

CHEMISTRY

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MODULE-I

ELECTRO CHEMISTRY AND CORROSION

1.0 Introduction:-

Chemistry is the Study of matter, its properties and the changes it may undergo. All matter is electrical in nature. An atom is made up of sub atomic particles like electrons, protons and neutrons etc.

Electro chemistry is a branch of chemistry which deals with the transformation of electrical energy into chemical energy or chemical into electrical energy.

1.1 Concept of electrochemistry:

Electrical Conduction: The substances are divided into 4 types depending upon their capability of flow of electrons.

Conductors: The Substances which allows electricity to pass through them are called conductors.

Ex: - Metals, metal sulphides, acids, alkalis, salt sol. and fused salts

The electrical conductors are of two types.

1. Metallic or Electronic conductors.
2. Electrolytic conductors

i) Non-conductors: The substances which do not allow electricity are called non-conductors. Ex: Pure water, dry wood, rubber, paper, non-metals etc.

ii) Semi-conductors: The substances which partially conduct electricity are called semi- conductors. The conducting properties of semi-conducting properties are increased by the addition of certain impurities called “dopping”.

Ex: ‘si’ and addition of V group elements like ‘p’ ‘si’ produces n-type semi-conductor. On addition of iii group element like ‘B’, Al, ‘si’ produces p-type of semi-conductor.

1.1.1. Electro chemical cell (or) Galvanic cell:-

Galvanic cell is a device in which chemical energy is converted into electrical energy. These cells are called Electrochemical cells or voltaic cells. Daniel cell is an example for galvanic cell.

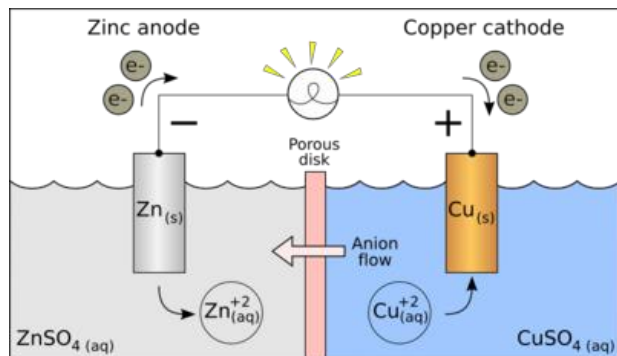


Fig1.1.1 Galvanic cell

This cell is made up of two half cells. One is oxidation or anodic half cell. The other is reduction or cathodic half-cell. The first half cell consists of 'Zn' electrode dipped in ZnSO_4 solution and second half cell consists of 'Cu' electrode dipped in CuSO_4 solution. Both the half cells are connected externally by metallic conductor. And internally by 'salt bridge' salt bridge is a U- tube containing concentrated solution of KCl or NH_4NO_3 in agar-agar gel contained porous pot. It provides electrical contact between two solutions.

The following reactions take place in the cell.

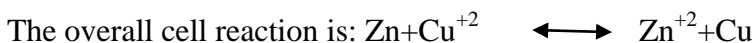
At anode:



At cathode:



The movement of electrons from Zn to Cu produces a current in the circuit.



The galvanic cell can be represented by



The passage of electrons from one electrode to other causes the potential difference between them which is called E.M.F.

1.1.2 EMF

The difference of potential which causes flow of electrons from an electrode of higher potential to an electrode of lower potential is called Electro motive force (EMF) of the cell.

The E.M.F of galvanic cell is calculated by the reduction half – cell potentials using to following ex.

$$E_{\text{cell}} = E_{(\text{right})} - E_{(\text{left})}$$

E_{cell} EMF of the cell.

E_{right} reduction potential of right hand side

electrode. E_{left} reduction potential of left hand side

electrode.

Applications of EMF measurement:-

1. Potentiometric titrations can be carried out.
2. Transport number of ions can be determined.
3. P^H can be measured.
4. Hydrolysis const, can be determined.
5. Solubility of sparingly soluble salts can be found.

1.1.3 Differences between Galvanic cell and Electrolytic cell.

Galvanic cell / Electrochemical cell	Electrolytic cell
<ol style="list-style-type: none">1. In this cell, chemical energy is converted into electrical energy.2. In this cell anode is –ve electrode and cathode is +ve electrode.3. Salt bridge is required.4. This process is reversible and spontaneous.5. EMF of the cell is +ve.	<ol style="list-style-type: none">1. In this cell electrical energy is converted into chemical energy.2. In this cell anode is +ve electrode and cathode is –ve electrode.3. Salt bridge is not required.4. This process is irreversible and not spontaneous.5. EMF of the cell is –ve.

1.2 Single electrode potential :- (E) When a metal rod dipped in its salt solution, the metal atom tends either to lose electrons (oxidation) or to accept electrons (reduction). The process of oxidation or reduction depends on the nature of metal. In this process, there develops a potential between the metal atom and its corresponding ion called the electrode potential. There is a dynamic equilibrium between the metal and metal ion and the potential diff. between the two is called electrode potential. It is measured in volts.

1.2.1 Standard electrode potential (E^0):-

The potential exhibited by single at unit concentration of its metal ion at 25°C is called standard electrode potential (E^0)

Eg: E of $\text{Cu}^{+2} / \text{Cu} = E^0$ when concentration of Cu^{+2} is 1M. E^0 value of single electrode is determined experimentally by combining the single electrode with standard hydrogen electrode.

1.3 Electrochemical series:-

The electrode potentials of different electrodes can be finding using standard hydrogen electrode. The potential of hydrogen electrode is assumed as zero volts. So the measured Emf. Itself is the standard electrode potential of that electrode.

The arrangement of different electrode potential s of different electrodes from highest -ve to highest +ve are called electrochemical series.

Electrode	Half-cell reaction	E^0 volts (standard reduction potential)
Li^+ / Li	$\text{Li}^+ + \text{e}^- \rightarrow \text{Li}$	-3.04
K^+ / K	$\text{K}^+ + \text{e}^- \rightarrow \text{K}$	-2.9
$\text{Ca}^{+2} / \text{Ca}$	$\text{Ca}^{+2} + 2\text{e}^- \rightarrow \text{Ca}$	-2.8
Na^+ / Na	$\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$	-2.7
$\text{Mg}^{+2} / \text{Mg}$	$\text{Mg}^{+2} + 2\text{e}^- \rightarrow \text{Mg}$	-2.3
$\text{Zn}^{+2} / \text{Zn}$	$\text{Zn}^{+2} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76
$\text{Fe}^{+2} / \text{Fe}$	$\text{Fe}^{+2} + 2\text{e}^- \rightarrow \text{Fe}$	-0.4
$\text{H}^+ / \text{H}_2, \text{pf}$	$\text{H}^+ + \text{e}^- \rightarrow \text{H}_2$	+ 0

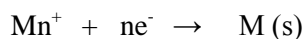
Cu^{+2}/Cu	$\text{Cu}^{+2} + 2\text{e}^{-} \rightarrow \text{Cu}$	+0.15
Ag^{+}/Ag	$\text{Ag}^{+} + \text{e}^{-} \rightarrow \text{Ag}$	+0.7
$\text{Pt}, \text{Cl}_2/\text{Cl}^{-}$	$\text{Cl}_2 + 2\text{e}^{-} \rightarrow 2\text{Cl}^{-}$	+1.3
$\text{Pt}, \text{F}_2/\text{F}^{-}$	$\text{F}_2 + 2\text{e}^{-} \rightarrow 2\text{F}^{-}$	+2.8

From the above series we can understand that the metals with higher –ve potentials are stronger reducing agents, and the metals with higher +ve potentials are stronger oxidizing agents. The metals with higher –ve potentials displaces a metals with lower –ve potentials.

1.4 Nernst Equation:

It tells us the effect of electrolyte concentration on-electrode potential

Consider a general electrode reaction



For this electrode reaction, free energy change (ΔG) can be calculated provided standard free energy change (ΔG^0)

Gas constant (R), temperature (T), activity of product and activity of reactant are known using the following equation.

$$\Delta G = \Delta G^0 + RT \ln (a_{\text{product}} / a_{\text{reactant}})$$

$$\text{Since } \Delta G = -nFE \quad \text{and} \quad \Delta G^0 = -nFE^0$$

Hence

$$E = E^0 - \frac{2.303 RT}{nF} \log (a_{\text{product}} / a_{\text{reactant}})$$

This is Nernst equation where

E = Electrode potential

E^0 = Standard electrode potential

F = faraday of electricity (96500 C)

T = temperature at 298k

R = Gas constant ($8.314 \text{ k}^{-1} \text{ mol}^{-1}$)

a = activity

at 298k

putting the value of F = faraday of electricity (96500 C) and R = Gas constant ($8.314 \text{ k}^{-1} \text{ mol}^{-1}$)

we get

$$E = E^0 - 0.0591/n \log (a_{\text{product}} / a_{\text{reactant}})$$

In dilute solutions, activities may be replaced by molar concentrations terms,

$$E = E^0 - 0.0591 / n \log ([M(s)] / [M^{n+}_{(aq)}])$$

For pure solid ($[M(s)] = 1$)

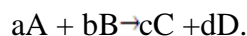
$$E = E^0 - 0.0591 / n \log (1 / [M^{n+}_{(aq)}])$$

$$E = E^0 - 0.0591 / n \log [M^{n+}_{(aq)}]$$

The above equation is Nernst equation for the electrode at 298 k

Nernst studied the theoretical relationship between electrode reaction and the corresponding cell e.m.f. This relationship generally Known as Nernst equation.

Consider a galvanic cell



Where a,b,c,d represents no. of moles respectively at equilibrium.

$$E = E^0 - 2.303 RT / nF \log ([C]^c [D]^d / [A]^a [B]^b)$$

Thus Nernst equation is applicable for the determination of Emf of cell

Similarly, for the cell reaction.

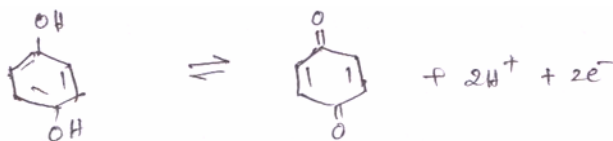
$$E = E^0 - 2.303 RT / nF \log ([Zn^{+2}(1m)/Cu^{+2}(1m)])$$

1.5 Reference Electrodes:-

Because of the inconveniences in the usage of Hydrogen electrode like maintenance of accurate pressure, inconvenience in handling gas secondary electrodes were developed.

1.5.1 Quinhydrone Electrode:-

It is a type of redox electrode which can be used to measure H^+ concentration of a solution. Quinhydrone is an equimolar (1:1) mixture of quinone and hydroquinone. The electrode consists of pt electrode dipped in an acid or base test solution which is saturated with quinhydrone. The electrode reaction is.



Quinone(Q)

Hydroquinone (QH₂)

Each one of the substances can be easily get oxidized or reduced to other.

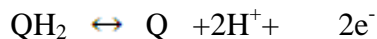


Quinone

Hydroquinone

Quinhydrone

The electrode reaction may be represented as



The electrode potential at 25⁰c is

$$E_Q = E_Q^0 - \log \frac{[Q]}{[QH_2]}$$

[Q] = [QH₂], because the concentration of

quinone and hydroquinone are equal

$$E_Q = E_Q^0 - \frac{RT}{2F} \log [H^+]^2$$

$$= E_Q^0 - \frac{RT}{F} \log [H^+]$$

By substituting the values of R, T, F,

$$E_Q = E_Q^0 - 0.0591 \log [H^+]$$

$$= E_Q^0 + 0.0591 P^H.$$

This eq' is used to calculate the p^H if E_Q and E_Q^0 values are known.

Advantages:-

- i. This electrode is simple to set up and needs no removal of air.
- ii. We can measure p^H value quicker than hydrogen gas electrode

Limitations:-

- i. This electrode cannot be used at P^H values greater than 8.
- ii. This electrode fails in presence of strong oxidizing and reducing agents.

Types of electrodes:

1.5.2 Standard calomel electrode (SCE)

The calomel electrode consists of a glass tube having two side tubes. A small quantity of pure mercury is placed at the bottom of the vessel and is covered with a paste of Hg and Hg_2Cl_2 . KCl solution of known concentration is filled through side tube, Shown on the right side of the vessel. The KCl sol. is filled in the left side tube which helps to make a connection through a salt bridge with the other electrode, which potential has to be determined.

A 'pt' wire is sealed into a glass tube as shown in the fig which is in contact with Hg.

When the cell is set up it is immersed in the given solution. The concentration of KCl. The electrode potentials of calomel electrode of different concentrations at 25°C are

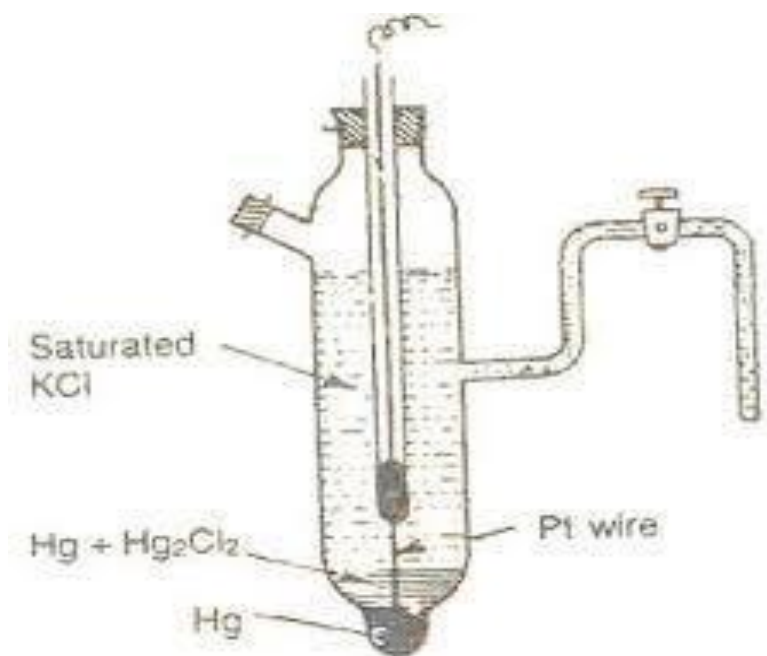


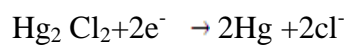
Fig1.5.2 Standard calomel electrode

0.1 M KCl / Hg_2Cl_2 (s) / Hg, pt \rightarrow 0.33v

1M KCl / Hg_2Cl_2 (s) / Hg, pt \rightarrow 0.28v

Saturated kcl / Hg_2Cl_2 (s) / Hg, pt \rightarrow 0.24v

The corresponding electrode reaction is



Nernst's expression is,

$$E_{\text{Hg}_2\text{Cl}_2/\text{Cl}^-} = E^{\circ}_{\text{Hg}_2\text{Cl}_2/\text{Cl}^-} - \frac{RT}{2F} \log a_{\text{Cl}^-}$$

$$= E^{\circ}_{\text{Hg}_2\text{Cl}_2/\text{Cl}^-} - \frac{RT}{2F} \log a_{\text{Cl}^-}$$

1.6 Battery Chemistry

Batteries:

When two or more electrochemical cells are electrically interconnected, each of which containing two electrodes and an electrolyte is called a Battery.

Batteries are classified into a two categories depending on their recharging capabilities.

Primary Batteries: “These are non-rechargeable and are meant for single use and to be discarded after use”.

These are non-reversed and are less expensive and are offer used in ordinary gadgets like torch lights, watches and toys.

Eg: Leclanche cell, Dry cell.

Secondary Batteries: - These are rechargeable and are meant for multi cycle use. After every use the electrochemical reaction could be reversed by external application fades or lost due to leakage or internal short circuit. Eg: Lead-acid cell, Ni/cd cell

Differences between Primary and secondary batteries:

Primary cells	Secondary cells
<ol style="list-style-type: none">1. These are non-rechargeable and meant for a single use and to be discarded after use.2. Cell reaction is not reversible.3. Cannot be rechargeable.4. Less expensive.5. Can be used as long as the materials are active in their composition. <p>Eg: Leclanche cell, ‘Li’ Cells.</p>	<ol style="list-style-type: none">1. These are rechargeable and meant for multi cycle use.2. Cell reaction can be reversed.3. Can be rechargeable.4. Expensive.5. Can be used again and again by recharging the cell. <p>Eg; Lead- acid cell, Ni-cd cells.</p>

1.6 Primary Batteries:

1.6.1 Dry cell (Leclanche cell):

Anode: Zinc

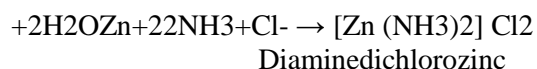
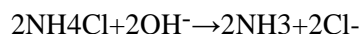
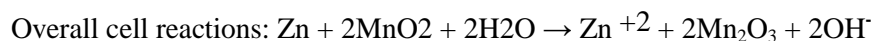
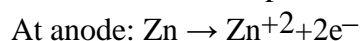
Cathode: Graphite rod

Electrolyte: paste of NH_4Cl and ZnCl_2

Emf: 1.5V.

Dry cell consists of a cylindrical Zinc container which acts as an anode. A graphite rod displaced in the center. The graphite rod does not touch the base and it acts as a cathode. The graphite rod is surrounded by powdered MnO_2 and carbon. The remaining Space in between cathode and anode is filled with a paste of NH_4Cl and ZnCl_2 . The graphite rod is fitted with a Metal cap and the cylinder is sealed at the top with a pitch.

The reactions takes place in the cell are:



The EMF of the cell is about 1.5volts.

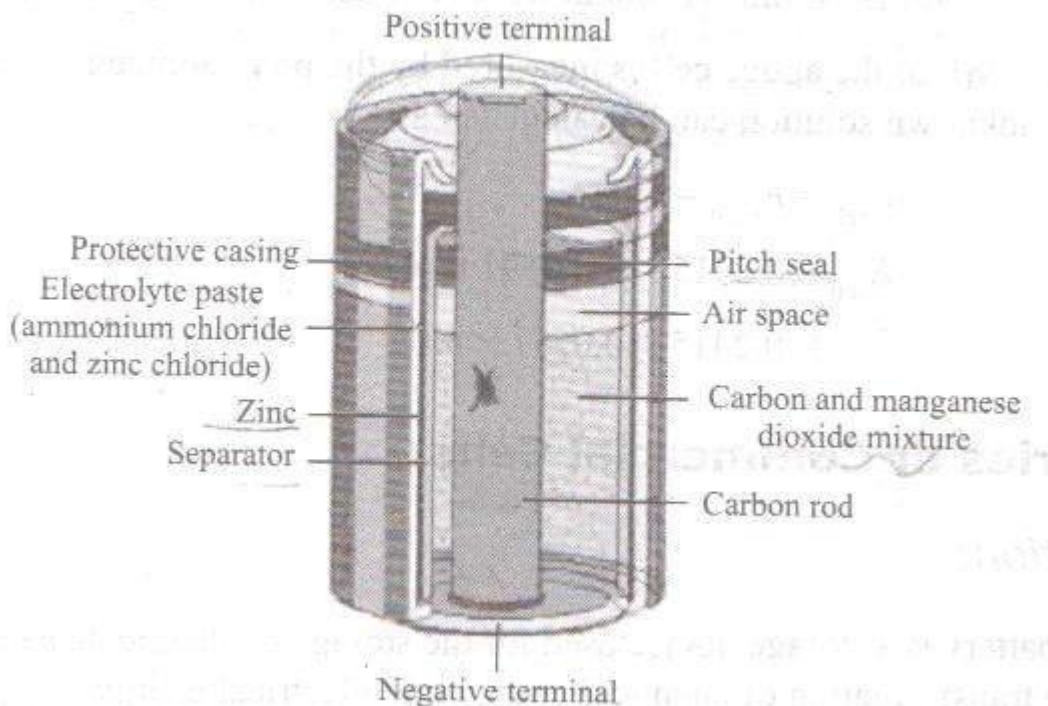


Fig 1.6.1 Dry Cell

1.6.2 Secondary Batteries:-

Lead – acidcell:

Anode: Sponge metallic lead

Cathode: Lead dioxide PbO_2

Electrolyte: Aqueous H_2SO_4 . **Emf: 2V**

Cell reactions:



The e.m.f. produced by the cell is 2v

Applications

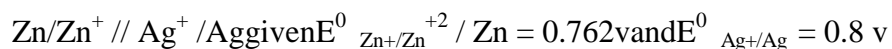
- i. Automobile and construction equipment.
- ii. Standby system for engine batteries

Advantages:-

Low cost, long life cycle, Ability to withstand mistreatment, perform well in high and low temperature.

1.7 Numerical Problems

Q: Calculate the emf for the cell,



A: Given cell is $\text{Zn}/\text{Zn}^{+2} // \text{Ag}^{+}/\text{Ag}$.

$$E^0_{\text{Zn}^{+2}/\text{Zn}} = 0.762\text{ v}$$

$$E^0_{\text{Ag}^{+}/\text{Ag}} = 0.8\text{ v}$$

$$\begin{aligned} E^0_{\text{cell}} &= E^0_{\text{right}} - E^0_{\text{left}} \\ &= 0.8 - (-0.762) \\ &= 1.562\text{ v}. \end{aligned}$$

4Q: Calculate the $E^0_{\text{Cu}^{+2}/\text{Cu}}$, given $E^-_{\text{Cu}^{+2}/\text{Cu}} = 0.296\text{ v}$ and $[\text{Cu}^{+2}] = 0.015\text{M}$.

A: cell reaction is $\text{Cu} \rightarrow \text{Cu}^{+2} + 2\text{e}^-$

$$E = E^0 + \frac{0.0591}{n} \log[\text{Cu}^{+2}]$$

$$0.296 = E^0 + \frac{0.0591}{2} \log[\text{Cu}^{+2}]$$

$$E^0 = 0.296 - \frac{0.0591}{2} \log(0.015)$$

$$= 0.296 - 0.2955 \quad (-1.8239)$$

$$= 0.296 + 0.0538$$

$$= 0.3498 \text{ V}$$

5Q: Write the half cell and net cell reactions for the following cell,

$\text{Zn} / \text{ZnSO}_4 (\text{aq}) // \text{CuSO}_4 (\text{aq}) / \text{Cu}$.

Calculate the standard emf of the cell given,

$E^0_{\text{Zn}^{+2}/\text{Zn}} = 0.76 \text{ V}$ and $E^0_{\text{Cu}^{+2}/\text{Cu}} = +0.34 \text{ V}$. A:

Half cell reactions

At anode: $\text{Zn} \rightarrow \text{Zn}^{+2} + 2\text{e}^-$

At cathode: $\text{Cu}^{+2} + 2\text{e}^- \rightarrow \text{Cu}$.

Net cell reaction = $\text{Zn} + \text{Cu}^{+2} \rightarrow \text{Zn}^{+2} + \text{Cu}$.

$$E^0_{\text{cell}} = E^0_{\text{Cathode}} - E^0_{\text{Anode}}$$

$$= E^0_{\text{Cu}^{+2}/\text{Cu}} - E^0_{\text{Zn}^{+2}/\text{Zn}}$$

$$= 0.34 - (-0.76)$$

$$= 1.1 \text{ V}$$

Causes and effects of corrosion

1.8 Corrosion

The surface of almost all the metals begin to decay more or less rapidly when exposed to atmospheric gases, water or other reactive liquid medium.

The process of decay metal by environmental attack is known as corrosion.

Metals undergo corrosion and convert to their oxides, hydroxides, carbonates, sulphides etc.

E.g. Iron undergoes corrosion to form reddish brown colour rust [$\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$].

Copper undergoes corrosion to form a green film of basic carbonate [$\text{CuCO}_3 + \text{Cu}(\text{OH})_2$]

1.8.1 Causes of corrosion

1. The metals exist in nature in the form of their minerals or ores, in the stable combined forms as oxides, chlorides, silicates, carbonates, sulphides etc.
2. During the extraction of metals, these ores are reduced to metallic state by supplying considerable amounts of energy.
3. Hence the isolated pure metals are regarded as excited states than their corresponding ores. So metals have natural tendency to go back to their combined state (minerals/ores).

When metal is exposed to atmospheric gases, moisture, liquids etc., and the metal surface reacts and forms more thermodynamically stabled compounds.

Effects of corrosion

1. Wastage of metal in the form of its compounds.
2. The valuable metallic properties like conductivity, malleability, ductility etc. are lost due to corrosion.
3. Life span and efficiency of metallic parts of machinery and fabrications is reduced.

1.8.2 Theories of corrosion

1.8.2.1 Dry corrosion or Chemical corrosion

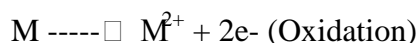
This type of Corrosion occurs mainly through the direct chemical action of atmospheric gasses like O_2 , halogens, H_2S , SO_2 , N_2 or anhydrous inorganic liquid with the metal surface.

There are three types of chemical Corrosion:

- (1) Oxidation corrosion
- (2) Corrosion due to other gases
- (3) Liquid metal corrosion

(1) Oxidation Corrosion: This is carried out by the direct action of oxygen low or high

Temperatures on metals in absence of moisture. Alkali metals and Alkaline earth metals are rapidly oxidized at low temperatures. At high temperature all metals are oxidized (except Ag, Au, and Pt).



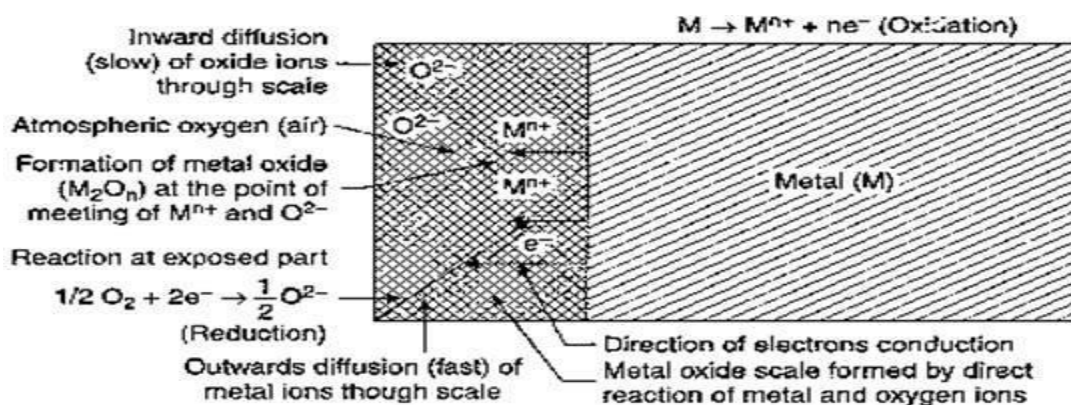
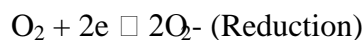


Fig.1.8.2.1 Oxidation corrosion

Mechanism: Initially the surface of metal undergoes oxidation and the resulting metal oxide scale forms a barrier which restricts further oxidation. The extent of corrosion depends upon the nature of metal oxide.

(a) If the metal oxide is stable, it behaves as a protective layer which prevents further Corrosion.

E.g., the oxide films of Al, Sn, Pb, Cu, Cr, W etc. are stable and therefore further corrosion is prohibited.

(b) If the metal oxide is unstable, the oxide layer formed decomposes back into metal and oxygen. Oxidation corrosion is not possible.

E.g., Ag, Au and Pt do not undergo oxidation corrosion.

(c) If the metal oxide layer is volatile, then the oxide layer volatilizes after formation and leaves the underlying metal surface exposed for further attack. This causes continuous corrosion which is excessive in molybdenum oxide (MoO_3).

(d) If the metal oxide layer is porous, the oxide layer formed has pores or cracks. In this case the atmospheric oxygen penetrates through the pores or cracks and corrode the underlying metal surface. This causes continuous corrosion till conversion of metal into its oxide is completed.

Ex: Alkali and alkaline earth metals (Li, Na, K, Mg etc.)

(2) Corrosion due to other gases: This type of corrosion is due to gases like SO_2 , CO_2 , Cl_2 , H_2S , F_2 etc. In this corrosion, the extent of corrosive effect depends mainly on the chemical affinity between the metal and the gas involved. The degree of attack depends on the formation

of protective or non protective films on the metal surface which is explained on the basis of Pilling Bed worth rule.

(i) If the volume of the corrosion film formed is more than the underlying metal, it is strongly adherent; non-porous does not allow the penetration of corrosive gases.



(ii) If the volume of the corrosion film formed is less than the underlying metal, it forms

Pores/cracks and allow the penetration of corrosive gases leading to corrosion of the underlying metal.

Ex. In petroleum industry, H_2S gas at high temperature reacts with steel forming a FeS scale. Fe (steel) + H_2S FeS (porous)

(3) Liquid metal corrosion: This corrosion is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. 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.

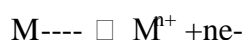
Eg. Coolant (sodium metal) leads to corrosion of cadmium in nuclear reactors.

1.8.2.2 Wet corrosion or electrochemical corrosion

- This type of Corrosion occurs where a conducting liquid is in contact with the metal. This corrosion occurs due to the existence of separate anodic and cathodic parts, between which current flows through the conducting solution.
- At anodic area, oxidation reaction occurs there by destroying the anodic metal either by dissolution or formation of compounds. Hence corrosion always occurs at anodic parts.

Mechanism: Electrochemical corrosion involves flow of electrons between anode and cathode.

The anodic reaction involves dissolution of metal liberating free electrons.



The cathodic reaction consumes electrons with either evolution of hydrogen or absorption of oxygen which depends on the nature of corrosive environment.

Evolution of hydrogen: This type of corrosion occurs in acidic medium.

E.g. Considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with

Liberation of electrons.

