H$ | $^{2}_{1}H$ | $^{12}_{6}C$ | $^{13}_{6}C$ | $^{14}_{7}N$ | $^{16}_{8}O$ | $^{19}_{9}F$ |
|---|---|---|---|---|---|---|---|
| Nuclear spin quantum number (I) | ½ | 1 | 0 | ½ | 1 | 0 | ½ |
| Number of spin states | 2 | 3 | 0 | 2 | 3 | 0 | 2 |

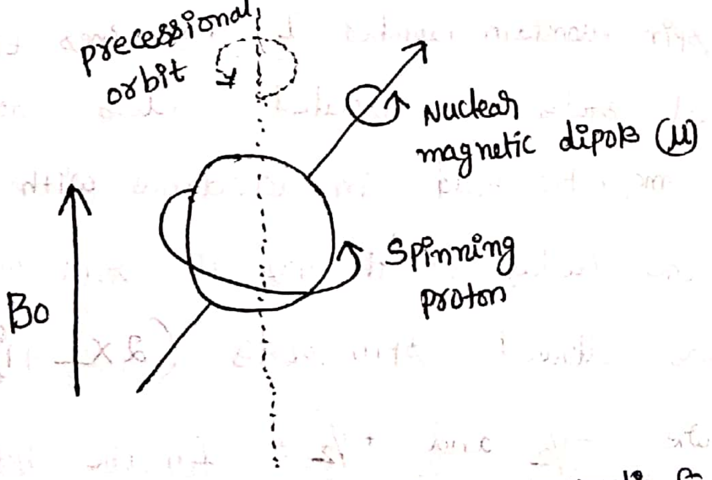
[redacted]

[redacted]

Because of the spin and charge, a nucleus can behave like a magnet. NMR spectroscopy involves application of magnetic field to nuclei and then measuring the amount of energy necessary to put various nuclei of the sample into resonance. Nuclei in different environments (shielded and unshielded) require different amount of energy to bring into resonance. An NMR spectrum provides a signal (or) peak representing the energy necessary to bring each nucleus into resonance.

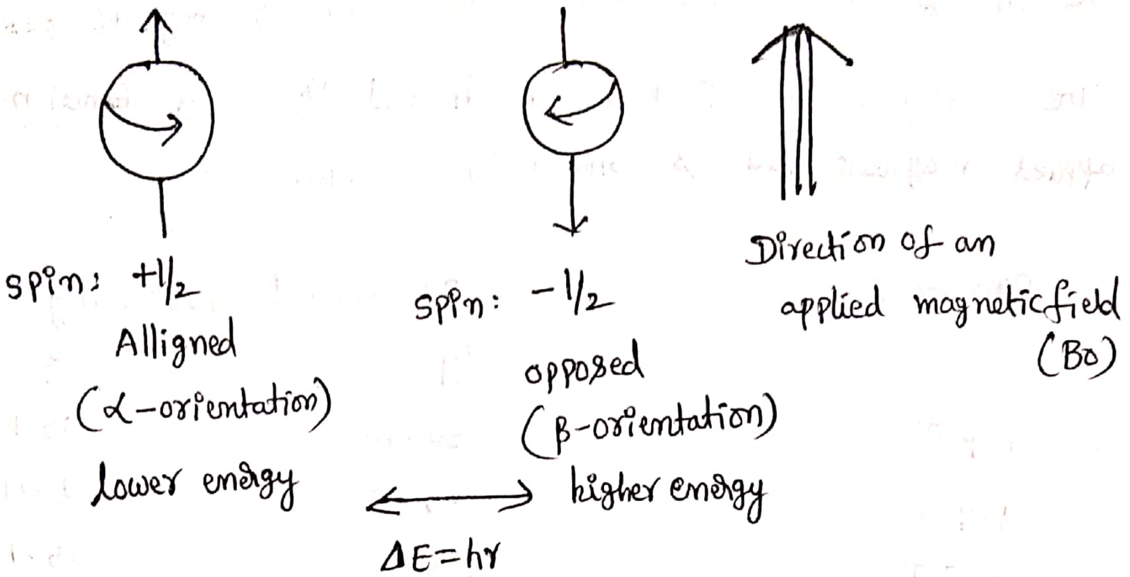
## Phenomenon of Nuclear Magnetic Resonance:

The magnetic nuclei ($^1H$, $^{13}C$ etc. under the influence of external magnetic field behave as a spinning bar magnet as they possess both electric charge and mechanical spin.



Spinning proton in a magnetic field Bo

The proton like a magnet tends to align itself with the external magnet (parallel) with the magnetic field, called α- orientation (low energy state) or opposed (anti-parallel) to the field, called β-orientation (higher energy state). In these α and β- states, the proton also spins around the axis of an applied magnetic field. This is called precessional motion.



precessional frequency: A transition from the lower energy state to the higher energy state can be brought about by applying radiation of exactly the required frequency (in the radiofrequency region) for a given stationary magnetic field of strength Bo. The fundamental NMR equation correlates to a particular value of the applied radiofrequency known as Lamor frequency ν, which is is directly proportional to the magnetic field strength. Thus

$$\nu \propto B_o$$

$$\nu = \left(\frac{\gamma}{2\pi}\right) B_o$$

Since $\Delta E = h\nu$

$$\Delta E = \left(\frac{h\gamma}{2\pi}\right) B_o \Rightarrow$$

$$\Delta E \propto B_o \quad (\because h, \gamma \text{ and } \pi \text{ are constants})$$

Here h is plank's constant

γ is gyromagnetic ratio and

Bo is the strength of the magnetic field.

The radio frequency ν is typically in the order of megahertz (MHz). A frequency of 300 MHz is needed at a magnetic field strength Bo of 7.05 T (tesla) for a proton. If an external field of strength

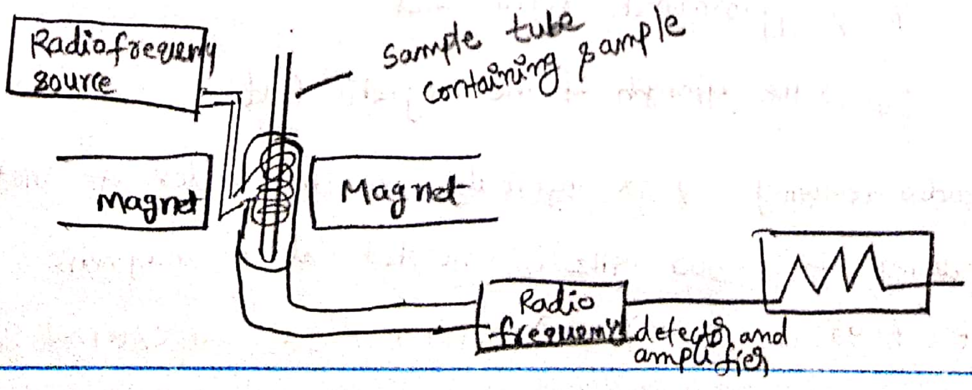
1.4 T will precess 60 MHz. At this ratio, the system is said to be in resonance, hence the name "nuclear magnetic resonance".

The frequencies of protons in $^1H$ and $^{13}C$ as a function of field of applied magnetic field is shown in Table.

| Bo (Tesla) | Precessional frequency (MHz) | |
|---|---|---|
| | $^1H$ | $^{13}C$ |
| 1.4 T | 60 MHz | 15.1 MHz |
| 1.9 T | 80 | 20.1 |
| 2.3 T | 100 | 25.1 |
| 4.7 T | 200 | 50.3 |
| 7.1 T | 300 | 75.5 |
| 11.7 T | 500 | 125.7 |
| 14.1 | 600 | 151 |

## Instrumentation of NMR Spectroscopy:

The early NMR instruments for proton magnetic resonance were built using permanent magnets (or) electromagnets, generally with field strengths of 1.4, 1.87, 2.20 (or) 2.35 tesla and corresponding frequencies of 60, 80, 90 (or) 100 MHz, respectively. The basic components, a detection system to measure the energy being absorbed by the nuclei from the radiofrequency beam and a display monitor. This is shematically represented as



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The sample under investigation is dissolved in deuterated solvent and the solution taken in a glass tube is placed in the probe with a spinner that spins the tube so that the non-homogenous components of the magnetic fields are averaged out. The transmitter and receiver coils also form part of the probe. The computer interface acquires the data and further processes to deliver the NMR spectrum, which appears as a series of peaks (corresponding to protons in different chemical environment) whose area are proportional to the number of protons they represent. The NMR spectrum obtained is useful for identification of compounds as well as quantitative analysis and purity of the sample.

**Q) CHEMICAL SHIFT :** The number of signals in an NMR spectrum tells the number of the sets of equivalent protons in a molecule. The position of the signals in the spectrum help us to know the nature of protons. Viz: aromatic, aliphatic, acetylinic, vinylic etc. Each of these type of protons will have different electronic environments and thus, they absorb at applied field strengths.

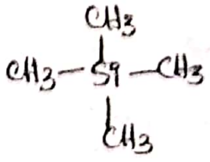
If the resonance frequency of all protons in a molecule were the same, then NMR spectrum would show only one peak for the compound. The field strength experienced by the protons in the sample is not same as the strength of the applied field. * A magnetic field induces electron circulations in the charge cloud in a plane perpendicular to the applied field, and in such a direction ~~so~~ as to produce a field opposing the applied field. The field felt by the proton, is dismissed and the proton is said to be "shielded".

"The induced field reinforces reinforces the applied field, the proton feels a higher field strength and thus, such a proton is said to be "deshielded".

"shielding shifts" the absorption upfield and "deshielding shifts" the absorption down field. [redacted]

Applied field.

"Such shifts in the positions of NMR absorptions which arise due to the shielding (or) deshielding of protons by the electrons are called "chemical shifts" (δ) for measuring chemical shifts of various protons in a molecule, the signal for tetramethyl silane (TMS) is taken as a reference, due to



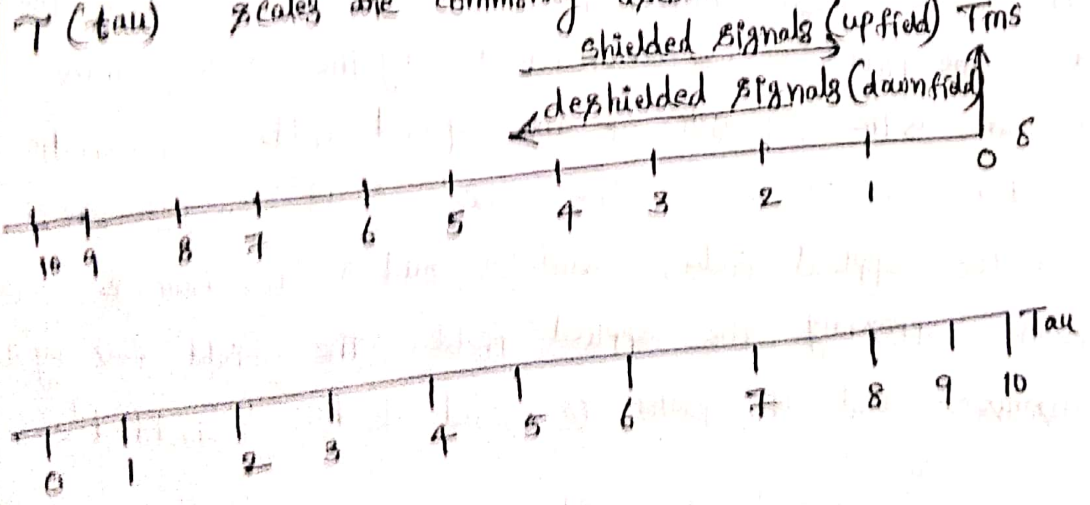
$(CH_3)_4Si$

TMS

(i) the low electronegativity of silicon.

(ii) the shielding of equivalent protons in TMS is greater than most of the organic compounds.

Protons with the same chemical shift are called equivalent protons. Non-equivalent protons are have different chemical shifts. δ (delta) or τ (tau) scales are commonly used.



The values of δ for a substance with respect to TMS can be obtained by measuring $\nu_s - \nu_{TMS}$

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where $\nu_S$ = Resonance frequency of the sample

$\nu_{TMS}$ = " " " TMS

$$\delta = \frac{\nu_{sample} - \nu_{reference}}{\text{operating frequency in megacycles}}$$

$$= \frac{\Delta\nu}{\text{operating frequency in megacycles}}$$

where $\Delta\nu$ = is the frequency shift.

The value of $\delta$ is expressed in parts per million (ppm). Most chemical shifts have $\delta$ values between 0 and 10. In the $\tau$ scale, signal for the standard reference, TMS is taken as 10 ppm.

$$\tau \text{ (tau)} = 10 - \delta$$

NMR signal is usually plotted with magnetic field strength increasing to the right. Thus the signal for TMS (highly shielded) appears at the extreme right of spectrum with $\delta = 0$ ppm. Greater the deshielding of protons, larger will be the value of $\delta$. The values of chemical shifts for protons in different environments are:

| Types of protons | Chemical shifts in ppm<br>$\delta$ |
|---|---|
| ① $R-CH_2$ | 0.9 |
|  | 2-3.5 |
| ② $C\equiv C-H$ | 6-9.0 |
| ③ $Ar-H$ | 0.23 |
| ④ $CH_4$ | 2.16 |
| ⑤ $CH_3-I$ | 2.68 |
| ⑥ $CH_3-Br$ | 3.25 |
| ⑦ $CH_3-Cl$ | 4.26 |
| ⑧ $CH_3-F$ |  |

## (a) Spin- Spin splitting ( Spin-spin coupling) :

"The splitting of signal lines in the spectrum into two (or) more components is called spin-spin splitting".

Consider a molecule of $\overset{a}{CH_3}-\overset{b}{CH_2}-Br$ (ethyl bromide). This molecule has two kinds of protons in it and thus, two signals are excepted in its own NMR spectrum. For "a" kind of protons ($CH_3$), a tripple i.e: a group of three peaks is observed and a quartet is noticed for "b" kind of protons ($CH_2$).

The spin of two protons ($-CH_2-$) can couple with the adjacent methyl group ($-CH_3-$) in three different ways relative to the external field. The three different ways of allignment are:

i) ↑↑ (~~Reinforcing~~)

ii) ↓↑ ↑↓ (~~No effect~~

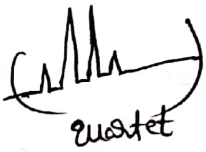
iii) ↓↓

↑ External field

Thus, a triplet of Peaks results with the intensity ratio of 1:2:1 which corresponds to the distribution ratio of allignment.

