



# **MALLA REDDY COLLEGE OF ENGINEERING & TECHNOLOGY**

**(An Autonomous Institution – UGC, Govt.of India)**

**Recognizes under 2(f) and 12(B) of UGC ACT 1956**

**(Affiliated to JNTUH, Hyderabad, Approved by AICTE –Accredited by NBA & NAAC-“A” Grade-ISO 9001:2015 Certified)**

## **ENGINEERING CHEMISTRY**

**B.Tech – I Year – II Semester**

**DEPARTMENT OF HUMANITIES AND SCIENCES**



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**(R18A0013) ENGINEERING CHEMISTRY**

**COURSE OBJECTIVES:**

1. To apply the electrochemical principles in batteries, understand the fundamentals of corrosion and development of different techniques in corrosion control.
2. To analyze microscopic chemistry in terms of atomic and molecular orbitals.
3. To analyze water for its various parameters and its significance in industrial and domestic applications.
4. To impart the knowledge of organic reaction mechanisms which are useful for understanding the synthesis of organic compounds.
5. To analyze different types of fuels and their applications in various engineering fields.

**Unit-I: Electrochemistry and Corrosion (12 lectures)**

**Electrochemistry:** Introduction to electrochemistry; Electrochemical cells - electrode potentials, construction and working of a galvanic cell, EMF and its applications - potentiometric titration; Nernst equation and its applications; Batteries - classification of batteries, primary cell - lithium cells and secondary cells - lead acid battery and lithium ion battery; Fuel cells - H<sub>2</sub>-O<sub>2</sub> fuel cell, its applications and advantages.

**Corrosion:** Introduction, causes and effects of corrosion; Theories of corrosion- chemical (oxidation corrosion) and electrochemical corrosion, mechanism of electrochemical corrosion; Corrosion control methods - cathodic protection - sacrificial anodic protection & impressed current cathodic protection; Methods of application of metallic coatings - hotdipping - galvanizing & tinning, electroplating (Cu plating) and electroless plating (Ni plating) - advantages and applications of electroplating/electroless plating.

**Unit -II: Atomic and Molecular Structure (8 lectures)**

Atomic and molecular orbitals; Postulates of molecular orbital theory - Linear Combination of Atomic Orbitals (LCAO); Molecular orbitals of diatomic molecules, molecular orbital energy level diagrams of N<sub>2</sub> and O<sub>2</sub>; Metallic bonding, limitations of Valence Bond Theory (VBT).

Crystal field theory (CFT) – Salient features of CFT, crystal field splitting of transition metal ion d-orbitals in tetrahedral and octahedral geometries.

**Unit -III: Water and its Treatment (6 lectures)**

Hardness of water- Types and units of hardness; Estimation of hardness of water by EDTA method; Softening of water by Ion exchange process; Potable water specifications, methods of disinfection-chlorination and ozonation; Desalination of water by Reverse Osmosis.

#### **Unit-IV: Organic Reactions (10 lectures)**

Introduction to Organic Reactions - Types of reactions; Substitution - Nucleophilic substitution reactions, mechanism of  $S_N1$  and  $S_N2$ ; Addition - electrophilic and nucleophilic addition reactions; addition of HBr to propene - Markownikoff and Anti- Markownikoff's additions; Elimination reactions - dehydrohalogenation of alkyl halides; Oxidation reactions - oxidation of alcohols using  $KMnO_4$  and chromic acid; Reduction reactions - reduction of carbonyl compounds using  $LiAlH_4$  and  $NaBH_4$ .

#### **Unit-V: Energy Sources (8 lectures)**

Fuels- Definition, classification (solid, liquid & gaseous fuels) - characteristics of a good fuel; Coal - analysis of coal - proximate and ultimate analysis and their significance; Petroleum - refining, knocking - octane and cetane number, cracking - fluid bed catalytic cracking; Natural gas, LPG, CNG - constituents, characteristics and uses.

#### **Suggested Text Books:**

1. Engineering Chemistry by P.C. Jain & M. Jain, Dhanpat Rai Publishing Company (P) Ltd, 16<sup>th</sup> Edition, New Delhi.
2. Engineering Chemistry by Prasanta Rath, B. Rama Devi, C. H. Venkata Ramana Reddy, Subhendu Chakroborty, Cengage Learning Publication, India Private Limited , 2018.

#### **Reference Books:**

1. University Chemistry by B. H. Mahan, Pearson, IV Edition.
2. Engineering Chemistry by Shashi Chawla, Dhanpat Rai Publishing Company (P) Ltd, New Delhi.
3. Reactions, Rearrangements and Reagents by S.N. Sanyal, Bharati Bhavan Publishers.

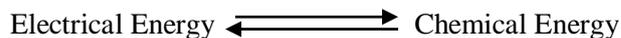
**COURSE OUTCOMES:** The basic concepts included in this course will help the student to:

1. Understand the operating principles of various types of electrochemical cells, including fuel cells and batteries. Analyze and develop a technically sound, economic and sustainable solution to corrosion problems related to engineering service.
2. Achieve basic concepts of atomic, molecular and electronic changes related to conductivity and magnetism.
3. Familiarize the student with the fundamentals of the treatment technologies and the considerations for its design and implementation in water treatment plants.
4. Gain knowledge on synthesis of organic compounds by using different reaction mechanisms.
5. Comprehend the types of fuels, characteristics and combustion systems with emphasis on engineering applications.

# UNIT - I: ELECTROCHEMISTRY AND CORROSION

## Introduction:

Electrochemistry is the branch of chemistry which deals with the transformation of electrical energy to chemical energy and vice versa. In brief it deals with the chemical applications of electricity.



Electric current is a flow of electrons generated by a battery, when the circuit is completed. Electrolysis is one process where electrical energy causes chemical changes. It is carried out in an apparatus called electrolytic cell. The cell contains electrolyte and electrodes. The electrode connected to the positive pole of the current source is called anode. The electrode connected to the negative pole of the current source is called cathode. When an electric current is passed through the electrolytic solution, cations move towards cathode (-ve electrode) and anions move towards anode (+ve electrode)

Ex: Electrolysis of water yields  $\text{H}_2$  and  $\text{O}_2$

In other process, certain chemical reactions take place in a vessel and produce electric energy. The device is called electrochemical cell. Eg. Galvanic cell, batteries and fuel cells. Broadly we can classify the cells as electrolytic cells and electrochemical cells.

**Electrolytic cell:** A device which converts electrical energy to chemical energy

**Electrochemical cell:** A device which converts chemical energy to electrical energy

## Types of Conductors:

**Electrical Conductors:** Substances which allow electric current to pass through them are known as electrical conductors. Eg. All metals, graphite, fused salts, aqueous solutions of acids and bases and salts.

**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 Ge on addition of V group elements like P produces n-type semi-conductor. On addition of III group element like B, Al, produces p-type of semi-conductor.

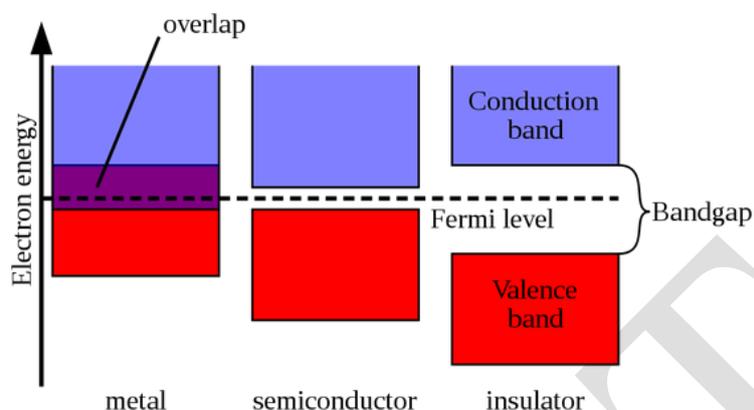
**Non-conductors or Insulators:** The substances which do not allow electricity are called non-conductors. . Eg. Rubber, wood, paper, all non-metals except carbon.

**Conductance:** The capacity of a conductor to allow the passage of current through it called conductance. It is a property of conductor which facilitates flow of electricity through it.

$$\text{Conductance (C)} = \frac{1}{R}$$

i.e. The reciprocal of resistance is called conductance. **Units:**  $\text{Ohm}^{-1}$

**Conductor:** The substance which allows the passage of electric current through it is called conductors. **E.g.:-** all metals, graphite, aqueous solution of acids and bases.



**Band Theory of Electrical Conductivity**

### Electric conductors are two types

Metallic conductor	Electrolytic conductors
Conductance due to the migration of electrons. <b>E.g.:</b> metals, graphite.	Conductance due to the migration of ions in a solution of fused electrolyte. <b>E.g.:</b> Acids and bases
Passage of current due to electron flow. No chemical reaction takes place.	Passage of current due to movement of ions. Some chemical reaction takes place.
Free electrons are responsible for electrical conduction.	Free ions are responsible for electrical conduction.
Mass is not transferred	Mass is transferred.
With increase of temp resistance increases and conductance decreases	With increase of temperature resistance decreases and conductance increases.

Electrolytes are classified into two types:

**Strong electrolytes:** The electrolytes which completely dissociates in solution at all concentrations. Their conductance is very high. Eg. NaCl, HCl, NaOH.

**Weak Electrolytes:** The electrolyte which partially dissociates at moderate concentration. Their conductance is low as they dissociate only to a small extent even at very high dilutions. Eg:  $\text{CH}_3\text{COOH}$ ,  $\text{NH}_4\text{OH}$ , sparingly soluble salts like AgCl, AgBr, AgI,  $\text{BaSO}_4$ ,  $\text{PbSO}_4$  etc

**CONDUCTANCE:**

**Ohm's Law:** Ohm's law states that the current (I) flowing through a conductor is directly proportional to potential difference (E) applied across the conductor and is inversely proportional to the resistance of conductor.

Thus,

$$E \propto I$$

Where I is the current in amperes, and E is potential difference applied across the conductor in volts.

Thus

$$E = IR$$

or

$$R = \frac{E}{I}$$



Where R is the proportionality constant and is known as the resistance of conductor in ohms. Thus, the resistance of a conductor is directly proportional to the potential difference applied across the conductor and inversely proportional to the current carried by the conductor.

**SPECIFIC RESISTANCE:** The resistance of a uniform conductor is directly proportional to its length (l) and inversely proportional to the area of the cross-section (a). Thus

$$R \propto l/a$$

$$R = \rho l/a$$

The proportionality constant ( $\rho$ ) is called as the specific resistance of an electrolytic solution of 1cm in length and 1cm<sup>2</sup> area of cross section. i.e. resistance of 1cm<sup>3</sup> of the electrolytic solution.

**UNITS: specific resistance units:** Ohm cm

**Cell constant:**

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

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

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

And specific conductance,  $K = \frac{1}{R} \times \frac{1}{a}$

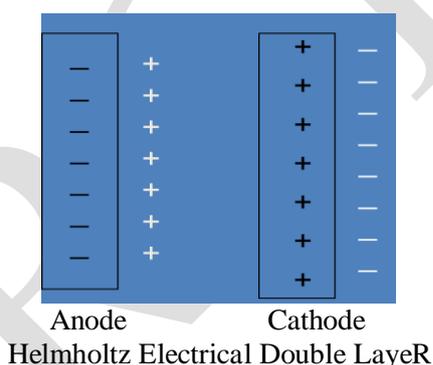
$$\therefore \text{Specific conductance} = \frac{\text{Cell constant}}{R}$$

$$\text{or } x = K \times R; \quad \text{or } x = \frac{K}{c} \quad (\because c = 1/R)$$

If area of cross-section is in  $\text{cm}^2$  and distance between the electrodes is in cm, the unit of cell constant is  $\text{cm}^{-1}$ .

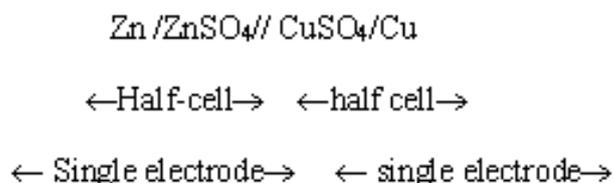
### ELECTRODE POTENTIAL:

- When a metal rod is dipped in its salt solution (electrolyte), 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.
- It is a measure of tendency of a metallic electrode to lose or gain electrons when it is in contact with its own ions in solution.
- **Reduction potential:** The tendency of an electrode to gain electrons and to get reduced is called *reduction potential*, its value is  $+x$  volts.
- **Oxidation potential:** Similarly the tendency of an electrode to lose electrons and to get oxidized is called *oxidation potential*, its value is  $-x$  volts
- The potential develop between electrode and electrolyte by the formation of charges and these charges are formed Helmholtz electrical double layer, through which potential develop between electrode and electrolyte.



### Single electrode potential:

Each electrochemical cell is made up of two electrodes, at one electrode electrons are evolved and at other electrode electrodes used up. Each electrode which is dipped in its salt solution is called Half Cell. The potential of half-cell i.e. the potential difference between the metal and its salt solution in which it is dipped is called single electrode potential. It cannot be measured directly.



The total cell E.M.F is equal to the sum of the single electrode potentials. Each electrode is affixed with a symbol corresponding to the reaction that takes place near the electrode.

$$E_{\text{cell}} = E_{\text{(anode)}} + E_{\text{(Cathode)}}$$

The half-cell reactions are as follows; the half-cell reaction which corresponds oxidation is



The electrode is called oxidation electrode and potential of the electrode is oxidation potential or the potential of left hand electrode which is represented as  $E_{\text{OX}}$  or  $E_{\text{L}}$ . The cell reaction of the electrode where reduction takes place is given below



The electrode is called reduction electrode or right hand electrode and the potential of this electrode is reduction potential and represented as  $E_{\text{(Red)}}$  or  $E_{\text{(R)}}$ .

The total cell reaction is  $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$ .

$$E_{\text{(cell)}} = E_{\text{(OX)}} + E_{\text{(Red)}}$$

E.M.F of the cell is equal to the sum of the oxidation potential and reduction potential, also expressed as the reduction potential of the right hand electrode minus reduction potential of the left hand electrode.

**GALVANIC CELL:** A galvanic cell is a system in which a spontaneous oxidation and reduction reaction occurs and generates electrical energy. Eg. Daniel cell

### Construction of Galvanic Cell

A galvanic cell is made up of two half cells. One is oxidation or anodic half- cell and other one is reduction or cathodic half cell. Daniel cell is an example of galvanic cell having zinc and copper electrodes. The first half cell consists of zinc electrode dipped in  $\text{ZnSO}_4$  solution and the second half is made of copper electrode dipped in copper sulphate solution. Both half cells are connected externally by metallic conductor and internally by a bent glass tube having saturated solution of a strong electrolyte (KCl) called salt bridge. It acts as a bridge between the two half cells.

### Working of Galvanic cell:

When two half cells are connected externally by a wire through a voltmeter, spontaneous redox reaction takes place at the electrode.

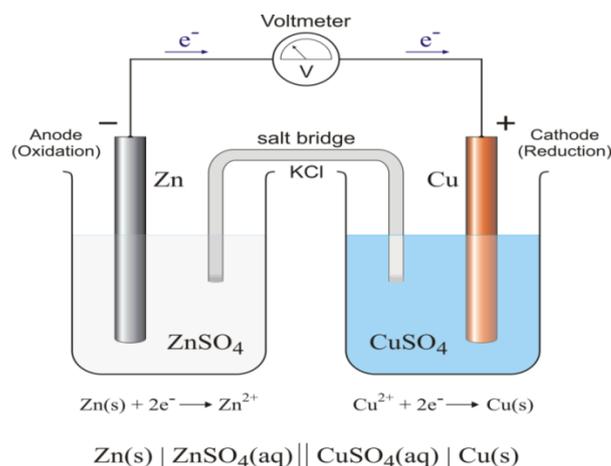
**At anode:** Oxidation takes place with the liberation of two electrons.