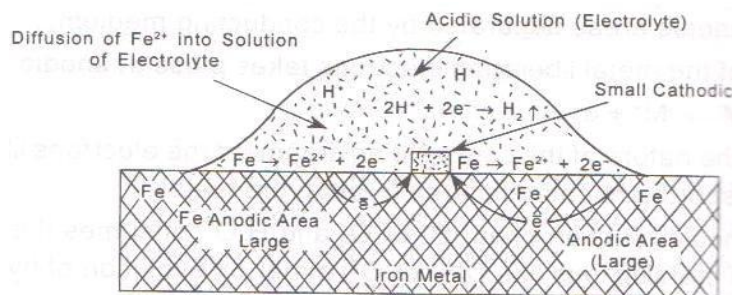
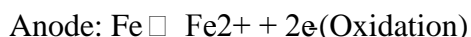
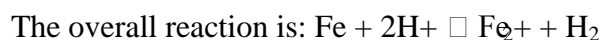
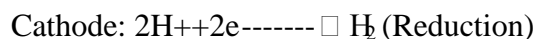


Fig.1.8.2.2 Hydrogen evolution



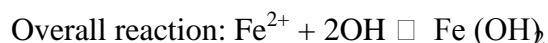
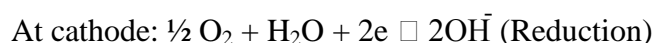
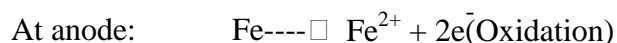
The electrons released flow through the metal from anode to cathode, whereas H^+ ions of acidic solution are eliminated as hydrogen gas.



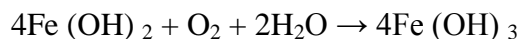
This type of corrosion causes displacement of hydrogen ions from the solution by metal ions. All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of H_2 gas. The anodes are large areas, whereas cathodes are small areas.

Absorption of oxygen: For example, rusting of iron in neutral aqueous solution of electrolytes in presence of atmospheric oxygen. Usually the surface of iron is coated with a thin film of iron oxide. If the film develops cracks, anodic areas are created on the surface. While the metal parts act as cathodes. It shows that anodes are small areas, while the rest metallic part forms large

Cathodes. The released electrons flow from anode to cathode through iron metal.



If oxygen is in excess, ferrous hydroxide is easily oxidized to ferric hydroxide.



The product called yellow rust corresponds to $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

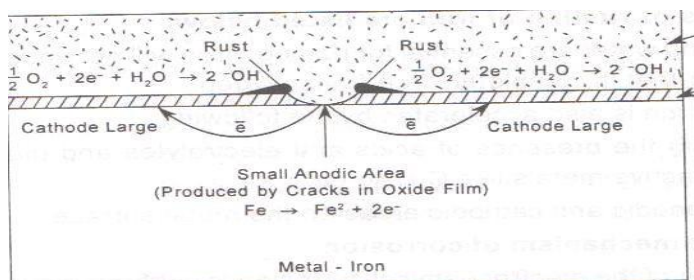


Fig.1.8.2.2 Oxygen absorption corrosion

1.8.3 Types of corrosion

1. Waterline corrosion or Concentration cell corrosion

This type of corrosion occurs due to electrochemical attack of the metal surface exposed to electrolyte of varying concentrations or varying aeration.

This type of corrosion is due to

- (i) Difference in concentration of metal ions.
- (ii) Difference in the exposure to air/oxygen (Differential aeration corrosion)
- (iii) Difference in temperature.
 - Differential aeration corrosion is the most common type of concentration cell corrosion. When a metal is exposed to different air concentrations, it has been found to be poorly oxygenated of the metal becomes anodic and well oxygenated part becomes cathodic.
 - The potential difference is created which causes the flow of electrons from anode (metallic part immersed in NaCl solution) to cathode (exposed to atmosphere).

Eg. Zn rod immersed deep in NaCl solution:

Anode Zn rod above NaCl solution: Cathode

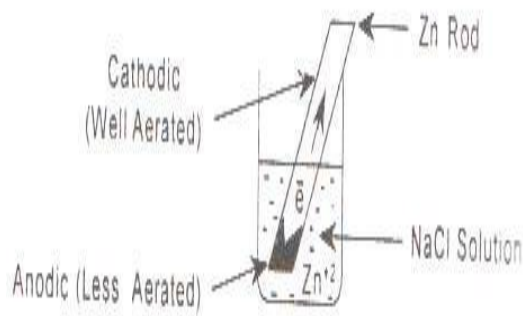


Fig 1.8.3 Concentration cell corrosion

Pitting Corrosion



Fig 1.8.4 Pitting Corrosion

Pitting corrosion is a localized form of corrosion that leads to the creation of small holes or “pits” in the metal. This form of corrosion is mainly found on passive metals. Passive metals and alloys, such as aluminium, titanium and stainless steel owe their corrosion resistance to a thin oxide layer on the surface with a thickness of only a few nanometers. The corrosion initiating process starts with a local break-down of the passive layer. Local corrosive attack can be initiated on stainless steels, for example, by chloride ions.

The most significant phases of this corrosion phenomenon on stainless steel. Pitting corrosion can be quite problematic. Whereas uniform corrosion can be seen clearly on the surface, pitting corrosion often appears only as small pinholes on the surface. The amount of material removed below the pinholes is generally unknown, as hidden cavities may form, making pitting corrosion more difficult to detect and predict. Technically, there is no reasonable way to control pitting corrosion. This form of corrosion must be excluded right from the start through design considerations and use of the right material

1.8.5 Factors effecting rate of corrosion

The rate and extent of corrosion depends upon various factors due to nature of metal and nature of corroding environment.

1.8.5.1 Factors due to nature of metal

1. Purity of the metal: Heterogeneity of the metal is due to the presence of impurities which form tiny electrochemical cells at the exposed parts. The anodic parts get corroded.

2. Electrode potentials: metals with higher reduction potentials do not corrode easily. They are noble metals like gold, platinum and silver. Whereas the metals with lower reduction potentials readily undergo corrosion (eg. Zn, Mg, Al etc.).

3. Position of metal in galvanic series: Metals which possess low reduction potentials and occupy higher end of galvanic series undergo corrosion easily.

Metals which possess high reduction potentials and occupy lower end of galvanic series do not undergo corrosion and they get protected.

- When two metals are in electrical contact in presence of an electrolyte, then the metal which is more active undergoes corrosion.
- The rate of corrosion depends on the difference in their position in Galvanic series. Greater the difference more will be the extent of corrosion at anode.

Eg. The potential difference between Fe and Cu is 0.78V which is more than that between Fe and Sn (0.30V). Therefore, Fe corrodes faster when in contact with Cu than that with Sn. on this account, the use of dissimilar metals should be avoided wherever possible (Eg. Bolt & nuts, screw & washer).

4. **Relative areas of anodic and cathodic cells:** the relative areas of corrosion is influenced by cathodic to anodic cells.
5. If the metal has small anodic and large cathodic area, the rate of corrosion is very high. This is because the electrons are liberated at anode which is consumed at cathode. If the cathodic area is larger, the liberated electrons are rapidly consumed at cathode. This further enhances the anodic reaction leading to increase the rate of corrosion.
6. **Hydrogen over voltage:** when a cathode reaction is hydrogen evolution type, the metal with Lower hydrogen over voltage on its surface is more susceptible for corrosion, since the liberation of hydrogen gas is easy at this condition. Hence the cathodic reaction is very fast which in turn Makes anodic reaction fast. Hence the rate of corrosion increases. Higher the over voltage, lesser is the corrosion.
7. **Physical state of metal:** Metals with small grain size have more tendencies to undergo corrosion. Metal with more stress/strain also undergoes corrosion easily.

8. **Nature of surface film:** If the corrosion product formed is more stable, insoluble and nonporous, it acts as protective layer and prevents further corrosion (Eg. Ti, Al and Cr). If the corrosion product is porous, volatile and soluble, it further enhances the corrosion (Fe, Zn and Mg).

1.8.5.2 Factors due to nature of corrosive environment

1. **Temperature:** the rate of corrosion reactions increases with increase in temperature.

2. **Humidity in air:** the moisture or humidity present in atmosphere furnishes water to the electrolyte which is essential for setting up of an electrochemical cell. The oxide film form as the tendency to absorb moisture which creates another electrochemical cell.

3. **Presence of impurities:** Atmosphere is contaminated with gases like CO_2 , SO_2 , H_2S ; fumes of H_2SO_4 , HCl etc. and other suspended particles in the vicinity of industrial areas. They are Responsible for electrical conductivity, thereby increasing corrosion.

4. **P^{H} value:** pH value of the medium has the greater effect on corrosion. Acidic pH increases the rate of corrosion.

5. **Amount of oxygen in atmosphere:** As the percentage of oxygen in atmosphere increases, the rate of corrosion also increases due to the formation of oxygen concentration cell. The decay of metal occurs at the anodic part and the cathodic part of the metal is protected.

1.8.5 Corrosion control methods

I. Cathodic protection

The method of protecting the base metal by making it to behave like a cathode is called as cathodic protection.

There are two types of cathodic protection

- (a) Sacrificial anode method
- (b) Impressed current method.

a. Sacrificial anode method

- In this protection method, the metallic structure to be protected (base metal) is connected by a wire to a more anodic metal so that all the corrosion is concentrated at this more anodic metal.
- The more anodic metal itself gets corroded slowly, while the parent structure (cathodic) is

protected. The more active metal so employed is called sacrificial anode. The corroded sacrificial anode is replaced by a fresh one, when consumed completely.

- Metals commonly employed as sacrificial anode are Mg, Zn, Al and their alloys which possess low reduction potential and occupies higher end in electrochemical series.

Eg. A ship-hull which is made up of steel is connected to sacrificial anode (Zn-blocks) which undergoes corrosion leaving the base metal protected.

Eg. The underground water pipelines and water tanks are also protected by sacrificial anode method. By referring to the electrochemical series, the metal with low reduction potential is connected to the base metal which acts as anode.

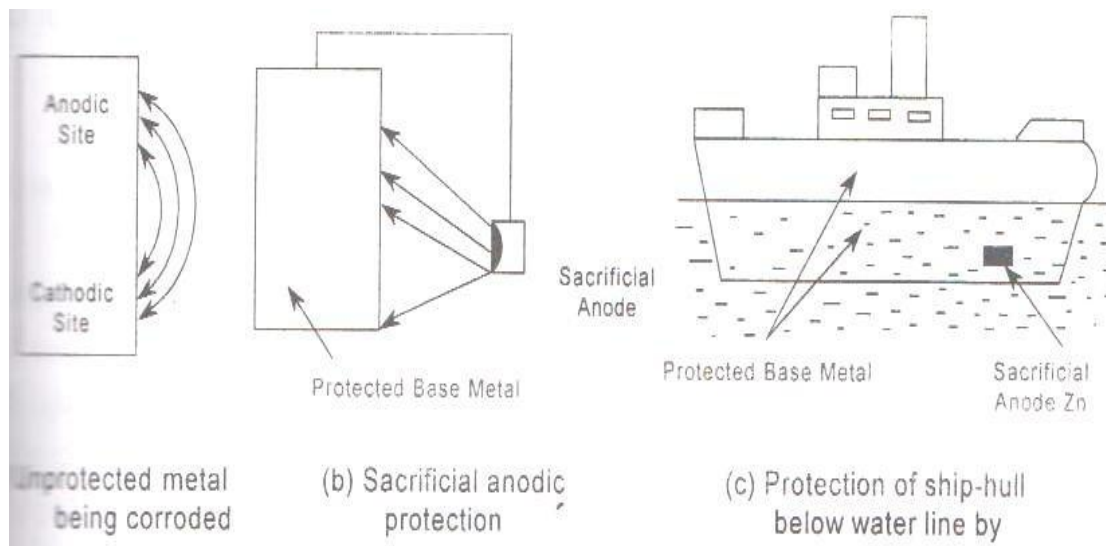


Fig.1.25 Sacrificial anode method: ship hull and underground water pipeline

b. Impressed current method

- In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode.
- The impressed current is slightly higher than the corrosion current. Thus the anodic corroding metal becomes cathodic and protected from corrosion.
- The impressed current is taken from a battery or rectified on A.C. line. The impressed current protection method is used for water tanks, water & oil pipe lines, transmission line towers etc.

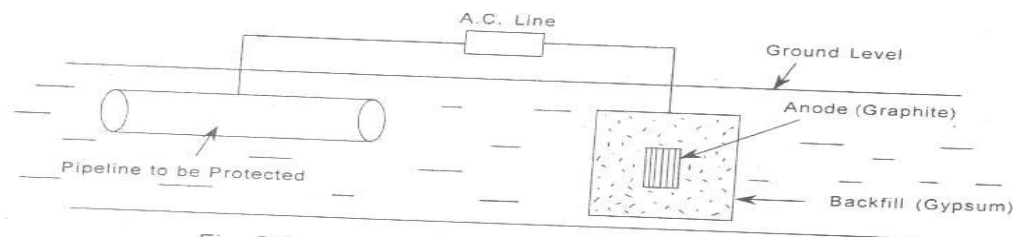


Fig.1.26 Impressed current method

1.8.4 Metallic coatings

The surface of the base metal is coated with another metal (coating metal). Metallic coatings are broadly classified into anodic and cathodic coatings.

1.8.4.1 Anodic coating: the metal used for the surface coating is more anodic than the base metal which is to be protected.

- For example, coating of Al, Cd and Zn on steel surface are anodic because their electrode potentials are lower than that of the base metal iron. Therefore, anodic coatings protect the underlying base metal sacrificially.
- The formation of pores and cracks over the metallic coating exposes the base metal and a galvanic cell is formed between the base metal and coating metal. The coating metal dissolves anodically and the base metal is protected.

1.8.7.2 Cathodic coating:

- Cathodic coatings are obtained by coating a more noble metal (i.e. metals having higher electrode potential like Sn, Au, Ag, Pt etc.) than the base metal. They protect the base metal as they have higher corrosion resistance than the base metal due to cathodic nature.
- Cathodic coating protects the base metal only when the coating is uniform and free from pores.
- The formation of pores over the cathodic coating exposes the base metal (anode) to environment and a galvanic cell is set up. This causes more damage to the base metal.

1.8.8 Methods of application of metallic coatings

1. Hotdipping

- Hot dipping process is applicable to the metals having higher melting point than the coating metal. It is carried out by immersing a well cleaned base metal in a bath

containing molten coating metal and a flux layer.

- The flux cleans the surface of the base metal and prevents the oxidation of the molten coating metal.

Eg. Coating of Zn, Pb, Al on iron and steel surfaces.

The most widely used hot dipping processes are galvanizing and tinning.

a. Galvanizing

- Galvanizing is a process in which the iron article is protected from corrosion by coating it with a thin layer of zinc.
- It is the anodic protection offered by the zinc. In this process, at first iron or steel is cleaned by pickling with dilute sulphuric acid solution at a temperature range of 60-90°C for 15 to 20 minutes. Therefore, it removes scale, rust and other impurities present and then washed well in a water bath and dried.
- Then after dipped in the bath containing molten zinc which is at 425-450°C. To prevent it from oxide formation, the surface of bath is covered with a ammonium chloride flux. When the iron sheet is taken out it is coated with a thin layer of zinc.
- To remove excess zinc, it is passed through a pair of hot rollers and then it is annealed at a temperature of 450°C followed by cooling.
- Galvanizing is widely used for protecting iron exposed to the atmosphere (roofs, wire fences, pipes etc.) Galvanized metallic sheets are not used for keeping eatables because of the solubility of zinc.

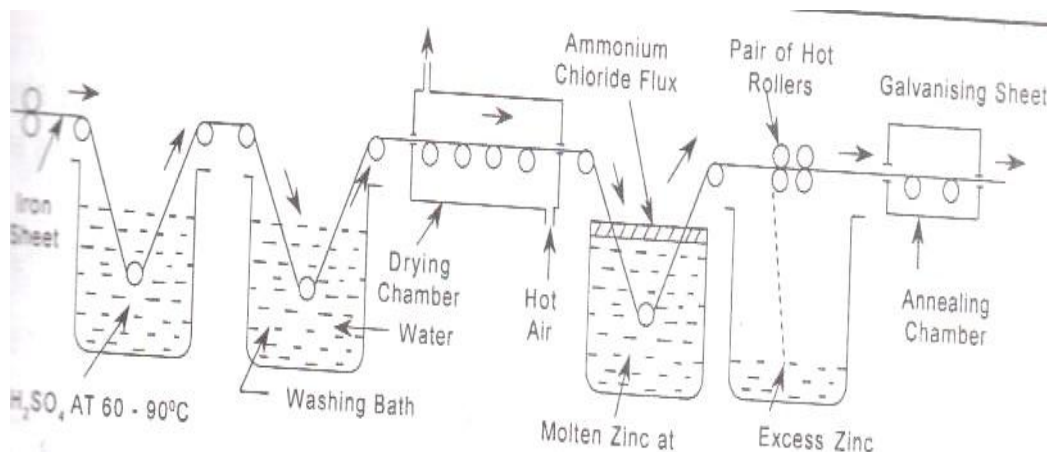


Fig.1.8.8 Galvanising

b. Tinning

- The process of coating tin over the iron or steel articles to protect them from undergoing corrosion is known as tinning.
- Tin is a noble metal and therefore it possess more resistance to chemical attack. It is the cathodic protection offered by the tin. In this process, iron sheet is treated in dilute sulphuric acid (pickling) to remove any oxide film, if present.
- A cleaned iron sheet is passed through a bath ZnCl_2 molten flux followed by molten tin and finally through a suitable vegetable oil. The ZnCl_2 flux helps the molten metal to adhere to the base metallic surface.
- . Palm oil protects the tin coated surface against oxidation. Tinning of mild steel plates is done mostly for the requirements of the food stuff industry.

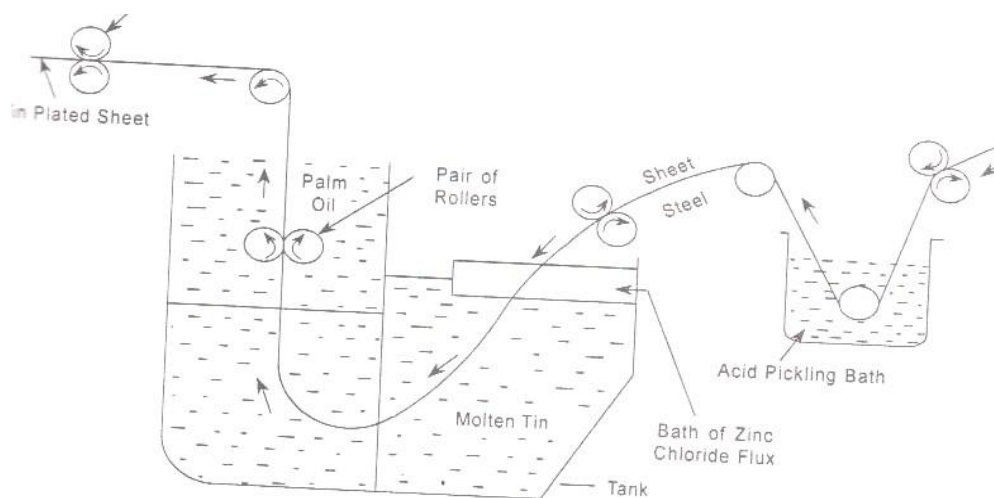


Fig.1.8.8 Tinning

3. Electroplating

Electroplating is the process of coating metals and protects them from corrosion, wear and chemical attack.

- Electroplating is the method of electro-deposition of metal by means electrolysis over surface of metals and alloys.
- The base metal is first subjected to acid pickling to remove any scales, oxides etc. The base metal is made as cathode of the electrolytic cell and the coating metal is made as anode.

- The two electrolytes are dipped in the electrolyte solution which contains the metal ions to be deposited on the base metal.
- When a direct current is passed from an external source, the coating metal ions migrate towards cathode and get deposited over the surface of base metal in the form of a thin layer.
- Low temperature, medium current density, low metal ion concentration conditions are maintained for better electro-plating.

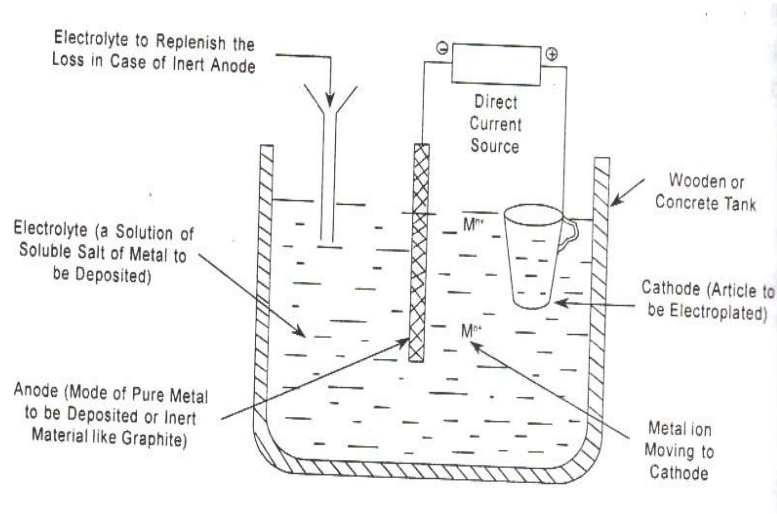


Fig1.30 Electroplating

MODULE- II

WATER AND ITS TREATMENT

2.0 Introduction

The pure water is composed of two parts of hydrogen and one part of oxygen by volume and dissolves many substances. These dissolved salts are the impurities in water. Water is a very good solvent. So it is called as universal solvent.

2.1 Hardness of water

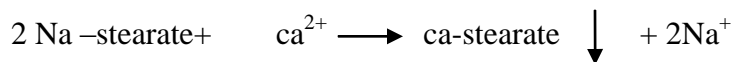
The water which does not give lather with soap is called Hard water. The Hard water contains dissolved calcium & magnesium salts.

Soft water: - The water which can give lather with soap easily is called as softwater.



Soap (softwater)

Stearic acid + Na-stearate \longrightarrow formation of lather



(Soluble salt)

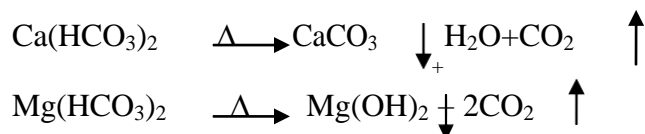
Hard water

1.2 Types of Hardness:-

Hardness in water is of two types.

- (1) Temporary hardness and (2) permanent hardness

Temporary hardness:- The hardness that can be removed simply by boiling is called the temporary hardness. It is due to the presence of boiling. On boiling $\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$ are precipitated as insoluble salts. Which can remove through filtration?



Permanent Hardness:- Permanent hardness cannot be removed by boiling . It is due to CaCl_2 , CaSO_4 , MgCl_2 , MgSO_4 and nitrates in H_2O . These salts cannot remove this hardness. Fe^{3+} , Al^{3+} & Mn^{2+} also cause hardness in water.

2.3 Units of Hardness

(1) Parts per million (ppm):- It is the number of parts of equivalents of CaCO_3 hardness causing salt present in one million parts (10^6 parts) of water.

(2).Miligram per litre (mg/l):-It is the number of milligrams of equivalent of CaCO_3 per litre of hard water. E.g.:- 1mg/li means 1 mg of equivalent CaCO_3 present in litre of hard water.

(3) Degree Clarke (o cl):-It is the number of grains of equivalent CaCO_3 equivalents of hardness causing salt in 70,000 parts of water.

(4) Degree French (o Fr):- It is a French unit. The number of parts of CaCO_3 equivalent hardness causing substance in 10^5 parts of water.

Inter conversion: - $1\text{ppm}=1\text{mg/l} == 0.07^\circ \text{cl} = 0.1^\circ \text{Fr}$

$$1^\circ \text{cl}=1.43^\circ \text{Fr} = 14.3 \text{ ppm}=14.3 \text{ mg/l}$$

2.4 Determination of Hardness of Water

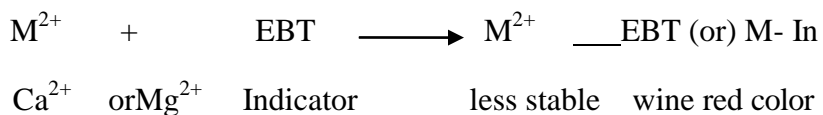
Two different methods are there

(1)**EDTA method:-**In EDTA methods, the known water sample is titrated against standard EDTA solution using EBT as indicator in the presence of basic buffer solution(PH=10). At the end point the wine red color changes to blue.

Principle:- The Ca^{2+} & Mg^{2+} ions present in water are responsible for hardness. These ions form selectable complexes with the indicator (EBT) and these metal ions form stable complexes with EDTA. This fact is used to estimate the hardness of water sample.

The metal ions Ca^{2+} & Mg^{2+} react with the EBT indicator and forms a stable complex at PH-10.

PH 9-10



Whenever we are adding EDTA solution to the wine- red color (M-In) solution, the metal ions form more stable complex with EDTA. When all the metal ions in the sample complexed with EDTA, further addition of EDTA liberates the free indicator solution at PH-10 which in blue color indicates the end point of the titration

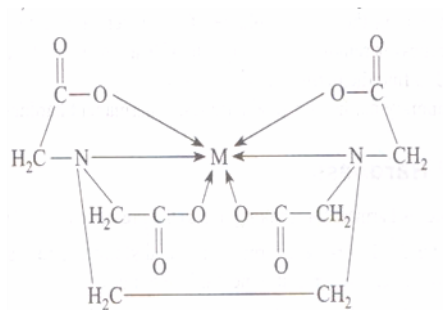


Fig3.1 Metal ion-EDTA complex

2.4.1 Experimental procedure:-

A known volume of Hardware sample is titrated with about 3 ml of buffer solution and 4- 5 drops of EBT indicator. This solution is treated against a standard EDTA solution. The end point is the color change from wine –red to blue.

Let the titer value = v_1 ml (End point) 1ml

of EDTA (0.01M) = 1 mg of CaCO_3

$V_1 \text{ ml of EDTA (0.01M)} = v_1 \text{ mg of CaCO}_3$

So v_1 mg of equivalent CaCO_3 hardness is presented in v ml of hard water

The total hardness of sample = ppm

A known volume of water sample is taken in a beaker and boiled for half an hour, after cooling it is filtered and the filtrate titrated against EDTA by adding EBT indicator & PH-10 buffer solution. Here the volume of EDTA consumed v_2 ml gives us the permanent hardness of water.

Permanent hardness of water= ppm

The total hardness of water= (Temporary hardness + permanent hardness)

Temporary hardness= (Total hardness-permanent hardness)

2.4.2 Effects of hardness: -

1. Hard water is harmful for drinking due to the presence of excess of Ca^{+2} and Mg^{+2} ions
2. Hard water used in boilers forms scales & sludge and results in corrosion, priming caustic embrittlement of the boilers.
3. Hard water used does not give lather with soap, so it sticks to clothes and body. (4) Hardness in water causes blockage in holes.
4. Hard water is not suitable for laboratory analysis, because hardness producing ions interfere in various reactions.

2.5 Boiler Troubles

Continues use of hard water in boilers causes boiler troubles that are

2.5.1 Priming

The carrying out of water droplets with steam is called “priming” Because of rapid and high velocities of steam, the water droplets move out with steam from the boiler. This process of wet steam generation is caused by (i) The presence of large amount of dissolved solids. (ii) High steam velocities (iii) sudden boiling (iv) improper designing of boilers (v) sudden increase in steam production rate and (vi) The high levels of water in boilers.

Prevention of priming

- a. The priming is avoided by fitting mechanical steam purifiers
- b. Avoiding rapid change in steaming rate
- c. Maintaining low water levels in boilers and
- d. Efficient softening and filtration of boiler feed water.

2.5.2 Foaming: -

Formation of stable bubbles at the surface of water in the boiler is called foaming. More foaming will cause more priming. It results with the formation of wet steam that harms the boiler cylinder and turbine blades. Foaming is due to the presence of oil drops, grease and some suspended solids. **Prevention of Foaming:-** Foaming can be avoided by

- i. Adding antifoaming chemicals like castor oil. The excess of castor oil addition can cause foaming.
- ii. Oil can be removed by adding sodium aluminates or alum.
- iii. Replacing the water concentrated with impurities with freshwater.

2.5.3 Scale & sludge formation:-

The water in boiler is continuously heated causes the increase in the concentration of dissolved and suspended solids. These are precipitated and slowly precipitate on the inner walls of the boiler plate. This precipitation takes place in two ways.

- (1) The precipitation in the form of soft loose and slimy deposits (sludge)
- (2) The precipitation in the form of hard deposits, which are sticky on the walls of boilers (scale)

Sludge: The muddy solid at the bottom of the boiler (or) the loose, slimy and soft deposits in the boiler are called sludge.

Causes of the sludge:- The sludge is caused by MgCO_3 , MgCl_2 , CaCl_2 which have more solubility in hot water.

Disadvantages of sludges: -

1. Sludges are bad conductors of heat and results in wastage of heat and fuel.
2. Sludges entrapped in the scale get deposited as scale causes more loss of efficiency of boiler.
3. Excessive sludge formation leads to setting of sludge in slow circulation. Areas such as pipe connections leading to choking (or) blockage of the pipes.

Prevention of sludge formation: - (1) By using soft water which is free from dissolved salts like MgCO_3 , MgCl_2 , CaCl_2 & MgSO_4 .

(2) Blow down operation can prevent sludge formation

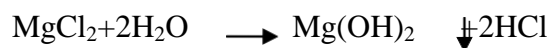
Scale: - Scales are hard sticky deposits on the inner walls of boiler. The scales are very difficult to remove.

Reason of Scale:- (1) Due to the decomposition of $\text{Ca(HCO}_3)_2$ at high temperature & pressure present in boiler, It forms CaCO_3 insoluble salt settles as ppt in the boiler.



(2) CaSO_4 present in water is highly soluble in cold water and less soluble in hot water. So the CaSO_4 in boiler water is precipitates out as hard scale, whenever the temp of boiler increases.

(3) Hydrolysis of MgCl_2 :- The dissolved MgCl_2 present in water is precipitates as $\text{Mg}(\text{OH})_2$ at high temperature, deposits as scale.



(4) SiO_2 present in water deposits as calcium silicate or magnesium Silicate. The deposits are very hard.

Disadvantages of Scale

As the scale is hardly sticky on the walls of the boiler and it is very bad conductor of heat. So there is loss of heat and fuel.

- Due to the scale formation we have to heat the boiler to high temperatures this causes the weakening of boiler material.
- Due to scale deposits the chocking of boiler is observed.
- Due to uneven heat there may be developing of cracks in Scale. Whenever the water passes through this crack comes to contact with boiler plate and generates sudden steam and high pressure results explosion of boiler.