Similarly, the spin of three protons ($-CH_3-$) can couple with the adjacent methylene group ($-CH_2-$) in four different ways

Thus, quartet of Peaks results with an intensity ratio of 1:3:3:1.



i) ↑↑↑ 1

ii) ↑↑↓ ↑↓↑ ↓↑↑ 3

iii) ↓↓↑ ↓↑↓ ↑↓↓ 3

iv) ↓↓↓ 1

* The multiplicity of the signal for any group of equivalent protons is clearly related to the number of protons of the adjacent atoms. As a simple rule the multiplicity of a given group is (n+1), where

n is the number of protons of the adjacent atoms. Accordingly, n-propyl iodide ($CH_3-CH_2-CH_2-I$) has three different types of protons. The NMR spectrum of 3H (triplet) (1:2:1), 2H (sextet) (1:5:10:10:5:1) and 2H (triplet) (1:2:1).

The peak intensities of the various multiplets can be described as under:

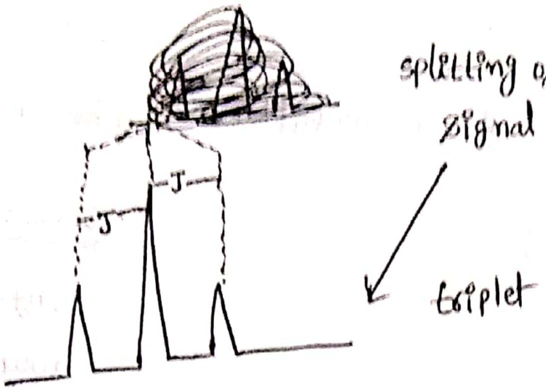
| Peak area ratio | Signal |
|---|---|
| 1 | Singlet |
| 1:1 | doublet |
| 1:2:1 | Triplet |
| 1:3:3:1 | quatet |
| 1:4:6:4:1 | quintet |
| 1:5:10:10:5:1 | sextet. |

## (Q) COUPLING CONSTANT (J):

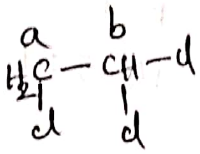
"The distance between the centres of the two adjacent peaks in a multiplet is usually constant and is called the coupling constant". The value of the coupling constant is independent of the external field. It is measured in Hertz (Hz) (or) in cps (cycles per second). It is denoted by the letter J. The spectrum of a particular compound at different radio-frequencies, the separation of signals due to different chemical shifts change but the separation of two adjacent peaks in a multiplet remains always constant. The value of "J" generally lies between 0 and 20 Hz.

Now let us consider a compound $>\overset{b}{CH}-\overset{a}{CH_2}-$. In this compound two signals are expected in the NMR spectrum.

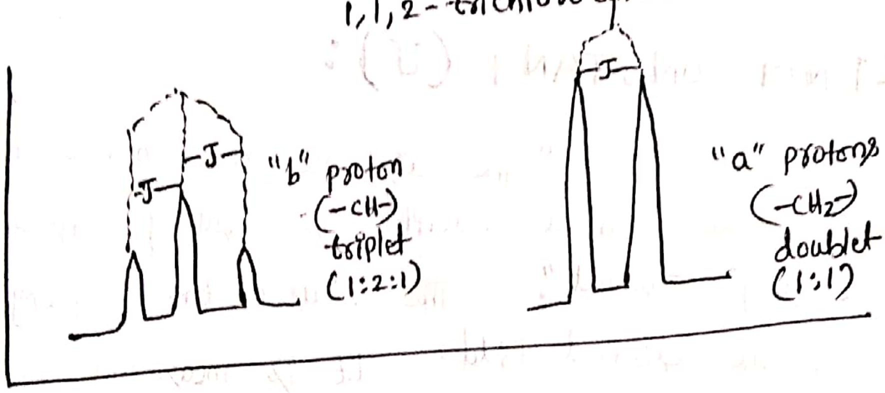
The influence of two equivalent protons "a" the signal for proton "b" will appear as a triplet. The distance between any two adjacent peaks in a multiplet will be exactly the same. The triplet formed due to spin-spin coupling is shown



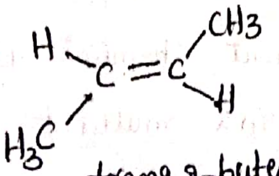
Similarly In the NMR spectrum of 1, 1, 2 trichloro ethane two multiples are observed.



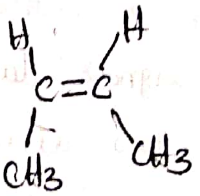
1,1,2-trichloro ethane



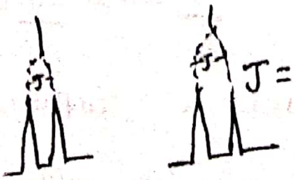
## Coupling constant in 2-butene:



trans 2-butene



J = cis = 6–10 Hz



J = trans 11–18 Hz

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# Module-V

## Fuels and Combustion

# Chapter 4: Fuels and Combustion

**Fuel:** "A fuel can be defines as a combustible substance containing carbon and releasing a large amount of heat, that can be used for domestic and industrial needs".

**"Combustion is the process of chemical reaction between fuel and oxygen. The combustion process is an** exothermic chemical reaction".

$$\text{Fuel} + O_2 \xrightarrow{high\ temp} \text{Combustion products} + \text{Heat}$$

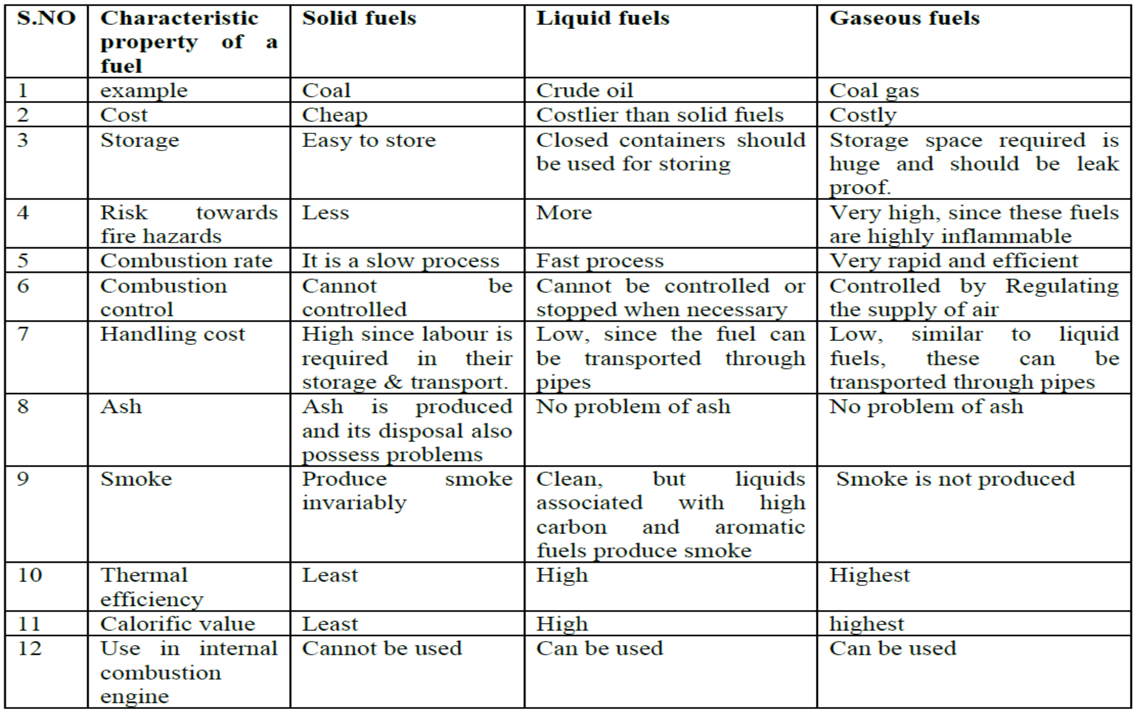
**As most of the fuels contain carbon or carbon and hydrogen, the combustion involves the oxidation of carbon to carbon dioxide and hydrogen to water. Sulphur, if present, is oxidised to sulphur dioxide while the mineral matter forms the ash.**

**Classification fuels**: Fuels can be classified into 2 types based on two factors

1. Their Occurrence
2. Physical state of aggregation.

1. Based on the occurrence, fuels can be further divided into 2 types (a) natural or primary fuels: Fuels which are found in nature are called natural (or) primary fuels. e.g.,wood, peat, coal, petroleum, natural gas etc.
(b) Artificial or secondary fuels: Fuels, which are prepared from the primary fuels. For example, charcoal, coke, kerosene, diesel, petrol, coal gas, oil gas, producer gas etc.

2. Based on the physical state of aggregation the fuels are divided in to solids, liquids and gases.



| S.NO | Characteristic property of a fuel | Solid fuels | Liquid fuels | Gaseous fuels |
|---|---|---|---|---|
| 1 | example | Coal | Crude oil | Coal gas |
| 2 | Cost | Cheap | Costlier than solid fuels | Costly |
| 3 | Storage | Easy to store | Closed containers should be used for storing | Storage space required is huge and should be leak proof. |
| 4 | Risk towards fire hazards | Less | More | Very high, since these fuels are highly inflammable |
| 5 | Combustion rate | It is a slow process | Fast process | Very rapid and efficient |
| 6 | Combustion control | Cannot be controlled | Cannot be controlled or stopped when necessary | Controlled by Regulating the supply of air |
| 7 | Handling cost | High since labour is required in their storage & transport. | Low, since the fuel can be transported through pipes | Low, similar to liquid fuels, these can be transported through pipes |
| 8 | Ash | Ash is produced and its disposal also possess problems | No problem of ash | No problem of ash |
| 9 | Smoke | Produce smoke invariably | Clean, but liquids associated with high carbon and aromatic fuels produce smoke | Smoke is not produced |
| 10 | Thermal efficiency | Least | High | Highest |
| 11 | Calorific value | Least | High | highest |
| 12 | Use in internal combustion engine | Cannot be used | Can be used | Can be used |

## Characteristics of a Good/ideal fuel:

While selecting an ideal fuel for domestic or industrial purpose we should keep in mind that the fuel selected must possess the following characteristic properties.

1. It should possess high calorific value. (Liberation of large amount of heat per unit mass/volume of the fuel)
2. It should have proper ignition temperature. The ignition temperature of the fuel should neither be too low nor too high.

3. It should not produce poisonous products during combustion. In other words, it should not cause pollution o combustion.
4. It should have moderate rate of combustion.
5. Combustion should be easily controllable i.e., combustion of fuel should be easy to start or stop as and when required.
6. It should not leave behind much ash on combustion.
7. It should be easily available in plenty.
8. It should have low moisture content.
9. It should be cheap.
10. It should be easy to handle and transport.

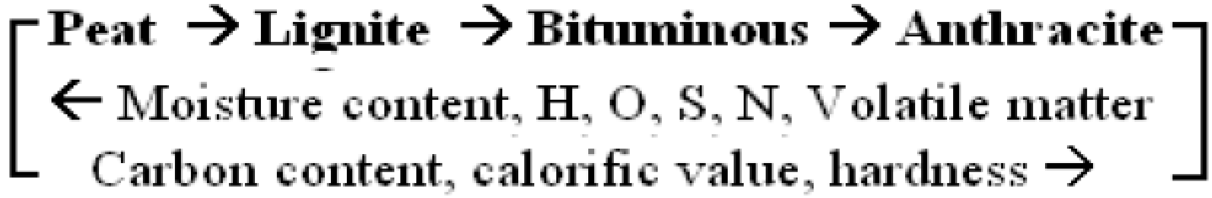
**Solid fuels:** The main solid fuel is wood. Wood contains higher percentage of carbon in the form of cellulose, lignocellulose. The process of conversion of wood into coal is called as **coalification**. The calorific value of wood is 4000-4500 Kcal/kg and thus is used as a domestic fuel. Wood can be converted into charcoal by a process is called **carbonization** (destructive distillation of wood). Charcoal is used as absorbent of gases and for decolourisation of sugars.

**Coal** is highly carbonaceous matter and is regarded as a fossil fuel produced from large accumulations of vegetable debris and alternation of vegetable matter like plants etc. under certain favourable conditions by the action of heat and pressure over a millions of years. Coal is mainly composed of carbon, oxygen, hydrogen and nitrogen.
Its formation can be explained by the following theories.

i) In-situ theory: this theory states that the coal formation took place at the same area where vegetation grew and accumulated originally. The great purity of coal appear more reasonable on the basis of this theory.

ii) Drift theory: according to this theory, trees when uprooted due climating conditions, in the deeper parts of the soil under transformation to coal due to high temperature, pressure absence of oxygen and presence of bacteria.

**Coal** has been classified in several ways. The most common method of classification is on the basis of rank. From the origin of coal it is clear the wood, after a long interval of time and under certain conditions was converted into coal. The successive stages in the transformation of vegetable matter into coal are wood, peat, lignite, bituminous coal and anthracite coal.
Coal is classified based on the carbon content. The following is sequence of conversion.



**Peat → Lignite → Bituminous → Anthracite**

← Moisture content, H, O, S, N, Volatile matter

Carbon content, calorific value, hardness →

**Peat**: peat is regarded as the first stage in the transformation of wood into coal. Brown, fibrous, jelly like mass. Un-economical fuel and contains 80-90% of $H_2O$. Composition C = 57%, H= 6%, O = 35%, ash 2.5 to 6%. Calorific value = 5400 kcal/kg.
**Lignite:** (Brown coal) soft, brown, coloured lowest rank coal moisture content is 20 to 60%. Composition: C = 60%, O = 20%, Calorific value = 6,500 to 7,100 k.cal/kg
**Bituminous coal:** Bituminous coal (common coal) Black to dark colored. This coal is largely used in industries for making metallurgical coke, coal gas and for domestic heating. It has laminated structure it is sub classified based on carbon content. Composition is % of C = 78 to 90%, VM = 20 to 45%, CV = 8000 to 8500 kcal/kg.
**Anthracite:** Highest rank of coal. These coals have very low volatile matter, ash & moisture. This coal is very hard, dense and lustrous in appearance. % of C = 98 % has lowest volatile matter hardest, dense, lustrous. CV = 8650 to 8700 k.cal/kg.

**Grading:** Coal is graded as caking coal and coking coal.
The coal which on heating becomes soft, plastic and fuse together are known as caking coal.
The coal which on heating gives porous, hard and strong residues are called coking coals.

## Analysis of coal

The composition of coal varies widely and hence it is necessary to analyse the coal samples so that types of coal can be selected for a particular industrial use. The following methods of analysis can be utilized for the selection of coal.
1. Proximate analysis: This analysis records moisture, volatile matter, ash and fixed carbon as percentages of the original weight of the coal sample. Proximate analysis is of significance in commercial classification and industrial utilization of coal.
2. Ultimate analysis: This consists of determination of C, H, S, N and O. The ultimate analysis is essential.

### Proximate Analysis of Coal

Proximate analysis is the study or analysis of coal sample in which

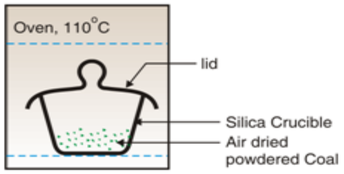
(i) moisture % (ii) volatile matter % (iii) ash % (iv) fixed carbon %, are found out.