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



The overall reaction is  $\text{Zn} + \text{Cu}^{2+} \rightleftharpoons \text{Zn}^{2+} + \text{Cu}$



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

At this stage, the salt bridge comes to the aid and restores the electrical neutrality of the solution in the two half cells. When the concentration of  $\text{Zn}^{2+}$  ions around the anode increases, sufficient number of  $\text{Cl}^-$  ions migrate from the salt bridge to the anode half cell. Similarly, sufficient number of  $\text{K}^+$  ions migrate from the salt bridge to cathode half cell for neutralizing excess negative charge due to the additional  $\text{SO}_4^{2-}$  ions in the cathodic half cell. Thus it maintains the electrical neutrality of the two solutions in the half cells.

### Representation of a galvanic cell:

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

Anode Half-Cell || Cathode Half-Cell

Electrode | Anode Soln || Cathode Soln | Electrode



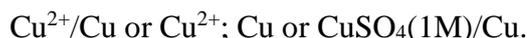
3. The electrode on left (i.e., anode) is written by writing the metal first and then the electrolyte. The two are separated by a vertical line or a semicolon. The electrolyte may be represented by the formula of the whole compound or by ionic species and concentration may also be mentioned in bracket.

Examples of representing anode half-cell as:

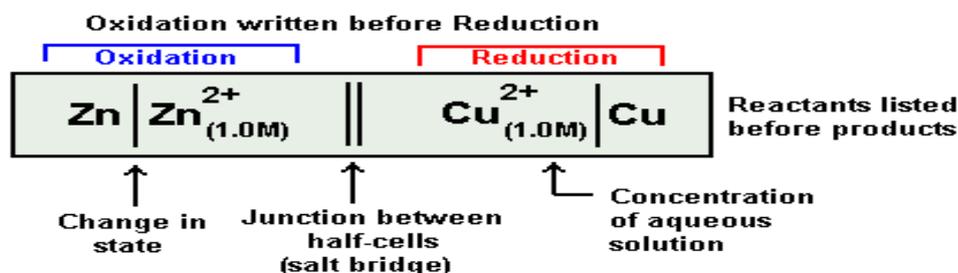
Eg:  $\text{Zn}/\text{Zn}^{2+}$  or  $\text{Zn};\text{Zn}^{2+}$  or  $\text{Zn}/\text{ZnSO}_4(1\text{M})$ .

4. The cathode of the cell (at which reduction takes place) is written on the right hand side. In this case, the electrolyte is represented first and then the metal. The two are separated by a vertical line or a semicolon.

Examples of representing cathode half-cell as:



5. A salt bridge is indicated by two vertical lines, separating the two half-cells.



### Electromotive Force or Cell Potential (EMF):

The flow of electricity from one electrode to another electrode in a galvanic cell indicates that the two electrodes have different potentials. The difference of potentials between the electrodes of a cell which causes flow of current from an electrode at higher potential to other electrode at lower potential is known as electromotive force or cell potential.

The EMF of the cell depends on (a) temperature (b) nature of reactants and (c) concentration of solutions in two half cells.

**Mathematically:**

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

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

Where

$E(\text{cell})$  = e.m.f of cell

$E(\text{right})$  = reduction potential of right hand side electrode (cathode)

$E(\text{left})$  = reduction potential of left hand side electrode (anode)

$$E_{\text{cell}} = E_{\text{ox}}(\text{anode}) + E_{\text{Red}}(\text{cathode})$$

$$E_{\text{cell}} = E_{\text{R}} - E_{\text{L}} \text{ (both are reduction potentials)}$$

$$E_{\text{cell}} = E_{\text{L}}(\text{anode}) - E_{\text{R}}(\text{cathode}) \text{ (both are oxidation potentials)}$$

**Salt bridge:** Salt bridge is a U shaped glass tube containing concentrated solution of an inert electrolyte such as KCl, KNO<sub>3</sub> and K<sub>2</sub>SO<sub>4</sub> or paste of inert electrolyte (whose ions do not take part in redox reaction and do not react with the electrolyte) in agar-agar medium or gelatin.

**Functions of salt bridge:**

1. Salt bridge helps to complete the circuit by allowing the ions to flow from one solution to the other without mixing the two solutions.

2. It helps to maintain electrical neutrality of the solution in the half cells.

## Applications of EMF

### Potentiometric Titration:

A potentiometric titration is one in which the end point is detected by measuring changes in the potential of a suitable electrode (after coupling it with a standard reference electrode) during the course of reaction. No indicator is used in this titration. The electrode whose potential varies during the reaction and which depends upon the concentration of ionic species is called the indicator electrode.

The potentiometric titrations are subdivided in terms of the type of chemical reaction involved in the titration, e. g. acid-base titration, redox titration, precipitation titration and complexometric titration.

**Acid-Base titration:** The acid solution whose strength has to be determined is taken in a beaker and the hydrogen electrode and calomel electrode were dipped in the solution. The electrodes were connected to the potentiometer and the e.m.f. is measured.

Reference Electrode: Saturated Calomel Electrode (SRP = 0.242 V) [Anode]

Indicator Electrode: Quinhydrone Electrode [Cathode].

Cell Notation:

(-) Pt / Hg, Hg<sub>2</sub>Cl<sub>2</sub> / KCl (sat) // H<sup>+</sup> Test Sol. / Q, QH<sub>2</sub> / Pt (+) Cell Reactions:

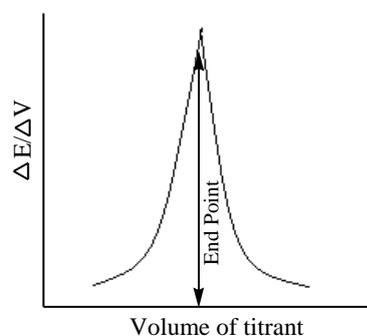
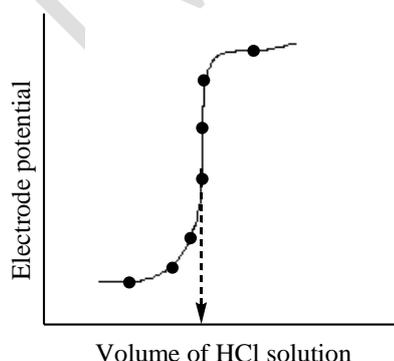
Anode:  $2\text{Hg} + 2\text{Cl}^- \rightarrow \text{Hg}_2\text{Cl}_2 + 2\text{e}^-$

Cathode:  $\text{Q} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{QH}_2$

$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = [0.0990 - 0.0591 \text{ pH}] - 0.242$  i.e.  $E_{\text{cell}}$  is a function of pH.

During titration, as base is added to the acid, the H<sup>+</sup> ion concentration in the half cell containing Quinhydrone will decrease. Correspondingly, there will be a decrease in the  $E_{\text{QE}}$  and  $E_{\text{cell}}$  values also.  $E_{\text{cell}}$  values are noted, graph is plotted, where equivalence point is located and concentration of test solution is calculated.

The steepest portion of the curve indicates the equivalent point of the titration. Instead  $\Delta E/\Delta V$  is plotted against the volume of the base.



**Nernst equation:**

**Derivation of Nernst equation:** Nernst found that the single electrode potential varies with the change in concentration of ions and temperature and hence the EMF of the cell also varies. He derived a mathematical relationship between the standard electrode potential, temperature and the concentration of ions. This relationship is known as the Nernst equation.

Consider the redox reaction:  $M^{n+} + ne^{-} \rightleftharpoons M$

In the above reversible reaction the free energy change (G) and its equilibrium constant (K) are related by the following equation which is popularly known as Van't Hoff reaction isotherm.

$$\Delta G = RT \ln K + RT \ln \frac{\text{product}}{\text{reactant}}$$

$$\Delta G = \Delta G^0 + RT \ln \frac{\text{product}}{\text{reactant}}$$

When  $\Delta G^0$  is the standard free energy change

The free energy change is equivalent to the electrical energy  $-nFE$

Where n = valency

F = Faraday (96500 coloumbs)

E = Electrode potential

R = 8.314 Joules K<sup>-1</sup> mole<sup>-1</sup> (Gas constant)

T = Temperature (K)

$$-nFE = -nFE^0 + RT \ln \frac{[M]}{[M^{n+}]} \quad (\text{Concentration of M is unity})$$

$$-nFE = -nFE^0 - RT \ln [M^{n+}]$$

$$= -nFE^0 - RT 2.303 \log_{10} [M^{n+}]$$

Dividing the equation by  $-nF$

$$E = E^{0+} + \frac{2.303RT}{nF} \log_{10} [M^{n+}]$$

Put the values of R, T and F then

$$\frac{2.303RT}{nF} = \frac{0.0591}{n}$$

$$E = E^0 + \frac{0.0591}{n} \log_{10} [M^{n+}]$$

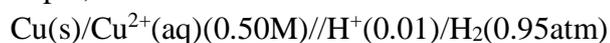
**APPLICATIONS OF NERNST EQUATION:**

1. It can be used to study the effect of electrolyte concentration on electrode potential.

$$E = E^{\circ} - \frac{RT}{nF} \ln\left[\frac{1}{M^{n+}}\right]$$

2. It can also be used for the calculation of the potential of a cell under non-standard conditions.

For example,

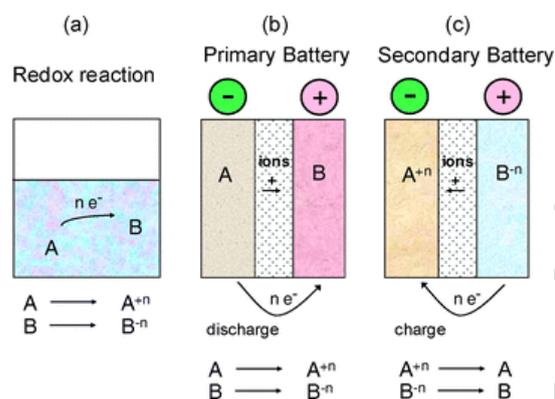


$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{2} \log(\text{Cu}^{2+})P_{\text{H}_2}/[\text{H}^{+}]^2$$

3. Determination of unknown concentration of one of the ionic species in a cell is possible with the help of Nernst equation, provided  $E_{\text{cell}}$  and concentration of other ionic species are known.
4. The pH of a solution can be calculated from the measurement of EMF and Nernst equation.
5. Nernst equation can also be used for finding the valence of an ion or the number of electrons involved in the electrode reaction.

# Batteries & Fuel Cell

Battery is an electrochemical cell or often several electrochemical cells connected in series that can be used as a source of direct electric current at constant voltages. A device which converts chemical energy to electrical energy is called battery cells, connected together electrically in series. Batteries are commercial electrochemical cells.



## ADVANTAGES OF BATTERIES:

- (1) Batteries act as a portable source of electrochemical energy.
- (2) The portability of electronic equipment in the form of handsets has been made possible by batteries.
- (3) A variety of electronic gadgets have been made more useful and popular with the introduction of rechargeable storage batteries having reliability, better shelf life and tolerance to service.
- (4) For all commercial applications, batteries are constructed for their service. For example batteries for automobiles and aircrafts, stand by batteries etc.

## Requirements of Battery:

A useful battery should fulfill the following requirements

1. It should be light and compact for easy transport.
2. It should have long life both when it is being used and when it is not used.
3. The voltage of the battery should not vary appreciably during its use.

### Differences between Primary, Secondary and Fuel cells:

Primary cell	Secondary cells	Fuel Cell
It acts as a simple galvanic cell.	It acts as a galvanic cell while discharging and electrolytic cell while charging.	It acts as a simple galvanic cell.
Cell reaction is not reversible.	Cell reaction can be reversed.	Cell reaction is not reversible
Cannot be recharged.	Can be recharged	Do not store energy
Can be used as long as the materials are active in their composition.  <b>E.g:</b> Leclanche or dry cell. Zn/NH <sub>4</sub> Cl (20%), ZnCl <sub>2</sub> /MnO <sub>2</sub> /C. emf =1.5V. Applications: Radios, torches, transistors, hearing aids.	Can be used again and again by recharging the cell  <b>E.g:</b> 1. Lead storage cell 2. Nicol or Nickel cadmium battery emf =1.4 Applications: Electronic calculators, electronic flash units & cordless electronic shavers etc.	Energy can be withdrawn indefinitely as long as outside supply of fuel is maintained  <b>E.g:</b> H <sub>2</sub> -O <sub>2</sub> , CH <sub>3</sub> OH-O <sub>2</sub> Applications: Space vehicles due to their light weight and the bi product H <sub>2</sub> O produced is a valuable source of fresh water for astronauts.

### PRIMARY CELLS:

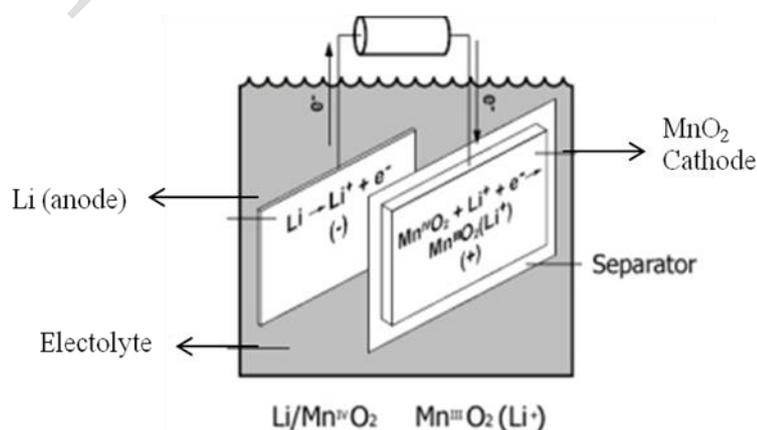
#### Lithium cells:

Lithium cells are primary cells in which lithium acts as anode and the cathode may differ. Lithium metal is used as anode because of its light weight, high standard oxidation potential ( $\geq 3V$ ) and good conductivity. As the reactivity of lithium in aqueous solution is more, lithium cells use non-aqueous solvents as electrolyte.

**Lithium cells are classified into two categories:**

#### (a) Lithium cells with solid cathode:

The electrolyte in this system is a solid electrolyte. The most widely used cell is lithium – manganese dioxide cell (3V). MnO<sub>2</sub> should be heated to over 300°C to remove water before keeping it in the cathode, thereby increasing the efficiency of the cell.

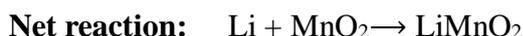
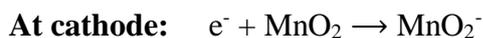


**Anode:** Lithium Metal,

**Cathode:** MnO<sub>2</sub> as an active material.

**Electrolyte:** LiBF<sub>4</sub> salt in a solution of propylene carbonate and dimethoxy ethane.

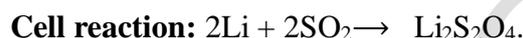
**Reactions:**



**Applications:**

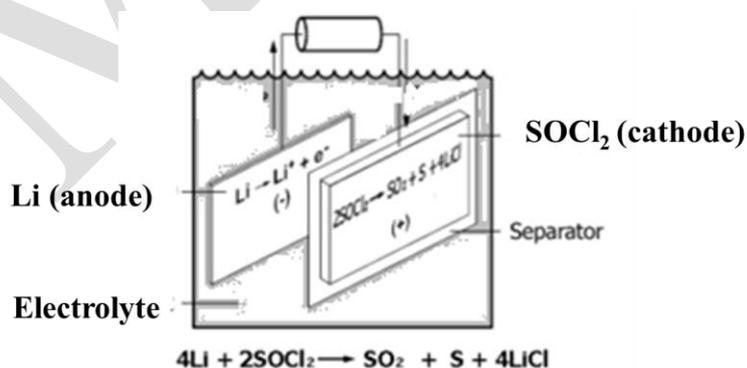
1. The coin type cells are used in watches and calculators.
2. Cylindrical cells are used in fully automatic cameras.