Removal of Scales:-

- If the scale is soft. It can be removed by scraper.
- By giving thermal shocks done by heating to higher temperature and suddenly cooling.
- The CaCO_3 scale is removed by the washing with 5-10% HCl Solution and CaSO_4 scale is removed washing with EDTA solution.
- Blow down operation also removes Scale

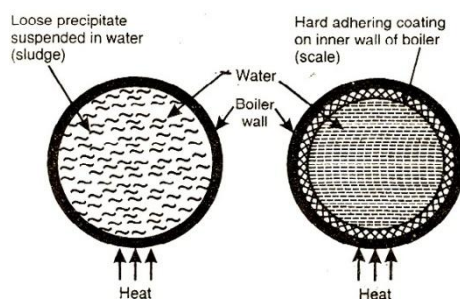
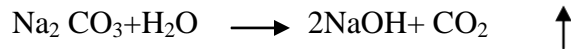


Fig3.2 Sludge Scale

2.5.4 Caustic embrittlement

The Na_2CO_3 present in water hydrolyzed to NaOH at high pressures in boilers.



The NaOH formed concentrates after long use. It causes inter-granular cracks on the boiler walls, especially at the stress points. The concentrated alkali is dissolved iron as sodium ferrote in cracks and cause brittleness of boiler.

The formation of cracks in boilers due to NaOH is called caustic embrittlement. The created concentration cell is explained.

Iron at bends	concentrated	Diluted	Iron at plane surface
(Anode)	NaOH	NaOH	(cathode)

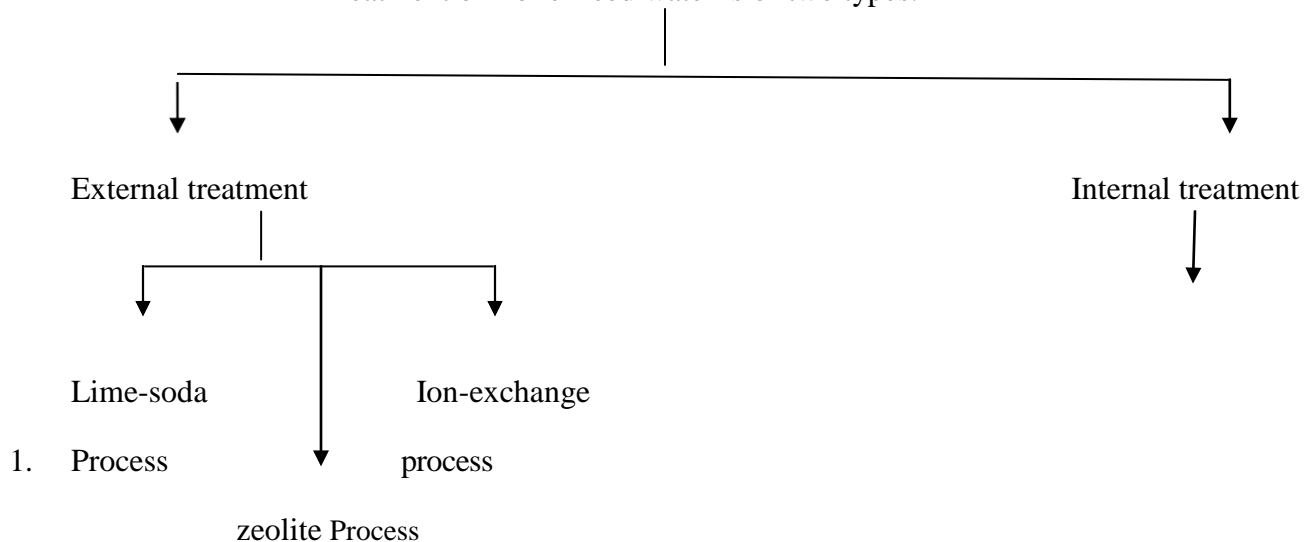
The iron is dissolved at anode i.e. undergoing corrosion

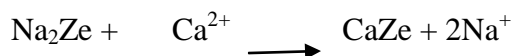
Prevention of caustic embrittlement :-

- (1) by using sodium phosphate as softening agent instead of Na_2CO_3 .
- 2) By adding tannin or lignin to boiler water which block the hair cracks and pits in boiler.
- 3) By adding sodium sulphate to soften the water and this also blocks the hair cracks present on the surface of the boilerplate.

2.5.5 Treatment of boiler feed water (Softening of water):-

Treatment of Boiler feed water is of two types.





Naturally occurring Zeolite is Natrolite $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$. The Synthetic Zeolites are also prepared with the help of feldspar & China clay on heating.

2.5.5.1 Ion exchange process (or) deionization or demineralization

Ion exchanges are of two types. Anionic & Cationic. These are co-polymers of styrene & di vinyl benzene. i.e. Long chain organic polymers with a micro porous structure.

cation exchange resins

The resins containing acidic functional groups such as $-\text{COOH}$, $-\text{SO}_3\text{H}$ etc. are capable of exchanging their H^+ ions with other cations are cation exchange resins, represented as RH^+

Anion exchange resins:

The resins containing amino or quaternary ammonium or quaternary phosphonium (or) Tertiary sulphonium groups, treated with "NaOH solution becomes capable of exchanging their OH^- ions with other anions. These are called as Anion exchanging resins

represented as R OH^-

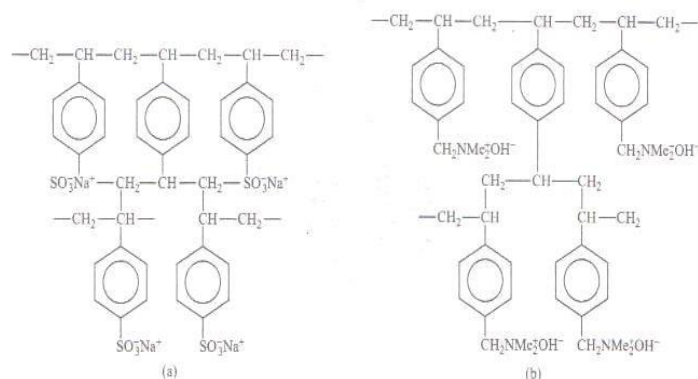
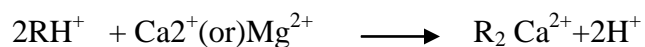


Fig 2.5.5 Cation exchange resin

Anion exchange resin

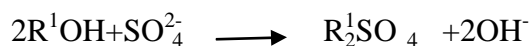
Process: The hard water is passed first through cation exchange column. It removes all the cation (Ca^{2+} & Mg^{2+}) and equivalent amount of H^+ ions are released from this column.



(Or)



After this the hard water is passed through anion exchange column, which removes all the anions like SO_4^{2-} , Cl^- , CO_3^{2-} etc and release equal amount of OH^- from this column.



The output water is also called as de-ionised water after this the ion exchanges get exhausted. The cation exchanges are activated by mineral acid (HCl) and anion exchanges are activated by dil NaOH solution.

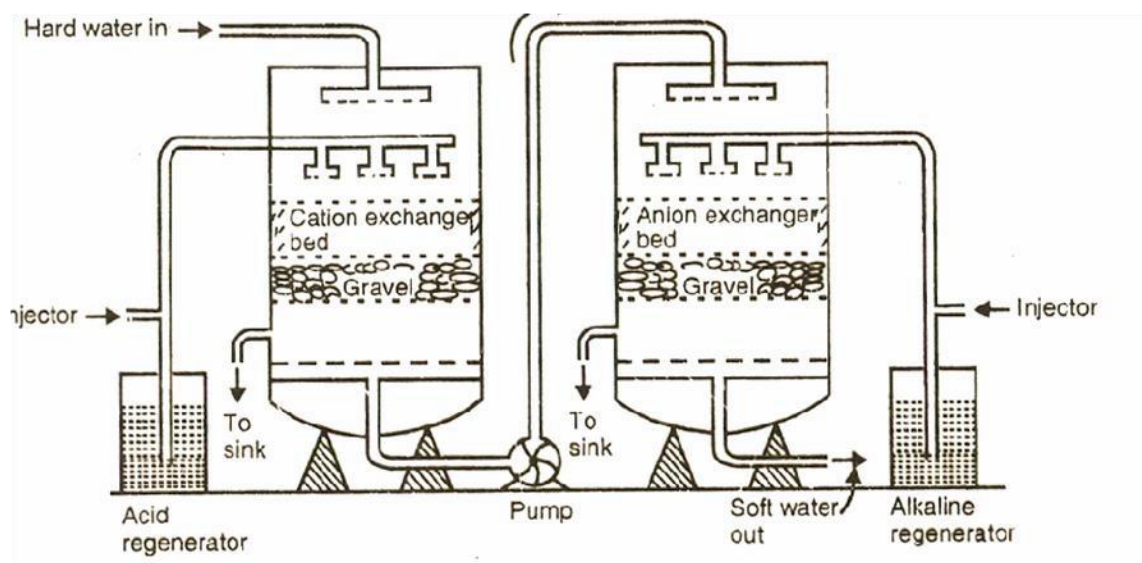
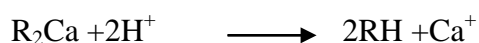


Fig2.5.5 Ion exchanger

Advantages:-

- i. The process can be used to soften highly acidic or alkaline waste.
- ii. It produces water of very low hardness. So it is very good for treating for use in high pressure boilers.

Disadvantages:-

- i. The equipment is costly and common expensive chemicals required.
- ii. If water contains turbidity, then output of this process is reduced. The turbidity must
- iii. be below 10 ppm

2.5.5.2 Internal treatment

In this method raw water is treated inside the boiler. This is a process of adding suitable chemical to reduce scale & sludge formation. It is mainly based on solubility. This is a corrective method. This method is also called conditioning method.

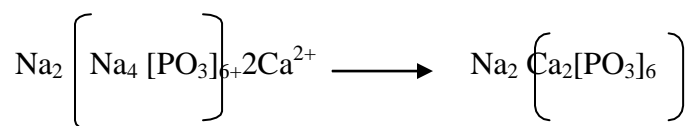
Conditioning of water:-

1) Carbonate conditioning:- In low pressure boilers scale formation can be avoided by treating the boiler water with Na_2CO_3 . Where CaSO_4 is converted into CaCO_3 .

CaSO_4 is precipitated as loose sludge in the boiler which can be scrapped off.

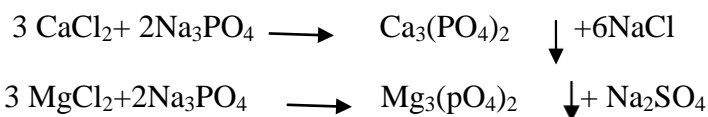
2) Calgon conditioning:- Calgon means calcium gone i.e. the removal of Ca^{2+} . Sodium hexameta phosphate is called calgon. It reacts with calcium ion and forms a water soluble compound.

Converted to scale which on drying converted to scale reduces the efficiency of the boiler.



At higher temperature NaPO_3 is converted to $\text{Na}_2\text{P}_2\text{O}_4$ that also reacts Ca^{2+} to form loose sludge of CaP_2O_7 , removed by blowing air.

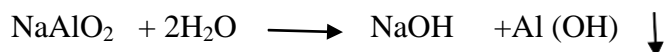
3) Phosphate conditioning:- It is applied to high pressure boilers. When sodium phosphate is added to boiler water, it reacts with Ca & Mg salt forming soft sludges.



Trisodium phosphate is used when the alkalinity of boiler water is 9.5 to 10.5 at that pH Ca gets precipitated.

If alkalinity is too high NaH_2PO_4 (acidic) is used and Na_2HPO_4 is used if sufficiently alkaline.

(4). Treatment with Sodium Aluminate:- when boiler water heated with Sodium aluminate it gets hydrolysed to give NaOH and gelatinous precipitate of $\text{Al}(\text{OH})_3$.



The NaOH formed reacts with MgCl_2 to form $\text{Mg}(\text{OH})_2$. These two precipitates entrap colloidal impurities like oil drops, sand and make them settle down.

2.5.6 Disadvantages of hard water in domestic and industrially

In Domestic use:-

(a) Washing

Hard water, when used for washing purposes, does not producing lather freely with soap.

As a result cleaning quality of soap is decreased and a lot of it is wasted.

(b) Hard water reacts with soap it produces sticky precipitates of calcium & Mg soaps. These are insoluble formations.

(c) Bathing

Hard water does not produce lather freely with soap solution, but produces sticky scum on the bath-tub and body. Thus, the cleaning quality of soap is depressed and a lot of it is wasted.

(d) Cooking:-

The boiling point of water is increased because of presence of salts. Hence more fuel and time are required for cooking.

(e) Drinking:-

Hard water causes bad effects on our digestive system. Moreover, the possibility of forming calcium oxalate crystals in urinary tracks is increased.

Industrial use:-

(a) Textile industry:-Hard water causes wastage of soap. Precipitates of calcium and magnesium soaps adhere to the fabrics and cause problem.

(b) Sugar Industry:-Water containing sulphates, nitrates, alkali carbonates etc. if used in sugar refining, causes difficulties in the crystallization of sugar. Moreover, the sugar so produced may be de-liquiscent.

(c) Dyeing industry:-The dissolved salts in hard water may reacts with costly dyes forming precipitates.

(d) Paper Industry:-Calcium, magnesium, iron salts in water may affect the quality of paper.

(e) Pharmaceutical Industry:-Hard water may cause some undesirable products while preparation of pharmaceutical products.

(f) Concrete making:-water containing chlorides and sulphates, if used for concrete making, affects the hydration of cement and the final strength of the hardened concrete.

(g) Laundry:- Hard water, if used in laundry, causes much of the soap used in washing to go as waste iron salts may even causes coloration of the cloths.

Why is hard water harm full to boilers?

Steam generation purpose boilers are used in Industries. If the hard water is fed directly to the boilers, there arise many troubles such as:

(a) Scale & Sludge formation:- The hardness of water fed to the many causes scale & sludge

formation.

- (b) **Corrosion:-** Hard water may cause caustic embrittlement which is a type of boiler corrosion.
- (c) **Priming & Foaming:-** Hard water used in boiler cause priming and foaming which results in the formation of wet steam
- (d) **Caustic embrittlement**

2.5.7 Hardness- Numerical problems:-

- (1) One litre of water from an underground reservoir in tirupathi town in Andhra Pradesh showed the following analysis for its contents. Mg (HCO₃)₂= 42 Mg, Ca(HCO₃)₂= 146 Mg, CaCl₂= 71 Mg, NaOH= 40 Mg, MgSO₄=48 Mg, organic impurities=100 Mg, Calculate temporary, permanent and total hardness?

<u>Hardness causing salt (H.C.S)</u>	<u>Quantity (H.C.S)</u>	<u>Mol.Wt.of (H.C.S)</u>	<u>Equivalent of CaCO₃</u>
CaCl ₂	71		_____
MgSO ₄	48	120	_____
Ca(HCO ₃) ₂	146	162	_____
Mg(HCO ₃) ₂	42	146	_____
NaOH	40	-	-

$$\begin{aligned}\text{Temporary Hardness} &= \text{Mg(HCO}_3\text{)}_2 + \text{Ca(HCO}_3\text{)}_2 \\ &= 28.7 + 90.1 = 118.8 \text{ ppm}\end{aligned}$$

$$\begin{aligned}\text{Permanent Hardness} &= \text{CaCl}_2 + \text{MgSO}_4 \\ &= 64 + 40 = 104 \text{ ppm}\end{aligned}$$

$$\begin{aligned}\text{Total Hardness} &= \text{Temporary Hardness} + \text{Permanent Hardness} \\ &= 118.8 + 104 = 222.8 \text{ ppm}\end{aligned}$$

- (2) One liter of water from khammam Dist in A.P showed the following analysis. Mg(HCO₃)₂=0.0256 gms, Ca(HCO₃)₂=0.0156 gms, NaCl=0.0167gms, CaSO₄=0.0065gms, and MgSO₄=0.0054gms. Calculate temporary, Permanent & total hardness.

S. No	Constituent	Amount Mg/l	Mol. Wt. of salt	Equivalent of CaCO ₃ mg/l
1	CaSO ₄	6.5	136	_____
2	MgSO ₄	5.4	120	_____
3	Ca(HCO ₃) ₂	15.6	162	_____
4	Mg(HCO ₃) ₂	25.6	146	_____
5	NaCl	16.7	—	—

Temporary hardness=Mg(HCO₃)₂+Ca(HCO₃)₂

$$= 17.5+9.6=27.1 \text{ ppm}$$

Permanent hardness=CaSO₄+MgSO₄

$$=4.77+4.5=9.27 \text{ ppm}$$

Total hardness=Temporary hardness +Permanent hardness

$$= 27.1+9.27=36.37 \text{ ppm}$$

- (3) Calculate the temporary & permanent hardness of 100 litre of water containing the following impurities per litre MgCl₂=19 mg, MgSO₄=60 mg, NaCl=36.5 mg, CaCl₂=11.1 mg, Ca(HCO₃)₂=32.4 mg & Mg(HCO₃)₂=7.3mg

S No	Constituent	Amount Mg/l	Mol.wt. of salt	Equivqlent of CaCO ₃ (Mg/l)
1	CaCl ₂	11.1	111	_____
2	MgCl ₂	19	95	_____
3	MgSO ₄	60	120	_____
4	Ca(HCO ₃) ₂	32.4	162	_____
5	Mg(HCO ₃) ₂	7.3	146	_____
6	NaCl	36.5	—	—

Temporary hardness=Mg (HCO₃)₂+Ca (HCO₃)₂

$$=5+20=25$$

Temporary hardness for 100ml = $25 \times 100 = 2500$ Mg/l

Permanent hardness = $\text{CaCl}_2 + \text{MgCl}_2 + \text{MgSO}_4$

= $10 + 20 + 50 = 80$ Mg/l

Permanent hardness for 100l = $80 \times 100 = 8000$ Mg/l

Total hardness = Temporary hardness + Permanent hardness

= $25 + 80 = 105$ Mg/l

Total hardness for 100 litre = $105 \times 100 = 10,500$ Mg/l

(4) A sample of hard water contains the following dissolved salts per liter

$\text{CO}_2 = 44$ Mg, $\text{Ca}(\text{HCO}_3)_2 = 16.4$ Mg, $\text{Mg}(\text{HCO}_3)_2 = 14.6$ Mg

$\text{CaCl}_2 = 111$ Mg, $\text{MgSO}_4 = 12$ Mg, & $\text{CaSO}_4 = 13.6$ Mg. Calculate the temporary &

Permanent hardness of water in $^\circ\text{Fr}$ & $^\circ\text{Cl}$. (2013)

S.No	Constituent	Amount Mg/l	Mol.wt. of salt	Equivqlent of CaCO_3 (Mg/l)
1	CO_2	44	44	_____
2	$\text{Ca}(\text{HCO}_3)_2$	16.4	162	_____
3	$\text{Mg}(\text{HCO}_3)_2$	14.6	146	_____
4	CaCl_2	111	111	_____
5	MgSO_4	12	120	_____
6	CaSO_4	13.6	136	_____

Temporary hardness of water = $\text{CO}_2 + \text{Ca}(\text{HCO}_3)_2 + \text{Mg}(\text{HCO}_3)_2$

= $100 + 10 + 10 = 120$ mg/l

Permanent hardness of water = $\text{CaCl}_2 + \text{MgSO}_4 + \text{CaSO}_4$

= $100 + 10 + 10 = 120$ mg/l

Conversion of hardness:-

1ppm = 1 mg/l = 0.07 $^\circ\text{cl}$ = 0.1 $^\circ\text{fr}$

Temporary hardness = 120 mg/l, 120 ppm, $120 \times 0.07 = 8.4^\circ \text{cl}$

$$= 120 \times 0.1 = 12^\circ \text{ French}$$

Permanent hardness = 120 mg/l, 120 ppm, $120 \times 0.07 = 8.4^\circ \text{cl}$

$$= 120 \times 0.1 = 12^\circ \text{french.}$$

- (5) Calculate the lime and soda needed for softening 50,000 litres of water containing the following salts: $\text{CaSO}_4 = 136 \text{ mg/l}$, $\text{MgCl}_2 = 95 \text{ mg/l}$, $\text{Mg}(\text{HCO}_3)_2 = 73 \text{ mg/l}$, $\text{Ca}(\text{HCO}_3)_2 = 162 \text{ mg/l}$. given that molar mass of $\text{Ca}(\text{HCO}_3)_2$ is 162 and that of MgCl_2 is 95.

S No	Constituent	Amount mg/l	Mol.wt	CaCO ₃ equivalent
1	CaSO_4	136	136	_____
2	MgCl_2	95	95	_____
3	$\text{Mg}(\text{HCO}_3)_2$	73	146	_____
4	$\text{Ca}(\text{HCO}_3)_2$	162	162	_____

Lime required= $(\text{Ca}(\text{HCO}_3)_2 + 2\text{Mg}(\text{HCO}_3)_2 + \text{MgCl}_2)$

$$\text{—} \quad 100 + 2 \times 50 + 100 + 100)$$

$$\text{—} \quad \text{—} \quad = * = 296 \text{ mg/l}$$

For 50,000 lit of water= $50,000 \times 296 = 148 \text{ kg}$ of lime required

Soda required= $\text{—} \quad 4 (\text{CaSO}_4 + \text{MgCl}_2)$

$$= \text{—} \quad \text{—} \quad * = 212 \text{ mg/l}$$

For 50,000 lit of water: $50,000 \times 212 = 10.6 \text{ kg}$ of soda required.

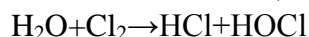
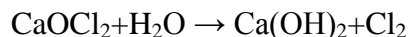
2.6 Disinfection:- The process of destroying/killing the disease producing bacteria, microorganisms, etc, from the water and making it safe are, is called Disinfection.

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 min. boiled, all the disease producing bacteria are killed and water become safe for use.

(b) **Bleaching powder:-**

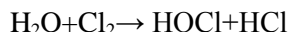
It is used to purify the drinking water from micro organisms. The purification process is achieved by dissolving 1 kg of bleaching powder in 1000 kilo litres of water. This dissolved water solution is left undisturbed for many hours when bleaching powder is mixed with water, the result of chemical reaction produces a powerful Germicide called Hypochlorous acid. The presence of chlorine in the bleaching powder produces disinfection action, kills germs and purifies the drinking water effectively.



$\text{HOCl} + \text{germs} \rightarrow \text{germs are killed} \rightarrow \text{water purified.}$

(c) **Chlorination:-**

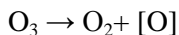
Chlorination is the process of purifying the drinking water by producing a powerful Germicide like hypochlorous acid. When this chlorine is mixed with water it produces Hypochlorous acid which kills the Germs present in water.



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.

(d) **Ozonisation:-**

Ozone is powerful disinfectant and is readily dissolved in water. Ozone being unstable decomposes by giving nascent oxygen which is capable of destroying the Bacteria. This nascent oxygen removes the colour and taste of water and oxidizes the organic matter present in water.

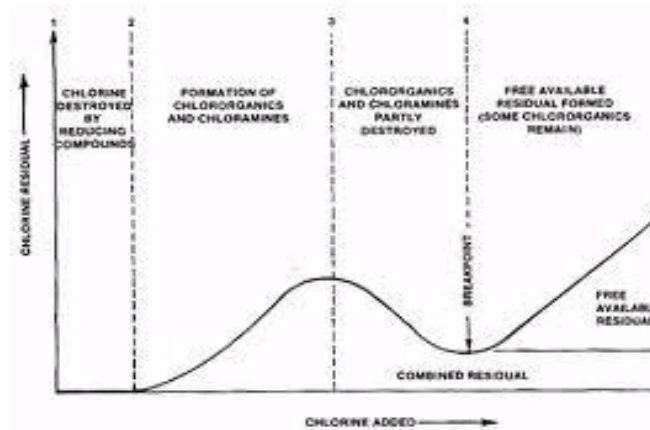


2.7 Break- Point Chlorination:-

Break Point Chlorination is a controlled process. In this process suitable amount of chlorine is added to water. In order to kill all the bacteria present in water, to oxidize the entire organic matter and to react with free ammonia the chlorine required should be appropriate.

Break point determines whether chlorine is further added or not. By chlorination, organic matter and disease producing bacteria are completely eliminated which are responsible for bad taste and bad odour in water. When certain amount of chlorine is added to the water, it leads to the formation of chloro-organic compounds and chloramines.

The point at which free residual chlorine begins to appear is terms as “Break-Point”.



2.8 Desalination

The removal of dissolve solids (NaCl) from water is known as desalination process. It can be carried out by

2.8.1 Reverse osmosis process:-

The membrane process used in the water purification system has been of much use now a days. Electro dialysis and reverse osmosis are part of the membrane process.

In osmosis, if a semi-permeable membrane separates two solutions, solvent from the lower concentration passes to the higher concentration to equalize the concentration of both. But in the reverse osmosis, pressure higher than osmotic pressure is applied from the higher concentration side so that the path of the solvent is reversed, i.e. from higher concentration to lower concentration.

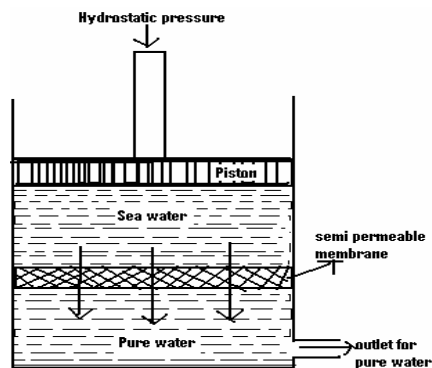


Fig 2.8.1 Reverse Osmosis

This method is applicable mainly for the desalination of sea water. Sea water and pure water are separated by a semi-permeable membrane made up of cellulose acetate fitted on both sides of a perforated tube. Inventions are in progress to search for better membrane. Polymethylmethacrylate and polyamides have been proved to be better membranes.

The process is very easy. It is used to make pure water. It removes the ionic and non ionic substances in the water. It also can remove suspended colloidal particles. The life of a membrane is nearly 2 years and it should be replaced after this period. By this process, sea water is made to fit for drinking water obtained after being treated by this process is used in boilers.

MODULE-III

MOLECULAR STRUCTURE AND THEORIES OF BONDING

3.0 Introduction

1. Atom is the smallest indivisible particle which aggregates to form matter. The word atom has been derived from Greek word 'atomos', meaning indivisible.
2. Atomic orbital is the region having the highest probability of finding an electron in an atom.
3. The energy levels about the nucleus contain group of these atomic orbitals.
4. Each orbital (designated as s, p, d, and f) has a unique energy associated with it, can contain a maximum of two electrons and varies in shape and spatial orientation.
5. We are mainly concerned with the s and p orbitals since most of the elements found in organic molecules have their electrons in the 1s, 2s and 2p orbitals.
6. The S orbital is in spherical shape. Each P orbital is in dumbbell shape.
7. Molecular orbital is the region having the highest probability of finding an electron of a molecule.
8. Molecular orbitals result from the combination of atomic orbitals.
9. Atomic orbitals with differing energies or the wrong spatial orientation do not combine, and are called non-bonding orbitals.
10. Molecular orbital properties can be explained by various theories like VSEPR, MOT.

3.1 Linear combination of orbitals

Molecular orbitals of a molecule, i.e. solutions to the molecular Schrodinger equation can be obtained by a method known as linear combination of atomic orbitals (LCAO). As per this method the formation of orbitals is because of addition or subtraction of atomic orbital wave function. For diatomic molecules, such a wave function takes the form,

$$\Psi = N(C_A \Psi_A \pm C_B \Psi_B)$$

Where Ψ is the wave function of MO; Ψ_A, Ψ_B are wave functions belonging AOs for atom A and atom B respectively; C_A, C_B are adjustable coefficients and N is normalizing factor.

3.2 Energy level diagrams of Diatomics:

Molecular orbital theory was introduced in 1928 by Mullikan, Huckel and Hund. The orbitals are associated with the molecule as a whole. The quantized molecular orbitals of varying energy levels surround both the nuclei of the bonded atoms. These molecular orbitals are formed by the coalescence of the individual atomic orbitals when the atoms lose their individual identity. The electrons are considered moving over the whole nuclear system instead of moving around a particular nucleus. The configuration of the molecule is obtained by placing electrons into these quantized molecular orbitals in an Aufbau order analogous to that employed in the filling of atomic orbitals. Corresponding to the particles indicating atomic orbitals by the letters S, P and d molecular orbitals are assigned similar Greek letter designations σ (sigma), π (pi), γ (delta).

3.3 Bonding and anti-bonding orbital's

Two atomic orbital's, one from each bonded atom, whose energies are comparable in value and which possess a large amount of overlap, coalesce to form two molecular orbital's. One of these molecular orbital's lower in energy than either of the atomic orbitals from which it was formed and hence gives rise to a repulsive state. This high energy molecular orbital is termed the anti-bonding orbital since electrons placed in this kind of orbital decrease the stability of the bond. The anti-bonding orbital's are represented by super script asterisks (ex: σ^* , π^*). The lower energy molecular orbital is called bonding orbital. Since electrons placed in such an orbital increase the stability of the bond.

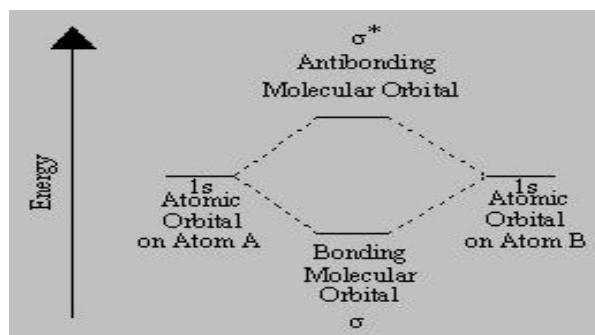


Fig 3.3 Bonding and anti-bonding orbital's

In case of molecular orbital's, the filling of electrons takes place in the following order of increasing energy.