**(i) Moisture %**

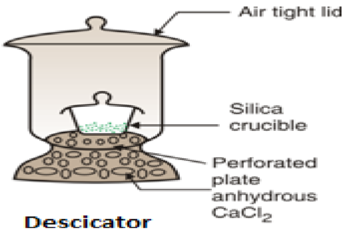
(a) Principle: All moisture in coal escapes on heating coal at 110°C for 1 hour.

(b) Method: A known weight of powdered and air dried coal sample is taken in a crucible and it is placed in an oven for 1 hour at 110°C. Then the coal is cooled in a desiccator and weighed out. If the initial weight of the coal is **m** gms and final weight is $\mathbf{m_1}$ gms. The loss in weight $(m - m_1)$ corresponds to moisture in coal.

(c) **Formula :** $\text{Moisture \%} = \dfrac{\text{Loss in weight}}{\text{Weight of coal sample}} \times 100 = \dfrac{m - m_1}{m} \times 100$



Silica Crucible



Descicator

(ii) Volatile Matter (V.M.) %
(a)Principle: At 925°C, coal molecules undergo thermal degradation to produce volatile matter.
(b)Method: Moisture free coal left in the crucible in first experiment $(m_1)$ is covered with a lid loosely. Then it is heated at 925°C in a muffle furnace for 7 minutes. The crucible is taken out and cooled in a descicator. Then it is weighed ($m_2$ gms). The loss in weight $(m_1 - m_2)$ is due to loss of volatile matter in the m gms of the coal sample. (Volatile matter is the thermally decomposed coal during burning of coal, that escapes without combustion, in the form of smoke).

(c) **Formula :** $\text{Volatile matter \%} = \dfrac{\text{Weight of volatile matter}}{\text{Weight of air dried coal}} \times 100 = \dfrac{m_1 - m_2}{m} \times 100$

The volatile matter % can also be determined by taking the fresh weight of the air dried coal but the loss in weight at 925°C, will be due to loss of moisture and volatile matter. If w is the weight of air dried coal and $w_1$ is the mass of coal left at 925°C heating, then

$$\text{Volatile matter \%} = \frac{\text{Loss in weight due to moisture and V.M.} \times 100}{\text{Weight of coal sample}} - \text{moisture \%}$$

$$= \frac{(w - w_1) \times 100}{w} - \text{moisture \%}$$

**(iii) Ash %**

(a)Principle: Inorganic matter in the coal gets oxidised to form metal oxides and silica, which is non-combustible and left as ash.

(b)Method: The residual coal in the above experiments is heated and burnt in a open crucible at above 750°C for half hour. The coal gets burnt. The ash left in crucible is cooled in a descicator and weighed ($m_3$ gm).

**(c) Formula :** $\text{Ash \%} = \frac{\text{weight of ash}}{\text{weight of coal}} \times 100 = \frac{m_3}{m} \times 100$

**(iv) Fixed carbon %**

Fixed carbon % = 100 – (% Moisture + % V. M. + % ash)

**Significance (Importance of Proximate Analysis)**

(i) High % of moisture is undesirable because it reduces the calorific value, increase the cost of transportation and causes wastage of heat.

(ii) The volatile matter present in coal may be due to coumbustible gases ($H_2$, CO, $CH_4$ etc) and non-coumbustible gases ($CO_2$, $N_2$). A high volatile matter containing coals give long flames, high smoke and low calorific value.

(iii) Ash is formed in the presence of non-coubustible elements like Fe, Mn, and Co. Many Indian coals have high ash content. High ash content in coal normally leads to (a) reduce the calorific value (b) ash if present as clinkers

(iv) The higher % of fixed carbon in a coal, greater is its calorific value and better the quality of coal.

**Ultimate Analysis of Coal**

Definition:The analysis of coal in which percentages of C, H, N, S and O elements are found out, is known as ultimate analysis.

**Carbon and Hydrogen.**

Method for determination :

• A known weight of powdered and air dried coal sample is burnt in the presence of pure oxygen, in a combustion apparatus. C and H are converted to $CO_2$ and $H_2O$ vapours respectively.

• The gaseous products are allowed to pass through first the preweighed U-tube containing anhydrous $CaCl_2$ or magnesium per chlorate (absorbing $H_2O$ vapours) and then through the KOH solution in a preweighed U-tube (absorption of $CO_2$).

• The increase in weight of U-tube containing anhydrous $CaCl_2$ corresponds to weight of water formed and increase in weight of U-tube containing KOH solution corresponds to $CO_2$ formed, by combusting the coal sample.

Reactions :

$$\underset{12}{C} + O_2 \longrightarrow \underset{44}{CO_2} \; ; \qquad 2\,KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

$$\underset{2}{2\,H} + \frac{1}{2} O_2 \longrightarrow \underset{18}{H_2O} \; ; \qquad CaCl_2 + 7\,H_2O \longrightarrow CaCl_2 \cdot 7\,H_2O$$

Formulae for calculation:

$$C\,\% = \frac{\text{Weight of } CO_2 \text{ formed} \times 12 \times 100}{\text{Weight of coal sample} \times 44}$$

$$H\,\% = \frac{\text{Weight of } H_2O \text{ formed} \times 2 \times 100}{\text{Weight of coal sample} \times 18}$$

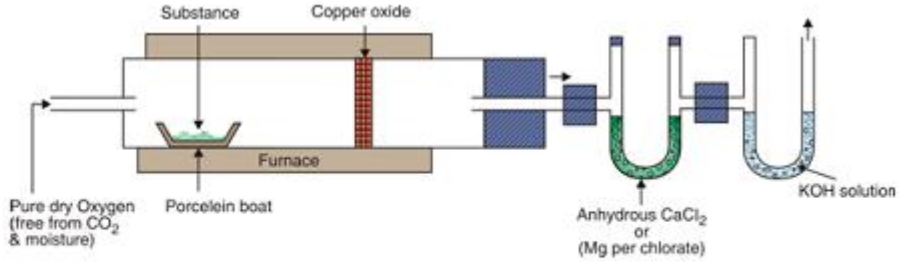


Fig. 4: Combustion apparatus

**Sulphur:**

Principle: Sulphur present in coal converts to first $SO_3$ which is soluble in water forming $H_2SO_4$. $H_2SO_4$ is then converted to $BaSO_4$ precipitate when treated with $BaCl_2$.

Sulphur is determined from the washings obtained from the known mass of coal, used in a bomb calorimeter for determination of calorific value. The washings are treated with barium chloride solution, barium sulphate is precipitated. The precipitate is filtered, washed and dried.

$$\% S = \frac{wt.of\ BaSO4\ formed\ X\ 32\ X\ 100}{wt.of\ coal\ sample\ taken\ X\ 233}$$

**Nitrogen:**

Principle:

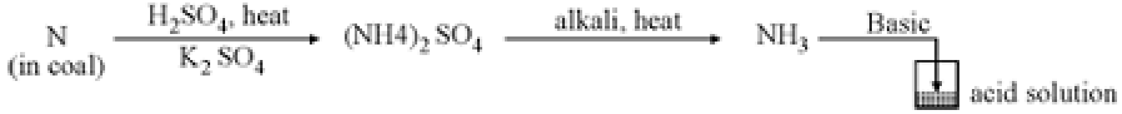
N in coal gets converted to ammonium sulphate, by action of hot concentrated $H_2SO_4$ and then on treatment with alkali solution, equivalent amount of $NH_3$ is liberated.

Method:

A known weight of powdered and air dried coal is heated with concentrated $H_2SO_4$ alongwith $K_2SO_4$ catalyst in a long necked Kjeldahl flask.

After the contents become clear, it is treated with alkali solution in a round bottom flask. The ammonia (basic gas) liberated is passed in known volume of standard acid solution.

The unused acid is determined by back titration with NaOH solution.



i)Mass of coal = m gm.

ii)$V_2$ ml = (Blank titration reading).

iii)$V_1$ ml = (Back titration reading, after passing $NH_3$)

iv)Volume of the acid consumed by $NH_3$ = $(V_2 – V_1)$ ml.

Formula :

$$N\ \% = \frac{\text{Volume of acid consumed x normality of NaOH x 1.4}}{\text{Weigth of coal sample}}$$

OR

$$N\ \% = \frac{\text{Volume of acid} \times \text{change in normality of acid} \times 1.4}{\text{Weight of coal sample}}$$

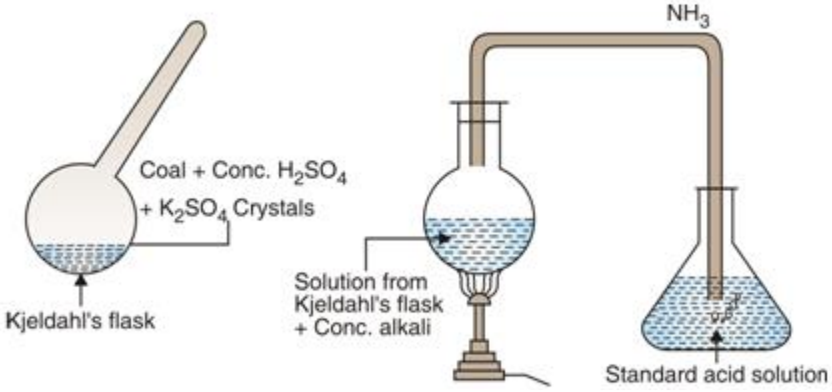


Fig. 5: Estimation of nitrogen in coal

Significances of Ultimate analysis: (1) Higher the % of carbon and hydrogen, the better is the quality of coal and its calorific value. (2) Nitrogen does not have any calorific value. It has no significance. (3) Sulphur increases calorific value. But the products of $SO_2$ and $SO_3$ are forms H2SO4 leading to corrosive effect on equipment. (4) Oxygen present in coal, it combined with moisture which causes low calorific value. An increases 1% of oxygen calorific value decreases by 1.7%. Hence a good quality of coal should be low % of oxygen.

**Ex. 1)** 0.25 gm of a coal sample on burning in a combustion chamber in the current of pure oxygen was found to increase weight of U-tube with anhydrous CaCl2 by 0.075 gm and of KOH U-tube by 0.52gm. Find C and H percentages in coal.

Given: Weight of coal = w = 0.25 gm

Increase in weight of U - tube containing $CaCl_2$ = Weight of moisture formed = 0.075 gm

Increase in weight of KOH U-tube = Weight of $CO_2$ formed = 0.52 gm

$$\underset{(2\times 1)}{2H} + \tfrac{1}{2}O_2 \rightarrow \underset{(18)}{H_2O}$$

$$\underset{(12)}{C} + O_2 \rightarrow \underset{(44)}{CO_2}$$

$$\%\,\text{hydrogen} = \frac{\text{Weight of moisture formed}}{\text{Weight of coat}} \times \frac{2}{18} \times 100$$

$$= \frac{2}{18} \times \frac{0.075}{0.25} \times 100 = 0.33\ \%$$

$$\%\,\text{carbon} = \frac{12}{44} \times \frac{\text{Weight of } CO_2}{\text{Weight of coal}} \times 100$$

$$= \frac{12}{44} \times \frac{0.52}{0.25} \times 100 = 56.73\ \% \qquad \text{...Ans.}$$

**Ex. 2)** One gram of coal sample was burnt in oxygen. Carbon Dioxide was absorbed in KOH and water vapour in CaCl2. The increase in weight of KOH and CaCl2 was 3.157 and 0.504 gm respectively. Determine % C and % H in the sample

Given: Weight of $CO_2$ absorbed in KOH = 3.157 gm

Weight of $H_2O$ absorbed in $CaCl_2$ = 0.504 gm

Weight of coal burnt = 1.0 gm

$$C\,\% = \frac{12}{44} \times \frac{\text{Weight of } CO_2}{\text{Weight of coal}} \times 100 = \frac{12}{44} \times \frac{3.157}{1} \times 100 = 86.1\ \% \qquad \text{...Ans.}$$

$$H\,\% = \frac{2}{18} \times \frac{\text{Weight of } H_2O}{\text{Weight of coal}} \times 100 = \frac{2}{18} \times \frac{0.504}{1} \times 100 = 5.6\ \% \qquad \text{...Ans.}$$

**Ex. 3)** Find the % of C and H in coal sample from the following data- 0.20 gm of coal on burning in a combustion tube in presence of pure oxygen was found to increase in the weight of CaCl2 tube by 0.08 gm and KOH tube by 0.12 gm.

Given: W = Weight of coal = 0.2 gm

Weight of $CO_2$ = increase in weight of KOH = 0.12 gm

Weight of $H_2O$ formed = increase in weight of $CaCl_2$ = 0.08 gm

$$C\,\%\ \text{in coal} = \frac{12}{44} \times \frac{\text{Weight of } CO_2}{\text{Weight of coal}} \times 100 = \frac{12}{44} \times \frac{0.12}{0.2} \times 100 = 16.36\ \% \qquad \text{...Ans.}$$

$$H\,\%\ \text{in coal} = \frac{2}{18} \times \frac{\text{Weight of } H_2O}{\text{Weight of coal}} \times 100 = \frac{2}{18} \times \frac{0.08}{0.2} \times 100 = 4.44\ \% \qquad \text{...Ans.}$$

**Ex. 4)** 2.4 gm of coal sample was weighed in silica crucible. After heating for one hour at 110°C, the residue weighed as 2.25 gm. The crucible was then covered with a vented lid and strongly heated for exactly 7 minutes

at 950°C. The residue weighed as 1.42 gm. The crucible was further heated without lid until a constant weight was obtained. The last residue was found to be 0.22 gm. Calculate the % results of the above analysis.
Given: W = weight of coal = 2.4 gm

$$\text{Weight of moisture} = \text{W} - \text{weight of residue at } 110^{\circ}\text{C} = 2.4 - 2.25 = 0.15 \text{ gm.}$$

$$\text{Moisture \%} = \frac{\text{Weight of moisture}}{\text{Weight of coal}} \times 100 = \frac{0.15}{2.4} \times 100 = 6.25\ \%$$

$$\text{Weight Volatile matter} = \text{Weight of coal after } 110^{\circ}\text{C} - \text{Weight of residue at } 950^{\circ}\text{C}$$

$$= 2.25 - 1.42 = 0.83 \text{ gm}$$

$$\text{VM \%} = \frac{\text{Weight of VM}}{\text{Weight of coal}} \times 100 = \frac{0.83}{2.4} \times 100 = 34.58\ \%$$

$$\text{Weight of ash residue} = 0.22 \text{ gm}$$

$$\text{Ash \%} = \frac{\text{Weight of ash}}{\text{Weight of coal}} \times 100 = \frac{0.22}{2.4} \times 100 = 9.17\ \%$$

$$\text{Fixed carbon \%} = 100 - (\text{Moisture \%} + \text{VM \%} + \text{ash \%})$$

$$= 100 - (6.25 + 34.58 + 9.17) = 50\ \%$$

The given coal contains,

| | | | |
|---|---|---|---|
| Moisture % | = 6.25 | Ash % | = 9.17 |
| VM % | = 34.58 | Fixed carbon % | = 50 |

**Ex. 5)** 0.5 gm of a coal sample on burning in a combustion chamber in the current of pure oxygen was found to increase weight of U tube with anhydrous CaCl2 by 0.145 gm and of KOH U tube by 0.90 gm. Find ‘C’ and ‘H’ percentage in coal.
Soln. :
Weight of coal burnt = 0.5 gm
Weight of $CO_2$ formed = Increase in weight of U-tube containing KOH = 0.9 gm
Weight of $H_2O$ formed = Increase in weight of U-tube containing anhydrous $CaCl_2$ = 0.145 gm

$$\text{C \% in coal} = \frac{12}{44} \times \frac{\text{Weight of } CO_2}{\text{Weight of coal}} \times 100 = \frac{12}{44} \times \frac{0.9}{0.5} \times 100 = 49.99\ \%$$

$$\text{H \% in coal} = \frac{2}{18} \times \frac{\text{Weight of } H_2O}{\text{Weight of coal}} \times 100 = \frac{2}{18} \times \frac{0.145}{0.5} \times 100 = 3.22\ \%$$

## LIQUID FUELS

Petroleum is one of the best primary liquid fuels. It is also known as crude oil. Petrol, diesel, kerosene are secondary liquid fuels and derived from petroleum. (i) The thermal efficiency of liquid fuels is higher than solid fuels. Low and high boiling fractions of petroleum are used in internal combustion of petrol and diesel engines, respectively. (ii) Liquid fuels possess higher calorific value per unit than solid fuels. (iii) Liquid fuels does not produce ash, dust, clinkers etc. during combustion.