(b) **Lithium cells with liquid cathode:** Lithium–sulphur dioxide cell is an example of liquid cathode. The co-solvents used are acrylonitrile or propylene carbonate (or) mixture of the two with SO<sub>2</sub> in 50% by volume.



Lithium thionyl chloride cell is another example of liquid cathode. It consists of high surface area carbon cathode, a non – woven glass separator. Thionyl chloride acts as an electrolyte and as a cathode.

**Cell reaction:**



In this cell no co-solvent is required as SOCl<sub>2</sub> is a liquid with moderate vapor pressure. The discharging voltage is 3.3 -3.5V.

**USES:**

1. They are used for military and space applications.
2. In medicinal devices such as neuro-stimulators, drugdelivery system, lithium batteries are widely used.
3. They are also used in electric circuit boards for supplying fixed voltage for memory protection and standby functions.

**Advantages:**

1. The energy output of a lithium cell is 2-4 times better than that of conventional zinc anode batteries.
2. Lithium batteries can work over temperature range of 40-70°C.
3. They have higher voltages of about 4V when compared to other primary cells with 1.5 V only.

**Secondary cell: E.g.: Lead – Acid cell:**

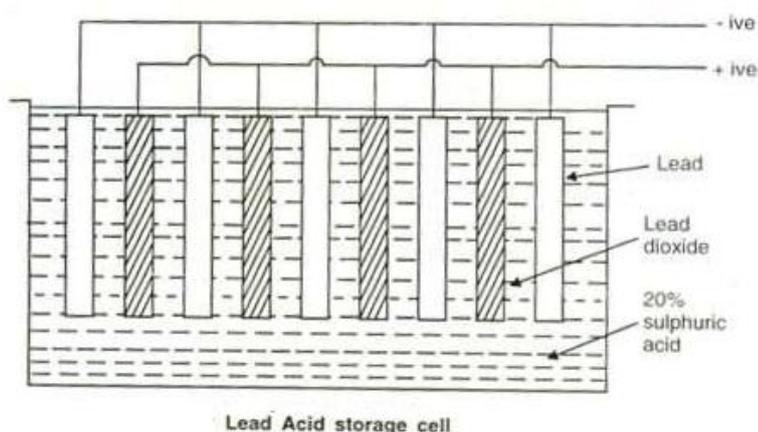
If a number of cells are connected in series, the arrangement is called a battery. The lead storage battery is one of the most common batteries that are used in the automobiles. A 12 V lead storage battery is generally used, which consists of six cells, each providing 2V. Each cell consists of a lead anode and a grid of lead packed with lead oxide as the cathode. These electrodes are arranged alternately, separated by a thin wooden piece and suspended in dil.  $\text{H}_2\text{SO}_4$  (38%), which acts as an electrolyte. Hence, it is called lead acid battery.

Anode: Pb

Cathode:  $\text{PbO}_2$

Electrolyte:  $\text{H}_2\text{SO}_4$  (20-22%)

EMF = 2 V



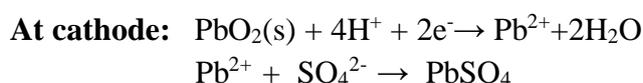
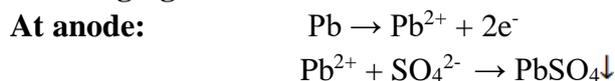
**Lead storage cells:** To increase the current output of each cell, the cathode and the anode plates are joined together, keeping them in alternate positions. The cells are connected parallel to each other.

The cell is represented as

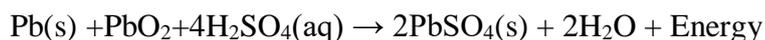


In the process of discharging, i.e., when the battery produces current, the reactions at the electrodes are as follows:

**Discharging reactions:**



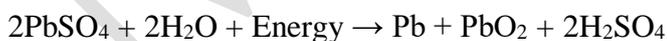
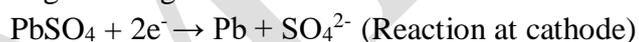
Therefore, the overall reaction is:



During discharging the battery,  $\text{H}_2\text{SO}_4$  is consumed, and as a result, the density of  $\text{H}_2\text{SO}_4$  falls. When it falls below  $1.20 \text{ g/cm}^3$ , the battery needs recharging. In discharging, the cell acts as a voltaic cell where oxidation of lead occurs.

**Recharging:**

During recharging, the cell is operated like an electrolytic cell, i.e. electrical energy is supplied to it from an external source. The electrode reactions are the reverse of those that occur during discharge.



During this process, lead is deposited at the cathode,  $\text{PbO}_2$  is formed at the anode and  $\text{H}_2\text{SO}_4$  is regenerated in the cell.

**Advantages:**

Lead-acid batteries are used for supplying current to railways, mines, laboratories, hospitals, automobiles, power stations, telephone exchange, gas engine ignition, UPS. Other advantages are its recharge ability, portability, and relatively constant potential and low cost.

**Disadvantages:** Use of conc.  $\text{H}_2\text{SO}_4$  is dangerous. Use of lead battery is fragile.

## Lithium-ion batteries (or) Lithium-ion cells:

Lithium-ion battery is a secondary battery. As in lithium cell, it does not contain metallic lithium as anode. As the name suggests, the movement of lithium ions are responsible for charging & discharging. Lithium-ion cell has the following three components.

1. A positive electrode (Layers of lithium-metal oxide) (cathode).
2. A negative electrode (Layers of porous carbon) (anode).
3. An electrolyte (Polymer gel) (separator)

Construction:

The positive electrode is typically made from a layers of chemical compound called lithium-cobalt oxide ( $\text{LiCoO}_2$ ).

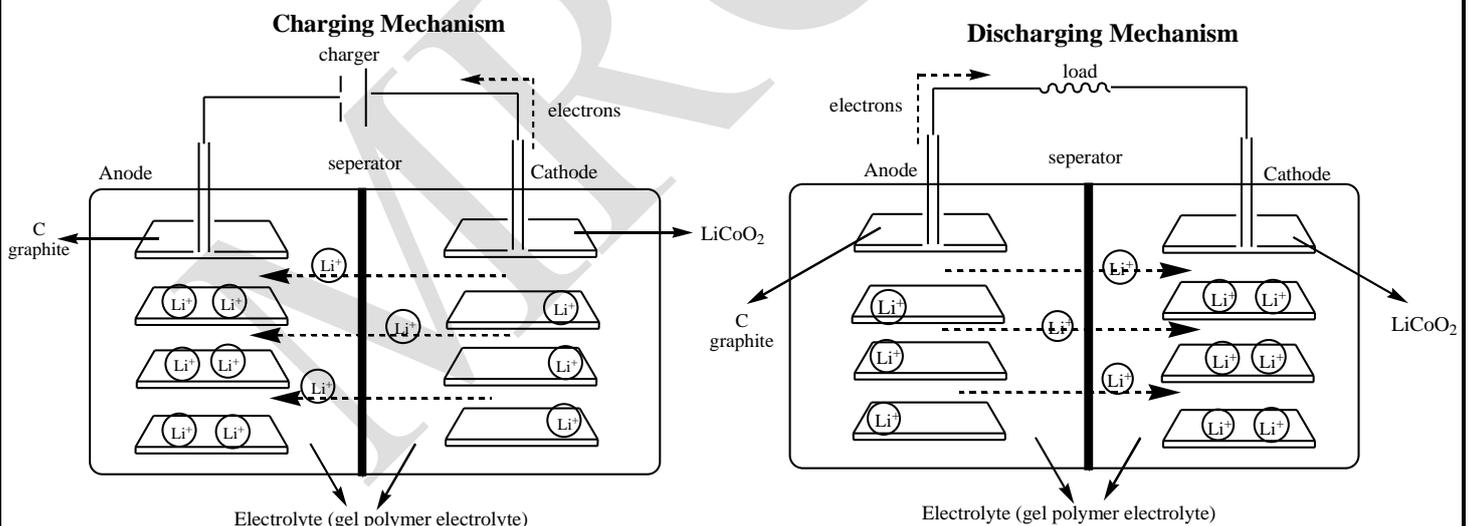
The negative electrode is made from layers of porous carbon (C) (graphite).

Both the electrodes are dipped in a polymer gel electrolyte (organic solvent) and separated by a separator, which is a perforated plastic and allows the  $\text{Li}^+$  ions to pass through.

### Working

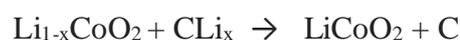
#### Charging Reaction:

During charging,  $\text{Li}^+$  ions flow from the positive electrode ( $\text{LiCoO}_2$ ) to the negative electrode (graphite) through the electrolyte. Electrons also flow from the positive electrode to the negative electrode. The electrons and  $\text{Li}^+$  ions combine at the negative electrode and deposit there as Li.



#### Discharging Reaction:

During discharging, the  $\text{Li}^+$  ions flow back through the electrolyte from negative electrode to the positive electrode. Electrons flow from the negative electrode to the positive electrode. The  $\text{Li}^+$  ions and electrons combine at the positive electrode and deposit there as Li.



**Advantages (or) Characteristics:**

1. Lithium-ion batteries are high voltage and light weight batteries.
2. It is smaller in size.
3. It produces three time the voltage of Ni-Cd batteries.
4. It has none of the memory effect seen in Ni-Cd batteries.

**Uses:**

It is used in cell phone, note PC, portable LCD TV, semiconductor driven audio, etc.

MRCET

# Fuel Cell

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

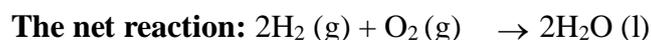
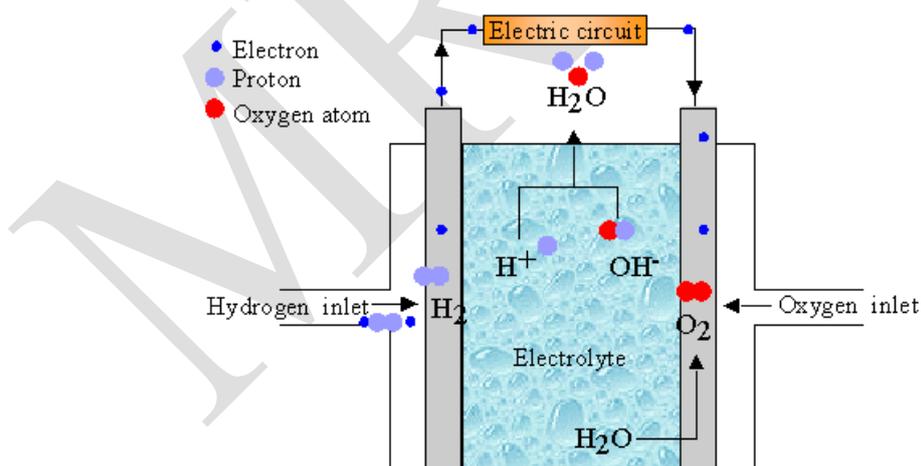
**Principle:** The basic principle of fuel cell is as same as that of an electrochemical cell. The fuel cell operates like a galvanic cell. The only difference is that the fuel and the oxidant are stored outside the cell. Fuel and oxidant are supplied continuously and separately to the electrodes at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



**Examples:** 1.  $\text{H}_2\text{-O}_2$  fuel cell  
2.  $\text{CH}_3\text{OH-O}_2$  fuel cell

### Hydrogen oxygen fuel cell:

This cell is a common type of fuel cell. Similar to a galvanic cell, fuel cell also have two half cells. Both half cells have porous graphite electrode with a catalyst (platinum, silver or a metal oxide). The electrodes are placed in the aqueous solution of NaOH or KOH which acts as an electrolyte. Hydrogen and oxygen are supplied at anode and cathode respectively at about 50 atmospheric pressure, the gases diffuse at respective electrodes. The two half-cell reactions are as follows;



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

**Advantages:**

1. The energy conversion is very high (75-82%).
2. Fuel cell minimizes expensive transmission lines and transmission losses.
3. It has high reliability in electricity generation.
4. The byproducts are environmentally acceptable.
5. Maintenance cost is low for these fuels.
6. They save fossil fuels.
7. Noise and thermal pollution are very low.
8. They have low maintenance cost.
9. They have quick start system.

**Disadvantages:**

1. The major disadvantage of the fuel cell is the high cost and the problems of durability and storage of large amount of hydrogen.
2. The accurate life time is also not known.

**APPLICATIONS:**

1. The most important application of a fuel cell is its use in space vehicles, submarine or military vehicles.
2. The product  $H_2O$  is valuable source of fresh water by the astronauts.
3. It is hoped that fuel cell technology will bring a revolution in the area of energy production.
4. Fuel cell batteries for automotive will be a great boom for the future.

**Limitations:**

1. The life time of fuel cells is not accurately known
2. It cannot store electricity
3. Electrodes are expensive and short lived.
4. Storage and handling of  $H_2$  gas is dangerous because it is inflammable.

# Corrosion & Its Control

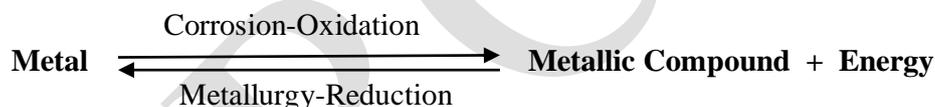
## Introduction:

Metals and alloys are used as fabrication or construction materials in engineering. If the metals or alloy structures are not properly maintained, they deteriorate slowly by the action of atmospheric gases, moisture and other chemicals. This phenomenon of destruction of metals and alloys is known as corrosion.

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.

## Corrosion

- *The process of decay of metal by environmental attack is known as corrosion.*
- Metals undergo corrosion and convert to their oxides, hydroxides, carbonates, sulphides, etc.
- Examples:-
- i) Rusting of iron – when iron is exposed to the atmospheric conditions, a layer of reddish scale and powder of  $\text{Fe}_3\text{O}_4$  is formed.
- ii) Formation of green film of basic carbonate-  $[\text{CuCO}_3 + \text{Cu}(\text{OH})_2]$  on the surface of copper when exposed to moist air containing  $\text{CO}_2$ .
- The corrosion of metals is measured in the units of *milli/inches/year or mm/year*.



Corrosion is an oxidation process and it is reverse of metal extraction.

## 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 and sulphides.
2. During the extraction of metals, these ores are reduced to metallic state by supplying considerable amount of energy.
3. Hence the isolated pure metals are in excited states than their corresponding ores.
4. So metals have natural tendency to go back to their combined state (minerals/ores).
5. When metal is exposed to atmospheric gases, moisture, liquids etc, the metal surface reacts and forms more thermodynamically stable 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

**Theories of corrosion:**

1. Dry corrosion
2. Wet corrosion

**Dry corrosion or Chemical corrosion:** The direct chemical action of environment on the surface of metal in absence of moisture is known as dry corrosion.