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

$$\text{Bond order} = \frac{1}{2}[\text{No. of electrons in bonding orbital's} - \text{No. of electrons in anti bonding orbital's}]$$

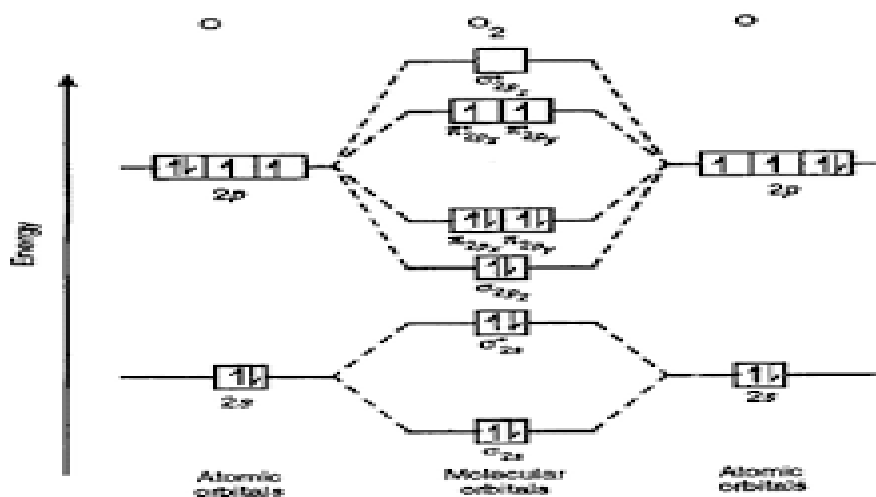
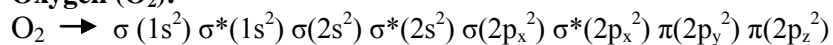


Fig 3.3 Energy level diagram of O₂

Examples:

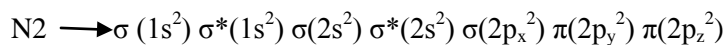
Oxygen (O₂):



$$\text{Bond order} = 1/2 [10-6] = 2$$

The number of covalent bonds in Oxygen is two.

Nitrogen(N₂):



$$\text{Bond order} = 1/2 [10-4] = 3$$

Number of covalent bonds in Nitrogen is 3.

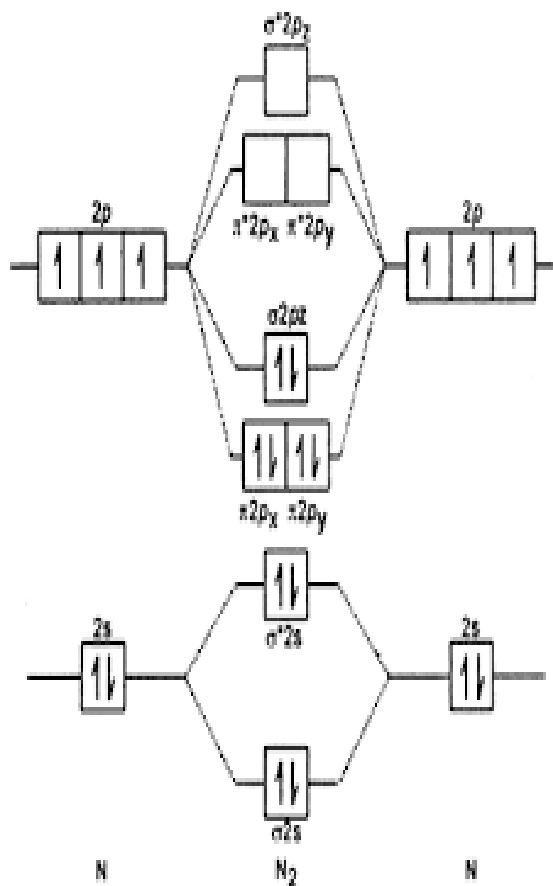
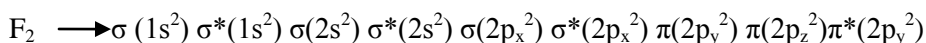


Fig 3.3 Energy level diagram of O₂

Fluoride(F_2) :



$$\text{Bond Order} = 1/2 [10-8] = 1$$

Number of covalent bond in Fluoride is 1.

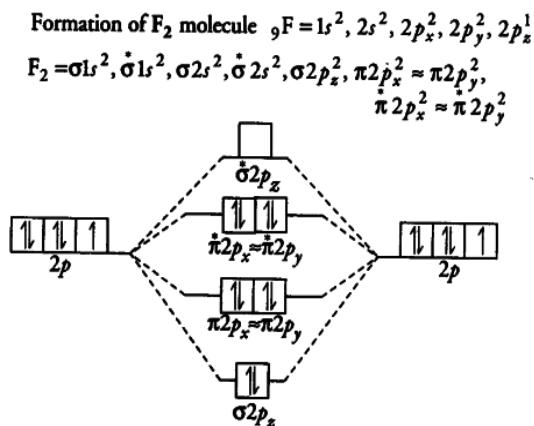


Fig 3.3 Energy level diagram of F_2

3.4 Crystal field theory:

Crystal field theory was developed to describe important properties of complexes (magnetism, absorption spectra, oxidation states, co-ordination etc.). CFT explains splitting in d-orbital. In free metal atom all d-orbital's have same energy, when a ligand coalescence with d-orbital splits into t_{2g} , e_g orbital's having different energies.

The important assumptions are

- Ligands are treated as point charges.
- There is no interaction between metal orbital's and ligand orbital's.
- In free metal atom all d-orbital's have same energy (degenerate) when a complex is formed d-orbital's have different energies.

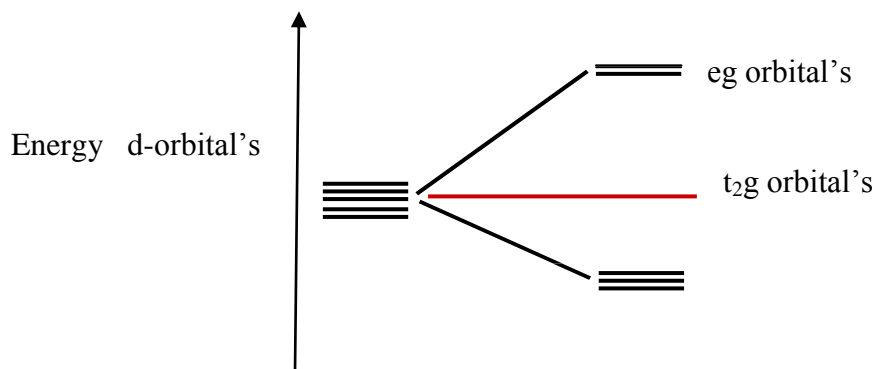


Fig 3.4 Crystal field theory

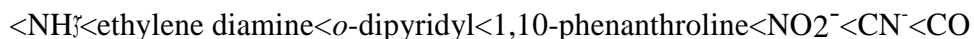
3.4.1 Octahedral Complexes

In the octahedral complexes, ligand approach along the axes. As a result, the d-orbitals where electron density is oriented along the axes, dx^2-y^2 and dz^2 are repelled much more by the ligands while the orbitals dxy , dyz , dxz having electron density oriented in between the axes are repelled lesser by the ligands. Thus two sets of orbital's eg and t2g, doubly and triply degenerate respectively, are formed.

Crystal field splitting of energy levels in an octahedral field of ligands

Noticeable features

1. The mean of these two sets of orbitals is zero and represented as Bari center.
2. The energy gap between these two sets of orbitals is known as Δ_0 , crystal field splitting parameter under the influence of octahedral field of ligands.
3. The value of Δ_0 in the complex $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ has been experimentally found as $20,300 \text{ cm}^{-1}$ or 243 kJ/mol ($1 \text{ kJ/mol} = 83.7 \text{ cm}^{-1}$) from the absorption spectrum in the visible region showing band at 500 nm or 5000 \AA .
4. The magnitude of Δ_0 depends on mainly on field strength of ligand, oxidation state of metal and down the group from 3d to 4d or 5d metals.
5. The ligands arranged in order of increasing ligand field strength constitute spectrochemical series-



the ligand with higher field, like CO or CN^- would produce more splitting or larger energy gap while I being weakest would produce minimum energy gap.

With increase in oxidation state of 3d metal ions from +2 to +3 there is almost 50% increase in Δ_0 .

Descending in a group, for example 3d to 4d series, Δ_0 increase by approximately 30%. 50

3.4.2 Crystal Field Stabilization Energy(CFSE) and pairing (P) Energy

The CFSE is defined as net gain in energy achieved by preferential filling of electrons in lower lying d orbitals over the energy of complete random occupancy of electrons in all five d orbitals. It is 2 to 10% of actual bond energy. The energy required to pair the electrons in the same orbital known as mean pairing energy and it is constant for the same metal ion.

Noticeable features

1. When magnitude of Δ_0 is higher than P, electrons tend to pair in the lower lying orbital thus spin paired or low spin complexes are formed. On the other hand, if Δ_0 is less than P, high spin or spin free complexes are formed. If Δ_0 is approximately equal to P, single temperature changes may affect spin changes. Sum of CFSE and P gives Total Stabilization Energy (TSE).
2. For d^4 and d^7 low spin systems only one P is added in CFSE to get TSE because only one electron is to be paired in the same orbital, rest are paired in natural configuration while for d^5 and d^6 low spin systems twice of pairing energy is required to be added to get TSE.
3. The 3d metals form high and low spin complexes, on the other hand 4d and 5d metals having very high CFSE form low spin complexes.

3.4.3 Tetrahedral Complexes

In tetrahedral geometry, the ligand approach is in between the axes. The e_g orbitals lie exactly between L-

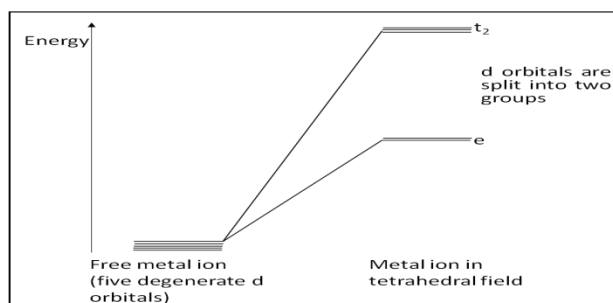


Fig 3.4.3 Tetrahedral Complexes

M-L bond, as a result, e_g -M-L bond angle is $109^\circ 28' / 2$, $54^\circ 44'$ while t_{2g} -M-L bond angle comes to be $35^\circ 16'$ ($90^\circ - 54^\circ 44'$).

Splitting of d orbitals in a tetrahedral field of ligands

Noticeable features

1. The t_2g orbitals are closer than e_g orbitals and therefore get repelled more than e_g orbitals.
2. It can simply be stated that the d orbital splitting diagram in tetrahedral complexes is just inverse of octahedral complexes.
3. The g subscript should be omitted in tetrahedral complexes as these are never symmetrical.
4. The crystal Field Splitting parameter Δ_t is $4/9$ of Δ_0 .
It is $2/3$ of Δ_0 due to number of ligands being 4 and 6 in tetrahedral and octahedral complexes respectively and $2/3$ of Δ_0 due to approach of ligands, t_2 - M-L bond angle $35^\circ 16'$ and e -M-L bond angle $54^\circ 44'$.
5. Tetrahedral complexes are high spin complexes as the energy gap between two sets of orbitals is roughly half of octahedral complexes.
6. As evident from the above data CFSE in tetrahedral complexes is much smaller than octahedral complexes, these should not be energetically favored. Since tetrahedral complexes are very much known to exist, their formation can be possible under the conditions when loss in CFSE.
 - A. Metal is in low oxidation state like in $Ni(CO)_4$, Ni is in zero oxidation state.
 - B. Ligand is weak field, for example Cl^- in $[MnCl_4]^{2-}$. Metal ion with d^0 , d^5 (weak field) or d^{10} configurations $[MnO_4]^-$, $[MnCl_4]^{2-}$ and $[ZnCl_4]^{2-}$ respectively where CFSE is zero in octahedral field.
 - C. In tetrahedral complexes the bond angle being $109^\circ 28'$ is larger than that in octahedral complexes, 90° . Therefore, bulky ligands may form tetrahedral complexes as have lesser steric hindrance.
 - D. The configurations of metal ions where symmetrical filling of electrons in degenerate orbitals is present, may form tetrahedral complexes. For example, $e^0 t^0$, $e^2 t^0$, $e^2 t^3$, $e^4 t^3$, $e^4 t^6$.

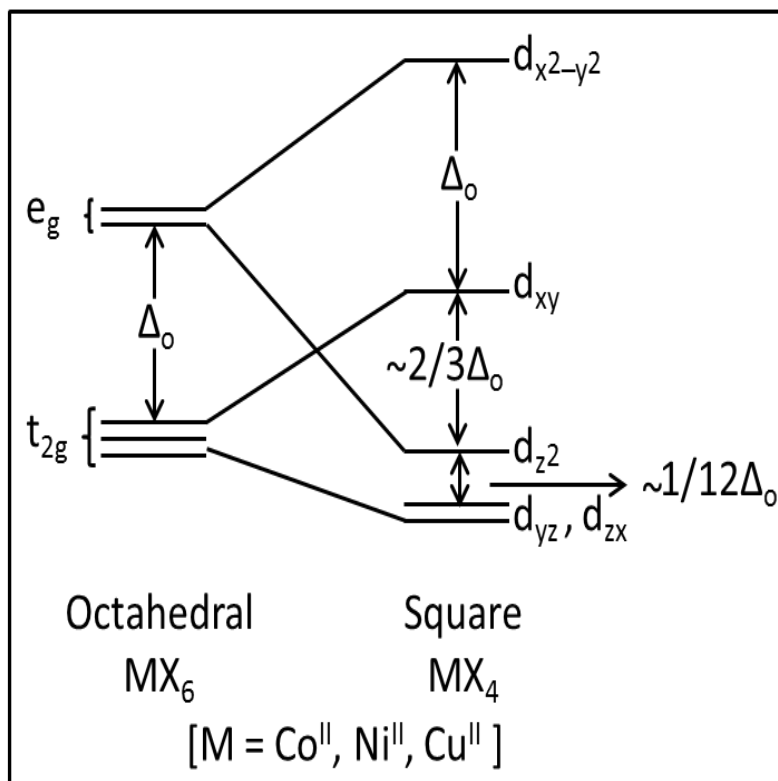


Fig 3.4.3 Square Planar Complexes

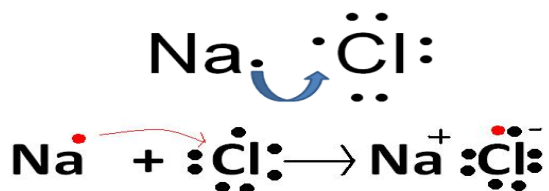
In a complex, like $[Ni(H_2O)_6]^{2+}$ with $t_2g^6 e_g^2$ configuration and symmetrical filling of electrons in both t_{2g} and e_g orbitals, no distortion is observed. In presence of strong field ligands like CN^- , electron in d_{z^2} is being repelled by two ligands while that in $d_{x^2-y^2}$ is repelled by four ligands. As a result, energy of $d_{x^2-y^2}$ increases and that of d_{z^2} decreases. The electrons present singly in $d_{x^2-y^2}$ and d_{z^2} are paired up in d_{z^2} and $d_{x^2-y^2}$ becomes vacant, therefore four ligands can now approach along x, y directions but experience too much repulsion along z direction. Consequently, square planar complex is formed instead of octahedral complex.

3.5 Band structure of solids:

Ionic bond:

- i. It forms a metal and non metal.
- ii. There is electron transfer from less electronegative atom to more electronegative atom.
- iii. Electrostatic attractions take place between opposite charged ions.
- iv. It is a non directional bond formed by strong electrostatic interactions.
- v. Due to strong electrostatic attractions ionic compounds has high melting and evaporation points, hard and brittle solids at room temperature.
- vi. They do not conduct electricity (except in molten state).

Example: NaCl



3.5.1 Covalent bond:

- i. It forms between non-metallic elements of the periodic table.
- ii. This bond involves the sharing of electrons between atoms.
- iii. Covalent bonds are directional in nature.
- iv. These compounds have low melting and boiling points.
- v. These are soft, brittle solids has poor electrical, thermal conductivity.

Example: H₂



3.5.2 Metallic compounds:

- i. In metal the outer energy levels tend to overlap. The valence electrons then moves about a group of metal atoms, making the metals positively charged.
- ii. The positively charged ion then attracts electrons from other metal atoms. The attraction of a positive metallic ion for delocalized electrons is called metallic bond.
- iii. The electron sea model proposes all metal atoms contribute their valence electrons to form a sea of electrons.
- iv. Metals owe their physical properties to their delocalised electrons for example metals are malleable, ductile, conductors, shiny etc.

Example: Metals

3.5.3 The role of doping on bond structures:

As isolated atoms brought together to form a solid, various interactions occurs between neighbouring atoms. In the process, important changes occur in the electron energy configuration. When the solid is formed the energy levels are so closely spaced that they form bands. The electrons can move freely through the material from conduction band (empty shell) to valence band (valence shell) and viseversa. Based on gap between conduction band and valence band solids are divided into three types

- i. Insulators
- ii. Semi conductors
- iii. Conductors

i. Insulators:

The gap between valence band and conduction band is quite high, electrons are fail to jump from valence band to conduction band. Such solids show less conductivity or no conductivity is called insulators.

Example: Glass.

ii. Semiconductors:

The gap between valence band and conduction band is small, some electrons jump from valence band to conduction band and thus show some conductivity. Such solids show less conductivity or no conductivity is called

semiconductors.

Examples: Germanium, Silicon.

iii. Conductors:

There is no band gap between valence band and conduction band, electrons can move through valence band to conduction band and shows conductivity. Such solids called as conductors.

Examples: Copper, Silver, Gold.

3.6 Doping:

Doping is the process of adding impurities to increase conductivity nature of semiconductors. Two of the most important materials silicon can be doped with, are boron and phosphorus. Other materials are aluminium, indium and arsenic, antimony.

Based on adding impurities doping process is two types

i. n-type

ii. p-type

i. n-type semiconductor:

n-type semiconductor is an excess negatively charged electrons containing semiconductor and obtained by adding extremely small quantity of a pentavalent element impurity (like phosphorous, arsenic or antimony) to pure semiconductor (like silicon, germanium, tellurium etc.) crystal lattice.

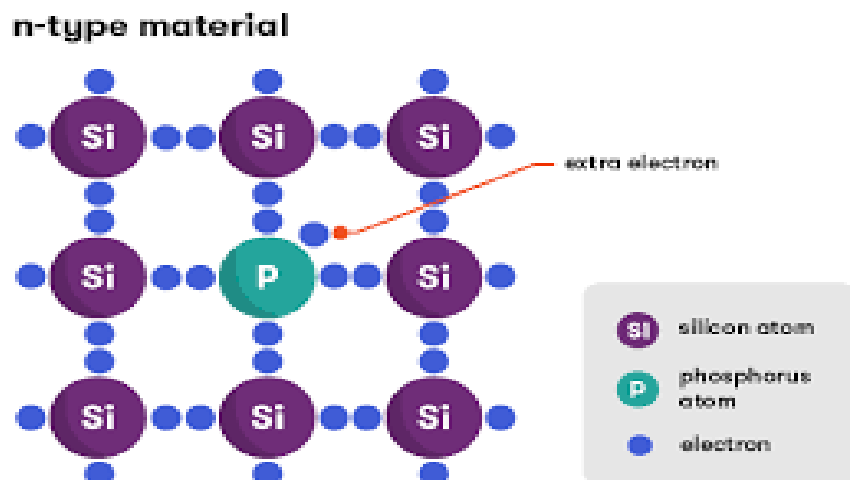


Fig 3.6 n-type semiconductor

ii. P-type semiconductor:

P-type semiconductor is an excess positivity charged holes-containing semiconductor and is obtained by adding an extremely small quantity of trivalent element (like boron, aluminium) to the pure semiconductor (like silicon, germanium, etc.) crystal lattice

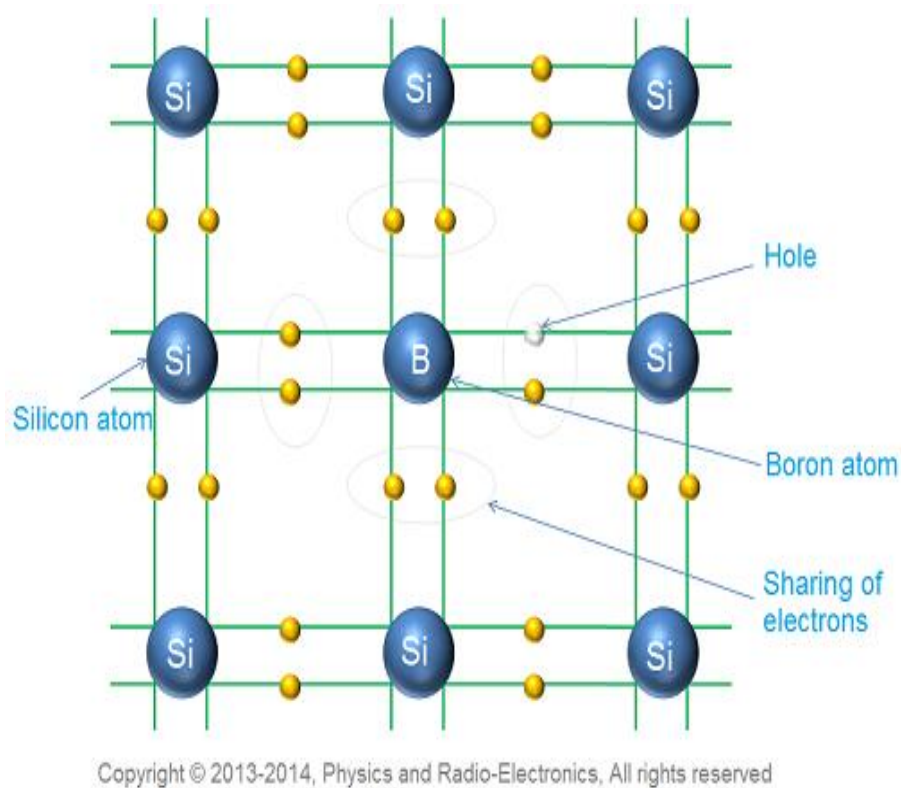


Fig 3.6 n-type semiconductor

MODULE - IV

STEREOCHEMISTRY, REACTION MECHANISM AND SYNTHESIS OF DRUG MOLECULES

5.0 Introduction

Stereochemistry is the study of the relative arrangement of atoms or groups in a molecule in three dimensional space. Stereochemical isomers are molecules, which have the same chemical formula and bond connectivity but different relative arrangement in three- dimensional space. In contrast, constitutional isomers have same molecular formula but different bond connectivity. Thus, n-butane and isobutene are structural isomers while the isomers of limonene, the compound which gives different taste to lemon and orange are examples of Stereochemical isomers (Figure 1).

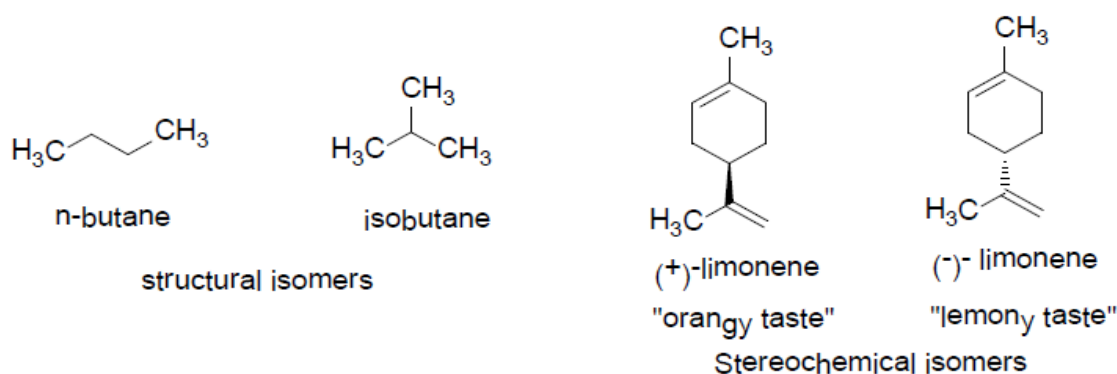


Figure 1

Fig 5.0 Structural isomers

To understand the difference between the two isomers of limonene, introduction to some new terms and concepts are required. The most important being the concept of chirality. A chiral object is one that cannot be superposed on its mirror image. The term originates from the greek term for “hand”. As it is with human hands, the left hand cannot be superimposed on the right hand. It is the same with chiral molecules. They are non- super imposable mirror images of each other. Achiral objects, on the other hand, are easily super imposable on each other. A tennis racquet and a spoon are examples of achiral objects.

The next question that comes to the mind is how to determine whether a molecule is chiral or achiral. At times, it becomes extremely difficult to determine with increasing molecular complexity, to determine the non superimposibility of a compound with its mirror image. Thus, a mathematical concept known as group

theory can be applied to determine the symmetry elements in a molecule. There are four symmetry elements which needs to be considered for this purpose:

5.1.1 Centre of symmetry (i)

The center of symmetry *i* is a point in space such that if a line is drawn from any part (atom) of the molecule to that point and extended an equal distance beyond it, an analogous part (atom) will be encountered. Thus the molecule 3,6-dimethylpiperazine-2,5-dione has centre of symmetry (sometimes referred to as centre of inversion) running through the centre of themolecule.

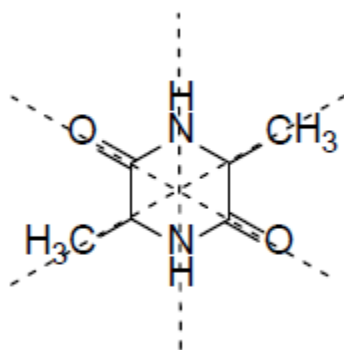


Fig 5.1.1 Centre of symmetry

5.1.2 Plane of symmetry (σ):

A plane of symmetry is a reflection plane which brings into coincidence one point of the molecule with another one through the mirror reflection. Thus, glyoxal has a plane of symmetry running through the molecular plane.

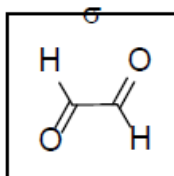


Fig 5.1. 2 Plane of symmetry

5.1.3 Axis of symmetry (C_n)

Symmetry axis C_n , also called n-fold axis, is an axis which rotates the object (molecule) around by $360^\circ/n$, such that the new position of an object is superimposable with the original one. For example, (1Z,4E,8E)- 3,7,11-trimethylcyclo-dodeca-1,4,8-triene has 3-fold rotation axis.

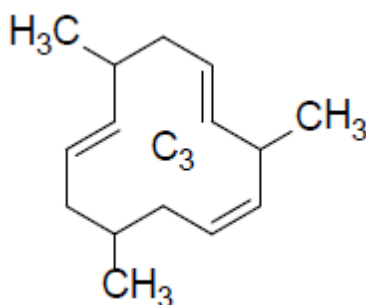


Fig 5.1.3 Axis of symmetry

5.1.4 Rotary reflection axis (S_n)

Rotary reflection axis is an axis which rotates the object (molecule) around by $360^\circ/n$, followed by rotation in a plane perpendicular to the axis, such that the new position of an object is superimposable with the original one. All odd values of S_n are identical with C_n . Thus, in **1**, there is a 4- fold rotary reflection axis.

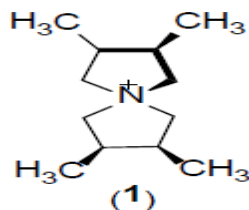


Fig 5.1.4 Rotatory reflection axis

If a molecule has only either centre of symmetry or plane of symmetry then it is achiral. However, in most cases, molecules have more than one element of symmetry. In such cases, it becomes important to know the point group to which the molecule belongs. A point group reflects the combination of symmetry elements present in the structure. The point group of a molecule can be determined by following the algorithm given below. The point groups of high symmetry are usually not important in simple organic molecules. The point groups C_1 , C_n and D_n are chiral groups and they contain chiral molecules while all other groups are achiral (Figure2).

5.2 Enantiomers

If a molecule is non-superimposable on its mirror image, then the molecule is said to have enantiomeric relationship with its mirror image molecule. For example, in 2-chloropropane, the molecule is superimposable with its mirror image, so they are identical molecules, but in 2-chlorobutane, the molecule is not superimposable with its mirror image and the two molecules are called enantiomers (Figure 3). Thus, enantiomers are stereoisomers since they differ only in the relative arrangement of the different groups in space but not in bond connectivity. Enantiomers are identical in all physical properties (except optical rotation) and chemical properties and reactivity compared to an achiral reagent in reactivity.

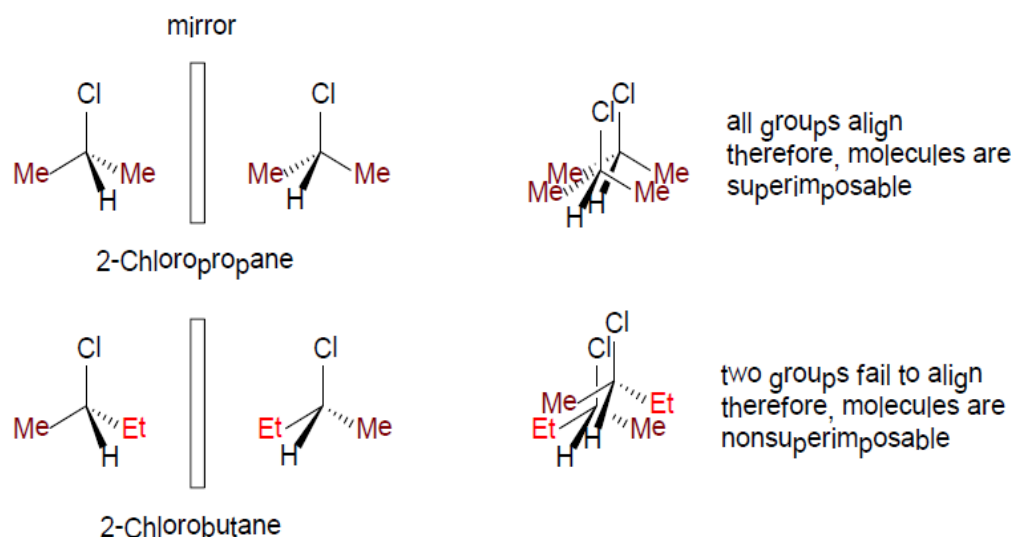


Fig 5.2 Enantiomers

Obviously, the next issue is how to detect and analyse the enantiomers physically. In this respect, in 1801, Haüy, a French mineralogist observed that some quartz crystals rotate polarized light clockwise, while other crystals rotate polarized light to the left. Haüy also noticed that quartz crystals exhibit the phenomenon of hemihedrism (externally, some crystals are non-identical mirror images of other crystals). This is referred to as optical activity. Followed by this, J. B. Biot observed the optical activity in certain organic compounds and was able to conclude that it is a molecular property. In 1884, Louis Pasteur in an in genius experiment crystallized and physically separated two types of crystals of tartaric acid –one of which was hemihedral to the left while the other washemihedral to the right. When he dissolved the two forms separately and measured their optical rotation, he observed that the crystals having the hemihedral to the left rotated the plane of polarized light to the left and vice-versa. Louis Pasteur thus proposed that the two forms of tartaric acid are mirror image of each other(enantiomers).