**PETROLEUM (OR) CRUDE OIL:** The crude oil (or) petroleum also known as rock oil (or) mineral oil. The unpleasant odour of petroleum is due to the presence of some foul smelling sulphur compounds. Petroleum does not have definite composition. It is a complex mixture of various hydrocarbons and small quantity optically active compounds of S, N, O and traces of Fe, Cu, V, etc.

## Composition of crude oil

Elemental composition

| Element | Percent range |
|---|---|
| Carbon | 80 to 87% |
| Hydrogen | 11 to 15% |
| Nitrogen | 0.4 to 0.9% |
| Oxygen | 0.1 to 0.9% |
| Sulfur | 0.1 to 3.0% |
| Metals | < 0.1% |

Molecular composition

| |
|---|
| Open chain Alkanes |
| Cycloalkanes |
| Aromatics |
| Asphaltenes |
| Resins |

Origin petroleum: **There are 2 theories to explain the origin of petroleum.**

(a) **Carbide theory (or) Mendeleev's theory:** This theory is also called inorganic theory. Metals inside the earth react with carbon to form metal carbides. These carbides are converted into hydrocarbons in the presence of moisture (or) steam, which on further hydrogenation, polymerise to give a complex mixture of paraffin's, olefins and aromatic hydrocarbons.

$Ca + 2C \xrightarrow{\text{high temp}} CaC_2$ (calcium carbide)
$4Al + 3Ca \longrightarrow Al_4C_3$ (aluminium carbide)

$CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$
$Al_4C_3 + 12H_2O \longrightarrow 4Al(OH)_3 + 3CH_4$

$C_2H_2 + H_2 \longrightarrow C_2H_4$ (ethylene)
$3C_2H_2 \longrightarrow C_6H_6$ (benzene)

Drawbacks: This theory was unable to explain the presence of N, S and optically active compounds in petroleum.

(b) **Engler's theory:** According to this theory, organic matter, animals, vegetation and marine accumulated in sea. They were decomposed under high temperature and pressure by anaerobic bacteria to a dark viscous liquid called petroleum. This theory is better accepted and presence of optically active compounds in petroleum favours Engler's theory.

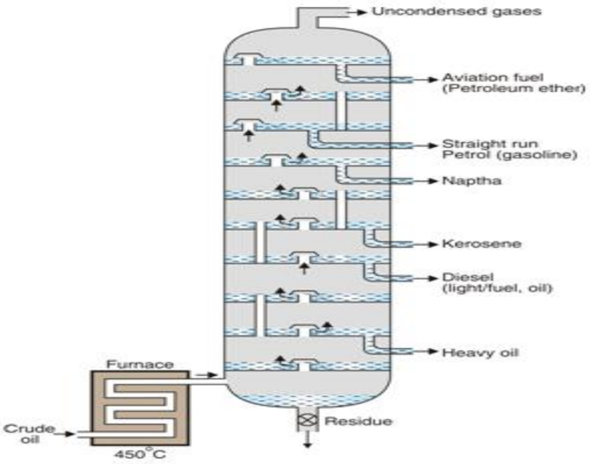
## REFINING OF PETREOLUEM

The crude oil is a mixture of several hydrocarbons and is not fit to be marketed. "The process of separating various fractions of crude oil is called **refining** and hence where the industry refining of crude oil is takes place is called **oil refinery**. Refining of petroleum involves the following 3 steps.

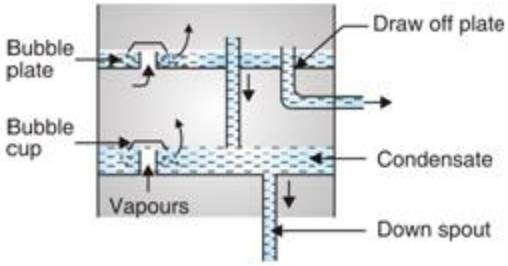
(a) **Separation of water (Cottrelle's process):** The crude oil is an emulsion of oil and water. This mixture was passed between two highly charged electrodes the emulsion films will destroy and the colloidal water droplets separated into bigger drops. They can be separated out from the oil.

(b) **Removal of sulphur compounds:** In order to remove sulphur compounds from crude oil, it is treated with copper oxide. The sulphur compounds converted to insoluble copper sulphide, which can be removed filtration.

(c) **Fractional distillation:** Crude oil obtained after (a) and (b) steps is then heated at about 400 $^0$C in an iron retort. All volatile constituents are evaporated leaving behind some residue. The hot vapours are passed through different fractionating columns. The apparatus is a long cylindrical vessel with several trays, each having chimney with a loose cap.

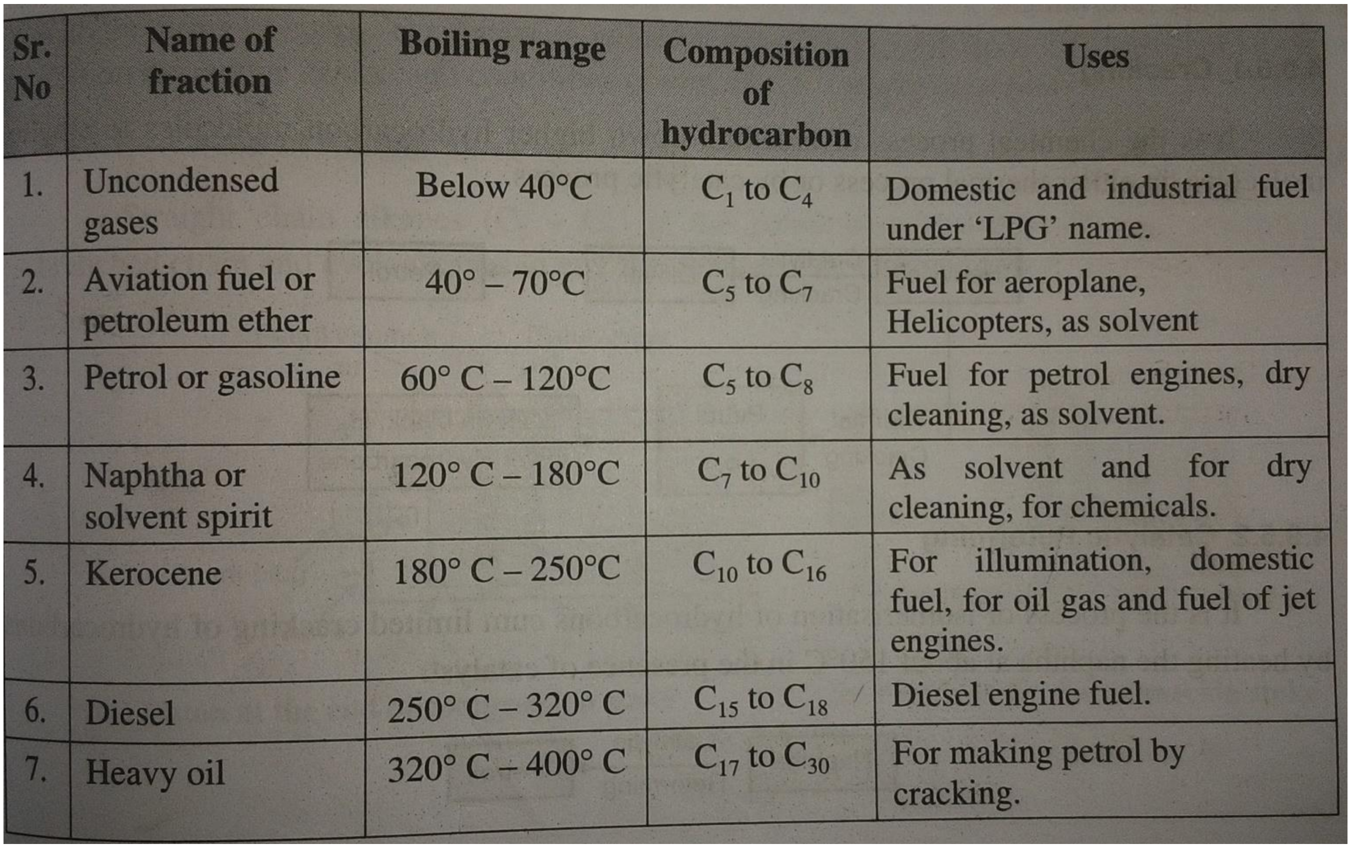


(a) Fractionating tower



(b) Portion of fractionating tower

The vapours go upward, they gradually become cool and their fractional condensation takes place at different levels in the column. The uncondensed gases escape from top of the fractionating column. These gases are liquefied and used as **LPG**. Different boiling fractions are condensed at different trays. Higher boiling fraction is condensed first and then gradually the lower ones.



| Sr. No | Name of fraction | Boiling range | Composition of hydrocarbon | Uses |
|---|---|---|---|---|
| 1. | Uncondensed gases | Below 40°C | $C_1$ to $C_4$ | Domestic and industrial fuel under 'LPG' name. |
| 2. | Aviation fuel or petroleum ether | 40° – 70°C | $C_5$ to $C_7$ | Fuel for aeroplane, Helicopters, as solvent |
| 3. | Petrol or gasoline | 60° C – 120°C | $C_5$ to $C_8$ | Fuel for petrol engines, dry cleaning, as solvent. |
| 4. | Naphtha or solvent spirit | 120° C – 180°C | $C_7$ to $C_{10}$ | As solvent and for dry cleaning, for chemicals. |
| 5. | Kerocene | 180° C – 250°C | $C_{10}$ to $C_{16}$ | For illumination, domestic fuel, for oil gas and fuel of jet engines. |
| 6. | Diesel | 250° C – 320° C | $C_{15}$ to $C_{18}$ | Diesel engine fuel. |
| 7. | Heavy oil | 320° C – 400° C | $C_{17}$ to $C_{30}$ | For making petrol by cracking. |

Heavy oil on re-fractionation produces
(a) Lubricating oil (as a lubricant)
(b) Petroleum jelly (in cosmetics, medicines and as a lubricant)
(c) Grease (as a lubricant)
(d) Paraffin wax (preparing wax papers, shoe polishes and candles)

Residue: Above 400 $^0$C residue the following products are obtained (>30 carbons) (a) Asphalt (or) tar (for laying roads and water proofing houses of the roofs (b0 Petroleum coke (for moulding the rods of arc lights and as a fuel)

**PETROL (OR) GASOLINE:** Petrol is highly volatile, inflammable secondary liquid fuel and used in the internal combustion engines of automobiles. Only 20% of the petrol is coming from petroleum fractionating column and it is called **straight run petrol**. 50% of the petrol is coming by process called **cracking** and remaining 30% of the petrol is produced by synthesis from coal and water, which is called **synthetic petrol**.

CRACKING: Cracking is familiar process of breaking of bigger hydrocarbons of high molecular weight, high boiling to simple, low boiling, low molecular weight hydrocarbons.
For eg: 1
$C_9H_{20} \xrightarrow{\text{cracking}} C_5H_{12} + C_4H_8$
(nonane) (n-pentane) (butane)

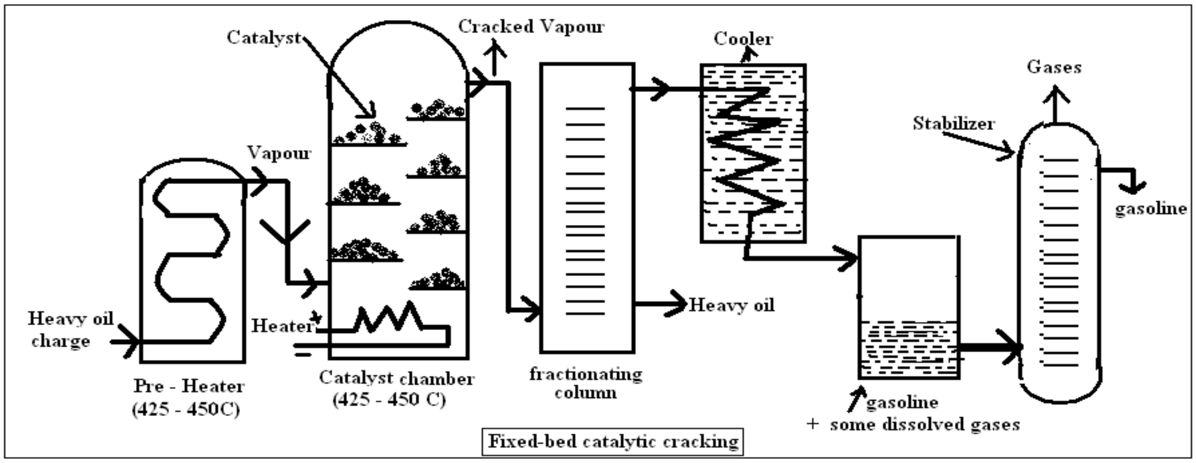
| $C_{10}H_{22}$ | $\longrightarrow$ | $C_5H_{12}$ | + | $C_5H_{10}$ |
|---|---|---|---|---|
| Decane | | n-Pentane | | Pentene |
| B.Pt : 174°C | | B.Pt : 36°C | | |

The process of cracking is mainly of two types. (1) Thermal cracking (2) Catalytic cracking

(1) **Thermal cracking:** Breaking heavier hydrocarbon molecules into simpler, low boiling, lower molecular weight hydrocarbons by use of temperature and pressure is called "thermal cracking". Thermal cracking is carried out by two ways. (a) Liquid phase thermal cracking (b) Vapour phase thermal cracking. The liquid phase cracking takes place at 475$^0$C to 530$^0$C at a pressure 100kg/cm$^2$. While the vapour phase cracking occurs at 600 to 650$^0$C at a low pressure of 10 to 20 kg/cm$^2$.