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

Example: (i) Silver materials undergo chemical corrosion by Atmospheric  $H_2S$  gas.

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

**There are three types of chemical Corrosion:**

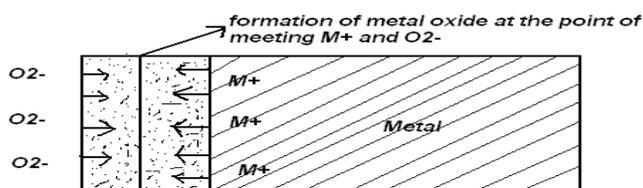
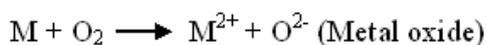
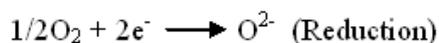
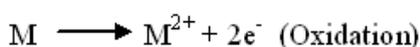
1. Oxidation corrosion
2. Corrosion due to other gases
3. Liquid metal corrosion

**Oxidation Corrosion:**

Direct action of oxygen at low or high temperatures on surface of metals in absence of moisture is known as oxidation corrosion. Alkali metals and Alkaline earth metals are rapidly oxidized at lower temperatures. At high temperature all metals are oxidized (except Ag, Au, Pt).

**Mechanism:**

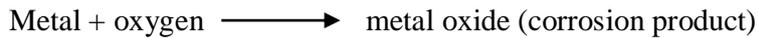
- 1) Oxidation takes place at the surface of the metal forming metal ions  $M^{2+}$
- 2) Oxygen is converted to oxide ion ( $O^{2-}$ ) due to the transfer of electrons from metal.
- 3) The overall reaction is of oxide ion reacts with the metal ions to form metal oxide film.

**Reactions in oxidation corrosion**

*Oxidation mechanism of metals*

**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.

**Nature of the oxide formed:** It plays an important role in further oxidation corrosion process.

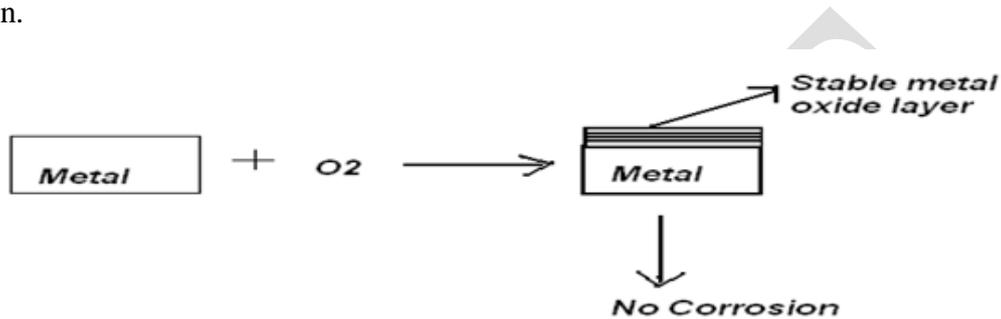


When the oxide film formed is:

### (a) Stable metal oxide layer

A stable layer is fine grained in structure and can get adhered tightly to the parent metal surface. Such a layer will be impervious in nature and hence behaves as protective coating, thereby shielding the metal surface. Consequently further oxidation corrosion is prevented.

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



**Example:**



### Unstable metal oxide layer

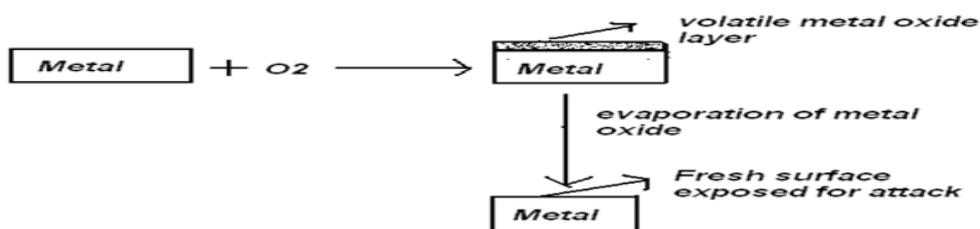
The oxide layer formed decomposes back into metal and oxygen. Consequently oxidation corrosion is not possible in such cases.

Eg: Ag, Au and Pt do not undergo oxidation corrosion.



### (c) Volatile Metal oxide layer

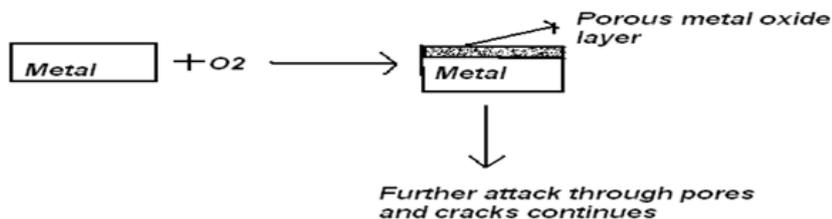
The oxide layer formed is volatile in nature and evaporates as soon as it is formed. There by leaving the under lying metal surface exposed for further attack. This causes rapid continuous corrosion, leading to excessive corrosion eg: Mo- molybdenum forms volatile  $\text{MoO}_3$  layer.



**(d) Porous Metal**

**oxide layer**

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 cause continuous corrosion till conversion of metal into its oxide is completed. **Eg:** Alkali and alkaline earth metals (Li, Na, K, Mg, Fe etc.)

**Example:****Pilling Bedworth rule:**

- To express the extent of protection given by the corrosion layer to the underlying metal Pilling Bedworth rule was postulated.
- It is expressed in terms of specific volume ratio.
- **Specific Volume ratio** =  $\frac{\text{Volume of metal oxide layer}}{\text{Volume of parent metal}}$
- Smaller the specific volume ratio, greater is the oxidation corrosion
- Eg. The specific volume ratio of W, Cr, and Ni are 3.6, 2.0 and 1.6 respectively. Consequently the rate of corrosion is least in Tungsten(W)
- If the volume of the corrosion film formed is more than the underlying metal, it is strongly adherent, non-porous and does not allow the penetration of corrosive gases. No further corrosion.
- 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.

## Wet Corrosion or Electrochemical Corrosion

- The direct chemical action of environment on the surface of metal in presence of conducting liquid with the formation of electrochemical cells.
- It a common type of corrosion which occurs usually in aqueous corrosive environment
- Occurs when metal comes in contact with a conducting liquid.
- Formation of galvanic cell on the surface of metal generating anodic and cathodic areas
- At anode oxidation takes place liberating electrons.
- Electrons at anode are transported to cathodic area where  $H^+$  or  $O_2$  and  $H_2O$  consumes the electrons generating non-metallic ions like  $OH^-$  or  $O^{2-}$
- Metallic ( $M^+$ ) and non metallic ( $OH^-$  or  $O^{2-}$ ) diffuse towards each other and results in the formation of corrosion product in between the anodic and cathodic area.

**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.

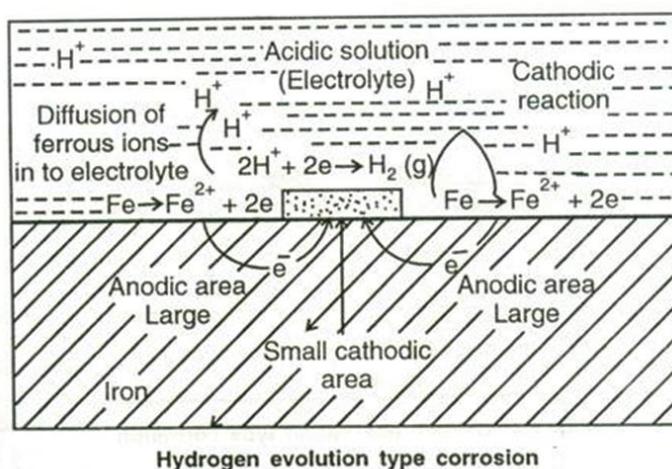
Wet corrosion takes place in two ways.

1. Evolution of Hydrogen
2. Absorption of Oxygen

### Evolution of Hydrogen:

This type of corrosion occurs in acidic medium.

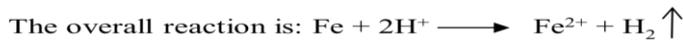
**Eg:** Rusting of iron metal in acidic environment takes place in the following way:



At Anode dissolution of iron to ferrous ion takes place with the liberation of electrons



The electrons released at anode flow through the metal from anode to cathode, where as  $H^+$  ions of acidic solution take up these electrons and eliminated as hydrogen gas.



This type of corrosion causes “displacement of hydrogen ions from the acidic solution by metal ions.

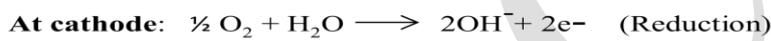
In hydrogen evolution type corrosion, the anodic areas are large and cathodic areas are small.

### Absorption of Oxygen:

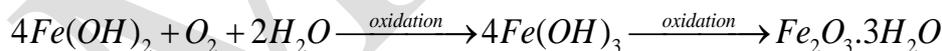
- This type of corrosion takes place in basic or neutral medium in presence of oxygen.
- For example, rusting of iron in neutral or basic aqueous solution of electrolyte in presence of atmospheric oxygen.
- Usually the surface of iron is coated with a thin film of iron oxide.
- If the film develops cracks, anodic areas are created on the surface and the rest of the metal surface acts as cathodes.
- It shows that anodic areas are small and the cathodic areas are large.



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

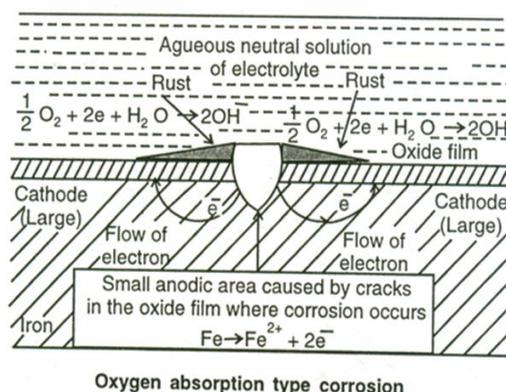


If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide and then to hydrated ferric oxide which is known as rust.



**Rust (hydrated ferric oxide)**

The product called rust corresponds to  $Fe_2O_3 \cdot 3H_2O$ .



**Corrosion control methods:**

1. Proper designing
2. Using Pure metals
3. Using metal alloys
4. Use of inhibitors
5. Modifying Environment
6. Cathodic protection
7. Application of protective coatings

**Cathodic Protection:**

The method of protecting the base metal by forcibly making it to behave like a cathode there by corrosion does not occur is called as cathodic protection.

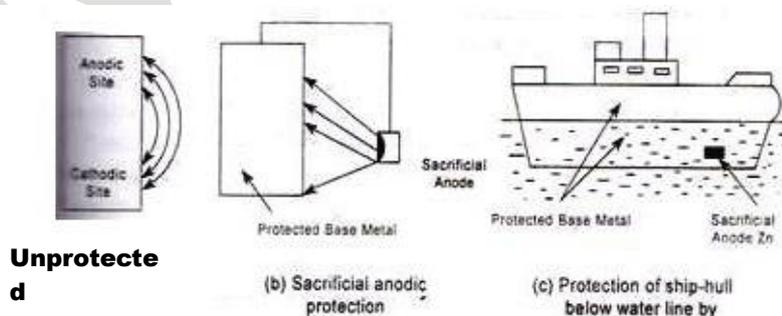
There are two types of cathodic protection

- (a) Sacrificial anodic protection
- (b) Impressed current cathodic protection

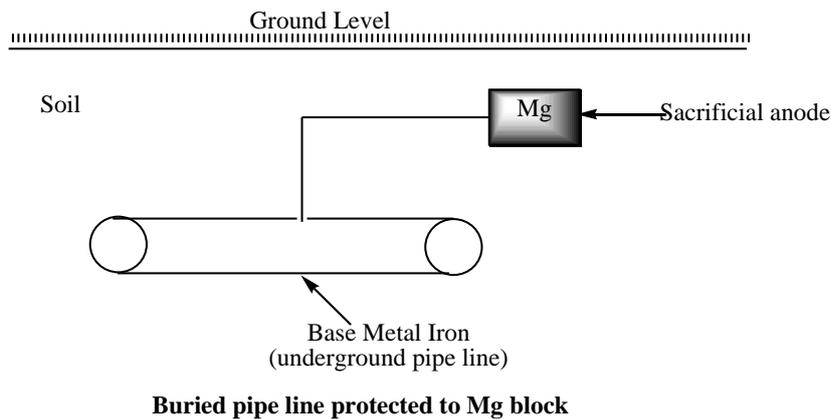
**Sacrificial anodic protection**

- In this protection method, the metallic structure to be protected (base metal) is connected by a conducting 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.
- The artificially made anode thus gets corroded gradually protecting the original metallic structure. Hence the process is known as sacrificial anodic protection.
- 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.



**Figure1. Sacrificial anode method: Ship hull and underground water pipeline**



### Applications of Sacrificial anodic protection:

By referring to the electrochemical series, the metal with low reduction potential is connected to the base metal which acts as anode.

1. To protect underground pipelines- Buried pipe line protected by connecting to Mg block
2. Protection of ship hulls and other marine devices.
3. Protection of water tank- by suspending Zn or Mg rods, body of the tank made cathode and protected.

### Advantages:

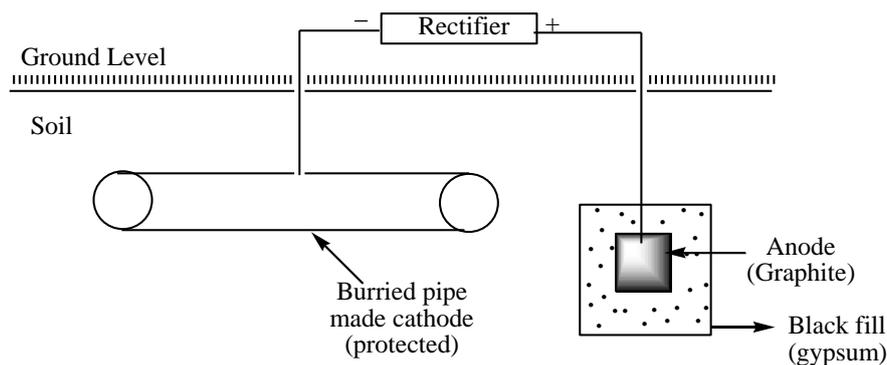
1. It is a simple method.
2. It does not require external power.
3. It has low maintenance and installation cost
4. Cathodic interferences are minimum.

### Disadvantages:

1. More than one anode is required some times.
2. It does not work properly in high corrosive environment.
3. Sacrificial anode must be replaced periodically as and when it is consumed

### Impressed current cathodic protection:

- In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode.
- 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 rectifier on A.C. line.
- The metal to be protected is made cathode by connecting to an external battery (-ve terminal)
- The anode is usually insoluble anode like graphite, stainless steel, or platinum connected to +ve terminal of the battery. Usually a sufficient D.C current is passed on to the insoluble anode kept in a black fill composed of coke or gypsum, so as to increase the electrical contact with the surrounding soil.
- In impressed current cathodic protection, electrons are supplied from an external cell, so that the object itself becomes cathodic and does not get oxidized.



### Applications:

1. The impressed current cathodic protection is used for the protection of water tanks, water & oil pipe lines, transmission line towers etc.

### Advantages

The method is mainly employed to protect large structures for long term operations.