The optical activity of a compound was found to be proportional to

- The concentration of the compound in solution(c)
- The length through light traverses through the solution(l)
- The wavelength used for the measurement (λ) and the temperature at which the measurement is made (t). Usually, the sodium D-line is used for polarimetric measurement.

Mathematically,

$$\alpha = [\alpha]_D/c \text{ at temperature } t$$

where $[\alpha]$ is the constant of proportionality

The constant of proportionality $[\alpha]$ is called specific rotation and is defined as the optical rotation in degrees of the plane of polarization of a ray of monochromatic light that passes through a tube 1 decimeter long containing the substance in solution at a concentration of 1 gram per millimeter in a polarimeter.

An enantiomer will thus rotate the plane of polarized light either clockwise or anticlockwise. The clockwise rotation is usually denoted by either of the prefix dextro or (+). Similarly anticlockwise rotation is denoted by laevo or (-). Thus, an equimolar mixture will not give any optical rotation at all. Such a mixture is referred to as a racemic mixture.

Whether a particular sample consists of a single enantiomer or a mixture of enantiomers can be determined by its observed specific rotation. For example, an enantiomerically pure sample-meaning only one enantiomer is present-of (*S*)-(+)-2-bromobutane will have an *observed specific rotation* of +23.1° because the specific rotation of (*S*)-(+)-2-bromobutane is +23.1°. If, however, the sample of 2-bromobutane has an observed specific rotation of 0°, we will know that the compound is a racemic mixture. If the observed specific rotation is positive but less than +23.1°, we will know that we have a mixture of enantiomers and the mixture contains more of the enantiomer with the *S* configuration than the enantiomer with the *R* configuration. From the observed specific rotation, we can calculate the **optical purity** of the mixture.

$$\text{optical purity} = \frac{\text{Observed specific rotation}}{\text{Specific rotation of the pure enantiomer}} \times 100$$

For example, if a sample of 2-bromobutane has an observed specific rotation of +9.2°, its optical purity is 0.40. In other words, it is 40% optically pure-40% of the mixture consists of an excess of a single enantiomer.

$$\text{Optical purity} = \frac{+9.2^\circ}{+23.1^\circ} \times 100 = 40\%$$

Because the observed specific rotation is positive, we know that the solution contains excess (*S*)-(+)-2-bromobutane. The **enantiomeric excess (ee)** tells us how much excess (*S*)-(+)-2-bromobutane is in the mixture. As long as the compound is chemically pure, enantiomeric excess and optical purity will be the same.

$$\begin{aligned} \text{Enantiomeric excess} &= \frac{\text{excess of a single enantiomer}}{\text{entire mixture}} \times 100\% \\ &= \frac{40\%}{100\%} = 40\% \end{aligned}$$

If the mixture has a 40% enantiomeric excess, 40% of the mixture is excess *S* enantiomer and 60% is a racemic mixture. Half of the racemic mixture plus the amount of excess *S* enantiomer equals the amount of the *S* enantiomer present in the mixture. Thus, 70% of the mixture is the *S* enantiomer and 30% is the *R* enantiomer.

Another class of stereoisomers is the so called diastereomers which have different chemical and physical properties. Such compounds may include geometrical isomers- the *cis* and *trans* isomers

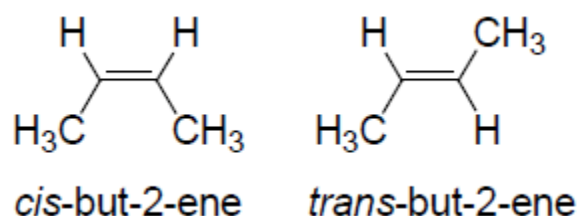


Fig 5.2 cis and trans isomers

A different type of isomerism may exist in disubstituted cyclic compounds. Thus, in 4- tert-butylcyclohexanol, two isomers-*cis* and *trans* exist (Fig 5).

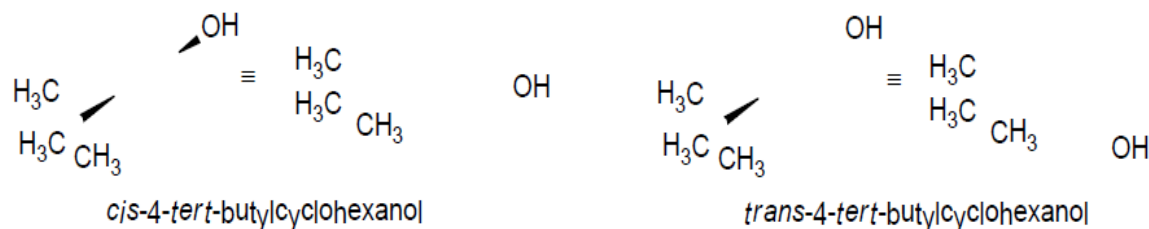
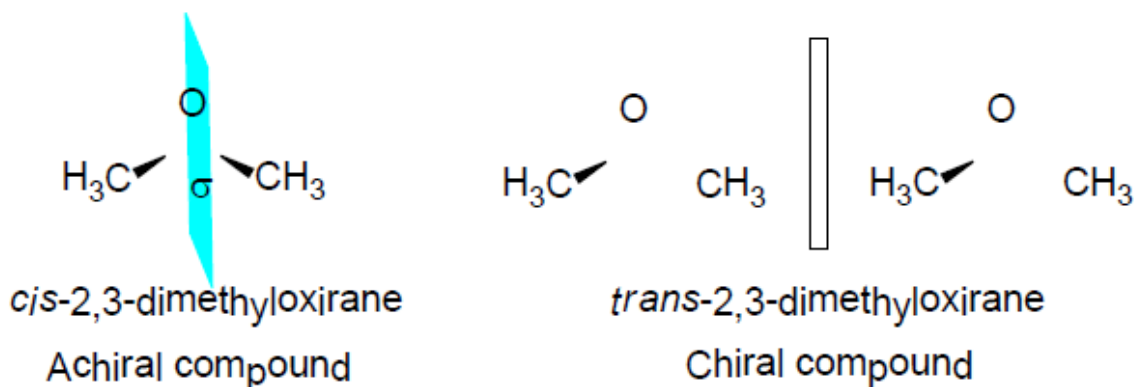


Fig 5.2 cis and trans isomers

Diastereomeric compounds may or may not be chiral. The above two examples are both achiral, each having a plane running through them. However, when *cis* and *trans* epoxides are compared, it can be easily seen that they may be chiral compounds. As an example, the comparison of *cis* and *trans* isomers of 2,3-dimethyloxirane, the *cis*-isomer is achiral having a plane of symmetry in the molecule. However, the *trans* isomer does not have any plane of symmetry through the molecule and as such it is a chiral molecule.



A similar observation can be made for 3-methyloxirane-2-carboxylic acid but here both the *cis* and *trans* isomers are chiral compounds each of which exist as a pair of enantiomers (Figure 7).

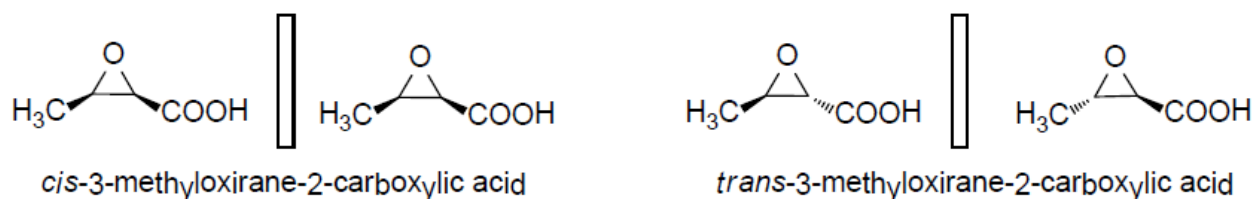


Fig 5.2 *cis* and *trans* isomers

The term chiral centre used so far is actually a subset of the term stereogenic centre. A stereogenic centre is defined as an element where the interchange of two substituents will lead to a stereoisomer. Not all stereogenic centres are chiral centres and even achiral molecules may have stereogenic centres.

The actual arrangement of the atoms or groups in a molecule about a stereo centre is called absolute configuration. It is mostly determined by X-ray crystallography or by inference based on chemical reactions of specific stereochemistry involving a compound whose absolute configuration is known, whereas the relative configuration is defined as the correlation between the different stereogenic centres within the molecule.

Though, here, the enantiomers are represented in the flying wedge form where two of the groups around the chiral centre are depicted in the plane of the paper and groups towards us in bold bonds and groups away from us in broken bonds, there are other forms of depictions of chiral compounds. These are discussed.

5.3 Fischer projection formula.

It is a representation of a 3D molecule as a flat structure where a tetrahedral carbon is represented as two crossed lines. The two vertical bonds about the stereocentre are above the plane of paper (towards the viewer) while the horizontal bonds are below the plane of the paper (away from the viewer) .

A few examples of depiction of molecules in Fischer projection formula is given below. It must be noted that when bonds are rotated by 180° , they result in the same identical molecule

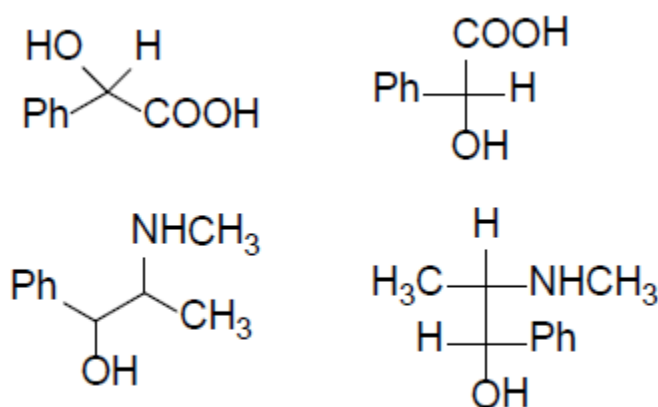
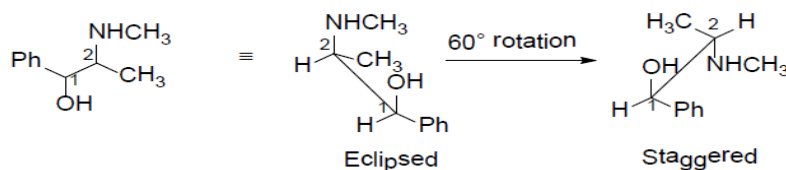


Fig 5.3 Fischer projection formula.

5.4 Sawhorse projection formula.

Sawhorse projection formulas are used to denote two principal stereocentres. It is a view of a molecule down a particular carbon- carbon bond, with the groups connected to both the front and back carbons are drawn using sticks at 120° angles. Sawhorse Projections can also be drawn so that the groups on the front carbon are staggered (60° apart) or eclipsed (directly overlapping) with the groups on the back carbon. The overall representation is given below.



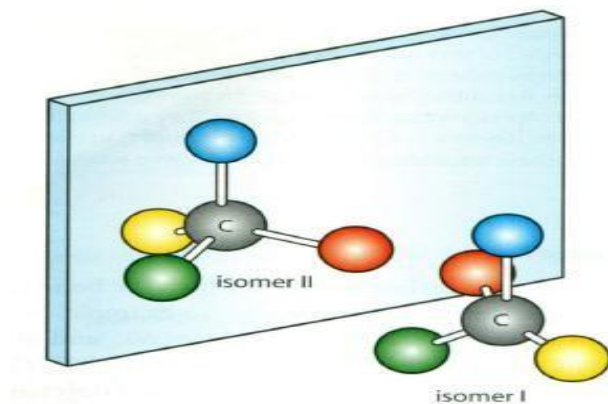
5.5 Newman projection formula.

In this notion, the molecule is again viewed by looking down a particular carbon-carbon bond. The front carbon of this bond is represented by a dot, and the back carbon is represented by a large circle. The three remaining bonds are drawn as sticks coming off the dot (or circle), separated by one another by 120° . Just like Sawhorse projection formula, Newman Projection can be drawn such that the groups on the front carbon are staggered (60° apart) or eclipsed (directly overlapping) with the groups on the back carbon.

5.6 Optical isomers

A carbon atom attached to four *different* atoms or groups is known as **asymmetric** or **chiral**. The four groups, arranged tetrahedrally around the carbon atom with bond angles of 109.5° , can be arranged in two different three-dimensional configurations which are mirror images of each other. This is known as **optical isomerism**. The term refers to the ways in which the isomers interact with plane-polarized light, discussed below. They are said to be **chiral molecules** and have no plane of symmetry.

In the following figure, an asymmetric, or chiral, carbon atom, shown in black, is bonded to four different atoms or groups shown here in different colors. This gives rise to two configurations which are mirror images of each other.



5.6 Optical isomers

The word *chiral* is derived from the Greek word for “hand”. Lord Kelvin first introduced the term into science in 1904 with the now celebrated definition: “I call any geometrical figure, or group of points, chiral, and say it has chirality if its image in a plane mirror, ideally realized, cannot be brought to coincide with itself.” His definition can therefore be applied much more generally to structures outside Chemistry, such as knots.

If you look at your two hands, you will see that they also are mirror images. When you put them directly on top of each other, the fingers and thumbs do not line up - we say they are non-superimposable. ⁶⁷



5.6 Enantiomers

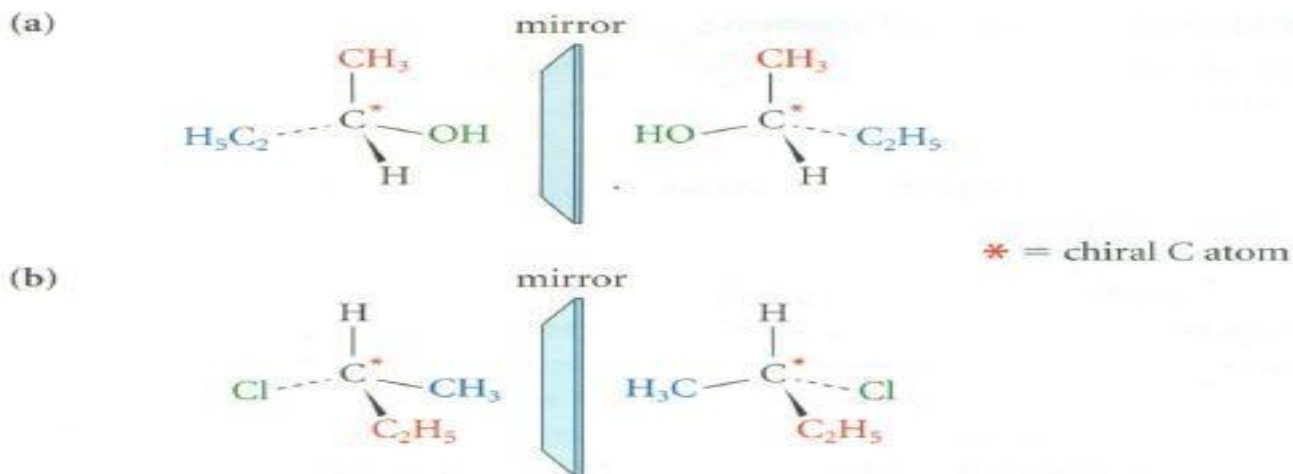
The same is true for optical isomers, and the two non-superimposable forms are known as enantiomers. A mixture containing equal amounts of the two enantiomers is known as a racemic mixture or a racemate. As we will see, such a mixture is said to be optically inactive.

A single chiral centre in a molecule gives rise to two stereoisomers. In general, a molecule with n chiral centres has a maximum of 2^n stereoisomers, although some may be too strained to exist. For example, cholesterol has eight chiral centres and so a possible $2^8 = 256$ stereoisomers. Only one is produced in biological systems.

We can find optical activity in many of the molecules we have already encountered in this chapter. The clue is to look for any carbon atom that is bonded to four different groups. It is often useful to mark that carbon with an asterisk.

When you are looking for a chiral carbon atom in a molecule, you must look at the whole group bonded to the carbon, not just the immediately bonded atom – for example CH_3 is a different group from C_2H_5 .

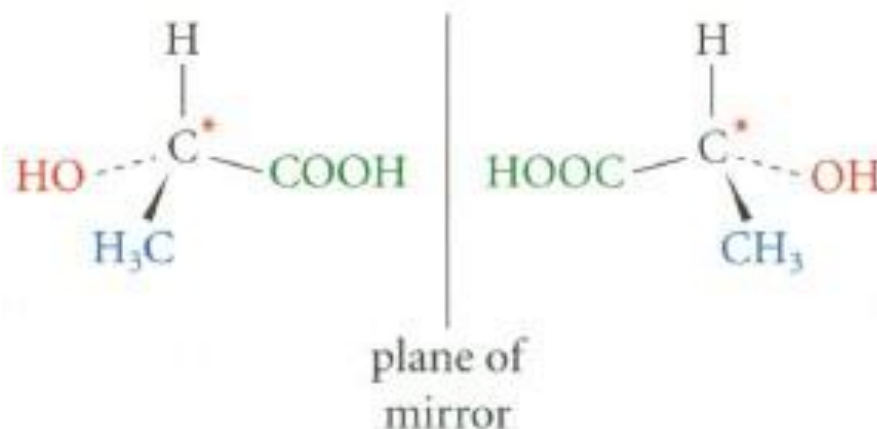
Worked example



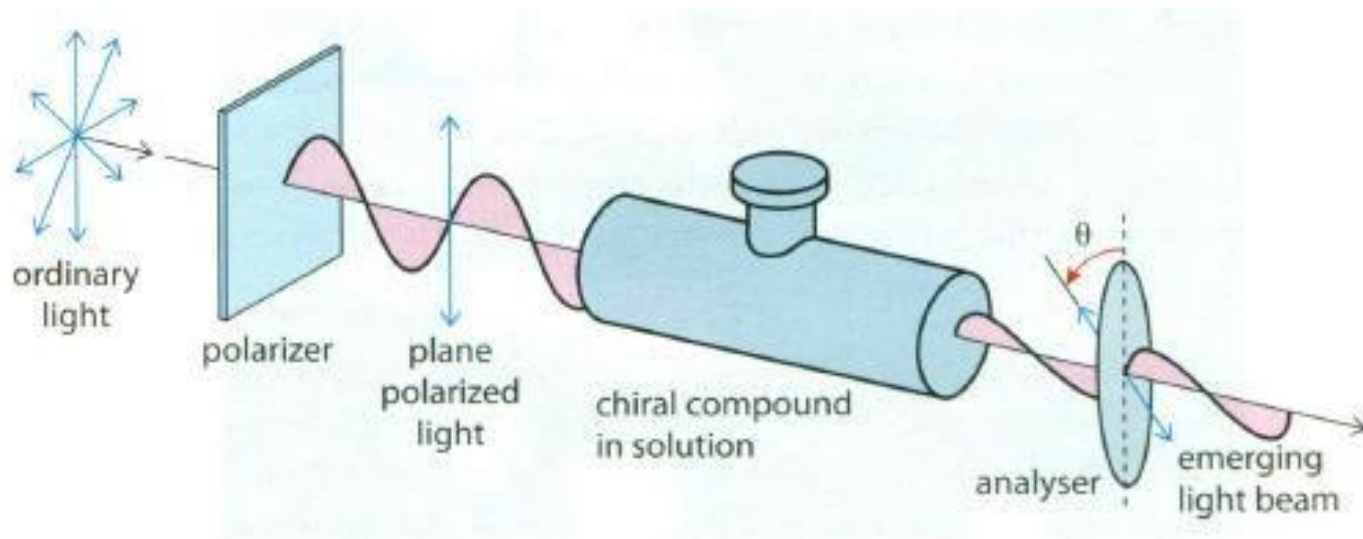
Draw the enantiomers of 2-hydroxypropanoic acid (lactic acid). Mark the chiral carbon atom and show the plane of the mirror.

Solution:

First draw out the full structure and identify the chiral carbon atom.

**Properties of optical isomers**

Optical isomers, the enantiomers, have identical physical and chemical properties – with two important exceptions:



- optical activity
- reactivity with other chiral molecules

5.7 Optical activity

As we know from their name, optical isomers show a difference in a specific interaction with light. A beam of ordinary light consists of electromagnetic waves that oscillate in an infinite number of planes at right angles to the direction of travel. If, however, this light is passed through a device called a **polarizer**, only the light waves oscillating in a single plane pass through, while light waves in all other planes are blocked out. This is known as **plane-polarized light**. A similar effect is achieved in polarized sunglasses or windshields to reduce glare. In the early 1800s, it was discovered that when a beam of plane-polarized light passes through a solution of optical isomers, they rotate the plane of polarization.

The amount and direction of rotation can be measured with an instrument called a **polarimeter**.

The solution of isomers is placed in the sample tube through which plane polarized light is passed. Rotation of the polarization plane occurs and the light then passes through a second polarizer called the analyser, which has been rotated until the light passes through it. Thus the extent and direction of rotation brought about by the sample can be deduced. In order to compare different solutions, the concentrations of the solutions, the wavelength of light used and the sample path length must all be kept the same.

The pioneer of polarimetry was Jean Baptiste Biot (1774-1862), a French physicist and older friend of the famous French bacteriologist Louis Pasteur (1822-1895). Biot showed that some crystals of quartz rotated the plane of polarized light while other crystals rotated it to the same extent in the opposite direction. Later, by showing the same effect in liquids such as turpentine, and in solutions of naturally occurring substances such as sugar, he realized it must be a molecular property and coined the term “optical activity”. In 1848, Pasteur was working on crystalline salts derived from wine and discovered that while tartaric acid showed optical activity, racemic acid – with the same chemical composition – did not. He deduced that this was because racemic acid contained an equal mixture of two isomers (such mixtures are now described as racemic). Pasteur saw the huge significance of this. He reasoned that reactions outside the cell always produce an optically inactive mixture whereas biological activity is specific to one isomer. In his later work on the origin of life, this became his guiding distinction between living and inanimate material.

Different notations are used to distinguish the two enantiomers of a pair: (+) and (-) refer to the direction in which the plane-polarized light is rotated; (+) for a clockwise direction and (-) for anticlockwise rotation. The lower-case letters d- (dextrorotatory) and l- (levorotatory) respectively have traditionally been used as alternatives for this but are becoming obsolete. Confusingly, D- and L- are a different, unrelated notation based on spatial configurations in comparison with the reference molecule glyceraldehyde. This system is widely used in naming many biological molecules such as amino acids and sugars.

Other molecules are described by their absolute configuration, using R (rectus) for right or clockwise and S (sinister) for left or counter-clockwise. The rules for determining the absolute configuration are based on atomic number and mass.

Happily, we will not adopt any particular system here and you will not be expected to identify the specific enantiomer in any of these examples.

Separate solutions of enantiomers, at the same concentration, rotate plane-polarized light in equal amounts but opposite directions. A racemic mixture does not rotate the light, which is why it is said to be optically inactive. Naturally occurring chiral molecules are optically active, in other words they exist as only one enantiomer. For example, morphine rotates plane-polarized light to the left so is said to be (-), whereas sucrose rotates plane-polarized light to the right and is said to be (+).

5.7.1 REACTIVITY WITH OTHER CHIRAL MOLECULES

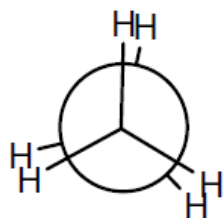
When a racemic mixture is reacted with a single enantiomer of another chiral compound, the two components of the mixture, the (+) and (-) enantiomers, react to produce different products. These products have distinct chemical and physical properties and so can be separated from each other relatively

easily. This method of separating the two enantiomers from a racemic mixture is known as resolution. The different reactivity of a pair of enantiomers with another chiral molecule is of particular significance in biological systems because these *are* chiral environments. An infamous example of the different reactivities of enantiomers occurred in the 1960s when thalidomide was prescribed to pregnant women for morning sickness. One enantiomer is therapeutic but the other produces severe malformations in the fetus. This tragedy largely spearheaded research into processes for the manufacture of a single enantiomer using a chiral catalyst. The process, known as asymmetric synthesis, was developed by three scientists who shared the Nobel Prize in Chemistry in 2001.

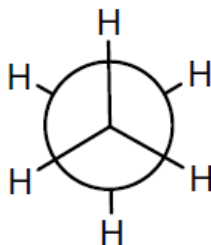
Other examples of the importance of chirality from biology include the fact that taste buds on the tongue and sense receptors in the nose contain chiral molecules and so interact differently with the different enantiomers. For example, D-amino acids all taste sweet, whereas L-amino acids are often tasteless or bitter. Similarly, we can distinguish between the smells of oranges and lemons due to the presence of different enantiomers of the compound limonene.

5.8 CONFORMATIONS

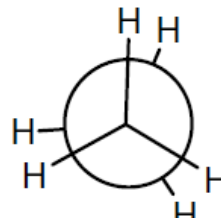
Electron distribution of carbon-carbon bond is cylindrically symmetrical about the line joining the two carbon nuclei. Rotation is possible about a single bond and this rotation means that, while localized arrangement of atoms stays the same, the molecule as a whole can adopt a number of different shapes. For example, ethane the simplest C-C bond possible molecule, could have an arrangement like **1** in which the hydrogen's exactly oppose each other, an arrangement like **2** in which the hydrogen's are perfectly staggered and an infinite number of intermediate arrangements **3** which is neither **1** nor **2**.



1



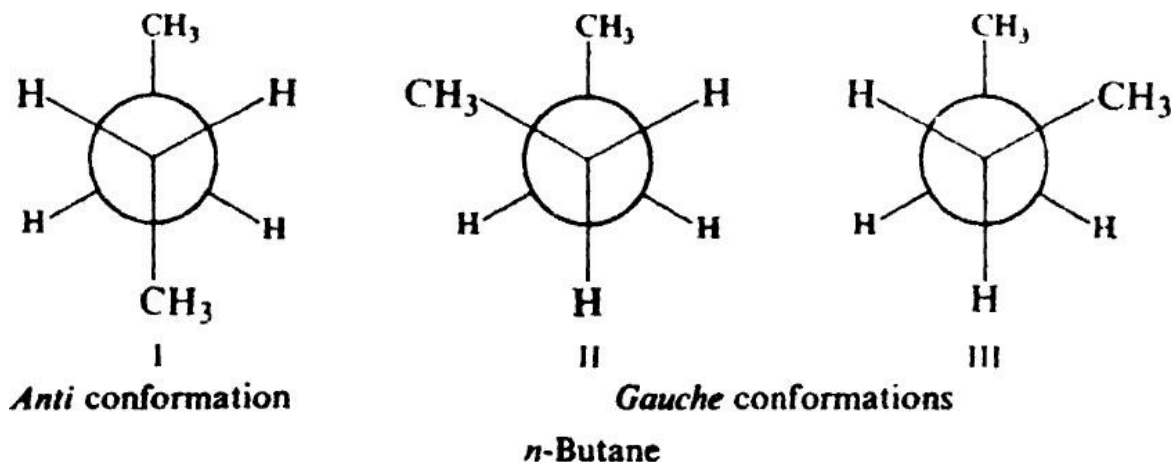
2



3

5.8.1 CONFORMATIONS OF n-Butane.

Let us look more closely at the n-butane molecule and the conformations in which it exists. Focusing our attention on the middle C- C bond, we see a molecule similar to ethane, but with a methyl group replacing one hydrogen on each carbon.



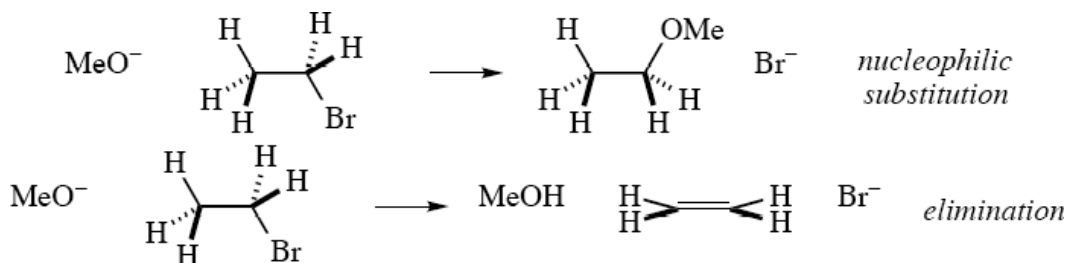
5.8.2 DEFINITIONS.

In an acid–base reaction such as $\text{CH}_3\text{CO}_2\text{H} + \text{NH}_3 \rightarrow \text{CH}_3\text{CO}_2^- + \text{NH}_4^+$ the N acts as a *nucleophile* (Greek for “loving the nucleus”), the H acts as an *electrophile* (“loves electrons”), and the O that accepts the pair of electrons acts as a *leaving group*. The acid–base reaction is the simplest model for a *substitution* reaction, which is a reaction in which a σ bond between atom 1 and atom 2 is replaced by a σ bond between atom 1 and atom 3. Substitution reactions are incredibly important in organic chemistry, and the most important of these involve substitutions at C. Foreexample:



This substitution reaction, discovered in 1849, involves the *nucleophilic* O making a new bond to the *electrophilic* C, and the bond between the electrophilic C and the *leaving group* I breaking. Any Brønsted base can also act as a nucleophile, and any nucleophile can also act as a Brønsted base, but some compounds are particularly good bases and particularly poor nucleophiles, whereas some are particularly poor bases and particularly good nucleophiles. Any Brønsted or Lewis acid can also act as an electrophile, but there are many electrophiles that are neither Brønsted nor Lewis acids (as in the example above). A haloalkane, e.g. $\text{CH}_3\text{CH}_2\text{Br}$, can in principle undergo either of two polar reactions when it encounters a lone pair nucleophile, e.g. MeO^- . First, MeO^- might *replace* Br^- at the

electrophilic C atom, forming a new C–O bond and giving an ether as the product. This is *substitution*, because the C–Br σ bond is replaced with a C–O σ bond. Second, MeO[–] might attack a H atom that is *adjacent* to the electrophilic C atom, giving MeOH, Br[–], and an alkene as products. The electrons in the C–H bond move to form the π bond, and the electrons in the C–X bond leave with X[–]. This is *elimination*, because a new π bond is formed, and because the elements of the organic starting material are now divided between more than one product. Elimination requires that the substrate have a C–X bond *and* adjacent C–H bonds, while substitution requires only that the substrate have a C–X bond.