(2) **Catalytic cracking:** In this type of cracking catalysts are used. The best one is **aluminosilicate** with some metal oxides (oxides of Ca, Fe, Mg, Cr, Na). This process completes at lower temperatures compared to the thermal cracking (300-400 $^0$C., 1-5 Kg/cm$^2$ pressure). Catalytic cracking is also of two types.
   - **(a)** Fixed-bed catalytic cracking
   - **(b)** Moving-bed catalytic cracking

### (a) Fixed-bed catalytic cracking:



Fixed-bed catalytic cracking

(i) In this method, vapours are heated in a pre-heater to cracking temperature 425-450 $^0$C (ii) The hot vapours are forced to catalytic chamber (containing artificial clay + $ZrO_2$) maintained at 425-450 $^0$C and 1.5 kg/cm$^2$ pressure. About 40% carbon is converted into gasoline and 2-4% carbon is deposited on catalytic bed. (iii) The vapours produced are then passed through a fractionating column, where heavy oil fractions are condensed. (iv) The vapours are then led through a cooler, where some of the gases are condensed along with gasoline. The uncondensed gases move on to stabilizer, where the dissolved gases are removed and pure gasoline is obtained. (v) The catalyst after 8-10 hr stop functioning due to deposition of carbon. This is reactivated by burning off the deposited carbon. During reactivation, the oil vapours are diverted through another catalytic chamber.

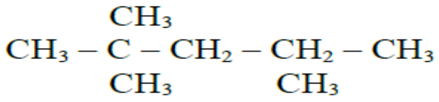
**Q. a) What is knocking? b) What is octane number & cetane number**
**c) What is leaded petrol? Discuss its advantages and disadvantages.**

In internal combustion engines, diesel or petrol mixed with air is used as fuel and ignited in the cylinder. In **petrol engines** the ignition brought by an electric spark (spark engines) and compressing air (compression engines) in **diesel engines**.
Premature and instantaneous ignition of petrol – air (fuel-air) mixture in a petrol engine, leading to production of an explosive violence is known as knocking. The resistance offered by gasoline to knocking cannot be defined in absolute terms. It is generally expressed on an arbitrary scale known as Octane rating.

**Knocking causes loss of efficiency of the engine, increase fuel consumption and damage to spark plug.**

The tendency of fuel constituents to knock in the following order. Straight – chain paraffins > Branched- chain paraffins (i.e.,iso paraffins)> Olefines> Cycloparaffins (i.e.,naphthalenes)> aromatics. Thus, olefins of the same carbon chain length possess better anti knock properties than the corresponding paraffins and so on.

The knocking of petrol can be measured by a test is called **octane rating** (or) **octane number**. The **n-heptane** knocks very badly and hence, anti-knocking value has been arbitrarily fixed as zero and **isooctane** (2,2,4-trimethy pentane) gives very little knocking, so its anti-knock value fixed as 100.



$$CH_3 - \underset{CH_3}{\overset{CH_3}{C}} - CH_2 - \underset{CH_3}{CH_2} - CH_3$$

2,2,4- trimethyl pentane
(isooctane) octane number 100 (good fuel)

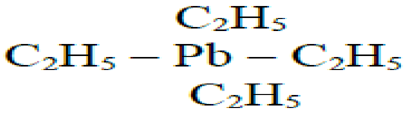
$CH_3 - (CH_2)_5- CH_3$

n-heptane
octane number zero (bad fuel)

Several mixtures of n-heptane and isooctane were prepared like **isooctane: n-heptane** -40:60, 50:50, 60:40, 70:30 etc. Each mixture is taken into an internal combustion engine and its knocking is observed and matched with the knocking characteristic of the petrol sample under examination.

For eg: Octane number of the petrol sample is matches with 70:30 mixture, the octane number of the test sample is 70. So "octane number can be defined as the percentage of isooctane in a mixture of isooctane and n-heptane and whose knocking of the petrol sample under examination".

**LEAD petrol:** The variety of petrol in which tetra ethyl lead is added, it is leaded petrol.



$$C_2H_5 - \underset{C_2H_5}{\overset{C_2H_5}{Pb}} - C_2H_5$$

Tetra ethyl lead (TEL)

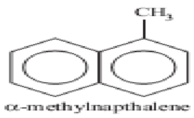
To improve the anti-knock of the petrol sample, TEL and diethyl telluride [$(C_2H_5)_2Te$] are added. These materials are extremely poisonous and about 1 to 1.5 ml of TEL is added per litre of petrol. When TEL is fed into the internal combustion engine along with petrol, TEL undergoes and converted to lead peroxide. This lead peroxide reacts with any hydrocarbon molecule, there by slowing down the reaction of pre-ignition. So TEL acts as a negative catalyst for pre-ignition of the petrol sample. This lead peroxide is deposited in I/C engine which is harmful. To eliminate lead peroxide, ethylene-dibromide is added, which converts lead peroxide to lead dibromide. The lead dibromide is volatile and easy escapes out along with other flue gases.

**Cetane number (knocking of diesel):** Diesel fraction is obtained between 250-320 $^0$C during fractional distillation of petroleum. The oil contains 85% C, 12% H and calorific value is 11,000 Kcal/mole.

"Diesel knock can be defined as the rattling sound produced due to ignition-lag (the delay in the ignition of the fuel)". The structure of diesel is responsible for knocking. The hydrocarbons possess antidisel knock property in the order.
n-alkanes > naphthalenes > alkenes > branched alkanes > aromatics.
"The diesel knock is measured by cetane number. For this **hexadecane** is selected which is having **100%** antiknock property. **2-methyl naphthalene** is aromatic compound having anti knock diesel property is **zero**".

$CH_3 — (CH_2)_{14} — CH_3$

*n*-hexadecane (cetane)



α-methylnapthalene

Antiknock: 100 antiknock: 0

The mixtures containing **n-hexadecane** and **2-methylnaphthalene** like 40:60, 50:50, 60:40, 70:30 etc. respectively are prepared and their anti-diesel knock property is measured by taking in a diesel engine. For eg: the diesel knock of the test sample matches with 60:40 mixtures, the cetane number of the diesel is 60.
"So the cetane number can be defined as the % of hexadecane in a mixture of 2-methyl naphthalene whose diesel knock matches with the diesel knock of the test sample under examination". For low speed diesel engines the cetane number is 25, for high speed diesel engines the cetane number is 45 and 35 for medium speed diesel engines.

## Gaseous Fuels

Natural gas is the primary gaseous fuel. A variety of secondary fuels are obtained from coal (or) petroleum. They include coal gas, producer gas, water gas derived from coal and LPG, CNG derived from petroleum and natural gas.

(a) **Natural Gas:** Natural gas is primarily methane gas and it is a fossil fuel. Commercially natural gas produced from oil fields and natural gas fields. It is also called **mars** gas. It consists of methane and other saturated hydrocarbons. The average composition of natural gas is as follows.

Composition: Average composition of a natural gas is;
$CH_4$ = 70-90%
$C_2H_6$ = 5-10%
$H_2$= 3%
$CO+CO_2$=0.7%
Its calorific value varies from 12,000 to 14,000 kcal/m$^3$. If natural gas contains lower hydrocarbons like methane and ethane it is called **lean or dry gas.** In the natural gas contains higher hydrocarbons like propane, butane along with methane it is called **rich or wet gas.**

Appreciable quantities of $H_2S$ can be removed from natural gas by scrubbing with monomethanol amine.

Applications: 1. It is used as a very good domestic fuel.
2. It is used in the preparation of ammonia (used for urea manufacturing).
3. It is used to prepare carbon-black which is used as filler for rubber industry.
4. A large number of chemicals are synthesised from natural gas.
5. It is also used for the generation of electricity by using it in fuel cells.

(b) **LPG (liquefied Petroleum Gas):** LPG is a common fuel for domestic and industries. The main components of LPG are n-butane, isobutane, butylene and propane. LPG is dehydrated and desulphurised. LPG is highly inflammable and consists of hydrocarbons can be readily liquefied under pressure and exists as gas at room temperature. Its Calorific Value is 27,800 kcals/m3 and LPG is supplied under different trade names like Indane, H.P etc.

**Composition**

Its approximate composition is
n-Butane = 70 %
Isobutane = 17 %
n-Propane = 11 %
Butylene and Ethane = rest.

**Uses**

i. It is used as a fuel for domestic cooking.
ii. Used for heating industrial furnaces.
iii. Used as an alternate for Gasoline in automobiles.

**Disadvantages**

1. It is difficult to handle as fuel.
2. Engines working at low compression ratio cannot use LPG as fuel.

**(c) CNG (Compressed Natural Gas)**: Natural gas contains mainly $CH_4$. When natural gas is compressed at high pressure (1000 atm) or cooled to –160°C, it is converted into CNG. It is now replacing gasoline as it releases less pollutant during its combustion. It is environmentally clean alternative to those fuels which produce toxic pollutants. In some of the metro cities, CNG-vehicles are used to reduce pollution. LNG (liquified natural gas) is different from CNG. LNG is costlier than CNG. Its calorific value is about 13000 kcal/m3

**Advantages of CNG**

1. Due to higher temperature of ignition, CNG is better fuel than petrol and diesel.
2. Operating cost of CNG is less. Cost of production is less. It can be easily stored.
3. It releases least pollutants like CO and unburnt hydrocarbons.
4. It undergoes regular combustion.

**Disadvantages**

1. Faint odour; leakage cannot be detected easily.
2. CNG tanks require a large tank space.
3. Refueling network for CNG is very expensive.

## COMBUSTION

**Combustion is an exothermic chemical reaction. It is defined as "the process of oxidation of the fuel by oxygen and subsequent liberation of energies like heat, light etc".** For example, combustion of carbon in oxygen:

$$C_{(s)} + O_{2(s)} \longrightarrow CO_{2\,(g)} + 97\ \text{kcal}$$

**Factors affecting the rate of combustion**

The rate of combustion depends on the following factors:
1. The concentration of the fuel and air.
2. The nature of the combustible substance
3. The temperature
4. With increase in pressure or surface area of the fuel the rate of combustion can be increased.
5. It increases with increase in pressure of air.
6. It Increases with preheating of fuel and air.

**Calorific value of a fuel:** "Calorific value can be defined as the amount of heat produced by the combustion of unit mass (or) unit volume of a fuel. The higher the calorific value, the better will be the quality of fuel. There are different units for measuring the quantity of heat. They are

**(a) Calorie:** It is the amount of heat required to increase the temperature of **1 gm** of water through **one degree centigrade.**

**(b) Kilocalorie:** The amount of heat required to increase the temperature of **1kg** of water through **one degree centigrade** (i.e. 15 $^{0}$C to 16 $^{0}$C).

**(c) British thermal unit (BTU):** The amount of heat required to raise the temperature of one pound of water by 1$^{o}$F (Fahrenheit) (60 $^{o}$F to 61 $^{o}$F) is BTU.

1 BTU = 252 cal = 0.252 kcal
1 kcal = 3.968 BTU

**(d) Centigrade heat unit (C.H.U):** It is the amount of heat required to raise the temperature of one pound of water through 1$^{o}$C.

1 kcal = 3.968 BTU = 2.2 CHU

**Inter conversion of various units of heat**

1 kcal = 1000 cal = 3.968 BTU = 2.2 CHU

**Types of calorific values**: (1) Gross calorific value (G.C.V.) or High calorific value

(2) Net calorific value (N.C.V.) or lower calorific value

**(1) Gross calorific value (G.C.V.) or High calorific value:** The higher calorific value can be defined as the total heat generated when a unit quantity of fuel is completely burnt and the products of combustion are cooled down to cooled down to 60 $^{0}$ For 15 $^{0}$ C.

For example, when a fuel containing hydrogen is burnt, it under goes combustion and will be converted to steam. If the combustion product is cooled to room temperature, the steam gets condensed into water and the latent heat is evolved. Therefore the latent heat of combustion of condensation of 'steam' so liberated is included in gross calorific value.

**(2) Net (or) Lower Calorific Value (NCV or LCV):** Lower the calorific value is defined as the net heat produced when a unit quantity of fuel is completely burnt and the products of combustion are allowed to escape into the atmosphere. LCV does not include latent heat of steam (or) water vapour.

**Relationship between HCV (GCV) and LCV (NCV)**

LCV (NCV) = HCV (GCV)-latent heat of condensation steam

(The energy required in calories to completely convert 1 gm of $H_2O$ to steam without increase the temperature is called latent heat of steam). **The latent heat of steam is 587 cal/gm.**

Since 1 part by weight of $H_2$ produces 9 parts by weight of $H_2O$ as given by the equation below

$$\begin{array}{cccccc} H_2 & + & \frac{1}{2}O_2 & \longrightarrow & H_2O \\ 2\text{gms} & & 16\text{gms} & & 18\text{gms} \\ 1 & & 8 & & 9 \end{array}$$

Hence, LCV = HCV-(mass of hydrogen X 9 X latent heat of steam)

$$\text{NCV} = \text{GCV} - \frac{9}{100}H \times 587 \quad \text{kcal/kg}$$
$$\text{NCV} = \text{GCV} - 0.09H \times 587 \quad \text{kcal/kg}$$

where , $H = \%$ of $H_2$ in the fuel.

## Dulong's formula (Theoretical calculation)

Dulong's formula for the theoretical calculation of calorific value is

$$\text{GCV (or) HCV} = \frac{1}{100}(8080\ C + 34500\ [H - \frac{O}{8}] + 2240\ S)\ \text{kcal/kg}$$

where, C, H, O & S represent the % of the corresponding elements in the fuel.

It is based on the assumption that the calorific values of C, H & S are found to be 8080, 34500 and 2240 kcal, when 1 kg of the fuel is burnt completely. However, all the oxygen in the fuel is assumed to be present in combination with hydrogen in the ratio H : O as 1 : 8 by weight. So the surplus hydrogen available for combustion is $H - \frac{O}{8}$.

**"**The amount of heat produced when 1 gm molecule of the reactants are burnt in the presence of oxygen" for example $C + O_2 \longrightarrow CO_2 + 96960$ cal

12 gm of carbon liberates 96960 calories of heat

1 gm of carbon liberates = 96960/12=8080 cal .