### Disadvantages

1. The method is expensive as it requires high current
2. Capital investment and maintenance costs are more
3. It is difficult to maintain uniform current over the entire metal surface as a result localized corrosion may occur.
4. The metal should not be over protected, ie, use of much high potential is avoided otherwise problems related to cathodic reactions like evolution of  $H_2$  and formation of  $OH^-$  Ions takes place leading to corrosion of base metal

### Metallic coatings:

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

#### 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.

#### 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.

## Methods of application of metallic coatings:

### 1. Hot dipping:

- 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.

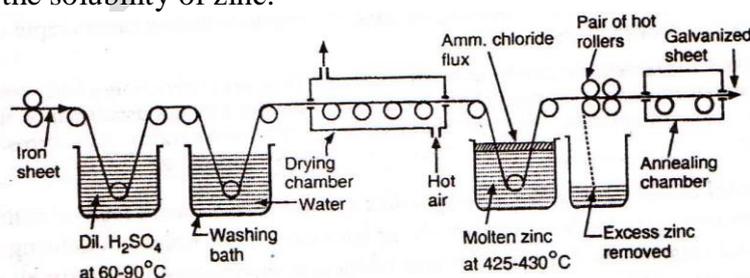
The most widely used hot dipping processes are

- (a) Galvanizing
- (b) Tinning

### 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 dil.  $H_2SO_4$  solution for 15-20 minutes at  $60-90^\circ C$ . In pickling any scale, dirt, oil, grease or rust and any other impurities are removed from the metal surface.
- The article is washed well and then dried.
- It is then dipped in bath of molten zinc maintained at  $425-430^\circ C$ .
- The surface of bath is kept covered with ammonium chloride – flux to prevent oxide formation. The article is covered with a thin layer of zinc when it is taken out of bath.
- It is then passed through a pair of hot rollers, which removes any excess of zinc and produces a thin film of uniform thickness
- Then it is annealed and finally cooled slowly.

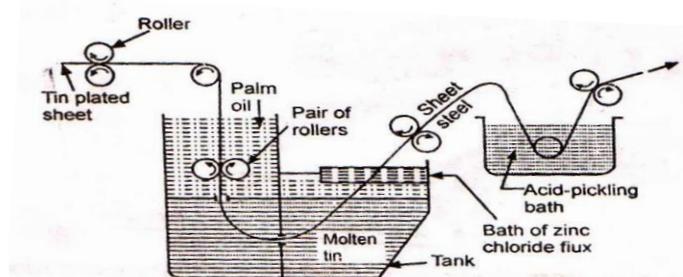
**Applications:** Galvanizing is widely used for protecting iron exposed to the atmosphere (roofs, wire fences, pipes etc.) Galvanized metallic sheets are not used for keeping eatables because of the solubility of zinc.



### 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 of  $ZnCl_2$  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.
- Finally the sheet is passed through rollers to remove excess of tin and produce thin coat of tin of uniform thickness

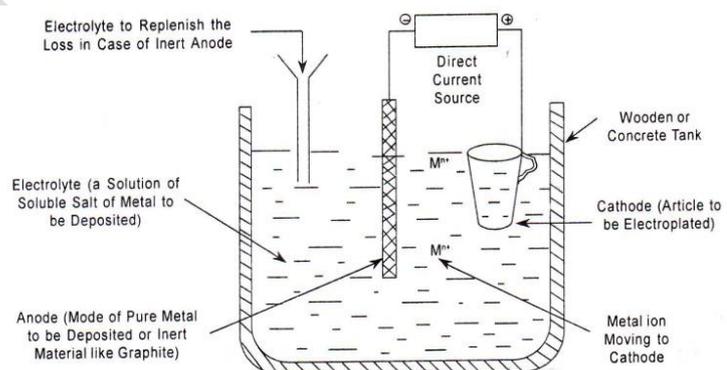


### Applications:

1. Tin metal possess good resistance against atmospheric corrosion. Tin is non-toxic and widely used for coating steel, copper and brass sheets
2. The containers coated with tin are used for storing food stuffs, ghee, oil etc and packing food materials.
3. Tinned copper sheets are used for making cooking utensils and refrigeration equipment.

### Electroplating:

- It is a process in which coating metal is deposited on the base metal by passing direct current through an electrolytic solution containing the soluble salt of the coating metal.
- 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.



### Objectives of Electroplating

1. To increase resistance to corrosion, chemical attack and wear resistance of the plated metal
2. To improve physical appearance and hardness
3. To increase the decorative and commercial values of metals
4. To increase the strength of non-metals like plastics, wood and glass etc.
5. To make surface conductive by using light weight non-metallic materials like wood and plastics

### Electroplating-Copper plating:

For example, for electroplating of copper on iron article the following are maintained

Electrolytic bath solution:  $\text{CuSO}_4$

Anode: Pure copper

Cathode: Base metal article

Temperature:  $20-40^\circ\text{C}$  (low temp for brighter and smooth surface)

Current density:  $20-30 \text{ mA/cm}^2$

When direct current is passed, the  $\text{Cu}^{2+}$  ions migrate to the cathode and deposit on the base metal article.

**Anode:**  $\text{Cu(s)} \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{e}^-$

**Cathode:**  $\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu(s)}$

### Electroless plating

- The method of deposition of a metal from its salt solution on a catalytically active surface by a suitable reducing agent without using electrical energy is called electroless plating.
- This process is also called chemical plating or autocatalytic plating.
- The metallic ions ( $\text{M}^+$ ) are reduced to the metal with the help of reducing agents ( $\text{R}^{-1}$ ). When the metal ( $\text{M}$ ) is formed, it gets plated over a catalytic surface.



### Electroless-Ni plating:

It is an auto-catalytic chemical technique used to deposit a layer of nickel-phosphorus or nickel-boron alloy on a solid work piece, such as metal or plastic. The process relies on the presence of a reducing agent.

It involves the following features

**Pretreatment and activation of the surface:** The surface to be plated is activated by treatment with organic solvents or alkali, followed by acid treatment

#### Composition of Bath:

Coating solution-  $\text{NiCl}_2$  solution

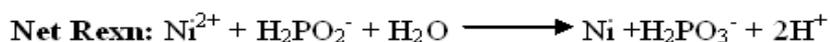
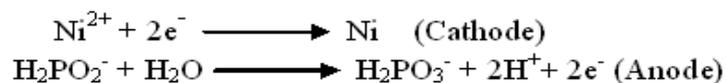
Reducing agent- Sodium hypophosphite ( $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ )

Buffer- Sodium acetate

Complexing agent- Sodium succinate

Optimum  $\text{pH}$ - 4.5

Optimum temperature -  $93^\circ\text{C}$

**Reactions:****Advantages of Electroless plating:**

1. Electrical energy is not required.
2. Even intricate parts (of irregular shapes) can be plated uniformly
3. There is flexibility in plating volume and thickness.
5. The process can plate recesses and blind holes with stable thickness.
6. Chemical replenishment can be monitored automatically.
7. Bright finishes can be obtained.
8. Plating on articles made of insulators (like plastics) and semiconductors can easily be carried out.
9. Electroless plated Ni objects has better corrosion resistance, deposits are pore free, hard and wear resistant.

**Applications:**

- 1) They are used in electronic industry for fabricating printed circuits and diodes.
- 2) It is used in domestic as well as automotive fields (eg. jewellery, tops of perfume bottles).
- 3) Its polymers are used in decorative and functional works.
- 4) Its plastic cabinets are used in digital as well as electronic instruments.

# UNIT - II: ATOMIC AND MOLECULAR STRUCTURE

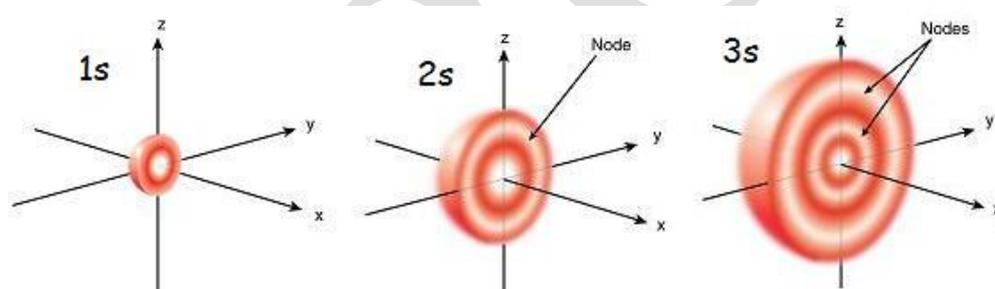
## Molecular Orbital Theory:

**Orbital:** An Orbital is a three dimensional space around nucleus where the probability of finding an electron is high. They represent the probability of finding an electron in any one place. They correspond to different energies. So an electron in an orbital has definite energy. Each orbital is denoted by a number and a letter. The number denotes the energy level of the electron in the orbital. Thus 1 refers to the energy level closest to the nucleus; 2 refers to the next energy level further out, and so on. The letter refers to the shape of the orbital. The letters go in the order s, p, d, f, g, h, i, j, etc.

**Atomic Orbitals:** Atomic orbitals are regions of space around the nucleus of an atom where an electron is likely to be found. Atomic orbitals allow atoms to make covalent bonds. An atomic orbital can have a maximum of two electrons. Atomic orbitals are labelled as s, p, d, and f sublevels.

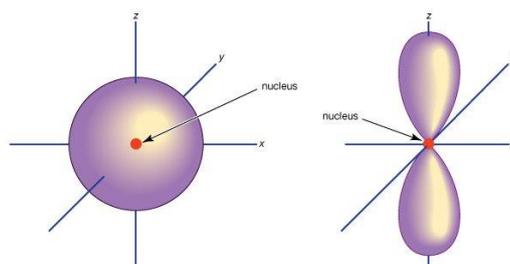
### s Orbitals

The s orbital is spherical and hold a maximum of two electrons. It has one sub-energy level. The order of size is  $1s < 2s < 3s < \dots$ , as shown below.



### p Orbitals:

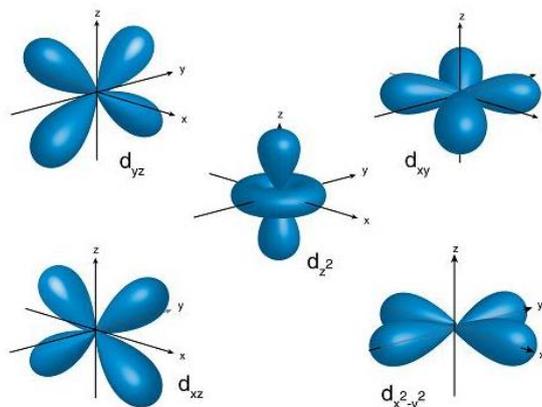
The p orbital is dumbbell shaped and can hold up to six electrons. It has three sub energy levels. These are given the symbols  $p_x$ ,  $p_y$  and  $p_z$ . The p orbitals at the second energy level are called  $2p_x$ ,  $2p_y$  and  $2p_z$ . There are similar orbitals at subsequent levels:  $3p_x$ ,  $3p_y$ ,  $3p_z$ ,  $4p_x$ ,  $4p_y$ ,  $4p_z$  and so on.



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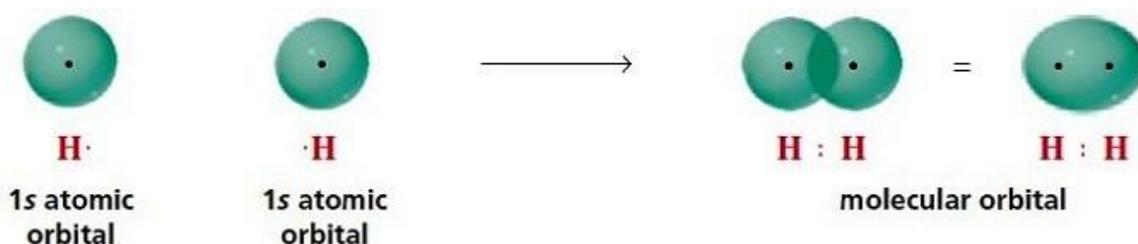
## d ORBITALS

The d and f orbitals have more complex shapes. The d level has five sub-energy groups and holds up to 10 electrons. The five 3d orbitals are called  $3d_{xy}$ ,  $3d_{xz}$ ,  $3d_{yz}$ ,  $3d_{x^2 - y^2}$ ,  $3d_{z^2}$



**Molecular orbital** (MO): Atoms join to form molecules. When two atoms move closer together to form a molecule, atomic orbitals overlap and combine to become molecular orbitals.

Molecular orbitals are regions around molecules where electrons are most likely to be found. The number of newly formed molecular orbitals is equal to the number of combined atomic orbitals. The molecular orbital surrounds the two nuclei of the atoms, and electrons can move around both nuclei. Similar to atomic orbitals, molecular orbitals maximally contain 2 electrons, which have opposite spins. Molecular orbitals are of two types, bonding molecular orbitals and antibonding molecular orbitals. Bonding molecular orbitals contain electrons in the ground state and antibonding molecular orbitals contain no electrons in the ground state. Electrons may occupy in the antibonding orbitals if the molecule is in the excited state.



## Differences between Atomic and Molecular Orbital

Atomic orbital	Molecular orbital
Atomic orbital is the region having the highest probability of finding an electron in an atom	Molecular orbital is the region having the highest probability of finding an electron of a molecule
Atomic orbitals are inherent property of an atom. Formed by the electron cloud around the atom	Molecular orbitals are formed by combination of atomic orbitals that have nearly the same energy
The shape is determined by the type of atomic orbital(s,p,d or f)	The shape is determined by the shapes of atomic orbitals that make the molecule. They have complex shapes.
Schrodinger equation is used	Linear combination of atomic orbitals (LCAO) is used
Monocentric as it is found around a single reaction	Polycentric as it is found around different nuclei

### Molecular Orbital Theory

Valence Bond Theory fails to answer certain questions like Why  $\text{He}_2$  molecule does not exist and why  $\text{O}_2$  is paramagnetic. Therefore in 1932 F. Hood and R.S. Mulliken came up with theory known as **Molecular Orbital Theory** to explain questions like above. According to Molecular Orbital Theory individual atoms combine to form molecular orbitals, as the electrons of an atom are present in various atomic orbitals and are associated with several nuclei.

**Molecular orbital (MO) theory** is a method for determining molecular structure in which electrons are not assigned to individual bonds between atoms, but are treated as moving under the influence of the nuclei in the whole molecule.

#### Postulates of MOT are:

- Two atoms come together, interact and forms a bond. All the atomic orbitals on either nuclei mix together to form a new orbital called molecular orbital.
- The molecular orbitals are formed by mixing of the atomic orbitals of same energy level and symmetry.
- After formation of molecular orbital, the atomic orbitals lose their identity.
- Each and every electron in the molecular orbital belongs to all the nuclei of the molecules.
- Atoms have atomic orbitals with one nuclei and Molecules have molecular orbitals with n nuclei. Thus, atoms are monocentric while molecules are polycentric.
- The number of molecular orbitals formed is equal to the atomic orbitals mixing.
- Molecular orbitals can be bonding, anti-bonding, and non-bonding orbitals.
- Bonding molecular orbitals are lower in energy than the corresponding anti-bonding orbitals.

- Each molecular orbital is described by a wave function  $\Psi$ , which in turn is associated with a set of quantum number.
- Electrons fill up these orbitals in the same way as atomic orbitals in accordance to the 3 principles (Aufbau, Hunds and Pauli Principle).
- The Aufbau principle states that orbitals are filled with the lowest energy first.
- The Pauli exclusion principle states that the maximum number of electrons occupying an orbital is two, with opposite spins.
- Hund's rule states that when there are several MOs with equal energy, the electrons occupy the MOs one at a time before two occupy the same MO.