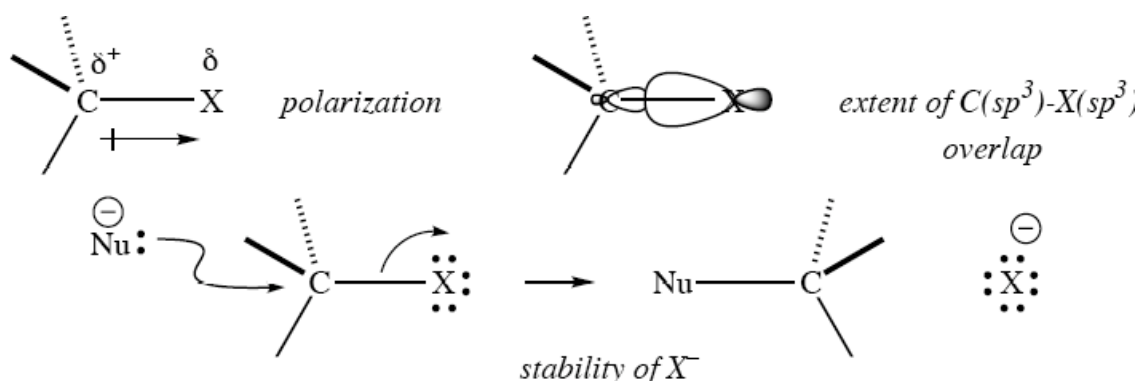


A reaction involves the formation and cleavage of bonds. A mechanism is a story we tell about the changes in the arrangement of the electrons in the starting materials that led to products. When multiple bonds are made or broken, they are usually not made and broken all at one time. A mechanism describes the order in which the different bonds are made and broken and which electrons moved to break and form particular bonds. A mechanism can also help us generate hypotheses about the rate and stereochemical results of a reaction that we can then use to test whether our idea about how the reaction occurred is correct.

5.8.3 Leaving Groups.

All substitution and elimination reactions require a σ bond electrophile. The most common such electrophile is a haloalkane, RX, where the leaving group is halide, X[–]. Different halides, though, have different *leaving group abilities*. The leaving group ability of X[–] is determined by two factors.

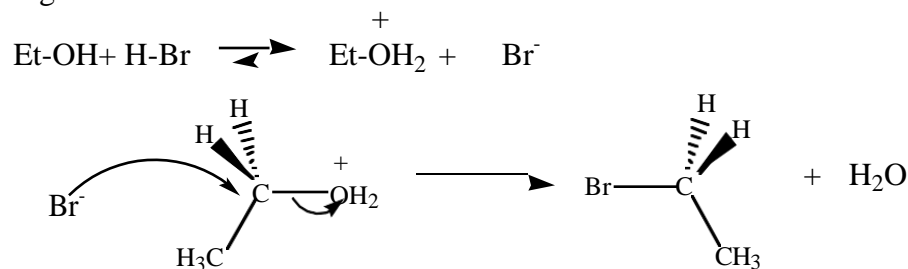
- The *strength* of the C–X bond. The weaker the bond, the better the leaving group. The strength of the bond depends on the amount of orbital overlap between C and X. C is a small element, so the overlap decreases as the size of X increases, i.e. F > Cl >> Br >> I.
- The *polarization* of the C–X bond. The more polarized the bond, the better the leaving group. The bond polarization decreases with decreasing electronegativity of X, i.e. in the order F > Cl > Br >> I. The actual order of leaving group ability is I[–] > Br[–] > Cl[–] >> F[–].



In fact, alkyl fluorides are nearly inert to substitution or elimination (hence the stability of Teflon). Other electronegative groups, e.g. RO^- , can also act as leaving groups in principle. Comparing F^- and HO^- , both are about the same size, but F^- is more electronegative. So we can conclude that HO^- is a worse leaving group than F^- . Since F^- is already a very bad leaving group, HO^- must be a *really* bad leaving group. HO^- usually leaves only when the mechanism is $E1cb$, which we haven't discussed, or when extremely harsh conditions are used (i.e., 50% aq.KOH).

There are several ways to make HO^- is better leaving group:

- (1) Protonate the alcohol with a strong acid to get the conjugate acid of the alcohol. E.g.

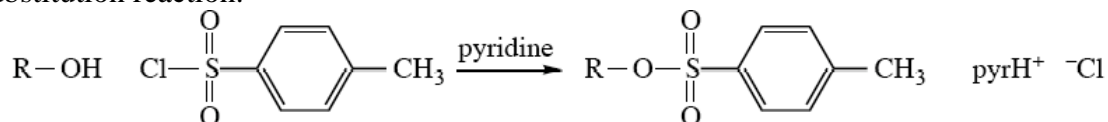


This converts a poor leaving group HO^- into the pretty good leaving group OH_2 (leaving group ability $\approx Cl^-$). Alcohols ROH are weak bases, with pK_a of their conjugate acids $ROH_2^+ \approx 0$, so an alcohol ROH is only protonated under acidic conditions to give ROH_2^+ , an electrophile with a pretty good leaving group. This does not happen under basic conditions. Alcohols are electrophiles under acidic conditions, but not under basic conditions.

- (2) Replace the H in HO^- with more electronegative groups.

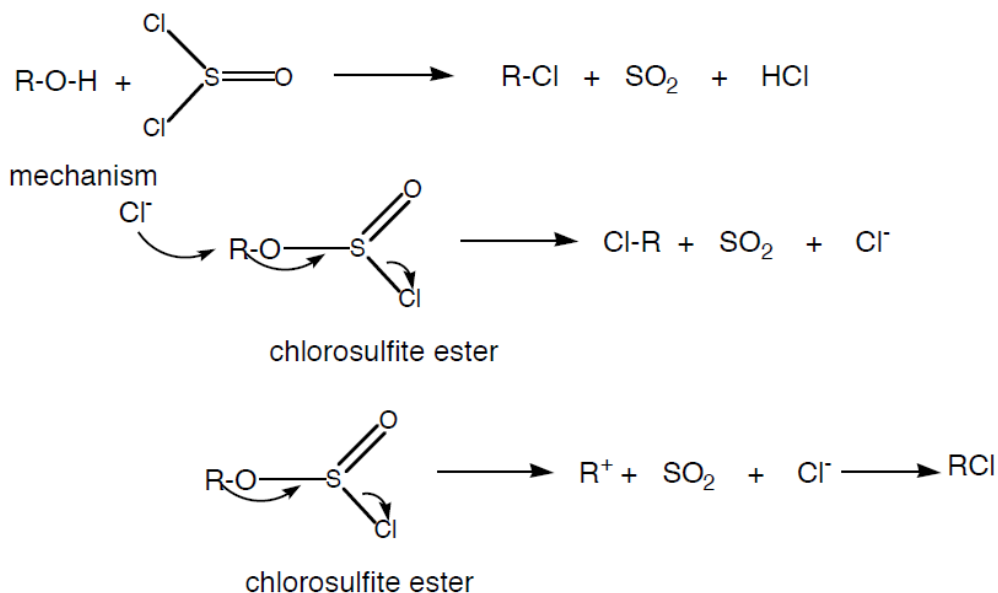
When H is replaced with $RS(O)_2$, one obtains a very important class of leaving groups, the sulfonate esters. The most common sulfonates, RSO_3^- , are tosylate (short for toluenesulfonate, $^-$ OTs) and mesylate ($^-$ OMs, short for methanesulfonate). Tosylates and mesylates are easily

made from alcohols and tosyl chloride TsCl or mesyl chloride MsCl. The O of the alcohol acts as a nucleophile toward electrophilic S, displacing the leaving group Cl^- by an $\text{S}_{\text{N}}2$ substitution reaction.



The conversion of an alcohol to a tosylate represents a way of turning a lousy leaving group, OH^- , into a good leaving group, OTs^- (leaving group ability $\approx \text{Br}^-$). Tosylates are sometimes called *pseudohalides*, because their properties are similar to the halides. From now on, whenever we say halides, we are also referring to tosylates and mesylates.

A variation on the sulfonate reaction involves treatment of alcohols with thionyl chloride SOCl_2 – this initially gives a chlorosulfite ester which can decompose by a $\text{S}_{\text{N}}2$ pathway or direct decomposition to SO_2 and ion recombination



This reactions results in conversion of the HO^- poor leaving group into a good one (SO_2 and Cl^-).

5.8.4 Nucleophiles.

A nucleophile is a compound that has a relatively high energy pair of electrons that is available to react with an electrophile. In other words, any Brønsted base is also a nucleophile.

In this Unit we will be talking about substitutions at $\text{C}(\text{sp}^3)$ electrophiles, and in these cases the nucleophile is generally either a metal salt (KOH , NaNH_2 , EtSK ,

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{ONa}$, NaBr) or a neutral compound with a lone pair (R_3N , H_2O , ROH , RCO_2H , R_2S , R_3P).

Remember that a metal salt such as KBr is dissociated into two ions, K^+ and Br^- , and the latter is the species that acts as a nucleophile. Sometimes we do not draw the counterion associated with the anionic nucleophile. Substitutions are usually carried out under basic or acidic conditions.

All nucleophiles are also Brønsted bases, but they may be strong bases or weak bases. **Only weak bases can exist under acidic conditions**, so under acidic conditions the nucleophiles we tend to see are weak bases only. This means either they are neutral or they are anionic but from the 3rd row of the periodic table or below (usually Cl^- , Br^- , or I^-). **Under basic conditions, though, any nucleophile can exist.**

5.9 MECHANISMS OF SUBSTITUTION REACTIONS.

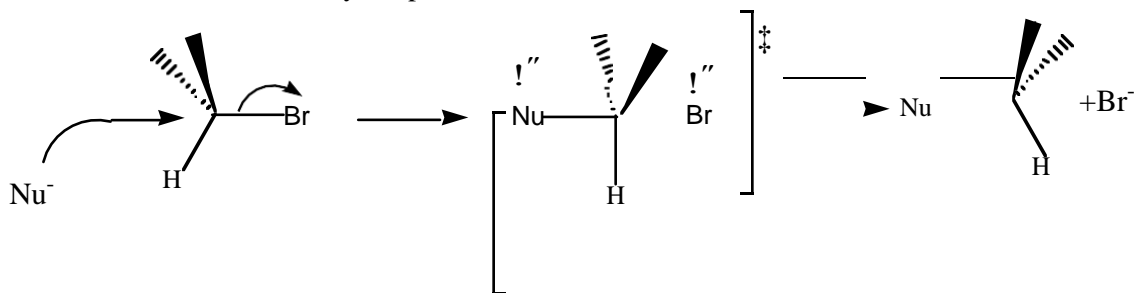
Let's look at the mechanism of nucleophilic substitution reactions. Substitution can in principle occur in three ways.

1. The nucleophile comes in at the same time as the leaving group leaves.
2. The leaving group leaves, then the nucleophile comes in.
3. The nucleophile comes in, then the leaving group leaves.

The third way requires a 10-electron C intermediate, though, so it doesn't occur at electrophilic tetrahedral C atoms. (It can occur in substitutions at transition metals and certain heavy atoms, however.)

5.9.1 $\text{S}_{\text{N}}2$ MECHANISM.

In the first mechanism for substitution, the nucleophile attacks the electrophilic C atom directly. As the nucleophile comes in, the C atom begins to acquire more than eight electrons, so the bond to the leaving group breaks simultaneously. In the TS, the C atom is partially bound to both the nucleophile and the leaving group. The nucleophile continues to come in and the leaving group continues to leave, until finally the product has been obtained.



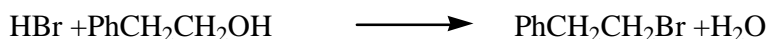
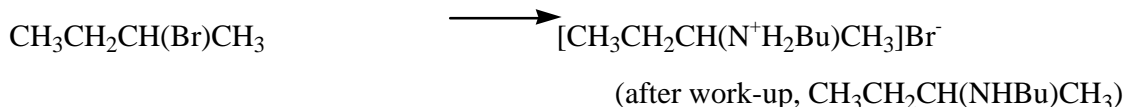
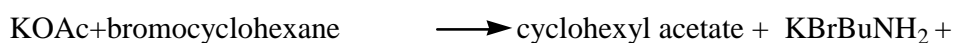
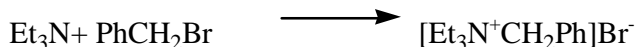
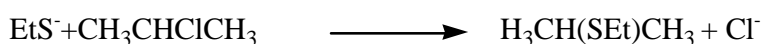
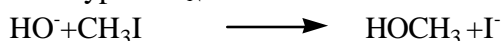
This mechanism has no intermediates. Because of this, the rate-determining step is bimolecular; that is, the rate of the reaction is described by the following equation:

$$\text{rate} = k [\text{Nu}^-][\text{alkyl halide}]$$

In other words, the rate of the reaction is proportional to *both* the concentration of the nucleophile *and* the concentration of the organic substrate. If one halves the concentration of nucleophile, the rate of the reaction should halve as well. This mechanism is called **SN2**, for

substitution/nucleophilic/bimolecular.

Some typical S_N2 substitution reactions:



Note that the electrophilic C in every example has at least one H attached; that is, the alkyl group in the alkyl halide is either Me, primary (1°, two H's), or secondary (2°, one H), but never tertiary (3°, no H's). The last phenomenon is due to steric hindrance of the S_N2 substitution reaction.

We can draw a reaction coordinate diagram for the S_N2 reaction. A reaction coordinate diagram is a way of showing the energy of the system as it moves from starting materials through the transition state to the products. The S_N2 substitution reaction has a particularly simple reaction coordinate diagram: starting materials, a single transition state, and products.

In the S_N2 mechanism the substrate goes from a four-coordinate C in the starting material to a very crowded five-coordinate C in the TS, so the reaction is very sensitive to steric hindrance about the electrophilic

Tertiary alkyl halides do not undergo S_N2 substitution reactions

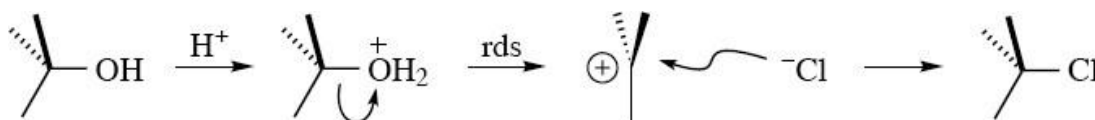
Note also that nucleophiles can be neutral or anionic. Also note that most entries are under basic conditions. (The last entry shows that the S_N2 reaction can occur under acidic conditions under special circumstances which we will discuss soon; for now, note that the OH acts as a leaving group in this case only because the conditions are acidic.)

5.9.2 S_N1 MECHANISM.

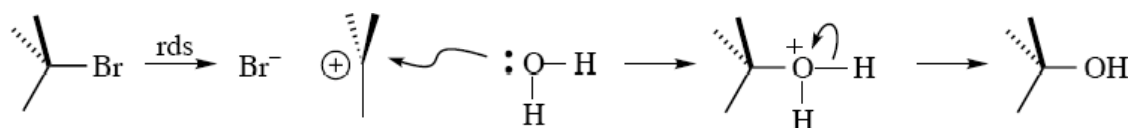
In the second possible mechanism for substitution, the leaving group might leave *first* to generate an electron-deficient intermediate called a *carbocation*. This intermediate then combines with a nucleophile to give the product. This mechanism for substitution is called S_N1.



The S_N1 mechanism is commonly called a two-step mechanism, but it is important to realize that usually additional steps are required. For example, protonation of the leaving group (or reaction of the leaving group with some other Lewis acid) often occurs in a fast, reversible step before the leaving group leaves.



On the other hand, if the nucleophile is water, an alcohol, or a carboxylic acid, then deprotonation of O after the nucleophile adds to C constitutes a third, fast step. The deprotonation is required to give a neutral product.



A carbocation is electron-deficient, so it is by definition a Lewis acid. **Lewis acids can be generated only under acidic conditions. Therefore, the S_N1 substitution mechanism can occur only under acidic conditions.**

We can draw a reaction coordinate diagram for the S_N1 reaction. The carbocation is electron deficient, so it is much higher in energy than either the starting materials or the product. The reaction coordinate diagram for the S_N1 mechanism then looks like a double-humped camel. There is a TS on the way from the starting material to the carbocation, and there is another TS on the way from the carbocation to the product.

The rate-limiting step in this reaction (the highest barrier the reactants have to surmount) is the formation of the high-energy, electron-deficient carbocation intermediate. Only one molecule is

involved in formation of the carbocation, so the rate of the reaction is described by the following equation.

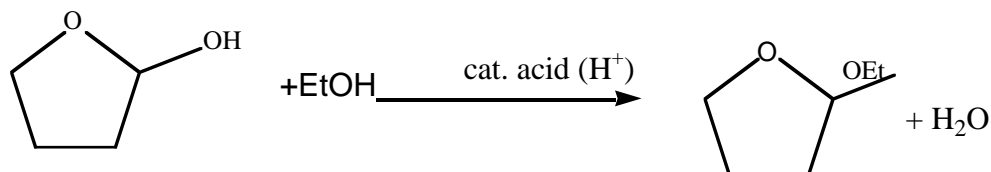
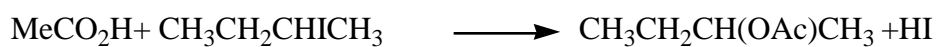
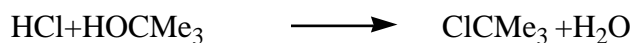
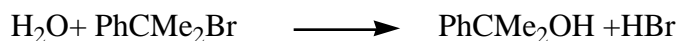
$$\text{rate} = k [\text{alkyl halide}]$$

In other words, the rate of the reaction is proportional *only to the concentration of the organic substrate*. We call this mechanism S_N1 , for

substitution/nucleophilic/unimolecular.

The dependence of the rate of a nucleophilic substitution reaction on the concentration of the nucleophile represents one way to determine whether a nucleophilic substitution is proceeding by the S_N1 or S_N2 mechanisms (S_N1 reactions are independent of nucleophile concentration)

Some typical S_N1 substitution reactions:

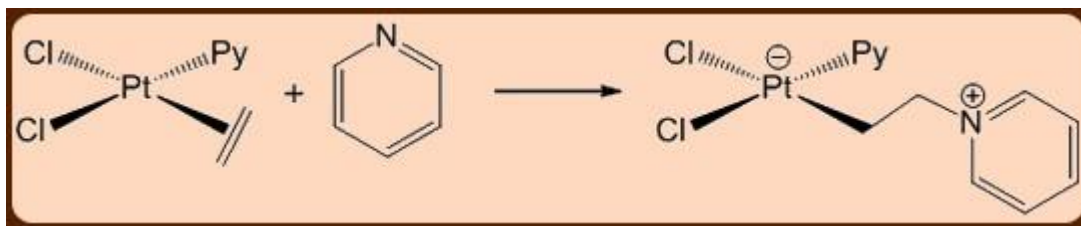


5.10 ELECTROPHILIC AND NUCLEOPHILIC ADDITION REACTIONS

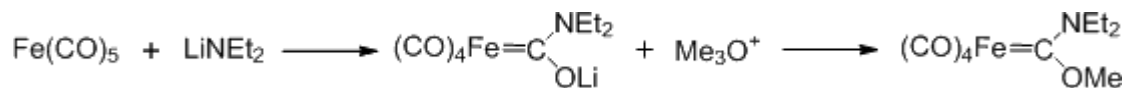
The nucleophilic and electrophilic substitution and abstraction reactions can be viewed as ways of activation of substrates to allow an external reagent to directly attack the metal activated ligand without requiring prior binding of the external reagent to the metal. The attacking reagent may be a nucleophile or an electrophile. The nucleophilic attack of the external reagent is favored if the L_nM fragment is a poor π -base and a good σ -acid *i.e.*, when the complex is cationic and/or when the other metal bound ligands are electron withdrawing such that the ligand getting activated gets depleted of electron density and can undergo an external attack by a nucleophile Nu^- , like $LiMe$ or OH^- . The attack of the nucleophiles may result in the formation of a bond between the nucleophiles and the activated unsaturated substrate, in which case it is called nucleophilic addition, or may result in an abstraction of a part or the whole of the activated ligand, in which case it is called the nucleophilic abstraction. The nucleophilic addition and the abstraction reactions are discussed below.

5.10.1 Nucleophilic addition

An example of a nucleophilic addition reaction is shown below

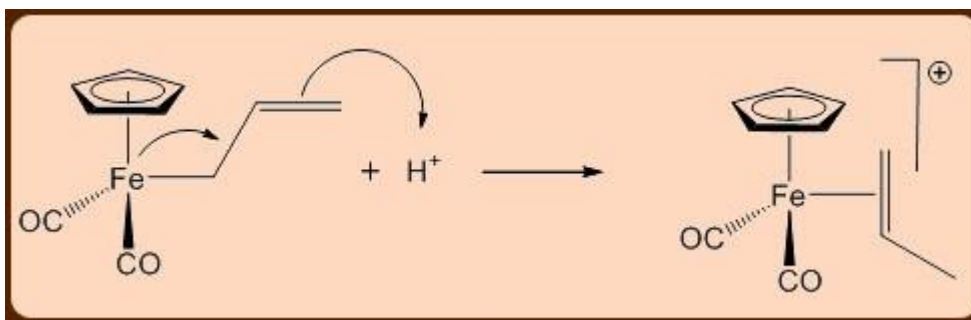


Carbon monoxide (CO) as a ligand can undergo nucleophilic attack when bound to a metal center of poor π -basicity, as the carbon center of the CO ligand is electron deficient owing to the ligand to metal σ -donation not being fully compensated by the metal to ligand π -back donation. Thus, activated CO ligand undergoes nucleophilic attack by the lithium reagent to give an anionic acyl ligand, which upon alkylation generates the famous Fischer carbenecomplex



5.10.2 ELECTROPHILIC ADDITION

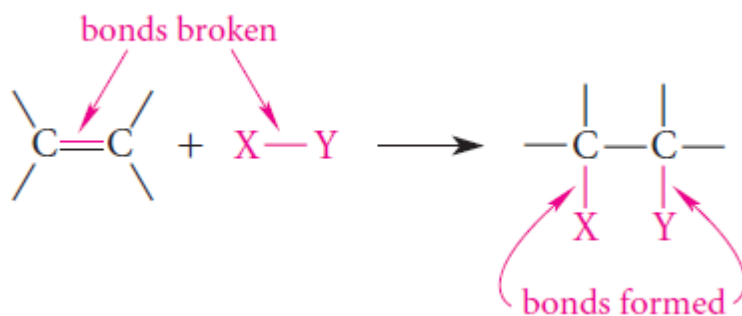
Similar to the nucleophilic addition and abstraction reactions, the electrophilic counterparts of these reactions also exist. An electrophilic attack is favored if the L_nM fragment is a good π -base and a poor σ -acid *i.e.*, when the complex is anionic with the metal center at low-oxidation state and/or when the other metal bound ligands are electron donating such that the ligand getting activated becomes electron rich from the π -back donation of the metal center and thus can undergo an external attack by an electrophile E^+ like H^+ and CH_3I . The attack of the electrophiles may result in the formation of a bond between the electrophile and the activated unsaturated substrate, in which case it is called electrophilic addition, or may result in an abstraction of a part or the whole of the activated ligand, in which case it is called the electrophilic abstraction.



5.11 ADDITION OF HYDROGEN HALIDES

The reaction with hydrogen halides, the reaction with hydrogen, called catalytic hydrogenation and the reaction with water, called hydration. These reactions will be used to establish some important principles of chemical reactivity that are very useful in organic chemistry.

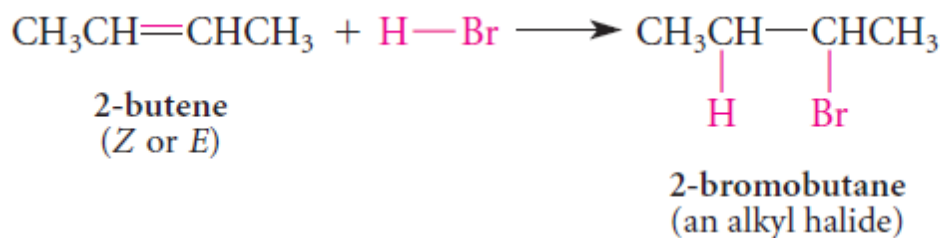
The most characteristic type of alkene reaction is **addition** at the carbon-carbon double bond. The addition reaction can be represented generally as follows



In an addition reaction, the carbon-carbon π bond of the alkene and the $X-Y$ bond of the reagents are

broken and new CL X and CL Y bonds are formed.

The hydrogen halides H F, H Cl, H Br, and H I undergo addition to carbon–carbon double bonds to give products called *alkyl halides*, compounds in which a halogen is bound to a saturated carbon atom.

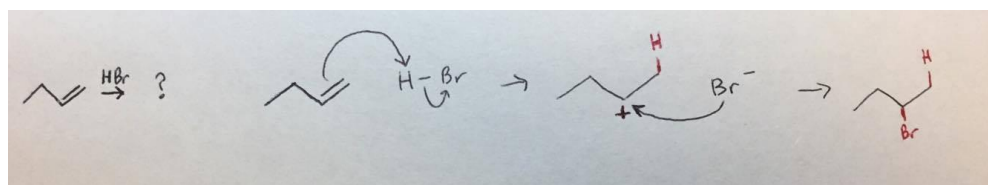


Although the addition of HF has been used for making alkyl fluorides, HF is extremely hazardous and is avoided whenever possible. Additions of HBr and HI are generally preferred to addition of HCl because additions of HBr and HI are faster.

5.11.1 Markovnikov's Rule:

In an addition reaction of a protic acid HX (hydrogen chloride, hydrogen bromide, or hydrogen iodide) to an alkene or alkyne, the hydrogen atom of HX becomes bonded to the carbon atom that had the **greatest number** of hydrogen atoms in the starting alkene or alkyne.

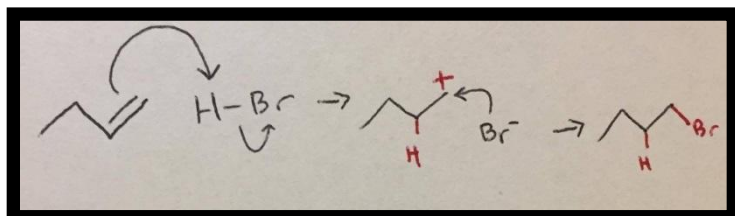
We will use Butene and H-Br as an example



Notice how the Hydrogen from the H-Br attaches at the terminal carbon of the alkene because that carbon originally had 2 hydrogens whereas the carbon on the other side of the double bond only has one.

5.11.2 ANTI-MARKOVNIKOV'S RULE:

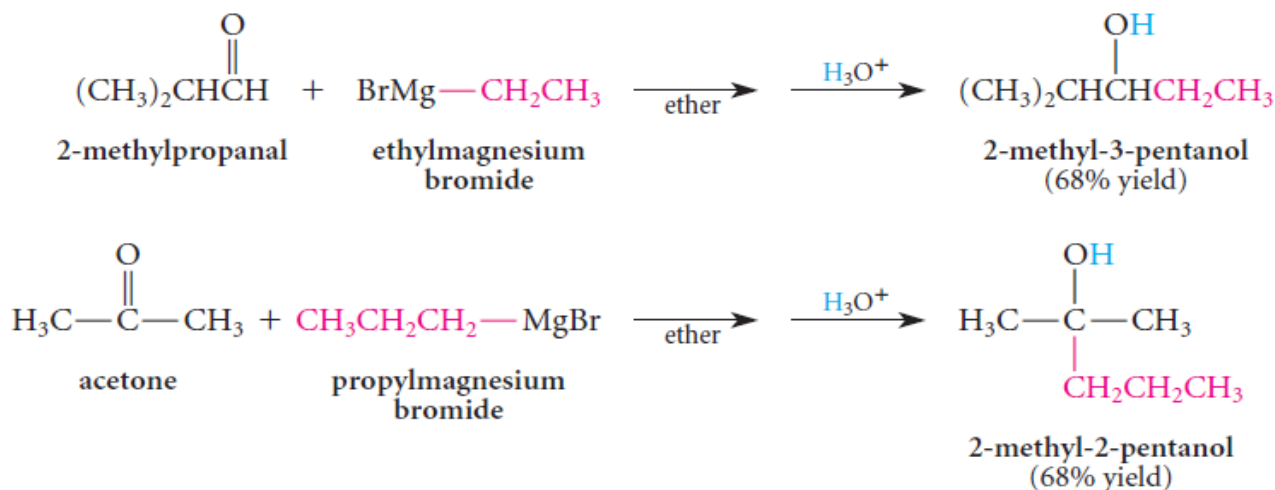
In an addition reaction of a generic electrophile HX to an alkene or alkyne, the hydrogen atom of HX becomes bonded to the carbon atom that had the **least number** of hydrogen atoms in the starting alkene or alkyne.



Notice that the Hydrogen from the H-Br is now attached at the carbon of the alkene that had only 1 hydrogen thus does not follow Markovnikov's rule and is the minor product.