Similarly $H_2$ burns in the presence of $O_2$, resulting in the formation of

$H_2 + 1/2O_2 \longrightarrow H_20 + 69000$ cal

2gm 16gm 18 gm

2 gm of $H_2$ liberates 69000 calories of heat, so 1gm of $H_2$ liberates = 69000/2= 34500 cal.

$S + O_2 \longrightarrow SO_2 + 71680$ cal

32 gm 32 gm 96 gm

1 gm of Sulphur produces = 71680/32= 2240 cal.

1) Calculate the gross and net calorific value of a coal sample having the following composition C= 80%, H=7%, O=3%, S=3.5 %, N=2% and ash 5%.

$$\text{GCV (or) HCV} = \frac{1}{100}(8080\ C + 34500\ [H - \frac{O}{8}] + 2240\ S)\ \text{kcal/kg}$$

=1/100 (8080x34500 (7-3/8)+2240x3.5

HCV=8828 Kcal/kg

And LCV=HCV-0.09HX587

8828-0.09x7587

LCV=8458 Kcal/kg

(2) Calculate the gross and net calorific value of coal containing the following composition. $C = 85\%$, $H_2 = 8\%$, $S = 1\%$, $N_2 = 2\%$, $O_2 = 2\%$, ash $= 2\%$ and latent heat of steam is 587 cal/gm.

∴ The gross calorific value of the fuel is calculated by making use of Dulong's formula.

$$GCV = \frac{1}{100}\left[8080 \times C + 34500\left(H - \frac{O}{8}\right) + 2240 \times S\right] \text{ cal/gm}$$

$$= \frac{1}{100}\left[8080 \times 85 + 34500\left(8 - \frac{2}{8}\right) + 2240 \times 1\right]$$

$$= \frac{1}{100}\left[68\ 6800 + 34500\,(7.75) + 2240\right]$$

$$= \frac{956415}{100} = 9565.15 \text{ cal/gm}$$

∴ Net calorific value $= GCV - (0.09 \times H \times 587)$

$$= 9564.15 - (0.09 \times 8 \times 587)$$

$$= 9564.15 - 422.64 = 9141.51 \text{ cal/gm.}$$

3) A coal has the following composition by weight $C = 90\%$, $O = 3\%$, $S = 0.5\%$, $N = 0.5\%$ and ash $= 2.5\%$. The net calorific value of the fuel was found to be 8490.5 kcal/kg. Calculate the percentage of hydrogen and HCV of the fuel.

∴ Higher calorific value $= \frac{1}{100}\left[8080 \times C + 34500\left(H - \frac{O}{8}\right) + 2240 \times S\right]$ cal/gm

$$= \frac{1}{100}\left[(8080 \times 90) + 34500\left(H - \frac{3}{8}\right) + 2240 \times 0.5\right]$$

$$= 7272 + (345H - 129.4) + 11.2 \text{ cal/gm}$$

$$= \left[7153.8 + 345H\right] \text{ cal/gm}$$

Lower calorific value (LCV) $= HCV - (0.09 \times H \times 587)$

$$HCV = LCV + 0.09H \times 587$$

$$= 8490.5 + 52.8H \text{ cal/gm}$$

$$7153.8 + 345H = 8490.5 + 52.8H$$

$$292.2H = 8490.5 - 7153.8$$

$$H = \frac{8490.5 - 7153.8}{292.2}$$

$$H = 4.575\%$$

% of $H = 4.58\%$

$$HCV = 8490 + (0.09 \times 4.58 \times 587)$$

$$= 8732.5 \text{ cal/gm.}$$

***1. Calculate the Gross and Net calorific values of a coal having the following compositions, $C = 80$ %, $H_2 = 08$ %, $O_2 = 08$ %, $S = 2$ % and ash=2. Latent heat of steam is = 587 cal/gm.***

**Solution**

***(i)Gross Calorific Value (GCV)***

$$\text{GCV} = \frac{1}{100}\left(8080\,C + 34500\,[H - \frac{O}{8}] + 2240\,S\right)$$

$$= \frac{1}{100}\left(8080 \times 80 + 34500\,[8 - \frac{8}{8}] + 2240 \times 2\right) \text{ kcal/kg}$$

$$= \frac{1}{100}(646400 + 241500 + 4480) \text{ kcal/kg}$$

$$= \frac{1}{100}(892380) \text{ kcal/kg}$$

$$= \mathbf{8923.8 \text{ kcal / kg.}}$$

***(ii) Net Calorific Value (NCV)***

$$= \text{GCV} - \frac{9}{100}H \times 587 \text{ kcal/kg}$$

$$= 8923.8 - \frac{9}{100} \times 8 \times 587 \text{ kcal/kg}$$

$$= 8923.8 - 422.64 \text{ kcal/kg}$$

$$= \mathbf{8501.16 \text{ kcal / kg}}$$

***2. Calculate the Gross and Net calorific values of a coal having the following compositions, $C = 63$ %, $H_2 = 19$ %, $O_2 = 03$ %, $S = 13$ % and ash=2. Latent heat of steam is = 587 cal/gm.***

**Solution**

***(i) Gross Calorific Value (GCV)***

$$\text{GCV} = \frac{1}{100}\left(8080\,C + 34500\,[H - \frac{O}{8}] + 2240\,S\right) \text{ kcal/kg}$$

$$= \frac{1}{100}\left(8080 \times 63 + 34500\,[19 - \frac{3}{8}] + 2240 \times 13\right) \text{ kcal/kg}$$

$$= \frac{1}{100}(509040 + 64562 + 29120) \text{ kcal/kg}$$

$$= \frac{1}{100}(1180722) \text{ kcal/kg}$$

$$= \mathbf{11807.22 \text{ kcal / kg.}}$$

***(ii) Net Calorific Value (NCV)***

$$= \text{GCV} - \frac{9}{100} H \times 587 \quad \text{kcal/kg}$$

$$= 11807.22 - \frac{9}{100} \times 19 \times 587 \quad \text{kcal/kg}$$

$$= 11807.22 - 1003.77 \quad \text{kcal/kg}$$

$$= \boldsymbol{10803.45 \text{ kcal / kg}}$$

***3. Calculate the Gross and Net calorific values of a solid fuel having 80% of carbon & 20% of hydrogen. Latent heat of steam is = 587 cal/gm.***

**Solution**

***(i) Gross Calorific Value (GCV)***

$$\text{GCV} = \frac{1}{100}(8080\, C + 34500\, [H - \frac{O}{8}] + 2240\, S) \quad \text{kcal/kg}$$

Here, the % of $H_2$ and S are Zero.

$$= \frac{1}{100}(8080 \times 80 + 34500\, [20 - \frac{0}{8}] + 2240 \times 0\,) \quad \text{kcal/kg}$$

$$= \frac{1}{100}[646400 + 690000\,] \quad \text{kcal/kg}$$

$$= \frac{1}{100}[1336400\,] \quad \text{kcal/kg}$$

$$= \boldsymbol{13364 \text{ kcal / kg.}}$$

***(ii) Net Calorific Value (NCV)***

$$= \text{GCV} - \frac{9}{100} H \times 587 \quad \text{kcal/kg}$$

$$= 13364 - \frac{9}{100} \times 20 \times 587 \quad \text{kcal/kg}$$

$$= 13364 - 1056.6 \quad \text{kcal/kg}$$

$$= \boldsymbol{12307.4 \text{ kcal / kg}}$$

***4. A coal sample on analysis gives C = 75%, $H_2$ = 6 %, $O_2$ = 3.5 % S = 03 % and the rest ash. Calculate the Gross and Net calorific values of the fuel. Latent heat of steam is = 587 cal/gm***

**Solution**

***(i) Gross Calorific Value (GCV)***

$$\text{GCV} = \frac{1}{100}(8080\, C + 34500\, [H - \frac{O}{8}] + 2240\, S) \quad \text{kcal/kg}$$

$$= \frac{1}{100}(8080 \times 75 + 34500\, [6 - \frac{3.5}{8}] + 2240 \times 3\,) \quad \text{kcal/kg}$$

$$= \frac{1}{100}[606000 + 191906 + 6720] \quad \text{kcal/kg}$$

$$= \frac{1}{100}[804626\,] \quad \text{kcal/kg}$$

$$= \boldsymbol{80462.6 \text{ kcal / kg.}}$$

***(ii) Net Calorific Value (NCV)***

$$= \text{GCV} - \frac{9}{100} H \times 587 \quad \text{kcal/kg}$$

$$= 80462.6 - \frac{9}{100} \times 6 \times 587 \quad \text{kcal/kg}$$

$$= 80462.6 - 316.98 \quad \text{kcal/kg}$$

$$= \boldsymbol{80145.62 \text{ kcal / kg}}$$

***5. On analysis, a coal sample has the following composition by weight; C = 75 %, $O_2$ = 04 %, S = 05 %, and ash = 3%. Net calorific value of the fuel is 9797.71kcal / kg. Calculate the percentage of hydrogen and gross calorific value of coal.***

## Solution

***(i) Gross Calorific Value (GCV)***

We know that,

$$\text{GCV} = [\text{NCV} + 0.09\text{H} \times 587]\ \text{kcal/kg}$$

$$= [9797.71 + 0.09\text{H} + 587]\ \text{kcal/kg}$$

$$= [9797.71 + 52.8\ \text{H}]\ \text{kcal/kg}\ \ldots\ldots\ldots\ldots(1)$$

$$\text{GCV} = \frac{1}{100}\left(8080\,C + 34500\left[H - \frac{O}{8}\right] + 2240\,S\right)\ \text{kcal/kg}$$

$$= \frac{1}{100}\left(8080 \times 75 + 34500\left[\text{H} - \frac{4}{8}\right] + 2240 \times 5\right)\ \text{kcal/kg}$$

$$= \frac{1}{100}[606000 + 34500\,H - 17250 + 11200]\ \text{kcal/kg}$$

$$= [6060 + 345\text{H} - 172.5 + 112]\ \text{kcal/kg}$$

$$= 5999.5 + 345\ \text{H kcal/kg}\ \ldots\ldots\ldots\ldots\ldots(2)$$

Equation (2) is substituted in equation (1)

$$9797.71 + 52.8\ \text{H} = 5999.5 + 345\ \text{H}$$

$$9797.71 - 5999.5 = 345\ \text{H} - 52.8\ \text{H}$$

$$3798.21 = 292.2\ \text{H}$$

$$\text{H} = \frac{3798.21}{292.2}$$

$$\%\ \text{of}\ H_2 = 12.99\ (\textit{i.e}\ 13\ \%)$$

Substituting the value of $H_2$ in the GCV equation

$$\text{GCV} = \frac{1}{100}\left(8080 \times 75 + 34500\left[13 - \frac{4}{8}\right] + 2240 \times 5\right)\ \text{kcal/kg}$$

$$\text{GCV} = \frac{1}{100}[606000 + 431250 + 11200]\ \text{kcal/kg}$$

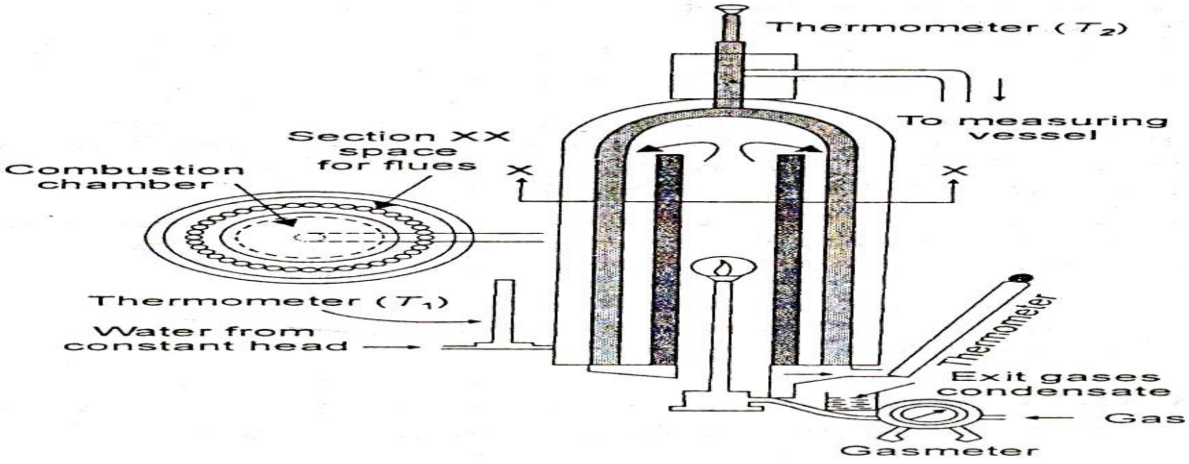
$$= \frac{1}{100}[1048450]\ \text{kcal/kg}$$

$$= \boldsymbol{10484.5\ \text{kcal/kg.}}$$

(Q**) Determination of calorific value of gaseous fuel by Junker's gas Calorimeter?**

The calorific value a fuel is determined by the combustion of the fuel in a special type apparatus called calorimeter. Junker's gas calorimeter is used for measuring the calorific values of gaseous and liquid fuels which get vaporised easily. This calorimeter works on junker's principle. According to this principle

**Calorific value of gaseous fuel X volume of gas=volume of water X rise in temperature of water**



Calorific value of gaseous fuel can be determined by using Junker's calorimeter; it consists of a vertical cylindrical combustion chamber where combustion of gaseous fuel can be carried out with the help of Bunsen burner. The supply of gaseous fuel is regulated with the help of pressure governor. The volume of gas, flowing in a particular time, is measured with the help of gasometer. The combustion chamber is surrounded by an annular water space. Inside the outer flues, heat exchanger coil are also fitted. Radioactive and convective heat loss from the calorimeter is prevented with the help of outer jacket which is chromium plated. Moreover, the outer jacket contains air which is very good heat insulator. Around the combustion chamber, there is an annular space where water is made to circulate. At the appropriate places there are the openings where thermometers arplaced for measuring the temperatures of the inlet and outlet water.

A known volume of gas is burned in excess of air at a constant rate in combustion chamber in such a manner that all the heat produced is absorbed in water. Water is flowing at a constant rate in annular space around the combustion chamber. The increase in the temperature of the water is measured and the heat evolved from the burning of the gas can be readily calculated. The weight of water flowing is also recorded for the calculation of calorific value of gaseous fuel.