Electrons may be considered either of particle or of wave nature. Therefore, an electron in an atom may be described as occupying an atomic orbital, or by a wave function  $\Psi$ , which are solution to the **Schrodinger wave equation**. Wave function is a mathematical function related to probability of finding the particle in a particular region of space.

Electrons in a molecule are said to occupy molecular orbitals. The wave function of a molecular orbital may be obtained by one of two methods:

1. Linear Combination of Atomic Orbitals (LCAO).
2. United Atom Method.

### Linear Combination of Atomic Orbitals (LCAO)

As per this method the formation of orbitals is because of Linear Combination (addition or subtraction) of atomic orbitals which combine to form molecule. Consider two atoms A and B which have atomic orbitals described by the wave functions  $\Psi_A$  and  $\Psi_B$ . If electron cloud of these two atoms overlap, then the wave function for the molecule can be obtained by a linear combination of the atomic orbitals  $\Psi_A$  and  $\Psi_B$  i.e. by subtraction or addition of wave functions of atomic orbitals

$$\Psi_{MO} = \Psi_A \pm \Psi_B$$

The above equation forms two molecular orbitals

### Bonding Molecular Orbitals

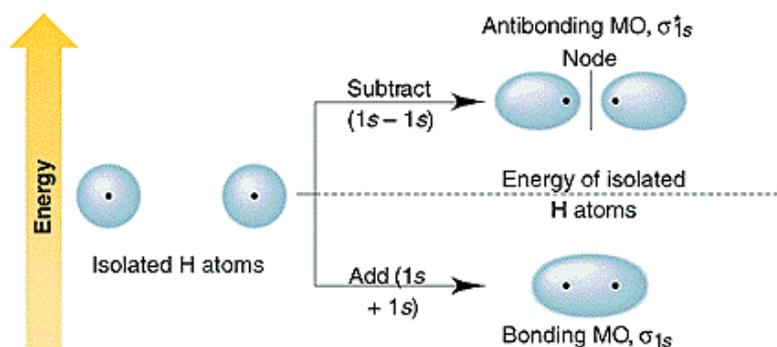
When addition of wave function takes place, the type of molecular orbitals formed are called Bonding Molecular orbitals and is represented by  $\Psi_{MO} = \Psi_A + \Psi_B$ .

They have lower energy than atomic orbitals involved. It is similar to constructive interference occurring in phase because of which electron probability density increases resulting in formation of bonding orbital. Molecular orbital formed by addition of overlapping of two s orbitals shown in Figure 1. It is represented by s.

### Anti-Bonding Molecular Orbitals

When molecular orbital is formed by subtraction of wave function, the type of molecular orbitals formed are called Antibonding Molecular Orbitals and is represented by  $\Psi_{MO} = \Psi_A - \Psi_B$ .

They have higher energy than atomic orbitals. It is similar to destructive interference occurring out of phase resulting in formation of antibonding orbitals. Molecular Orbital formed by subtraction of overlapping of two s orbitals are shown in figure no. 2. It is represented by  $\sigma^*$  (\* is used to represent antibonding molecular orbital) called Sigma Antibonding.



**Fig. 1 Formation of Bonding and Anti-Bonding Orbital**

Therefore, Combination of two atomic orbitals results in formation of two molecular orbitals, bonding molecular orbital (BMO) whereas other is anti-bonding molecular orbital (ABMO).

BMO has lower energy and hence greater stability than ABMO. First BMO are filled then ABMO starts filling because BMO has lower energy than that of ABMO.

Formation of molecular orbitals occurs by the combination of atomic orbitals of proportional symmetry and comparable energy. Therefore, a molecular orbital is polycentric and atomic orbital is monocentric. Number of molecular orbitals formed is equal to the number of atomic orbitals.

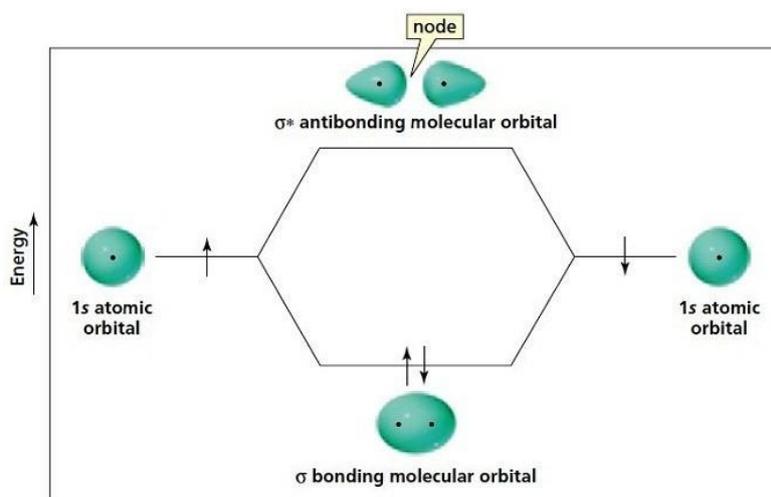
### Relative Energies of Molecular Orbitals

**Bonding Molecular Orbitals (BMO)** - Energy of Bonding Molecular Orbitals is less than that of Anti Bonding Molecular Orbitals because the attraction of both the nuclei for both the electron (of the combining atom) is increased.

**Anti-Bonding Molecular Orbitals (ABMO)** - Energy of Anti Bonding Molecular Orbitals is higher than Bonding Molecular Orbitals because the electrons move away from the nuclei and are in repulsive state.

The Energies of Bonding Molecular Orbitals and Anti-Bonding Molecular Orbitals are shown in

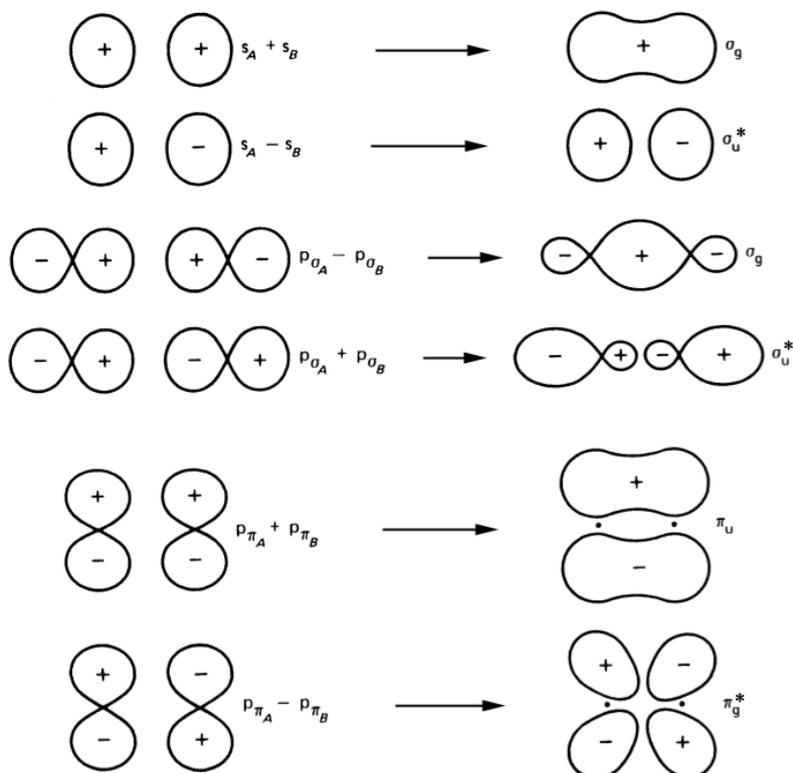
Fig 2 :



**Fig: 2**

**Molecular orbitals of diatomic molecules:**

Molecular Orbitals for diatomic Molecules formed from a Linear Combination of Atomic Orbitals is shown below:

**Filling Electrons in MO Diagrams**

The next step in constructing an MO diagram is filling the newly formed molecular orbitals with electrons. Three general rules apply:

- The Aufbau principle states that orbitals are filled starting with the lowest energy
- The Pauli exclusion principle states that the maximum number of electrons occupying an orbital is two, with opposite spins.
- Hund's rule states that when there are several MOs with equal energy, and the electrons occupy the MOs one at a time before two occupy the same MO.

The filled MO that is highest in energy is called the Highest Occupied Molecular Orbital, or HOMO; the empty MO just above it is the Lowest Unoccupied Molecular Orbital, or LUMO. The electrons in the bonding MOs are called bonding electrons, and any electrons in the antibonding orbitals are called antibonding electrons. The reduction in these electrons' energy is the driving force for chemical bond formation.

## Energy Level Diagram

The factors upon which relative energies of molecular orbitals depend are:

- (i) Energies of the Atomic orbitals combining to form Molecular Orbitals.
- (ii) The extent of overlapping between the atomic orbitals. The greater the overlap, the more the bonding orbital is lowered and the anti-bonding orbital is raised in energy relative to AOs

1s Atomic Orbitals (AOs) of two atoms form two Molecular Orbitals (MOs) designated as  $\sigma 1s$  and  $\sigma^* 1s$ . The 2s and 2p orbitals (eight AOs of two atoms) form four bonding MOs and four anti-bonding MOs as:

**Bonding MOs:**  $\sigma 2s, \sigma 2p_z, \pi 2p_x, \pi 2p_y$

**Anti – Bonding MO:**  $\sigma^* 2s, \sigma^* 2p_z, \pi^* 2p_x, \pi^* 2p_y$

The order of increasing energy of molecular orbitals obtained by combination of 1s, 2s and 2p orbitals of two atoms is  $\rightarrow$

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

(Energy Increases from left to right)

### Bond order:

It may be defined as the half of difference between the number of electrons present in the bonding orbitals and the antibonding orbitals that is,

Bond order (B.O.) = (No. of electrons in BMO - No. of electrons in ABMO) / 2

Those with positive bonding order are considered stable molecule while those with negative bond order or zero bond order are unstable molecule.

**Magnetic Behavior:** If all the molecular orbitals in species are spin paired, the substance is diamagnetic. But if one or more molecular orbitals are singly occupied it is paramagnetic.

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

The electronic configuration of nitrogen atom is  $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$  and  $N_2$  molecule has 14 electrons. The Molecular orbital diagram is shown in Fig. 3

The molecular orbital electronic configuration of the molecule is:

$N_2: KK (\sigma 2s)^2 < (\sigma^* 2s)^2 < (\pi 2p_x)^2 = (\pi 2p_y)^2 < (\sigma 2p_z)^2$

Bond Order =  $\frac{8-2}{2} = 3$

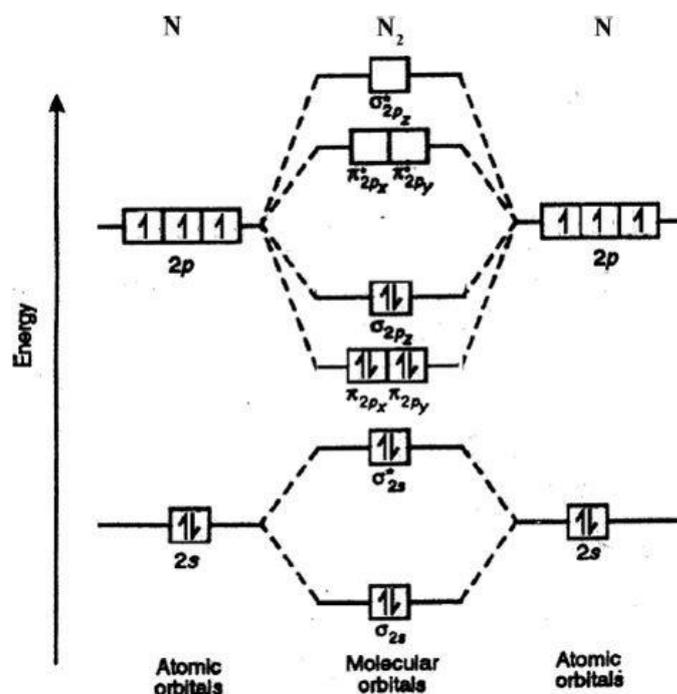


Fig 3: Molecular orbital energy level diagram of  $N_2$  molecule

Thus, nitrogen molecule has three bonds, one  $\sigma$  and two  $\pi$ -bonds. This is in accordance with very high bond dissociation energy ( $945 \text{ kJ mol}^{-1}$ ) and small bond length (110 pm) of the molecule. The molecule has no unpaired electrons and therefore it is **diamagnetic**.

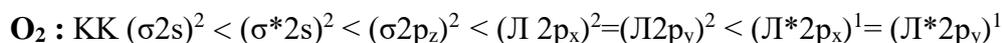
#### Molecular orbital energy level diagram of Oxygen molecule ( $O_2$ )

Oxygen atom has electronic configuration of  $1s^2 2s^1 2p_x^2 2p_y^1 2p_z^1$ . Therefore, oxygen molecule has 16 electrons. In the formation of molecular orbitals, the electrons in the inner shells are expressed as KK denoting  $(\sigma 1s)^2 (\sigma^* 1s)^2$ . The remaining 12 electrons are filled in molecular orbitals as shown in figure 4

For  $O_2$



The electronic configuration of the molecule is



$$\text{Bond Order} = \frac{8-4}{2} = 2$$

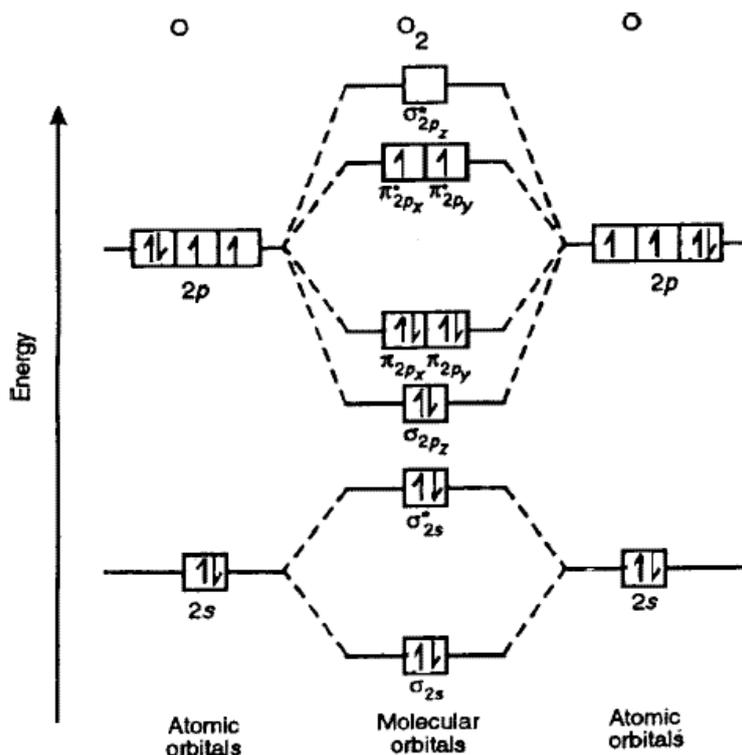
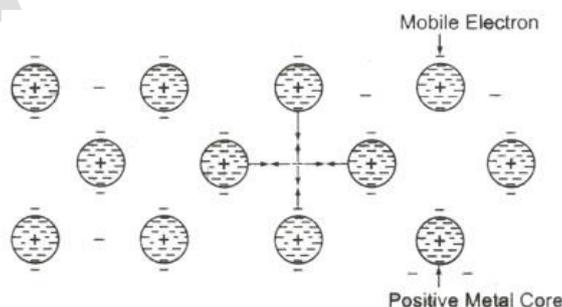


Fig 4: Molecular orbital energy level diagram of  $O_2$

Thus, oxygen molecule has **two bonds** one  $\sigma$  and one  $\pi$ . Further, in accordance with Hund's rule, the last two electrons in  $\pi^*2p_x$  and  $\pi^*2p_y$  orbitals will remain unpaired. Therefore, the molecule has **paramagnetic** character due to the presence of two unpaired electrons. These facts are in accordance with experimental observations. The bond dissociation energy in  $O_2$  molecule is  $498 \text{ kJ mol}^{-1}$  and bond length is 121 pm.