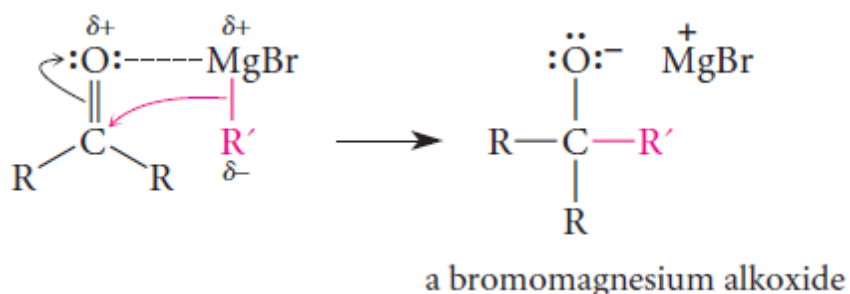
5.12 GRIGNARD ADDITIONS ON CARBONYL COMPOUNDS

The reaction of Grignard reagents with carbonyl groups is the most important application of the Grignard reagent in organic chemistry. Addition of Grignard reagents to aldehydes and ketones in an ether solvent, followed by protonolysis, gives alcohols.



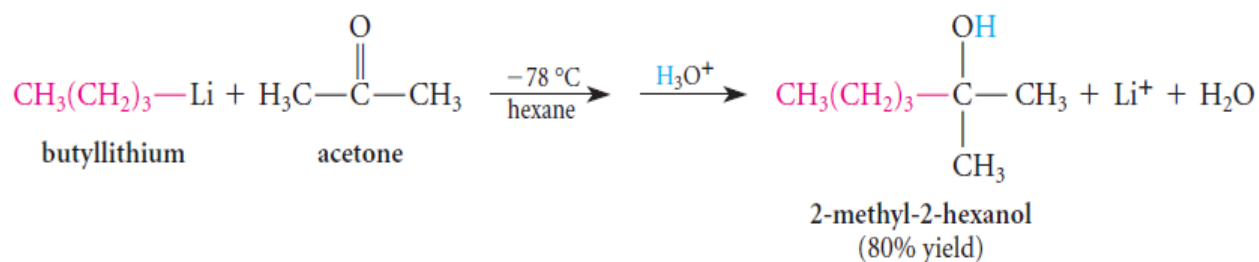
The reaction of Grignard reagents with aldehydes and ketones is another example of *carbonyl addition*. In this reaction, the magnesium of the Grignard reagent, a Lewis acid, bonds to the carbonyl oxygen. This bonding, much like protonation in acid-catalyzed hydration, makes the carbonyl carbon more electrophilic (that is, makes it more reactive toward nucleophiles) by making the carbonyl oxygen a better acceptor of electrons. The carbon group of the Grignard reagent reacts as a nucleophile at the carbonyl carbon. Recall

that this group is a strong base that behaves much like a *carbanion*.

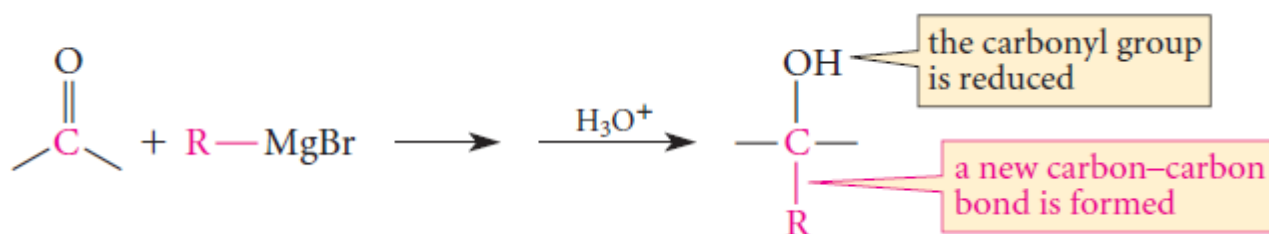


The product of this addition, a bromomagnesium alkoxide, is essentially the magnesium salt of an alcohol. Addition of dilute acid to the reaction mixture gives an alcohol.

Because of the great basicity of Grignard reagents, this addition, like hydride reductions, is irreversible, and it works with just about any aldehyde or ketone. The reactions of organolithium and sodium acetylide reagents with aldehydes and ketones are fundamentally similar to the Grignard reaction.



The reaction of Grignard and related reagents with aldehydes and ketones is important not only because it can be used to convert aldehydes or ketones into alcohols, but also because it is an excellent method of carbon–carbon bondformation.



5.13 DEHYDRO HALOGENATION OF ALKYL HALIDES

Dehydrohalogenation is a chemical reaction that involves removal of (elimination of) a hydrogen halide from a substrate. The reaction is usually associated with the synthesis of alkenes, but it has wider applications.

5.14 SAYTZEFF'S RULE

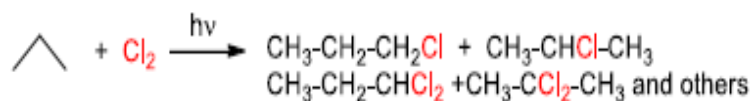
A double bond is formed due to loss of water molecule. It is an elimination reaction. According to Saytzeff's rule (also Zaitsev's rule), during dehydration, more substituted alkene (olefin) is formed as a major product, since greater the substitution of double bond greater is the stability of alkene.

Preparation of Alkyl Halides

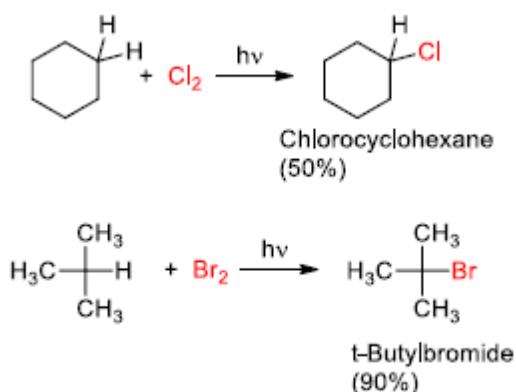
Free Radical Halogenation

Usually this method gives mixtures of mono-, di-, tri- etc halogenated compounds, which is considered an inefficient method for the synthesis of a desired compound.

Consider propane:



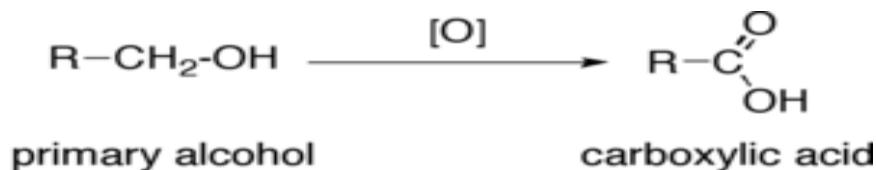
Sometimes if there can be control over the selectivity of halogenation this is a useful route



5.15 Oxidation Reactions

The **oxidation of primary alcohols to carboxylic acids** is an important oxidation reaction in organic chemistry.

When a primary alcohol is converted to a carboxylic acid, the terminal carbon atom increases its oxidation state by four. Oxidants able to perform this operation in complex organic molecules, featuring other oxidation-sensitive functional groups, must possess substantial selectivity. The most common oxidants are potassium permanganate (KMnO_4), Jones reagent, PCC in DMF, Heyns oxidation, ruthenium tetroxide (RuO_4) and TEMPO.



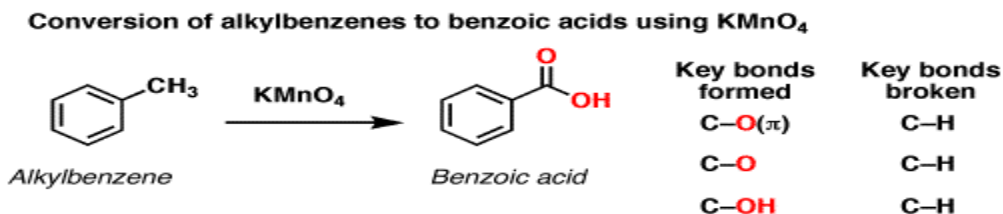
$[\text{O}] = \text{KMnO}_4$, Jones oxidation, PDC in DMF, Heyns oxidation, RuO_4 or TEMPO

Potassium permanganate (KMnO_4) is a very strong oxidant able to react with many functional groups, such as secondary alcohols, 1,2-diols, aldehydes, alkenes, oximes, sulfides and thiols. Under controlled conditions, KMnO_4 oxidizes primary alcohols to carboxylic acids very efficiently.

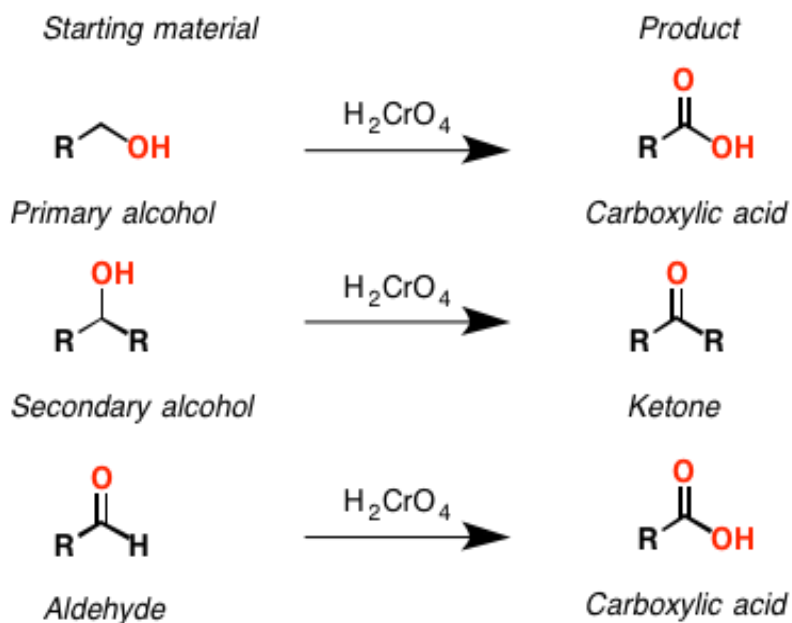
This reaction, which was first described in detail by Fournier is typically carried out by adding KMnO_4 to a solution or suspension of the alcohol in an alkaline aqueous solution. The resulting mixture is stirred until the oxidation is complete. For the reaction to proceed efficiently, the alcohol must be at least partially dissolved in the aqueous solution. This can be facilitated by the addition of an organic co-solvent such as dioxane, pyridine, acetone or *t*-BuOH. KMnO_4 will readily react with a carbon-carbon double bond before oxidizing a primary alcohol.

Normally, these oxidations are performed under strong alkaline conditions using a ca. 1N NaOH or KOH solution, because this promotes a greater oxidation speed and selectivity. In substrates sensitive to strong base, the reaction can be carried out at a lower pH—or even under acidic conditions—at the cost of a greatly decreased reaction velocity.

KMnO_4 is decomposed in water, resulting in formation of manganese dioxide (MnO_2) and gaseous oxygen. This decomposition is catalyzed by acid, base and MnO_2 . As the extent of this decomposition is difficult to estimate during the oxidation of primary alcohols, the quantity of KMnO_4 must be adjusted during the oxidation by adding it sequentially until the oxidation is complete.

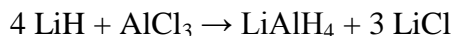


Once deciphered, chromic acid is a fairly straightforward reagent. It oxidizes primary alcohols to carboxylic acids and secondary alcohols to ketones. It will also oxidize aldehydes to carboxylic acids.



5.16 REDUCTION REACTIONS

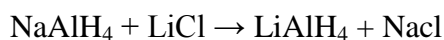
Preparation: LiAlH was first prepared from the reaction between lithium hydride (LiH) and aluminium chloride:



In addition to this method, the industrial synthesis entails the initial preparation of sodium aluminium hydride from the elements under high pressure and temperature



LiAlH₄ is then prepared by a salt metathesis reaction according to:



* **Lithium aluminium hydride**, LiAlH_4 , also abbreviated as **LAH**, is a **reducing agent** commonly employed in modern organic synthesis.

* It is a nucleophilic reducing agent, best used to reduce polar multiple bonds like $\text{C}=\text{O}$.

* LiAlH_4 can reduce aldehydes to primary alcohols, ketones to secondary alcohols, carboxylic acids and esters to primary alcohols, amides and nitriles to amines, epoxides to alcohols and lactones to diols.

* Lithium aluminium hydride cannot reduce an isolated non-polar multiple bond like $\text{C}=\text{C}$. However, the double or triple bonds in conjugation with the polar multiple bonds can be reduced.

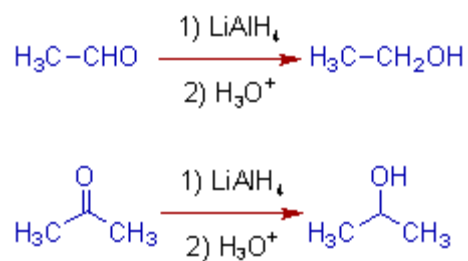
* LiAlH_4 is a powerful reducing agent compared to sodium borohydride, NaBH_4 , since the Al-H bond is weaker and thus less stable than B-H bond.

There is a tetrahedral arrangement of hydrogens around aluminium in aluminium hydride, AlH_4^- ion. It is formed by coordination of hydride, H^- ions to aluminium, Al^{3+} ion. The hybridization in central aluminium is sp^3 .

LiAlH_4 is prepared by the reaction between lithium hydride and aluminium chloride.

The **aldehydes or ketones** are reduced by LiAlH_4 to the corresponding primary or secondary alcohols respectively.

E.g. Acetaldehyde is reduced to ethyl alcohol and acetone is reduced to isopropyl alcohol



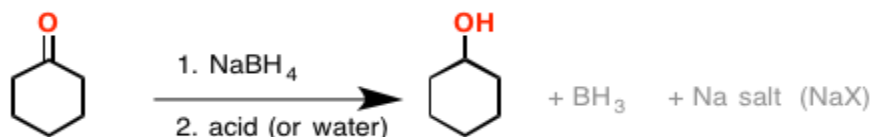
5.16.1 SODIUM BOROHYDRIDE

Sodium borohydride is a good reducing agent. Although not as powerful as lithium aluminum hydride (LiAlH_4), it is very effective for the reduction of aldehydes and ketones to alcohols. By itself, it will generally not reduce esters, carboxylic acids, or amides (although it will reduce acyl chlorides to alcohols).

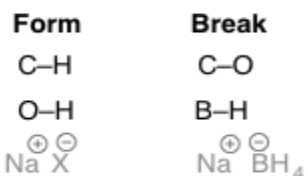
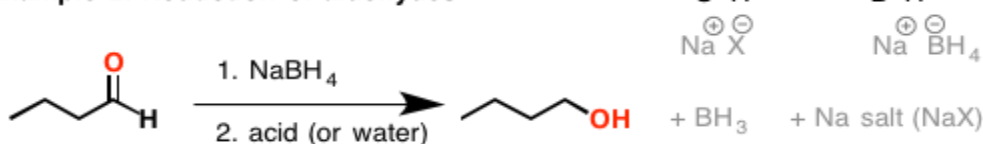
It is also used in the second step of the oxymercuration reaction to replace mercury (Hg) with H . **Similar to:** lithium aluminum hydride (LiAlH_4) although less reactive. For our purposes, sodium borohydride is

really useful for one thing: it will reduce aldehydes and ketones. In this sense it traverses one rung on the oxidation ladder. Here are some examples of it in action.

Example 1: Reduction of ketones



Example 2: Reduction of aldehydes

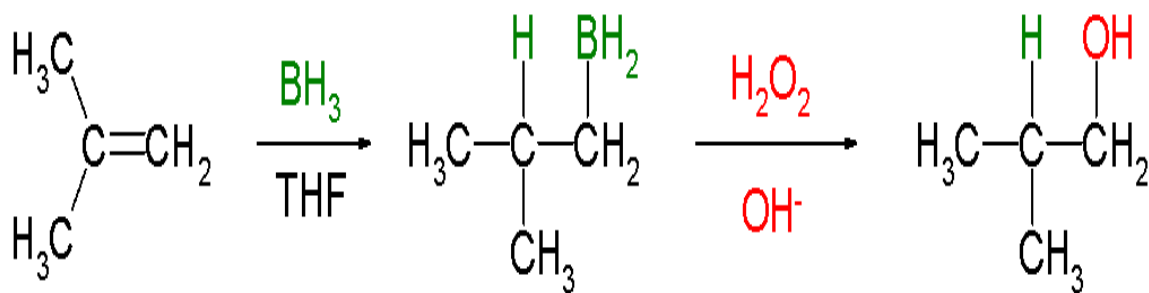


5.17 Hydroboration of alkenes

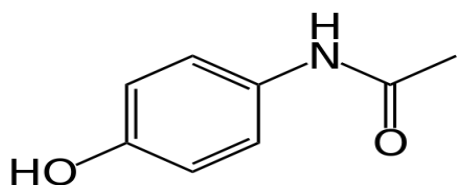
Oxidation is a two step pathway used to produce alcohols. The reaction proceeds in an Anti-Markovnikov manner, where the hydrogen (from BH₃ or BHR₂) attaches to the more substituted carbon and the boron attaches to the least substituted carbon in the alkene double bond.

Furthermore, the borane acts as a Lewis Acid by accepting two electrons in its empty p orbital from an alkene that is electron rich. This process allows boron to have an electron octet.

A very interesting characteristic of this process is that it does not require any activation by a catalyst. The Anti-Markovnikov Hydroboration mechanism has the elements of both hydrogenation and electrophilic addition and it is a stereospecific (*syn addition*), meaning that the hydroboration takes place on the same face of the double bond, this leads to *cis* stereochemistry.



5.18 Structure of Paracetamol

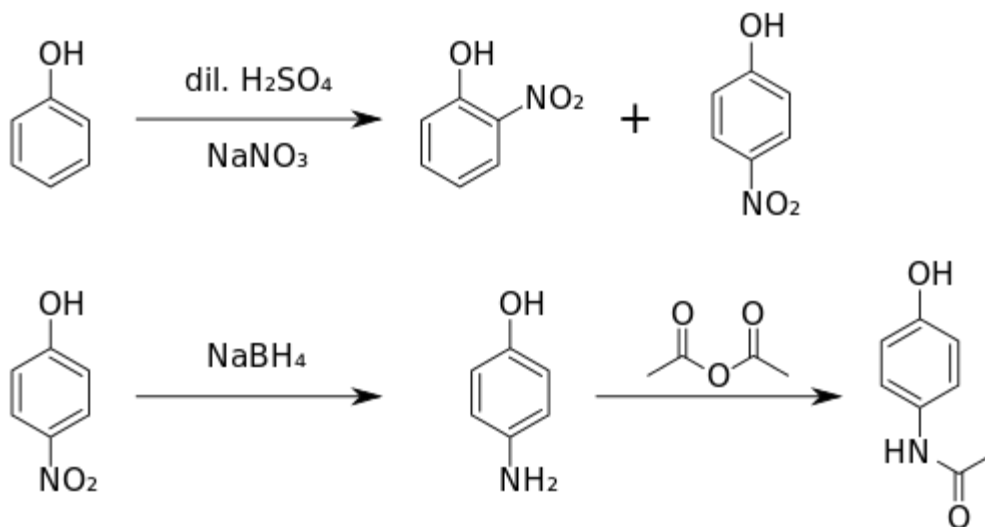


Paracetamol, also known as **acetaminophen** or **APAP**

The original method for production involves the nitration of phenol with sodium nitrate gives a mixture of two isomers, from which the wanted 4-nitrophenol (bp 279 °C) can easily be separated by steam distillation

In this electrophilic aromatic substitution reaction, phenol's oxygen is strongly activating, thus the reaction requires only mild conditions as compared to nitration of benzene itself. The nitro group is then reduced to an amine, giving 4-aminophenol. Finally, the amine is acetylated with acetic anhydride.

Industrially direct hydrogenation is used, but in the laboratory scale sodium borohydride serves.



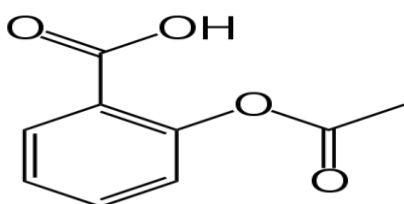
5.18.1 PHARMACEUTICAL APPLICATIONS OF PARACETOMOL

1. It is a medicine used to treat pain and fever.
2. It is typically used for mild to moderate pain relief.

3. Evidence for its use to relieve fever in children is mixed. It is often sold in combination with other medications, such as in many cold medications

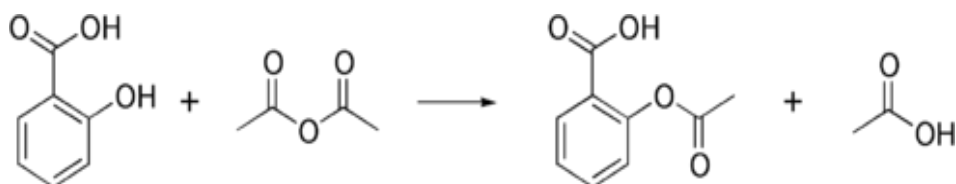
5.18.2 ASPIRIN

Structure of Aspirin



Synthesis

The synthesis of aspirin is classified as an esterification reaction. Salicylic acid is treated with acetic anhydride, an acid derivative, causing a chemical reaction that turns salicylic acid's hydroxyl group into an ester group ($R-OH \rightarrow R-OCOCH_3$). This process yields aspirin and acetic acid, which is considered a byproduct of this reaction. Small amounts of sulfuric acid (and occasionally phosphoric acid) are almost always used as a catalyst.



Pharmaceutical applications of Aspirin:

Aspirin is used in the treatment of a number of conditions, including fever, pain, rheumatic fever, and inflammatory diseases, such as rheumatoid arthritis, pericarditis, and Kawasaki disease

Lower doses of aspirin have also been shown to reduce the risk of death from a heart attack, or the risk of stroke in some circumstances

MODULE - V

FUELS & COMBUSTION

Introduction:-

Fuels are the main energy sources for industry and domestic purposes.

“A fuel is a substance containing carbon as the major substituent which provides energy on combustion for industry and domestic purposes”.

The combustion is the process of oxidation that provides heat energy. Every combustion is an oxidation but every oxidation is not combustion.

Ex: - Combustion of wood, Petrol and kerosene gives heat energy.

a. Classification of Fuels:-

Classification of fuels is based on two factors.

1. Occurrence (and preparation)
2. The state of aggregation

On the basis of occurrence, the fuels are further divided into two types.

A. natural or primary fuels: - These are found in nature such as Wood, peat, coal, Petroleum, natural gas etc.

B. artificial or secondary fuels: - These are prepared artificially from the primary fuels.

Ex: - charcoal, coke, kerosene, diesel, petrol, coal gas, oil gas, producer gas, blast Furnace gas etc.

5.2.1 Characteristics of a good fuel:-

- i. The fuel should be easily available.
- ii. It should be dry and should have less moisture content. Dry fuel increases its calorific value.
- iii. It should be cheap, easily transportable and has high calorific value.
- iv. It must have moderate ignition temperature and should leave less ash after combustion.
- v. The combustion speed of a good fuel should be moderate.
- vi. It should not burn spontaneously to avoid fire hazards.
- vii. Its handling should be easy and should not give poisonous gases after combustion.
- viii. The combustion of a good fuel should not be explosive.

The second classification is based upon their state of aggregation like:

- a) Solid fuels;
- b) Liquid fuels and
- c) Gaseous fuels.

Type of fuel	Natural or primary fuel	Artificial or secondary fuel
Solid	Wood, peat, lignite, dung, bituminous coal and anthracite coal	Charcoal, coke etc.
Liquid	Crude oil	Petrol, diesel and various other fractions of petroleum

Gaseous	Natural gas	Coal gas, oil gas, bio gas, water gas etc.
---------	-------------	--------------------------------------------

5.2.1 Characteristic properties of solid, liquid and gaseous fuels:

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 leakproof.
4	Risk towards firehazards	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 poses 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	Calorific value	Least	High	Highest
11	Heat efficiency	Least	High	Highest efficiency

b. Solid Fuels:-

The main solid fuels are wood, peat, lignite, coal and charcoal.

Coal: - Coal is a fossil fuel which occurs in layers in the earth's crust. It is formed by the partial decay of plant materials accumulated millions of years ago and further altered by action of heat and pressure. The process of conversion of wood into coal can be represented as

Wood □ Peat □ Lignite □ Bituminous Coal □ Anthracite

- 1) **Peat:-** Peat is brown-fibrous jelly like mass.
- 2) **Lignite:-** these are soft, brown coloured, lowest rank coals

- 3) Bituminous coals:- These are pitch black to dark grey coal
- 4) Anthracite:- It is a class of highest rank coal

Fuel	Percentage of carbon	Calorific value (k.cal/kg)	Applications
Wood	50	4000-4500	Domestic fuel
Peat	50-60	4125-5400	Used if deficiency of high rank coal is prevailing
Lignite	60-70	6500-7100	For steam generation in thermal power plants
Bituminous	80-90	8000-8500	In making coal gas and Metallurgical coke
Anthracite	90-98	8650-8700	In households and for steam raising

c. Analysis of Coal:-

The analysis of coal is helpful in its ranking.

The assessment of the quality of coal is carried out by these two types of analyses.

- A) Proximate analysis
- B) Ultimate analysis

A. Proximate analysis: In this analysis, the percentage of carbon is indirectly determined. It is a quantitative analysis of the following parameters.

1. Moisture content
2. Volatile matter
3. Ash
4. Fixed carbon

1. **Moisture Content:** About 1 gram of finely powdered air-dried coal sample is weighed in a crucible. The crucible is placed inside an electric hot air-oven, maintained at 105 to 110°C for one hour. The crucible is allowed to remain in oven for 1 hour and then taken out, cooled in desiccators and weighed. Loss in weight is reported as moisture.

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

Weight of coal taken

2. **Volatile Matter:** The dried sample taken in a crucible in and then covered with a lid and placed in an electric furnace or muffle furnace, maintained at 925 + 20C. The crucible is taken out of the oven after 7 minutes of heating. The crucible is cooled first in air, then inside desiccators and weighed again. Loss in weight is reported as volatile matter on percentage-basis.

$$\text{Percentage of volatile matter} = \frac{\text{Loss in weight}}{\text{Weight of coal taken}} \times 100$$

3. **Ash:** The residual coal sample taken in a crucible and then heated without lid in a muffle furnace at 700 + 50 C for ½ hour. The crucible is then taken out, cooled first in air, then in desiccators and weighed. Hearing, cooling and weighing are repeated, till a constant weight is obtained. The residue is reported as ash onpercentage-basis.

Thus,

$$\text{Percentage of ash} = \frac{\text{Weight of ash left}}{\text{Weight of coal taken}} \times 100$$

Weight of coal taken

4. **Fixedcarbon:**

$$\text{Percentage of fixed carbon} = 100 - \% \text{ of (Moisture + Volatile matter + ash)}$$

Significance of proximate analysis: Proximate analysis provides following valuable information's in assessing the quality of coal.

1. **Moisture:** Moisture is coal evaporates during the burning of coal and it takes some of the liberated heat in the form of latent heat of evaporation. Therefore, moisture lowers the effective calorific value of coal. Moreover over, it quenches the fire in the furnace, hence, lesser, the moisture content, better the quality of coal as a fuel. However, presence of moisture, up to 10%, produces a more uniform fuel-bed and less of ‘fly-ash’.

2. **Volatile matter:** a high volatile matter content means that a high proportion of fuel will distil over as gas or vapour, a large proportion of which escapes un-burnt, So, higher volatile content in coal s undesirable. A high volatile matter containing coal burns with a long flame, high smoke and has low calorific value. Hence, lesser the volatile matter, better the rank of the coal.

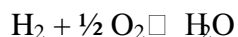
3. **Ash:** Ash is a useless, non-combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature. Also, it often causes trouble during firing by forming clinkers, which block the interspaces of the grate, on which coal is being burnt. This in-turn causes obstruction to air supply; thereby the burning of coal becomes irregular. Hence, lower the ash content, better the quality of coal. The presence of ash also increases transporting, handling and storage costs. It also involves additional cost in ash disposal. The presence of ash also causes early wear of furnace walls, burning of apparatus and feeding mechanism.

4. **Fixed carbon:** Higher the percentage of fixed carbon, greater is it’s calorific and betters the quality coal. Greater the percentage of fixed carbon, smaller is the percentage of volatile matter. This also represents the quantity of carbon that can be burnt by a primary current of air drawn through the hot bed of a fuel. Hence, high percentage of fixed carbon is desirable. The percentage of fixed carbon helps in designing the furnace and the shape of the fire-box, because it is the fixed carbon that burns in the solidstate.

B. Ultimate analysis: This is the elemental analysis and often called as qualitative analysis of coal. This analysis involves the determination of carbon and hydrogen, nitrogen, sulphur and oxygen.

1. Carbon and Hydrogen: About 1 to 2 gram of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus. C and H of the coal are converted into CO_2 and

H₂O respectively. The gaseous products of combustion are absorbed respectively in KOH and CaCl₂ tubes of known weights. The increase in weights of these are then determined.



$$\text{Percentage of C} = \frac{\text{Increase in weight of KOH tube} \times 12 \times 100}{\text{Weight of Coal sample taken} \times 44}$$

$$\text{Percentage of H} = \frac{\text{Increase in weight of CaCl}_2 \text{ tube} \times 2 \times 100}{\text{Weight of Coal sample taken} \times 18}$$

$$\text{Percentage of N} = \frac{\text{Volume acid} \times \text{Normality of acid} \times 1.4}{\text{Weight of coal taken}}$$

$$\text{Percentage of S} = \frac{\text{Weight of washings} \times 100}{\text{Weight of coal taken}}$$

2. Nitrogen: About 1 gram of accurately weighed powdered coal is heated with concentrated H₂SO₄ along with K₂SO₄ (catalyst) in a long-necked Kjeldahl's flask. After the solution becomes clear, it is treated with excess of KOH and the liberated ammonia is distilled over and absorbed in a known volume of standard acid solution. The unused acid is then determined by back titration with standard NaOH solution. From the volume of acid used by ammonia liberated, the percentage of N in coal is calculated as follows:

$$\text{Percentage of N} = \frac{\text{Volume acid} \times \text{Normality of acid} \times 1.4}{\text{Weight of coal taken}}$$

$$\text{Percentage of S} = \frac{\text{Weight of washings} \times 100}{\text{Weight of coal taken}}$$

3. Sulphur: Sulphur is determined from the washings obtained from the known mass of coal, used in bomb calorimeter for determination of calorific value. During this determination, S is

converted in to Sulphate. The washings are treated with Barium chloride solution, when Barium-sulphate is precipitated. This precipitate is filtered, washed and heated to constant weight.

$$\text{Percentage of Sulphur} = \frac{\text{Weight of BaSO}_4 \text{ obtained} \times 32 \times 100}{\text{Weight of coal sample taken in bomb} \times 233}$$

Weight of coal sample taken in bomb X 233

4. Ash: The residual coal taken in the crucible and then heated without lid in a muffle furnace at $700 + 50^\circ\text{C}$ for $\frac{1}{2}$ hour. The crucible is then taken out, cooled first in air, then in desiccators and weighed. Hearing, cooling and weighing are repeated, till a constant weight is obtained. The residue is reported as ash on percentage-basis.