Experimental calculations and observations: Let "V" be the volume of gaseous fuel burnt at a given temperature and pressure in a certain time "t"
Volume of water used for cooling combustion products in the "t"= w
Weight of steam condensed in time "t"=m
Temperature of inlet water= $t_1{}^0C$
Temperature out let water= $t_2{}^0C$
Rise in temperature= $(t_2-t_1)$
Mass of water condensed in the out let water in time "t" is "m" kg and hence =m/v
If **L** kcal/volume is the calorific value of gaseous fuel, then Heat produced by fuel=V x L
Heat absorbed by water (w kg) = Wx $(t_2-t_1)$
**By junker's principle V x L = W x $(t_2-t_1)$ (gross calorific value)**
HCV or calorific value of gas L = **W x $(t_2-t_1)$/V**
If latent heat of steam is 587 kcal/kg, then

$$HCV=\frac{(M \times 587)}{V}$$

So, Net calorific value (NCV) = $(L-\frac{(M \times 587)}{V}$ kacl/m3

## RENEWABLE ENERGY SOURCES

The term energy means capacity to do work. Energy can neither be created nor destroyed, but transformed one form to another. Energy is present in a number of forms such as mechanical, thermal, biological energy etc. There are two types of energy sources namely

(1) Renewable energy sources
(2) Non-renewable energy sources

Energy exists freely in nature. Some of them exists infinitely (never run out called renewable). The important renewable energy sources are (1) solar energy (2) wind energy (3) hydropower energy (4) biomass energy

**(1) Solar energy:** The energy is derived from the sun is known as solar energy. It can be used for direct heating (or) sun's heat is converted into electricity. Solar cells (or) photovoltaic cells are devices that convert light energy directly into electrical energy. Solar cells consist of two semiconductor materials joined together. Silicon is "doped" with phosphorous to create an "n" type semiconductor, which is joined to silicon "doped" with boron "p" type semiconductor to create a p-n junction.

When the solar cell is exposed to sunlight, energy from sunlight excites electron from n-type silicon to the holes of p-type silicon. From the p-type silicon, electrons flow through the external circuit as an electric current. The voltage of solar cell is not large, so a series of solar cells are connected to get a solar panel.

**Advantages:**

Solar cells make absolutely no noise at all.

Solar cells create absolutely no pollution (oil burning release harmful greenhouse gases, carcinogens and $CO_2$ into air).

Very little maintenance is required to keep solar cells running.

Solar panels may quite expensive, long you run can use.

A number of solar equipment's have been developed to utilize to heat water, to cook food, to pump water, to certain machines and used for street lighting, railway signals etc.

**Disadvantages:**

The major disadvantage is solar energy does not produce during cloudy weather, night time, rains and other natural conditions.

**(2) Wind energy:** Moving air is called wind. Energy recovered from the force of wind is called wing energy. The energy possessed by wind is of its high speed. The earth's surface has both land and water. When the sun fall down, the air over the land heats up quicker than that over water. The heated air is lighter and its rises.

The moving air (wind) has huge amounts of kinetic energy (K.E), and this can be transferred into electrical energy using wind turbines and connects to a generator.

**Advantages:**

(a) It does not cause any air pollution.
(b) Reduce fossil fuel consumption.
(c) Environmentally friendly (not cause for any pollution).
(d) Low operating/maintenance costs.
(e) High net energy yield.

**Disadvantages:**

(a) Public resists for locating the wind forms in populated areas due to noice generated by machines and loss of aesthetic appearance**.**
(b) Wind forms located on the migratory routes of birds will cause hazards.
(c) Wind forms produce unwanted sound.
(d) Wind turbines interface with electromagnetic signals (TV, Radio signals).
(e) Low energy density of wind (Must use large areas of land).
(f) Wind turbines cannot work, if there is no wind (or) if wind speed is so high it would damage them.

- The Largest wind turbine in the world is located in Hawaii, and has blades length of a football court.
- The average wind speed of 14 miles per hour is needed to convert wind energy into electricity.
- One wind turbine can produce enough electricity to power up to 300 homes.

**(3) Hydropower:** Hydropower is one of the oldest methods of producing power. Hydropower is energy is obtained from flowing water. Electrical power is generated by hydro-electric projects in which dams are constructed across the river. The kinetic energy of flow water is converted into mechanical energy by means of turbines and in turn, the mechanical energy transferred into electrical energy by generators.

**Advantages:**

1. Cheap to operate.
2. Long life and lower operating costs than all other power plants.

3. Renewable.
4. High yield of energy obtained.
5. Lower energy cost than any other method.
6. Some countries depend almost entirely on it.
7. Not intermittent (if reservoir is large enough).
8. Reservoirs have multiple uses.
9. Flood control, drinking water, aquaculture, recreation.
10. Less air pollution than fossil fuel combustion.

**Disadvantages:**

1. Human population displacement.
2. Reduces availability of water downstream

**(a) Ecosystem impacts:**

1. Barriers to migrating fish
2. Loss of biodiversity both upstream and downstream
3. Coastal erosion
4. Reduces nutrient flow (dissolved and particulate)

**(b) Water pollution problems:**

1. Low dissolved oxygen (DO)
2. Increased $H_2S$ toxicity; other DO-related problems
3. Siltation a big problem (also shortens dam life).

**(4) Biomass energy:** Bio-mass is an organic material from living beings or its residues. It is a renewable sources of energy derived from the waste of various human and natural activities. The bio-mass energy sources include wood, animal manure, sugar cane waste, agriculture crops, house hold waste, roots of plants, garbage etc.

The simplest way of using bio-mass energy sources is to allow them to dry out in the sun and burn them. Liquid fuels including ethanol, methanol, biodiesel and gaseous fuels such as methane ($CH_4$) derived from bio-mass feed stocks. Ethanol is made from starch (or) sugar.

Bio gas is a mixture of methane ($CH_4$) (68%), $CO_2$ (31%) and $N_2$ (1%). Bio gas produced from natural organic wastes of cattle dung, human excretia, poultry waste, plant leaves, paddy husk. Bio gas used as cooking gas whose calorific value is 4400-6200 kcal. Heat value of bio gas can be improved by reducing its $CO_2$ content. “Bio gas another name is also called gobar gas”.

**Advantages:**

(a) It is renewable energy.
(b) No harmful emissions.
(c) It is clean energy source.
(d) Reduce dependency on fossil fuels
(e) Reduce land fills (waste is harmful to the environment and occupy the land. So waste be burned to create useful biomass energy)
(f) Prepare different products from biofuels.
(g) Emits less $SO_2$ and $NO_x$ than fossil fuel.

**DISADVANTAGES:**

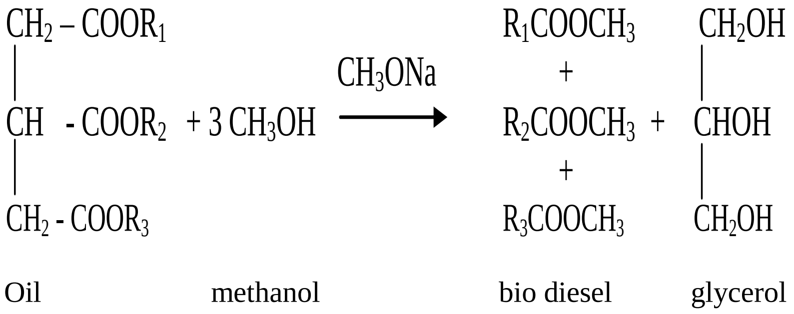
(a) Low energy density/yield: In some cases (eg, corn-derived bioethanol) may yield no net energy
(b) Land conversion:
(i) Biodiversity loss.
(ii) Possible decrease in agricultural food productivity
(iii)Usual problems associated with intensive agriculture, (a) Nutrient pollution (b) Soil depletion (c) Soil erosion

**Biodiesel**: Biodiesel is renewable and clean burning fuel that is made from waste vegetable oils, animal fats and restaurant wastes. “Biodiesel can be defined as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils (or) animal fats, designated as B100”.

Biodiesel is made through a chemical process is called “trans esterification”. There are 3 basic routes to biodiesel production oils and fats.
(a) Base catalysed trans- esterification of the oil.
(b) Acid catalysed trans- esterification of the oil.
(c) Conversion of the oil to its fatty acids and then bio diesel.

Reaction for Biodiesel Formation: Generally base catalysed trans-esterification method widely used for the synthesis of biodiesel.

During the chemical conversion of vegetable oil to biodiesel we get water soluble glycerol and a small amount of sodium soaps. The water soluble part can be easily separated from biodiesel by washing the mixture with water. The alkaline sodium methoxide catalyst, saponifies some small amount of oil to give soap.



$$\begin{array}{l} CH_2-COOR_1 \\ | \\ CH\ -COOR_2 \\ | \\ CH_2-COOR_3 \end{array} + 3\,CH_3OH \xrightarrow{CH_3ONa} \begin{array}{c} R_1COOCH_3 \\ + \\ R_2COOCH_3 \\ + \\ R_3COOCH_3 \end{array} + \begin{array}{l} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Compounds present in biodiesel are like,

| | |
|---|---|
| methyl palmitate | $H_3C - (CH_2)_{14} - COOCH_3$ |
| methyl stearate | $H_3C - (CH_2)_{16} - COOCH_3$ |
| methyl oleate | $H_3C - (CH_2)_7 - CH = CH - (CH_2)_7 - COOCH_3$ |
| methyl linoleate | $H_3C - (CH_2)_5 - (CH = CH)_2 - (CH_2)_7 - COOCH_3$ |

Biodiesel produces less toxic pollutants and greenhouse gases than petroleum diesel. It can be used pure form (B100) or blended with diesel in the form of B2 (2% biodiesel, 98% diesel), B5 (5% biodiesel, 95% diesel), B20 (20% biodiesel, 80% diesel). Biodiesel can be used in any diesel engine with little (or) no modification to the engine (or) fuel system.

**Advantages of Biodiesel**:
(i) Biodiesel is renewable unlike petroleum based diesel.
(ii) Biodiesel is safer to handle compared to standard diesel.
(iii) Biodiesel can be easily blended with standard diesel.
(iv) Biodiesel can help cut our reliance on fossil fuels.
(v) Biodiesel emitting significantly less harmful carbon emission compared to standard diesel.
(vi) Biodiesel has very good lubricating properties, significantly better than standard diesel.
(vii) Biodiesel has shorter ignition delay compared to standard diesel.
(viii) Biodiesel has no sulphur content, and it does not acid formation.

**Limitations of Biodiesel:**
(i) Biodiesel is currently mostly produced from corn, which could lead to food shortages and increased fodd prices.
(ii) Biodiesel is 20 times more susceptible to water contamination compared to standard diesel. This could lead to corrosion.
(iii)Cloud and pour points of biodiesel are higher than diesel and can cause problem in fuel flow line. So it cannot be used in cold regions.
(iv) Biodiesel is significantly more expensive compared to around 11% to standard diesel.
(v) Biodiesel can release nitrogen oxide, which can lead to the formation smog.

## Calculation of Air for Combustion

Substances always combine in definite proportions. These proportions are determined by their molecular masses.

$C + O_2 \rightarrow CO_2$ (12:32:44)

(i) 22.4 L of any gas at 0°C and 760mm pressure (STP) has a mass equal to its 1 mol.

(ii) Air contain 21% of oxygen by volume and 23% of oxygen by mass.

(iii) 28.94 g/mol is taken as molar mass of air.

(iv) $O_2$ required for combustion = theoretical $O_2$ required - $O_2$ present in the fuel.

(v) Dry flue gases means products of combustion except moisture.

For solid or Liquid fuels:

$$O_2\text{ quantity} = \left(\frac{32}{12}C + 8H + S - O\right)\text{ kg.}$$

Where C, H, S and O are amounts of elements in Kg.

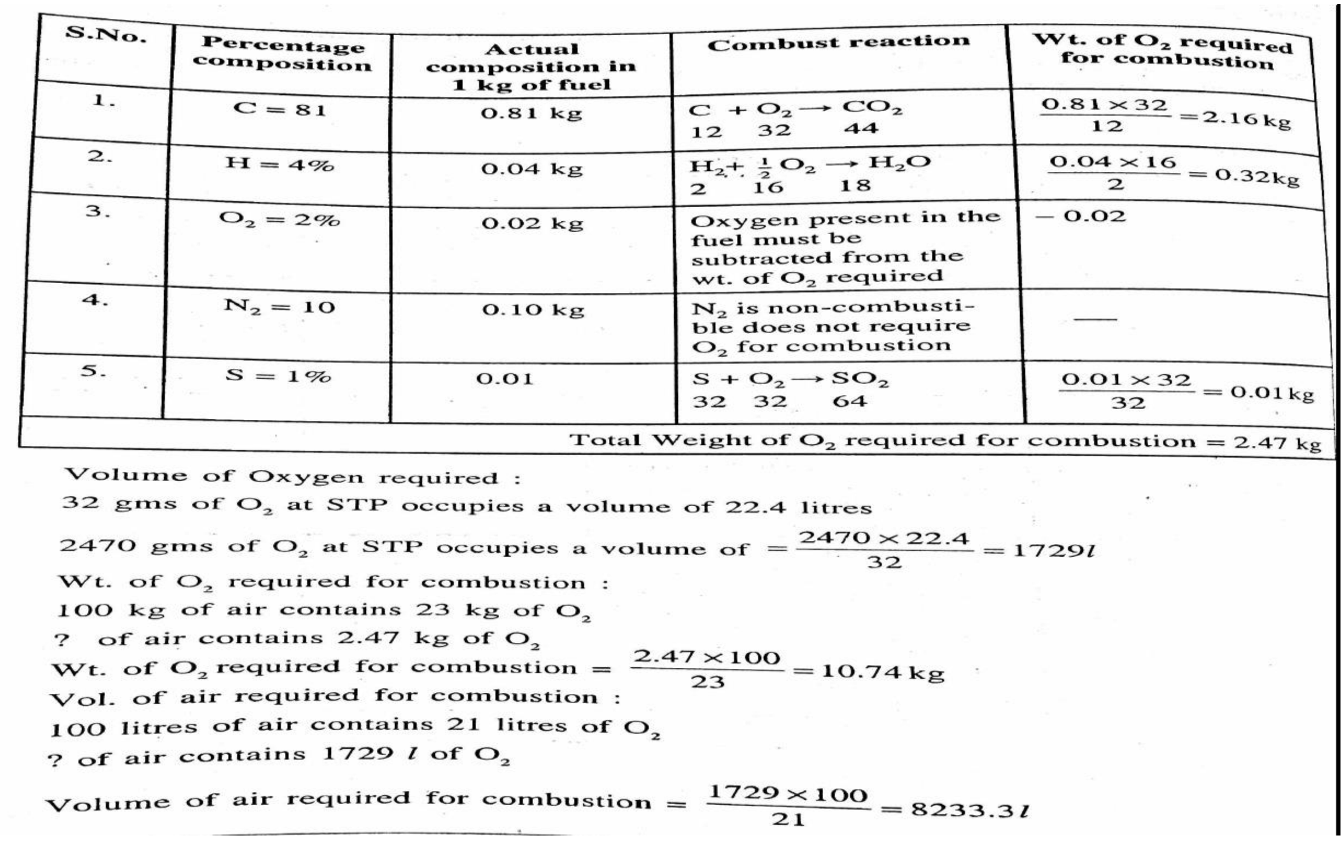
$$\text{Air quantity} = \frac{\textbf{Oxygen quantity X (100+\% excess air)}}{\textbf{23}}\ \text{Kg.}$$