### Metallic Bonding:

The force that holds the atoms of pure metal together in a crystal as a result of the attraction between positive ions and surrounding freely mobile delocalized electrons is known as metallic bond.



## Valence bond theory

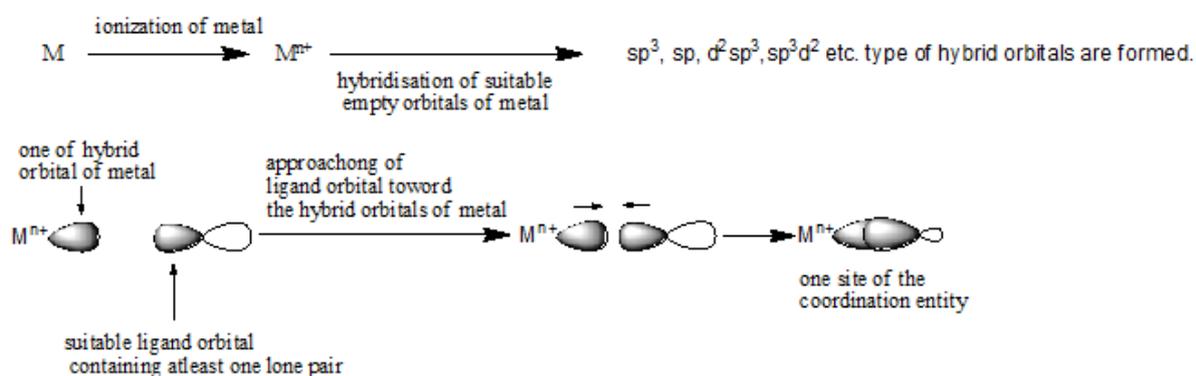
Valence bond theory explains the geometry of the complex compound using the concept of hybridization. This theory is a chemical bonding theory that explains the bonding between two atoms is caused by the overlap of half-filled atomic orbitals. The two atoms share each other's unpaired electron to form a filled orbital to form a hybrid orbital and bond together. According to this theory, a covalent bond is formed between the two atoms by the overlap of half filled valence atomic orbitals of each atom containing one unpaired electron.

Based on the pattern of overlapping, there are two types of covalent bonds: sigma bond and a pi bond. The covalent bond formed by sidewise overlapping of atomic orbitals is known as pi bond whereas the bond formed by overlapping of atomic orbital along the inter nucleus axis is known as a sigma bond.

According to VBT theory, a coordination entity is formed as a result of coordinate covalent bond formation by electron pairs from ligands (Lewis bases) through overlap of appropriate atomic orbitals (usually hybrid orbitals) of the metal (Lewis acid) and ligand.

A coordination entity is composed of central atom, usually that of metal, to which is attached a surrounding array of other atoms or group of atoms, each of which is called ligand.

Hypothetical sequence of steps for the formation of a coordination entity;



### Limitation of the VBT:

1. Fail to explain the colour & characteristics of absorption spectra of complex compounds.
2. Orbital contribution and temperature dependency on magnetic moment of coordination complex are not properly explained by VBT.
3. It is not helpful to predict the mystery of formation of outer or inner orbital coordination complex.
4. VBT fails to predict any distortion in the shapes of the coordination complexes from regular geometry.

## Crystal Field Theory:

### Coordination compounds /Complex compounds

They are molecular compounds which retain their identities even when dissolved in water and their properties are completely different from those constituents.

Ex.  $[\text{K}_4\text{Fe}(\text{CN})_6]$  is a complex compound.

Compounds containing complex ions are called complex compounds. These complex ions have coordinate bonds in their structure and known as coordinate ions and the compounds are called coordinate compounds.

**Central ion** The cation to which one or more neutral molecules or anions are attached is called central ion

**Ligands.** Any atom or ion or molecule which is capable of donating a pair of electrons to the central metal atom are called ligands.

The particular atom which donates pair of electrons is called a donor atom.

Ex. Donor atoms-N, O, S and halogens

**Unidentate ligands** The ligands containing one donor atom is called unidentate ligand.

Ex.  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$ .

**Bidentate ligands.** The ligands which contains two donor atoms are called bidentate ligands.

Ex. Ethylene diammine

**Coordination Number** The total number of ligands attached to the central atom is called coordination number Ex.  $[\text{Ag}(\text{NH}_3)_2]^{2+}$  / CN-2 ;  $[\text{Cu}(\text{H}_2\text{O})_4]^{2+}$  / CN-4

Crystal field theory is very much different from valence bond theory. According to valence bond theory, bonding between the metal ion and the ligands is purely covalent, while according to crystal field theory, the interaction between the metal ion and ligands, is purely electrostatic, i.e metal-ligand bonds are 100% ionic.

Crystal field theory (CFT) describes the breaking of orbital degeneracy in transition metal complexes due to the presence of ligands. CFT qualitatively describes the strength of the metal-ligand bonds. Based on the strength of the metal-ligand bonds, the energy of the system is altered. This may lead to a change in magnetic properties as well as color. This theory was developed by Hans Bethe and John Hasbrouck van Vleck.

Crystal Field Theory was developed to describe important properties of complexes (magnetism, absorption spectra, oxidation states, coordination,).

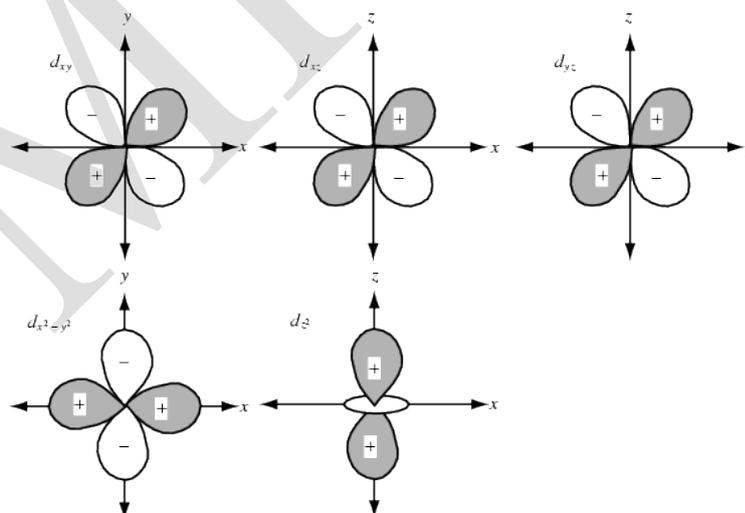
**Salient features of crystal-field theory are:**

1. The transition metal ion is surrounded by the ligands with lone pairs of electrons and the complex is a combination of central ion surrounded by other ions or molecules or dipoles i.e. ligands.
2. All types of ligands are regarded as point charges.
3. The ionic ligands, like F-, Cl-, CN-, etc., are regarded as negative point charges, or point charges and the neutral ligands, like H<sub>2</sub>O, NH<sub>3</sub>, etc., are regarded as point dipoles or just dipoles. (CFT regards neutral ligands as dipolar) If the ligand is neutral, the negative end of this ligand dipole is oriented towards the metal atom.
4. The interactions between the metal ion and the negative ends of anion (or ion dipoles) are purely electrostatic, i.e. the bond between the metal and ligand is considered 100 percent ionic.
5. The ligands surrounding the metal ion produce electrical field and this electrical field influences the energies of the orbitals of central metal ion, particularly d-orbitals.
6. In the case of free metal ion, all the five d-orbitals have the same energy. Such orbitals having the same energies are called degenerate orbitals.

**Crystal field splitting of d orbitals:**

In a free transition metal or ion, there are five d-orbitals which are  $d_{xy}$ ,  $d_{yz}$ ,  $d_{zx}$ ,  $d_{z^2}$  and  $d_{x^2-y^2}$ . These are divided into 2 sets based on their orientation in space:

- **$t_{2g}$**  : The 3d-orbitals ( $d_{xy}$ ,  $d_{yz}$  and  $d_{zx}$ ) which orient in the regions between the coordinate axes . These are non-axial orbitals .  $t_{2g}$  are three fold degenerate.
- **$e_g$**  : the other two orbitals ( $d_{z^2}$  and  $d_{x^2-y^2}$ ) which orient along the axis . These are two fold degenerate and also known as axial orbitals.



In an isolated gaseous atom, all the five d orbital are degenerate. (They have same energy). On the approach of the ligands in a complex, the electrons in the d orbital of the central ion

are repelled by the lone pairs of the ligands. This repulsion will raise the energy level of the d orbitals. All the ligands approaching the energy of each orbital will increase by the same amount.

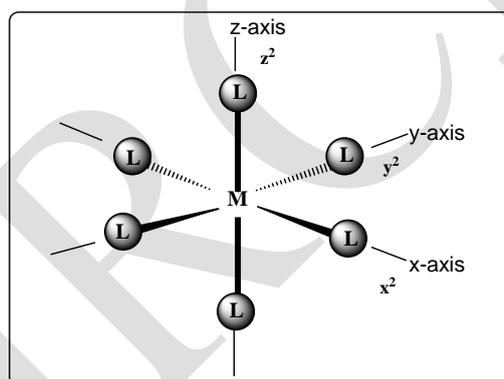
In other words, they will remain degenerate. Since d-orbitals differ in their orientation, those orbitals lying in the direction of the ligands is raised to a larger extent than the others. So, five degenerate d-orbitals will split into two sets, having different amount of energies. This splitting of five degenerate d-orbitals of the metal ion under the influence of approaching ligands, into two sets of orbitals having different energies is called as Crystal- field splitting.

This splitting is affected by the following factors:

1. Nature of the ligands. The stronger the ligand, the greater is the splitting.
2. Oxidation state of the central metal ion. A higher oxidation state leads to larger splitting.
3. Size of d orbitals (i.e., transition series).
4. Geometry of the complex.
5. Nature of the metal ion
6. Arrangement of the ligands around the metal ion.

### Crystal Field Splitting in Octahedral Complexes

The octahedral arrangement of six ligands surrounding the central metal ion is as shown in the figure.



In an octahedral complex, the metal ion is at the centre and the ligands are at the six corners.

In the figure, the directions x, y and z point to the three adjacent corners of the octahedron. The lobes of the  $e_g$  orbitals ( $dx^2-y^2$  and  $dz^2$ ) point along the x, y and z axis while the lobes of the  $t_{2g}$  orbitals ( $dxy$ ,  $dxz$  and  $dyz$ ) point in between the axes. As a result, the approach of six ligands along the x, y z, -x,-y and -z directions will increase the energy of  $dx^2-y^2$  and  $dz^2$  orbitals (which point towards the ligands) much more than that it increases the energy of  $dxy$ ,  $dxz$  and  $dyz$  orbitals ( which point in between the metal-ligand bond axis).

The approach of the ligands is considered as a two step process. In the first step, it is assumed that the ligands approach the metal ion spherically, i.e. at an equal distance from each of the d-orbitals. At this stage all the d- orbitals are raised in energy by the same amount (The five d-orbitals remain degenerate).

In the second step the spherical field changes to octahedral field leading to splitting of orbitals.

The energy difference between  $t_{2g}$  and  $e_g$  orbitals is known as crystal field splitting and it is denoted by the symbol  $\Delta_o$  or  $10Dq$

Thus, under the influence of an octahedral field, the d orbitals split into triply degenerate orbitals with less energy and another as doubly degenerate orbitals with higher energy. The main energy level between these two sets of orbitals is taken as zero, which is called **bari centre**. The splitting between these two orbitals is called crystal field splitting. The magnitude of stabilization will be  $0.4 \Delta_o$  and the magnitude of destabilization will be  $0.6 \Delta_o$ .

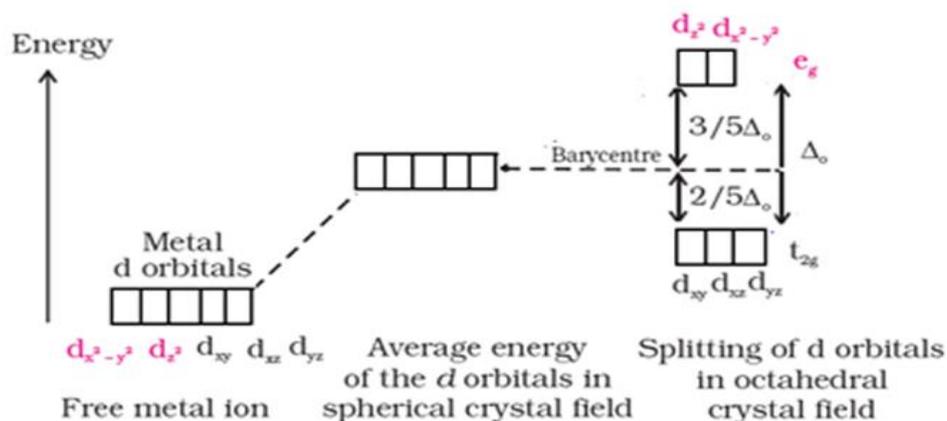
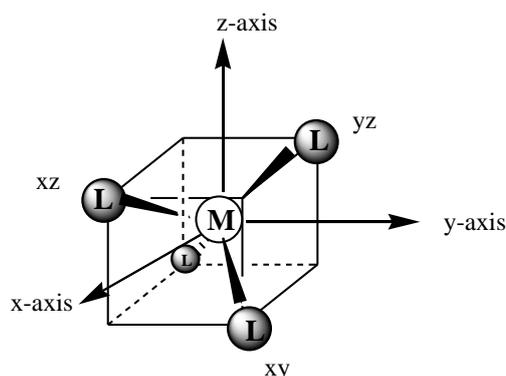


Fig: Splitting of d-orbitals in an octahedral complex

### Crystal Field Splitting in Tetrahedral Complexes:

The tetrahedral arrangement of four ligands surrounding the metal ions is as shown in the figure.

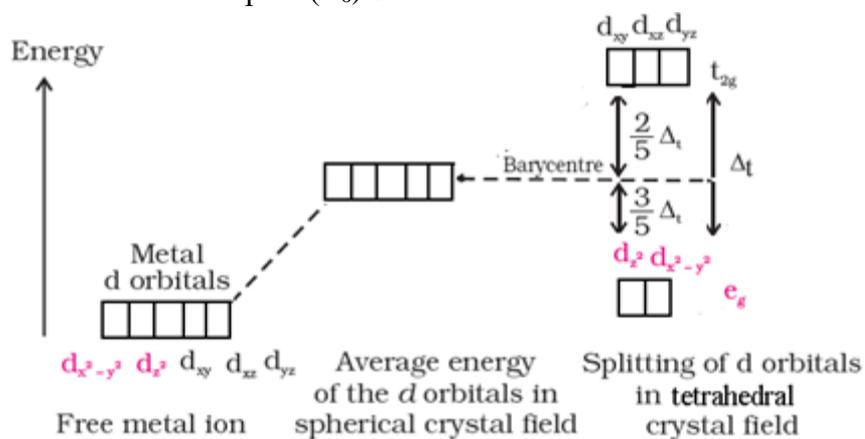


A regular tetrahedron is a cube. One atom is at the centre of the cube and four of the eight corners of the cube are occupied by ligands. The directions x, y and z point to the face centres. The  $dx^2-y^2$  and  $dz^2$  orbitals point along the x, y and z directions and  $d_{xy}$ ,  $d_{zx}$  and  $d_{yz}$  orbitals point in between x, y and z directions.