Thus,

$$\text{Percentage of ash} = \frac{\text{Weight of ash left}}{\text{Weight of coal taken}} \times 100$$

Weight of coaltaken

5. Oxygen: It is determined indirectly by deducting the combined percentage of carbon, hydrogen, nitrogen, sulphur and ash from 100.

$$\text{Percentage of Oxygen} = 100 - \text{percentage of (C + H + S + N + Ash)}$$

Significance of ultimate analysis:

Carbon and Hydrogen: Greater the percentage of carbon and hydrogen better is the coal in quality and calorific value. However, hydrogen is mostly associated with the volatile mater and hence, it affects the use to which the coal is put.

Nitrogen: Nitrogen has no calorific value and hence, its presence in coal is undesirable. Thus, a good quality coal should have very little Nitrogen content.

Sulphur: Sulphur, although contributes to the heating value of coal, yet on combustion produces acids like SO_2 , SO_3 , which have harmful effects of corroding the equipments and also cause atmospheric pollution. Sulphur is, usually, present to the extent of 0.5 to 0.3% and derived from ores like iron, pyrites, gypsum, etc., mines along with the coal. Presence of sulphur is highly undesirable in coal to be used for making coke for iron industry. Since it is transferred to the iron metal and badly affects the quality and properties of steel. Moreover, oxides of sulphur pollute the atmosphere and leads to corrosion.

Ash: Ash is a useless, non-combustible matter, which reduces the calorific value of coal. Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature. Hence, lower the ash content, better the quality of coal. The presence of ash also increases transporting, handling and storage costs. It also involves additional cost in ash disposal. The presence of ash also causes early wear of furnace walls, burning of apparatus and feeding mechanism.

Oxygen: Oxygen content decreases the calorific value of coal. High oxygen-content coals are characterized by high inherent moisture, low calorific value, and low coking power. Moreover, oxygen is a combined form with hydrogen in coal and thus, hydrogen available for combustion is lesser than actual one. An increase in 1% oxygen content decreases the calorific value by about 1.7% and hence, oxygen is undesirable. Thus, a good quality coal should have low percentage of oxygen.

d. Liquid Fuels

Liquid fuels are the important commercial and domestic fuels used these days. Most of these fuels are obtained from the naturally occurring petroleum or crude oil.

Primary Petroleum:-

Petroleum or crude oil is a dark greenish brown, viscous oil found deep in the earth crust. Crude oil is a source of many liquid fuels that are in current use. The composition of crude petroleum approximately is C = 80-85%, H= 10-14%

S= 0.1-3.5% and N=0.1-0.5%.

Refining of Petroleum:-

Crude oil obtained from the mine is not fit to be marketed. It contains a lot of soluble and insoluble impurities which must be removed. Previously the purification of crude oil is done by simple fractional distillation. Further treatment of the products is done by refining. Refining can be defined as the process by which petroleum is made free of impurities, division of petroleum into different fractions having different boiling points and their further treatment to impart specific properties.

Refining of petroleum is done in different stages:

- a. Removal of solid impurities: The crude oil is a mixture of solid, liquid and gaseous substances. This is allowed to stand undisturbed for some time, when the heavy solid particles settle down and gases evaporate. The supernatant liquid is then centrifuged where in the solids get removed.
- b. Removal of water (Cottrell's process): The crude oil obtained from the earth's crust is in the form of stable emulsion of oil and brine. This mixture when passed between two highly charged electrodes will destroy the emulsion films and the colloidal water droplets coalesce into bigger drops and get separated out from the oil.
- c. Removal of harmful impurities: In order to remove sulphur compounds in the crude oil. It is treated with copper oxide. The sulphur compounds get converted to insoluble copper sulphide, which can be removed by filtration. Substances like NaCl and $MgCl_2$ if present will corrode the refining equipment and result in scale formation. These can be removed by techniques like electrical desalting and dehydration.
- d. Fractional distillation: Heating of crude oil around $400^{\circ}C$ in an iron retort, produces hot vapor which is allowed to pass through fractionating column. It is a tall cylindrical tower containing a number of horizontal stainless trays at short distances and is provided with small chimney covered with loose cap. As the vapors go up they get cooled gradually and fractional condensation takes place. Higher boiling fraction condenses first later the lower boiling fractions.

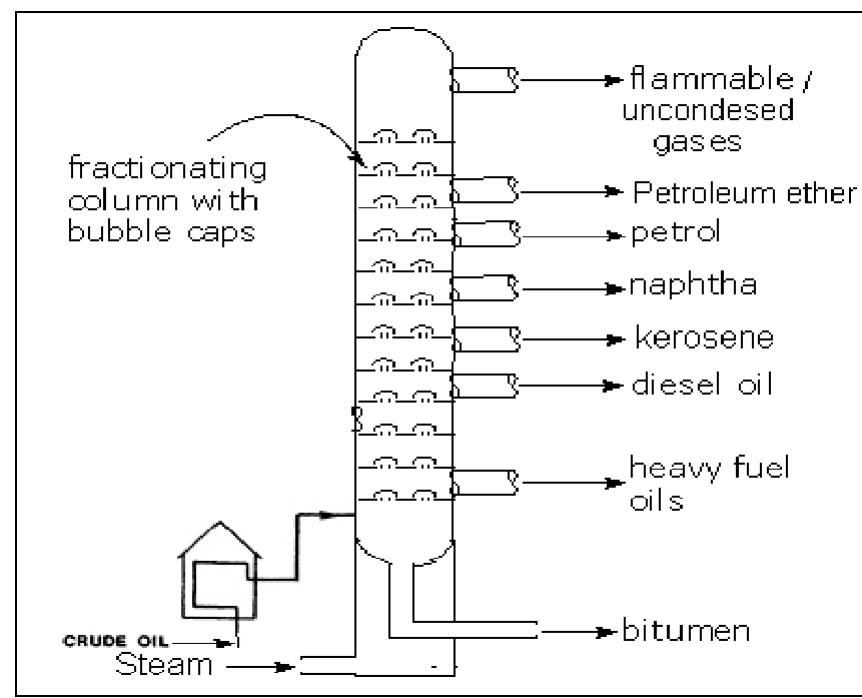
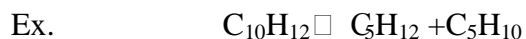


Fig. 4.1 Refining of Petroleum

e. Cracking:-

Decomposition of larger hydrocarbon molecules to smaller molecules is cracking.

Cracking



(Decane) (Pentane) (Pentene)

Cracking is mainly two types:

- A. ThermalCracking
- B. CatalyticCracking

A. **Thermal cracking:** If the cracking takes place at high temperature then it is thermalcracking.

It may take place by two ways. They are i) Liquid-phase Thermal cracking

ii) Vapour-phase Thermal cracking

The liquid phase cracking takes place at 475°C to 530°C at a pressure $100\text{kg}/\text{cm}^2$. While the vapor phase cracking occurs at 600 to 650°C at a low pressure of 10 to $20\text{ kg}/\text{cm}^2$

B. Catalytic cracking: If the cracking takes place due to the presence of catalyst than it is named as catalytic cracking. Catalytic cracking may be fixed bed type or moving bedtype.

i) Fixed bed catalytic cracking: The oil vapors are heated in a pre-heater to cracking temperatures ($420 - 450^{\circ}\text{C}$) and then forced through a catalytic chamber maintained at $425 - 450^{\circ}\text{C}$ and $1.5\text{ kg}/\text{cm}^2$ pressure. During their passage through the tower, about 40% of the charge is converted into gasoline and about 2 – 4% carbon is formed. The latter adsorbed on the catalyst bed. The vapour produced is then passed through a fractionating column, where heavy oil fractions condense. The vapors are then led through a cooler, where some of the gases are condensed along – with gasoline and uncondensed gases move on. The gasoline containing some dissolved gases is then sent to a ‘stabilizer’, where the dissolved gases are removed and pure gasoline is obtained.

The catalyst, after 8 to 10 hours, stops functioning, due to the deposition of black layer of carbon, formed during cracking. This is re-activated by burning off the deposited carbon. During the re-activated interval, the vapors are diverted through another catalyst chamber.

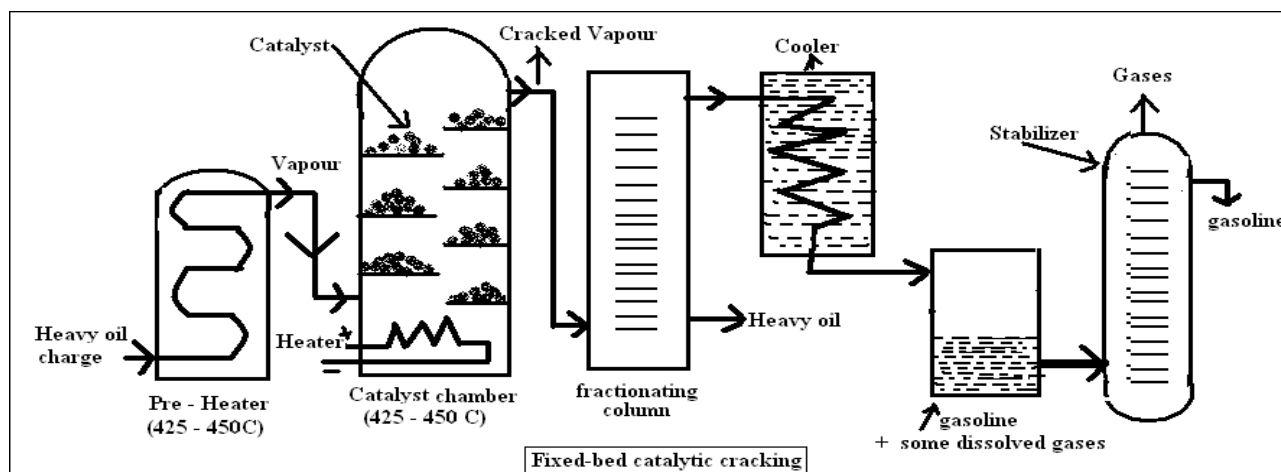


Fig. 4.2 Fixed-Bed Catalytic Cracking

f. Knocking

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.

In an internal combustion engine, a mixture of gasoline vapor and air is used as a fuel. After the initiation of the combustion reaction, by spark in the cylinder, the flame should spread rapidly and smoothly through the gaseous mixture; thereby the expanding gas drives the piston down the cylinder.

The ratio of the gaseous volume in the cylinder at the end of the suction-stroke to the volume at the end of compression ratio. The efficiency of an internal combustion engine increases with the compression ratio, which is dependent on the nature of the constituents present in the gasoline used. In certain circumstances (due to the presence of some constituents in the gasoline used), the rate of oxidation becomes so great that the last portion of the fuel air mixture gets ignited instantaneously, producing an explosive violence, known as knocking. The knocking results in loss of efficiency.

Some of the effects of knocking or detonation are:

- a. Carbon deposits on liners and combustion chamber
- b. Mechanical damage
- c. increase in heat transfer
- d. Noise and roughness
- e. decrease in power output and efficiency
- f. preignition

The knocking can be controlled or even stopped by the following methods:

- i. increasing engine speed
- ii. reducing pressure in the inlet manifold by throttling
- iii. Retarding spark
- iv. Making the ratio too lean or rich, preferably latter.
- v. Water injection increases the delay period as well as reduces the flame temperature.
- vi. Use of high octane fuel can eliminate detonation. High octane fuels are obtained by adding additives known as dopes like tetraethyl lead, benzol, xylene to petrol

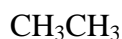
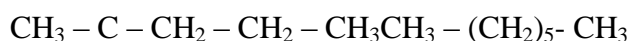
Chemical structure and knocking: The tendency of fuel constituents to knock in the following order.

Straight-chain paraffins > Branched-chain paraffins (i.e., iso paraffins) > Olefins > Cyclo paraffins (i.e., naphthalenes) > aromatics.

Thus, olefins of the same carbon chain length possess better anti knock properties than the corresponding paraffin and so on.

5.8 Octane number:-

The knocking characteristic of a fuel can be easily expressed by octane number. The anti-knocking value of n-heptane is taken as 0 (zero) because n-heptane knocks very badly. Whereas the anti-knock value of iso-octane is approximately taken as 100 because iso-octane knocks very little. Actually the octane number is the percentage of iso-octane in a mixture of n-heptane in order to match the knocking characteristics of the fuel. In this way, an “80-octane” fuel is one which has the same combustion characteristics as an 80:20 mixture in iso-octane and n-heptanes. Gasoline with octane rating as high as 135 are used for aviation purposes. The octane number of poor fuels can be raised by the addition of extremely poisonous materials as tetra ethylene lead $(C_2H_4)_4Pb$ and diethyl-telluride $(C_2H_4)_2Te$



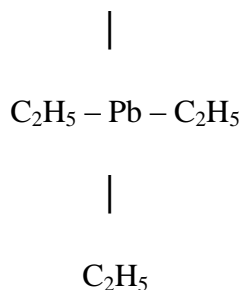
2, 2, 4-trimethylpentane n-heptane

(Isooctane) octane number 100 (good fuel)

Octane number zero (bad fuel)

Lead petrol: The variety of petrol in which tetra ethyl lead is added, it is leaded petrol.





Tetra ethyl lead (TEL)

g. Octane rating:

It has been found that n-heptane, Knocks very badly and hence, its anti-knock value has arbitrarily been given zero. On the other hand, isooctane (2: 2: 4 – trimethyl pentane). It gives very little knocking, so its anti-knock value has been given as ‘100’. Thus, octane number (or rating) of a gasoline (or any other internal combustion engine fuel) is the percentage of isooctane in a mixture of isooctane and n-heptane, which matches the fuel under test in

knocking characteristics. In this way, an “80-octane” fuel is one which has the same combustion characteristics as an 80:20 mixture of isooctane and n-heptane.

Advantages: Usually petrol with low octane number is not good quality petrol. It often knocks (i.e., produces huge noise due to improper combustion). As a result of knocking, petrol is wasted; the energy produced cannot be used in a proper way.

When tetra ethyl lead is added, it prevents knocking, thereby saves money and energy. Usually 1 to 1.5 ml of TEL is added per 1 lit of petrol.

The mechanism of action is as follows:

First TEL will be transformed into finely divided particles of PbO which looks like a cloud. This takes place in the cylinder. Then the PbO particles react with hydrocarbon peroxide molecules formed, thus slowing down the oxidation process and prevent early detonation. Thus either knocking may be stopped or greatly reduced.

Disadvantages: Deposits of PbO are harmful to engine. So PbO must be eliminated from the engine. For this purpose, little amount of ethylene dibromide is added to petrol. It converts the harmful PbO to volatile PbBr₂ and eliminated through exhaust. Presence of any sulphur

compounds reduces the efficiency of TEL.

Cetane Number:-

Cetane number is defined as the percentage of hexadecane (n-cetane) present in a mixture of hexadecane and 2-methyl naphthalene, which has the same ignition characteristic of diesel fuel in test. Generally diesel fuels with cetane numbers of 70-80 are used.

The knocking tendency of diesel fuel is expressed in terms of cetane number. Diesel engines work on the principle of compression ignition. Cetane (n-cetane) or hexadecane [$\text{CH}_3 - (\text{CH}_2)_{14} - \text{CH}_3$] is a saturated hydrocarbon, its cetane number is arbitrarily fixed as 100. A methyl naphthalene is an aromatic hydrocarbon, its cetane number is arbitrarily fixed as zero.

h. Gaseous Fuels:-

The gaseous fuels are most preferred because of their ease of storage, transport, handling and ignition. These are classified into two types.

- i. Primary fuels Ex:- Natural gas
- ii. Secondary fuels ex: - Coal gas, producer gas, water gas.

5.9.1 Natural Gas:-

The natural gas is obtained from the wells dug in the earth during mining of petroleum. It is mainly composed of methane and small quantities of ethane along with other hydrocarbons.

If the lower hydrocarbons are present, the gas is called dry gas or lean gas but if the hydrocarbons having the higher molecules are present, the gas is known as rich or wet gas.

The average composition of natural gas is as follows.

Methane – 88.5%, Ethane – 5.5%, Propane – 3.7%

Butane – 1.8%,

Pentane, hydrogen and higher hydrocarbons – 0.5%

The calorific value of natural gas varies from 8000-14000 K.cal/m³.

Applications:-

- i. It is an excellent domestic fuel and industrial fuel.
- ii. It is also used as raw material for the manufacture of carbon-black, methanol, formaldehyde etc.
- iii. Methane on microbiological fermentation gives synthetic proteins which are used as animal feed.

5.9.2 LPG (Liquefied Petroleum Gas)

The gas is obtained from natural gas or as a byproduct in refineries during cracking of heavy petroleum products. Nowadays LPG has been a common fuel for domestic work and also in most of the industries. The main components of LPG are n-butane, isobutane, butylenes and propane (traces of propene and ethane). The hydrocarbons are in gaseous state at room temperature and 1 atmospheric pressure but can be liquefied under higher pressure.

LPG is kept in metallic cylinder attached with burner through pipe. It has two stoppers, one at the cylinder and other at burner. LPG has special odour due to the presence of organic sulphides which are added specially for safety measure.

Characteristics of LPG:-

1. It has high calorific value ($27,800 \text{ kcal/m}^3$)
2. It gives less CO and least unburnt hydrocarbons. So it causes least pollution.
3. It gives moderate heat which is very good for cooking
4. Its storage is simple. It is colourless
5. It has tendency to mix with air easily
6. Its burning gives no toxic gases though it is highly toxic
7. It neither gives smoke nor ash content
8. It is cheaper than gasoline and used as fuel in auto vehicles also

9. It is dangerous when leakage is there

Applications

1. In Food industry: LPG is widely used in the food industry like hotels, restaurants, bakeries, Canteens etc. Low sulphur content and controllable temperature makes LPG the most Preferred fuel in the food industry.
2. In Glass & Ceramic: The use of a clean fuel like LPG enhances the product quality thereby reducing technical problems related to the manufacturing activity of glass and ceramic products.
3. In Building Industry: LPG being a premium gaseous fuel makes it ideal for usage in the Cement manufacturing process.
4. In Automotive Industry: The main advantage of using automotive LPG is, it is free of lead, Very low in sulphur, other metals, aromatics and other contaminants.
5. In Farming industry: LPG in the farming industry can be used for the following:
 - Drying of crops
 - Cereal drying
 - Curing of tobacco and rubber
 - Soil conditioning
 - Horticulture etc
6. LPG is used in metal industry, aerosol industry, textile industry and it can also be used in steam rising.

5.9.3 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 to CNG. It is stored in cylinder made of steel. It is now replacing gasoline as it releases less pollutant during its combustion. In some of the metro cities, CNG vehicles are used to reduce pollution.

Characteristics of CNG:-

1. Natural Gas being lead/sulphur free, its use substantially reduces harmful engine emissions.

2. Natural gas being lighter than air, will rise above ground level and disperse in the atmosphere, in the case of leakage.

3. Natural Gas in the gaseous state, and is colourless.

4. Predominantly Methane is available in the lean gas, hence CNG contains mostly methane

Applications:-

1. It was used to generate electricity, heat buildings, fuel vehicles, power industrial furnaces and Airconditioners.

2. Natural gas is also consumed in homes for space heating and for water heating

3. It is used in stoves, ovens, clothes dryers and other appliances.

4. In some of the metro cities, CNG vehicles are used to reduce pollution.

5.10 Combustion

Combustion may be defined as the exothermic chemical reaction, which is accompanied by heat and light. It is the union of an element or a compound with oxygen.

Example: $\text{C(s)} + \text{O}_2 \text{ (g)} \rightarrow \text{CO}_2 \text{ (g)} + 97\text{kcal}$

In common fuels it involves the burning of carbon and hydrogen in air and also to a much smaller extent of sulphur.

The presence of moisture in coal is undesirable, because it causes waste of heat; moisture may be present in coal naturally or by adding i.e. moistening the coal before use. The presence of some sort of moisture in coal helps to keep the temperature of the fire bars low and prevents the formation of clinkers. The excess presence of moisture leads to heavy smoking and leads to slow starting of combustion process. Optimum free moisture content is 7 to 9% when coal has minimum density. The presence of moisture in combustion makes the combustion process successful.

5.10.1 Calorific value:

The prime property of a fuel is its capacity to supply heat. Fuels essentially consist of carbon, hydrogen, oxygen and some hydrocarbons and the heat that a particular fuel can give is due to the oxidation of carbon and hydrogen. Normally when a combustible substance burns the total heat depends upon the quantity of fuel burnt, its nature, air supplied for combustion and certain other conditions governing the combustion. Further the heat produced is different for different fuels and is termed as its calorific value.

Calorific value of fuel may be defined as “the total quantity of heat liberated, when a unit mass (or volume) of a fuel is burnt completely”.

Or

“Calorific value is the amount of heat liberated by the complete combustion of a unit weight of the fuel and is usually expressed as cal gm^{-1} or kcal gm^{-1} or B.Th.U.

Or

The calorific value of a fuel can be defined as “the total quantity of heat liberated when a unit mass of the fuel is completely burnt in air or oxygen”.

There are different units for measuring the quantity of heat. They are:

- | | |
|----------------|----------------------------------|
| 1. Calorie | 3. British thermal unit (B.Th.U) |
| 2. Kilocalorie | 4. Centigrade heat unit (C.H.U) |

1. Calorie: It is the amount of heat required to increase the temperature of 1 gram of water through one degree centigrade.

2. Kilocalorie: This is the unit of heat in metric system, and is defined as the quantity of heat required to raise the temperature of one kilogram of water through one degree centigrade.

$$1 \text{ k.cal} = 1000 \text{ cal}$$

$$1 \text{ k.cal} = 3.968 \text{ B.Th.U}$$

3. British thermal unit (B.Th.U):_ This is the unit of heat in English system, it is defined as “the quantity of heat required to increase the temperature of one pound of water through of one degree of Fahrenheit.

$$1 \text{ B.Th.U} = 252 \text{ cal} = 0.252 \text{ k.cal}$$

4. Centigrade heat unit (C.H.U): It is the quantity of heat required to raise the temperature of one pound of water through one degree centigrade.

$$1 \text{ k.cal} = 3.968 \text{ B.Th.U} = 2.2 \text{ C.H.U}$$

Inter conversion of various units of heat:

On the basis that $1 \text{ kg} = 2.2 \text{ lb}$ and $1^\circ\text{C} = 1.8^\circ\text{F}$ we have

$$1 \text{ k.cal} = 1000 \text{ cal} = 3.968 \text{ B.Th.U} = 2.2 \text{ C.H.U}$$

$$1 \text{ B.Th.U} = 252$$

Units of calorific value:

For solid or liquid fuels: cal/g or k.cal/kg, B.Th.U/lb

For gaseous fuels: k.cal/cubic meter or

k.cal/m³ B.Th.U/ft³ or B.Th.U/cubic feet

Relation between various units:

$$1 \text{ k.cal/kg} = 1.8 \text{ B.Th.U/lb} = 1 \text{ cal/g}$$

$$1 \text{ k.cal/m}^3 = 0.1077 \text{ B.Th.U/ft}^3$$

$$1 \text{ B.Th.U/ft}^3 = 9.3 \text{ k.cal/m}^3$$

Gross calorific value is the heat liberated when a unit quantity of fuel is completely burnt and the products of combustion are cooled to room temperature. This heat includes the latest heat of condensation of water. Because when a fuel containing hydrogen is burnt, the hydrogen present is converted to steam. As the products of combustion are cooled to room temperature, the steam

gets condensed into water and the latent heat is evolved. Thus the latent heat of condensation of steam, so liberated, is included in the gross calorific value.

Higher calorific value (HCV) or gross calorific value is defined as the total amount of heat liberated, when unit mass or unit volume of the fuel has been burnt completely and the products of combustion are cooled down to 60 °F or 15 °C.

Net calorific value or lower calorific value (LCV): lower calorific value is defined as “the net heat produced, when unit mass or unit volume of the fuel is burnt completely and the combustion products are allowed to escape.

Net calorific value is the gross calorific value excluding the latent heat of condensation of water (the weight of water formed is nine times the weight of hydrogen in the fuel).

Therefore,

$$\text{LCV or NCV} = \text{HCV} - \text{Latent heat of water vapour formed}$$

$$\text{Net calorific value} = \text{Gross calorific value} - (\text{Mass of hydrogen per weight of fuel burnt} \times 9 \times \text{latent heat of vaporization of water}).$$

Latent heat of steam is 587 kcal/g.

$$\text{Net calorific value} = \text{Gross calorific value} - 52.83 \times \%H$$

Where % H = percentage of hydrogen.

The gross and net calorific values of coal can be calculated by bomb calorimeter.

Calorific value of a fuel may be defined as “the total quantity of heat liberated, when a unit mass (or volume) of a fuel is burnt completely”.

Air quantity required for complete combustion of fuel:

The amount of volume of air required theoretically for combustion of 1Kg of fuel is give as

$$=100/21[32/12 \times C + 8[H-O/8] + S] \text{Kg}$$

Or

$$[32/12C + 16/2H_2 + 32/12S] - O_2 \times$$

5.10.2 Numerical problems on combustion:

1. The following data are obtained in a Bomb Calorimeter experiment.

Weight of coal burnt = 0.95g

Weight of water taken = 700g

Water equivalent of calorimeter = 2000g

Increase in temperature = 2.48°C

Acid correction = 60.0cal

Cooling correction = 0.02°C

Fuse wire correction = 10.0cal

Latent heat of condensation = 587 cal/g

Calculate the GCV and NCV of the fuel if the fuel contains 92% of C. 5% of H and 3% of ash.

Sol:

$$\text{GCV} = \frac{(W+w)(T_2 - T_1 + T_c) - (T_A + T_f + T_t)}{0.95}$$

X

$$= \frac{(2200+700)(2.48+0.02) - (60+100)}{0.95}$$

0.95

$$= 7031.6 \text{ cal/g}$$

$$\begin{aligned}
 \text{NCV} &= \text{GCV} - 0.09\text{H} \times 587 \\
 &= 7031.6 - 0.09 \times 5 \times 587 \\
 &= 6767.45 \text{ cal/g}
 \end{aligned}$$

2. On burning 0.72g of a solid fuel in a Bomb calorimeter, the temperature of 250g of water is increased from 27.3°C to 29.1°C. If the water equivalent is 150g, calculate the HCV of the fuel.

Sol:

$$x = 0.72\text{g}$$

$$W = 250\text{g}$$

$$T_1 = 27.3^\circ\text{C}$$

$$T_2 = 29.1^\circ\text{C}$$

$$w = 150\text{g}$$

$$\text{HCV of fuel} = \frac{(W+w)(T_2 - T_1)}{x} \text{ cal/g}$$

$$\times$$

$$= \frac{(250+150)(29.1 - 27.3)}{0.72}$$

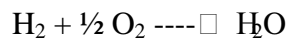
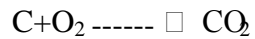
$$0.72$$

$$= 1000 \text{ cal/g}$$

3. A sample of coal was found to have the following percentage composition. C= 75%, H= 5.2%, O= 12%, N= 3.2% and ash =4.5%. Calculate the minimum air required for complete combustion of 1 kg of coal.

Sol:

Combustion reactions are:



Weight of O_2 required for combustion of 12g of C = 32

Hence, weight of O_2 required by 1 kg of carbon = $\frac{32}{12} \times 1$

Weight of O_2 required for combustion of 2g of H = 16

Hence, weight of O_2 required by 1kg carbon = $\frac{16}{2} \times 1$

1 kg of coal contains:

$$75\% \text{C} = 750\text{g}$$

$$5.2\% \text{H} = 52\text{g}$$

$$12\% \text{O} = 120\text{g}$$

$$3.2\% \text{N} = 32\text{g}$$

$$4.5\% \text{ash} = 45\text{g}$$

The net weight of O_2 required for complete combustion

$$\begin{aligned} &= 750 \times \frac{32}{12} + \frac{16}{2} \times 52 - \text{oxygen present in 1kg of coal} \\ &= 2000 + 416 - 120 \\ &= 2296\text{g} \end{aligned}$$

Since air contains 23% oxygen, the weight of air require for complete combustion of 1kg of coal

$$\begin{aligned} &= 2296 \times \frac{100}{23} \\ &= 33 \end{aligned}$$

$$= 9978\text{g}$$

4. In an experiment in a Bomb calorimeter, a solid fuel of 0.90g is burnt. It is observed that increase of temperature is 3.8°C of 4000g of water. The fuel contains 1% of H. calculate the HCV and LCV value (equivalent weight of water = 385g and latent heat of steam = 587cal/g)

Sol:

$$\text{Weight of fuel (x)} = 0.90\text{g}$$

$$\text{Weight of water (W)} = 4000\text{g}$$

$$\text{Equivalent weight of water (w)} = 385\text{g}$$

$$\text{Rise in temperature (T}_2\text{-T}_1\text{)} = 3.8^\circ\text{C}$$

$$\text{Percentage of carbon} = 1\%$$

$$\text{Latent heat of steam} = 587 \text{ cal/g}$$

$$\text{HCV} = \frac{(W+w) (T_2 - T_1)}{x} \text{ cal/g}$$

$$\times$$

$$= \frac{(400+385) (3.8)}{0.90} \text{ cal/g}$$

$$0.90$$

$$= 18514.5 \text{ cal/g}$$

$$\text{LCV} = (\text{HCV} - 0.09H \times 587)$$

$$= 18514.5 - 0.09 \times 1 \times 587$$

$$= 18461.6 \text{ cal/g}$$