For Gaseous fuels:

$O_2$ volume required = volume gas component in $m^3$ x volume of $O_2$ per volume of gas.

$$\text{Air volume required} = \frac{\textbf{Oxygen volume X (100+\% excess air)}}{\textbf{21}}\ m^3.$$

**Ex 10) A sample of a fuel contains the following by weight C=81%, H= 4%, O2= 2%, N2=10%, S= 1% the reminder is ash. Calculate the volume of air required for the perfect combustion of 1kg of fuel assuming STP conditions.**



| S.No. | Percentage composition | Actual composition in 1 kg of fuel | Combust reaction | Wt. of $O_2$ required for combustion |
|---|---|---|---|---|
| 1. | C = 81 | 0.81 kg | $C + O_2 \rightarrow CO_2$<br>12 32 44 | $\frac{0.81 \times 32}{12} = 2.16$ kg |
| 2. | H = 4% | 0.04 kg | $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$<br>2 16 18 | $\frac{0.04 \times 16}{2} = 0.32$ kg |
| 3. | $O_2$ = 2% | 0.02 kg | Oxygen present in the fuel must be subtracted from the wt. of $O_2$ required | − 0.02 |
| 4. | $N_2$ = 10 | 0.10 kg | $N_2$ is non-combustible does not require $O_2$ for combustion | — |
| 5. | S = 1% | 0.01 | $S + O_2 \rightarrow SO_2$<br>32 32 64 | $\frac{0.01 \times 32}{32} = 0.01$ kg |
| | | | | Total Weight of $O_2$ required for combustion = 2.47 kg |

Volume of Oxygen required :

32 gms of $O_2$ at STP occupies a volume of 22.4 litres

2470 gms of $O_2$ at STP occupies a volume of $= \frac{2470 \times 22.4}{32} = 1729l$

Wt. of $O_2$ required for combustion :

100 kg of air contains 23 kg of $O_2$

? of air contains 2.47 kg of $O_2$

Wt. of $O_2$ required for combustion $= \frac{2.47 \times 100}{23} = 10.74$ kg

Vol. of air required for combustion :

100 litres of air contains 21 litres of $O_2$

? of air contains 1729 $l$ of $O_2$

Volume of air required for combustion $= \frac{1729 \times 100}{21} = 8233.3l$

**Ex.11)** A petrol sample contains 14 % H and 86 % carbon. Calculate the quantity of air required for complete combustion of 1 kg petrol.

Soln. :

Given : Weight of petrol fuel = 1 kg. C % = 86 and H % = 14,

$$C = \text{Weight of carbon in 1 kg petrol} = \frac{86}{100} \times 1 = 0.86 \text{ kg}$$

$$H = \text{Weight of hydrogen in 1 kg petrol} = \frac{14}{100} \times 1 = 0.14 \text{ kg.}$$

$$O_2 \text{ quantity} = \left(\frac{32}{12} C + 8\,H + S - O\right) \text{ kg.}$$

$$= \left(\frac{32}{12} \times 0.86 + 8 \times 0.14 + 0 + 0\right) \text{ kg.}$$

$$= 2.293 + 1.12 = 3.413 \text{ kg oxygen}$$

$$\text{Excess air used} = \text{zero}$$

$$\text{Air quantity} = \frac{\text{Oxygen quantity} \times (100 + 0 \text{ excess})}{23}$$

$$= \frac{3.413 \times 100}{23} = 14.839 \text{ kg air} \qquad \text{...Ans.}$$

**Ex. 12)** Volumetric analysis of producer gas is, $H_2$ = 20 % CO = 22 % $N_2$ = 50 %, $CH_4$ = 2 % and $CO_2$ = 6 %. Find volume of air required for complete combustion of 1 $m^3$ of the gas

Soln. :

$$\text{Volume of } H_2 \text{ in } 1\,m^3 \text{ gas} = \frac{20}{100} \times 1\,m^3 = 0.2\,m^3$$

$$\text{Similarly, Volume of CO} = 0.22\,m^3$$

$$\text{Volume of } CH_4 = 0.02\,m^3$$

($N_2$ and $CO_2$ are not combustible)

| Reaction | Volume of $O_2$ required |
|---|---|
| $H_2 + \frac{1}{2}\,O_2 \rightarrow H_2O$<br>1 vol. 1/2 vol. | $\frac{1}{2} \times \text{volume of } H_2 = \frac{1}{2} \times 0.2 = 0.1\,m^3$ |
| $CO + \frac{1}{2}\,O_2 \rightarrow CO_2$ | $\frac{1}{2} \times 0.22 = 0.11\,m^3$ |
| $CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O$ | $2 \times \text{volume of } CH_4 = 2 \times 0.02 = 0.04\,m^3$ |

$$\text{Total volume of } O_2 \text{ required} = 0.25\,m^3$$

$$\text{Volume of air required} = \frac{\text{Volume of } O_2 \times (100 + 0)}{21}$$

$$= \frac{0.25 \times 100}{21} = 1.19\,m^3 \qquad \text{...Ans.}$$

**Ex. 13)** A gas has following composition by volume, H2 = 20 %, CH4 = 6 %, CO = 18 %, O2 = 5 %, N2 = 43 %. If 25 % excess air is used. Find volume of air actually supplied per m3 of the gas.

Soln. : 1 $m^3$ of the gaseous fuel contains,

$$H_2 = \frac{20}{100} \times 1 = 0.2\,m^3,\ CH_4 = \frac{6}{100} \times 1 = 0.06\,m^3,$$

$$CO = \frac{18}{100} \times 1 = 0.18\ m^3,\ O_2 = \frac{5}{100} \times 1 = 0.05\ m^3.$$

| Reaction | Volume of $O_2$ required |
|---|---|
| $H_2 + \frac{1}{2}\ O_2 \rightarrow H_2\ O$<br>1 vol. $\frac{1}{2}$ vol. | Volume of gas $\times \frac{1}{2} = 0.2 \times \frac{1}{2} = 0.1\ m^3$ |
| $CH_4\ +\ 2\ O_2 \rightarrow CO_2 + H_2\ O$<br>1 vol. 2 vol. | Volume of gas $\times\ 2 = 0.06 \times 2 = 0.12\ m^3$ |
| $CO + \frac{1}{2}\ O_2 \rightarrow CO_2$<br>1 vol. ½ vol. | Volume of gas $\times \frac{1}{2} = \frac{0.18}{2} = 0.09\ m^3$ |
|  | Total $O_2$ required = 0.1 + 0.12 + 0.09<br>= 0.31 $m^3$ |
|  | Less $O_2$ present in fuel = – 0.05 |
|  | Net $O_2$ required = 0.26 $m^3$ |

Volume of $O_2$ = 0.26 $m^3$

Volume of air with 25 % excess

$$= \frac{\text{Volume of oxygen} \times (100 + 25)}{21} = \frac{0.26 \times 125}{21}$$

= **1.548 $m^3$.** **...Ans.**

∴ Actual volume of air supplied with 25 % excess for combusting 1 $m^3$ of the gaseous fuel is 1.548 $m^3$.

**Ex. 14)** A gas has following composition by volume : $H_2$ = 20 %; $CH_4$ = 6% ; CO = 22%; =
CO2 O = 4% 2 N = 4% 2 = 44%
Find the volume of air actually supplied per m3 of this gas.

Soln. :

$$\text{Volume of } H_2 \text{ in } 1m^3 \text{ gas} = \frac{20}{100} \times 1 = 0.2\ m^3$$

$$\text{Volume of } CH_4 \text{ in } 1m^3 \text{ gas} = \frac{6}{100} \times 1 = 0.06\ m^3$$

$$\text{Volume of } CO \text{ in } 1m^3 \text{ gas} = \frac{22}{100} \times 1 = 0.22\ m^3$$

$$\text{Volume of } O_2 \text{ in } 1m^3 \text{ gas} = \frac{4}{100} \times 1 = 0.04\ m^3$$

($CO_2$ and $N_2$ do not burn and do not require air).

| Reaction | Volume of $O_2$ required = Volume of gas × Volume of $O_2$ per molecule |
|---|---|
| $H_2 + \frac{1}{2} O_2 \longrightarrow H_2O$ | $0.2 \times \frac{1}{2} = 0.1\ m^3$ |
| $CH_4 + 2\ O_2 \longrightarrow CO_2 + 2\ H_2O$ | $0.06 \times 2 = 0.12\ m^3$ |
| $CO + \frac{1}{2} O_2 \longrightarrow CO_2$ | $0.22 \times \frac{1}{2} = 0.11\ m^3$ |
|  | Total $O_2$ = 0.33 $m^3$ |
|  | Less $O_2$ in fuel = 0.33 – 0.04 = 0.29 |

**Ex. 15)** A sample of coal was found to have the following composition :
 H    C = 75%, 2  O    = 5.2%, 2  N     S = 1.2%,     = 12.8%, 2  ash = 2.1%    = 3.7%,
Calculate the minimum amount of air necessary for complete combustion of 1 kg of coal

Soln. :

$$\text{Amount of C in 1 kg coal} = \frac{75}{100} \times 1\ \text{kg} = 0.75\ \text{kg}$$

$$\text{Amount of H in 1 kg coal} = \frac{5.2}{100} \times 1\ \text{kg} = 0.052\ \text{kg}$$

$$\text{Amount of O in 1 kg coal} = \frac{12.8}{100} \times 1\ \text{kg} = 0.128\ \text{kg}$$

$$\text{Amount of S in 1 kg coal} = \frac{1.2}{100} \times 1\ \text{kg} = 0.012\ \text{kg}$$

(N and ash do not get burnt, do not require air, during combustion of coal).

$$O_2\ \text{quantity} = \left[\frac{32}{12}\text{C} + 8\ \text{H} + \text{S} - \text{O}\right]\text{kg}$$

(C, H, S, O are the amount of elements in the fuel )

$$\therefore\ O_2\ \text{quantity} = \left(\frac{32}{12} \times 0.75 + 8 \times 0.052 + 0.0128 - 0.128\right)$$

$$= (2 + 0.416 + 0.0128 - 0.128)$$

$$= 2.3\ \text{kg oxygen}$$

$$\text{Air quantity} = \frac{O_2\ \text{quantity}\ (100 + \%\ \text{excess air})}{23}$$

$$= \frac{2.3\ (100 + 0)}{23} = 10\ \text{kg air}$$

**Ex. 16)** A sample of coal requires 20% excess air for complete combustion. Calculate weight of air for 250 gm of the coal, if its composition is C = 81%, H = 4%, N = 1.5%, S = 1.2%, O = 3%, ash = 9.35.May 2010

Soln. :

$$\text{Weight of coal} = 250\ \text{gm}$$

$$\text{Weight of carbon in 250 gm coal} = \frac{81}{100} \times 250\ \text{gm} = 202.5\ \text{gm}$$

$$\text{Weight of hydrogen in 250 gm coal} = \frac{4}{100} \times 250\ \text{gm} = 10\ \text{gm}$$

$$\text{Weight of sulphur in 250 gm coal} = \frac{1.2}{100} \times 250\ \text{gm} = 3\text{gm}$$

$$\text{Weight of oxygen in 250 gm coal} = \frac{3}{100} \times 250 = 7.5\ \text{gm}$$

(N and ash do not burn, do not require oxygen)

$$O_2\ \text{quantity} = \left[\frac{32}{12}\text{C} + 8\ \text{H} + \text{S} - \text{O}\right]\text{gm}$$

(C, H, S, O are the weights of elements in gms)

$$\therefore\ O_2\ \text{quantity} = \frac{32}{12} \times 202.5 + 8 \times 10 + 3 - 7.5\ \text{gm}$$

$$= 615.5\ \text{gm oxygen}$$

$$\text{Quantity of air} = \frac{O_2\ \text{quantity}\ (100 + \%\ \text{excess air})}{23}$$

$$= \frac{615.5\ (100 + 20)}{23}$$

$$= 3211.3\ \text{gm air}$$

$$= 3.2113\ \text{kg air}$$

**Ex. 17)** A gas used in internal combustion engine contains, $H_2$ = 45 %, CO = 15% , $CH_4$ =35% $N_2$= 5 % Find the minimum quantity (volume ) of air required per 1 $m^3$ of the gas for complete combustion.

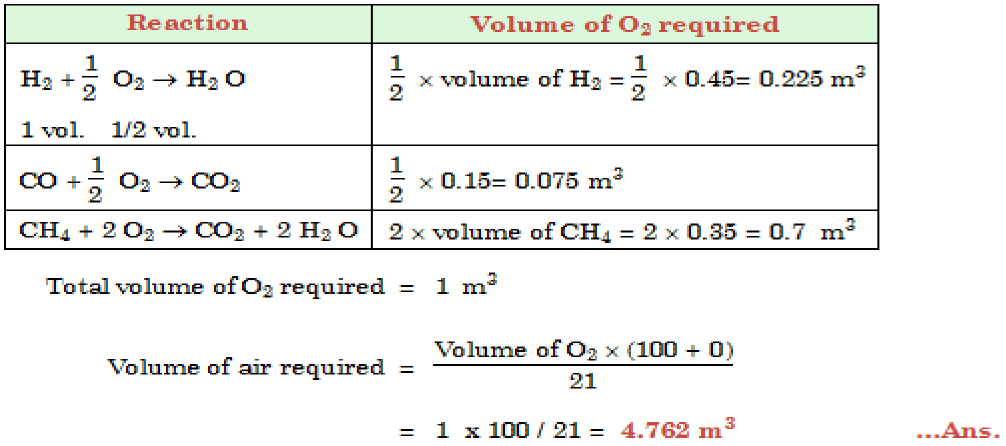
Soln. :

Volume of $H_2$ in 1 $m^3$ gas = 45 × 1 $m^3$ / 100 = 0.45 $m^3$

Similarly, Volume of $CH_4$ = 35 × 1 / 100 = 0.35 $m^3$

Volume of CO = 15 × 1 / 100 = 0.15 m3

($N_2$ is not combustible)



| Reaction | Volume of $O_2$ required |
|---|---|
| $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$<br>1 vol. 1/2 vol. | $\frac{1}{2} \times$ volume of $H_2 = \frac{1}{2} \times 0.45 = 0.225\ m^3$ |
| $CO + \frac{1}{2} O_2 \rightarrow CO_2$ | $\frac{1}{2} \times 0.15 = 0.075\ m^3$ |
| $CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$ | $2 \times$ volume of $CH_4 = 2 \times 0.35 = 0.7\ m^3$ |

Total volume of $O_2$ required = 1 $m^3$

$$\text{Volume of air required} = \frac{\text{Volume of } O_2 \times (100 + 0)}{21}$$

$$= 1 \times 100 / 21 = 4.762\ m^3$$

...Ans.