The direction of approach of ligands does not coincide exactly with either the e or  $t_2$  orbitals. The  $t_2$  orbitals are pointing close to the direction in which the e orbitals are lying in between the ligands. As a result, the energy of  $t_2$  orbitals increases compared to the energy of e orbitals. Thus, d orbitals again split into two sets- triply degenerate  $t_2$  of higher energy and

doubly degenerate e orbitals of lower energy. That is,  $t_2$  orbitals are raised by  $0.4 \Delta_t$  in energy and the e orbitals are stabilized by  $0.6 \Delta_t$  in energy.

The energy difference between the two sets of orbitals ( $\Delta_t$ ) will be about half the magnitude of that in an octahedral complex ( $\Delta_o$ ).



# UNIT - III : WATER AND ITS TREATMENT

## Introduction:

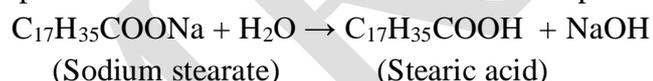
Like air water is one of the few basic materials which is of prime importance for the preservation of life on this earth. All are aware of the uses of water for drinking, cooking, bathing and farming etc., but few know the importance of water as an engineering material. For the existence of all living beings (humans, animals and plants) water is very crucial. Without water we cannot survive and almost all human activities—domestic, agricultural and industrial demand use of water. Although water is nature's most wonderful and abundant compound but only less than 1% of the world's water resources are available for the ready use. As engineering material water is used for producing steam in boilers to generate hydroelectric power, furnishing steam for engines, for refrigeration and air conditioning, for construction of concrete structures for manufacturing purposes and as a solvent in the chemical process.

## Hardness:

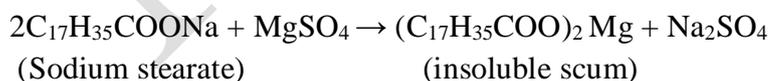
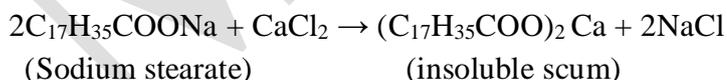
Hardness of water is defined as the property which prevents the lathering of soap. This is due to presence of certain salts of  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$  and other heavy metals dissolved in it. Soaps are sodium or potassium salts of higher fatty acids like oleic acid or palmitic acid or stearic acids ( $\text{C}_{17}\text{H}_{35}\text{COONa}$ ). Hard water does not give lather with soap while soft water gives lather readily with soap.

## Soap with hard water reactions:

When soap comes in contact with soft water lather is produced due to sodium stearate.



When soap comes in contact with hard water, sodium stearate will react with dissolved calcium and magnesium salts and produce calcium stearate or magnesium stearate which is white precipitate. This insoluble white precipitate prevents lathering of soap.



Different types of water have different degrees of hardness. The different types of water are commercially classified on the basis of degree of hardness as follows:

Hardness	Name of water
0-70mg/liter	Soft water
70-150mg/liter	Moderate hard water
150-300mg/liter	Hard water
300mg/liter and above	Very hard water

### Degree of hardness:

The total hardness of water is caused by eight different dissolved salts of calcium and magnesium, [Ca(HCO<sub>3</sub>)<sub>2</sub>, Mg(HCO<sub>3</sub>)<sub>2</sub>, CaCl<sub>2</sub>, MgCl<sub>2</sub>, CaSO<sub>4</sub>, MgSO<sub>4</sub>, Ca(NO<sub>3</sub>)<sub>2</sub> and Mg(NO<sub>3</sub>)<sub>2</sub>]. Hence the hardness of water is expressed in terms of calcium carbonate equivalents. The weight of different hardness salts causing hardness are converted to weight equivalent to that of calcium carbonate. CaCO<sub>3</sub> is selected for expression of hardness because the molecular weight of CaCO<sub>3</sub> is 100, which is easy for calculation and it is the most insoluble salt and all the dissolved salts of calcium are precipitated as CaCO<sub>3</sub>.

Name of the salt	Molecular weight
Ca(HCO <sub>3</sub> ) <sub>2</sub>	162
Mg(HCO <sub>3</sub> ) <sub>2</sub>	146
CaCl <sub>2</sub>	111
MgCl <sub>2</sub>	95
CaSO <sub>4</sub>	136
MgSO <sub>4</sub>	120
CaCO <sub>3</sub>	100

The method for calculating degree of hardness will be clear from the following formula:  
Hardness of water in terms of calcium carbonate equivalents

$$= \frac{\text{Amount of hardness causing salts}}{\text{Molecular weight of hardness causing salts}} \times 100$$

### Causes of hardness:

The natural water is usually contaminated by different types of impurities. They are mainly 3 types

1. Physical impurities
2. Chemical impurities
3. Biological impurities
4. Collodial impurities

## Expression of hardness – Units

### Units of Hardness:

**1Parts Per Million:** Parts of  $\text{CaCO}_3$  equivalent hardness per  $10^6$  parts of water.

1 ppm = 1 part of  $\text{CaCO}_3$  equivalent hardness present in  $10^6$  parts of water.

**Milligram per liter:** Number of milligrams of calcium carbonate equivalent hardness present in 1 liter of water.

1mg / L = 1 mg of  $\text{CaCO}_3$  equivalent hardness present in 1 liter of water.

1 L = 1 Kg = 1000 g = 1000 x 1000 mg =  $10^6$  mg.

1mg /L= 1 mg of  $\text{CaCO}_3$ eq per  $10^6$  mg of  $\text{H}_2\text{O}$  = 1ppm

**Degree Clark: ( $^\circ\text{Cl}$ ):** It is the number of grains (1/7000 lb) of  $\text{CaCO}_3$  equivalent hardness per 70,000 parts of water.

1Clark = 1 grain of  $\text{CaCO}_3$  equivalent hardness per gallon of water.

= 1 part of  $\text{CaCO}_3$  of hardness per 70,000 parts of water.

**Degree French ( $^\circ\text{Fr}$ ):** It is the parts of  $\text{CaCO}_3$  equivalent hardness per  $10^5$  parts of water.

1 $^\circ\text{French}$  = 1 part of  $\text{CaCO}_3$  per  $10^5$  parts of hard water

**Milliequivalents per litre :** - No of milliequivalents of hardness present per liter of water.

1m eq/L= 1 m eq of  $\text{CaCO}_3$  per / liter of water = 50 mg /L of  $\text{CaCO}_3$ eq = 50ppm

### Relation between various units of hardness:

$$1 \text{ ppm} = 1 \text{ mg /L} = 0.1^\circ\text{Fr} = 0.07^\circ\text{Cl} = 0.02 \text{ meq /L}$$

Total hardness of the sample water=121ppm=121mg/L

121x0.07=8.47 $^\circ\text{cl}$  and 121x0.1=12.1 $^\circ\text{Fr}$

Permanent hardness=101mg/l,101ppm,7.07 $^\circ\text{cl}$ ,10.1 $^\circ\text{Fr}$

Temporary hardness=20mg/l,20ppm,1.4 $^\circ\text{cl}$  and 2 $^\circ\text{Fr}$

### Types of Hardness:

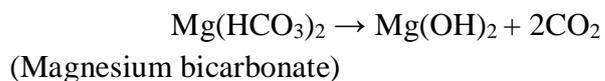
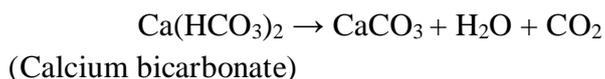
Hardness of water is mainly two types

1. Temporary Hardness
2. Permanent Hardness

#### 1. Temporary Hardness:

It is caused mainly due to the presence of dissolved bicarbonates of calcium, magnesium and other heavy metals. The salts mainly responsible for temporary hardness of water are Calcium bicarbonate  $\text{Ca}(\text{HCO}_3)_2$  and Magnesium bicarbonate  $\text{Mg}(\text{HCO}_3)_2$ .

When bicarbonates are decomposed, yielding insoluble carbonates or hydroxides, which gets deposited as a crust at the bottom of vessel. Temporary hardness can be largely removed by mere boiling of water. On boiling bicarbonates converts into corresponding carbonates which are insoluble. They can be removed by filtration.



## 2. Permanent Hardness:

It is due to the presence of dissolved chlorides and sulphates of calcium, magnesium, iron and other metals. The salts responsible for permanent hardness are  $\text{CaCl}_2$ ,  $\text{MgCl}_2$ ,  $\text{CaSO}_4$ ,  $\text{MgSO}_4$ ,  $\text{FeSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ . Permanent hardness cannot be removed by boiling but it can be removed by the use of chemical agents.

Total hardness of water = Temporary hardness + Permanent hardness

## Estimation of temporary & permanent hardness of water:

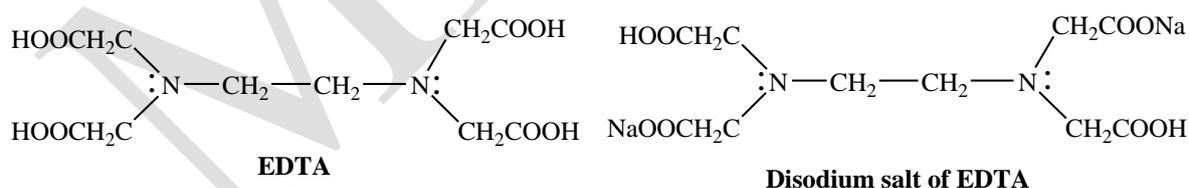
### Estimation of Hardness of Water by EDTA method (Complexometric titration):

#### Estimation of Hardness of Water by EDTA method (Complexometric titration)

Hardness in water is due to the presence of dissolved salts of calcium and magnesium. It is unfit for drinking, bathing, washing and it also forms scales in boilers. Hence it is necessary to estimate the amount of hardness producing substances present in the water sample.

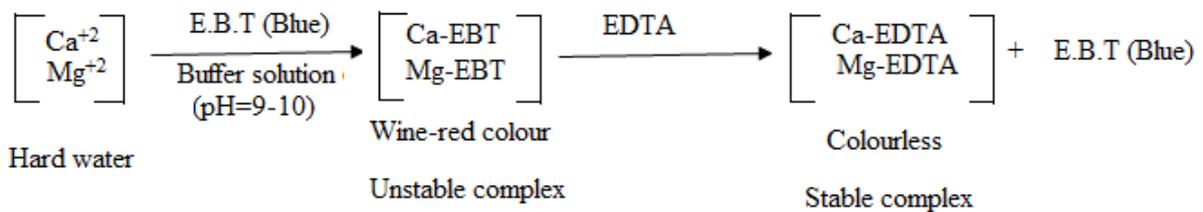
The estimation of hardness is based on complexometric titration. Hardness of water is determined by titrating with a standard solution of ethylene diamine tetra acetic acid (EDTA) which is a complexing agent. Ethylene Diamine Tetra Acetic acid (EDTA) is a reagent that forms EDTA-metal complexes with many metal ions. In alkaline conditions ( $\text{pH} > 9$ ) it forms stable complexes with the alkaline earth metal ions  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .

EDTA is Ethylene Diamine Tetra Acetic acid. The structure of EDTA is as shown below. Since, EDTA is insoluble in water, its disodium salt is used as a complexing agent.

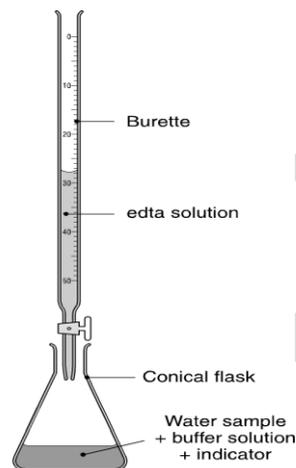


### Basic Principle:

Total hardness is due to the presence of bicarbonates, chlorides and sulphates of calcium and magnesium ions. The total hardness of water is estimated by titrating the water sample against EDTA using Eriochrome Black-T (EBT) indicator. Initially EBT forms a weak EBT- $\text{Ca}^{2+}/\text{Mg}^{2+}$  wine red coloured complex with  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ions present in the hard water. On addition of EDTA solution,  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ions preferably forms a stable EDTA- $\text{Ca}^{2+}/\text{Mg}^{2+}$  complex with EDTA leaving the free EBT indicator in solution which is steel blue in colour in the presence of ammonia buffer. Thus the end point is the change of color from wine red to blue.



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.



**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  $\text{CaCO}_3$

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

So  $v_1$  mg of equivalent  $\text{CaCO}_3$  hardness is presented in  $v$  ml of hard water

The total hardness of sample =  $\frac{v_1 \times 1000}{v}$  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 =  $\frac{v_2 \times 1000}{v}$  ppm

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

Temporary hardness = (Total hardness-permanent hardness)

## Softening of water by Ion exchange resin process or deionization process or demineralization process:

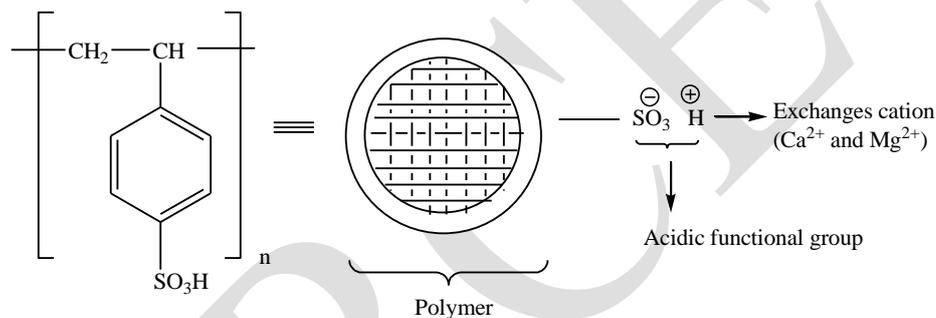
- The process of complete removal of all ions present in water is known as demineralization process.
- The process is done by using ion exchange resin process.
- These resins are highly insoluble cross linked organic polymers with porous structure.
- They contain functional groups attached to the polymeric chains are responsible for ion exchange property.
- The functional groups used is either acidic or basic in nature.
- Depending on functional groups Ion exchange resins are classified into two types.

### 1. Cation Exchange Resins

#### 2. Anion Exchange Resins

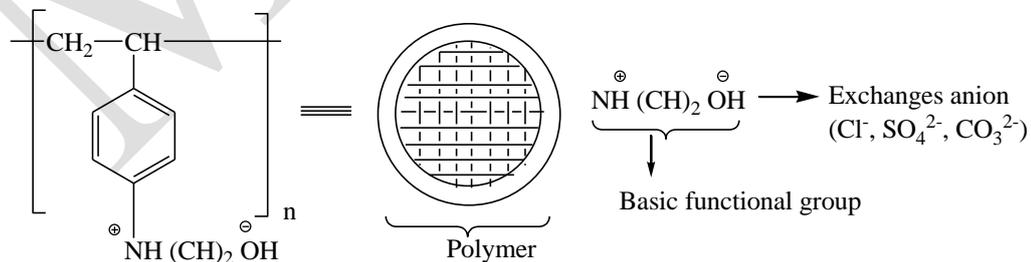
### 1. Cation Exchange Resins:

- These are mainly poly-styrene polymers which contain acidic functional groups.
- The acidic functional group is capable of exchanging its  $H^+$  ions with cations present in water.

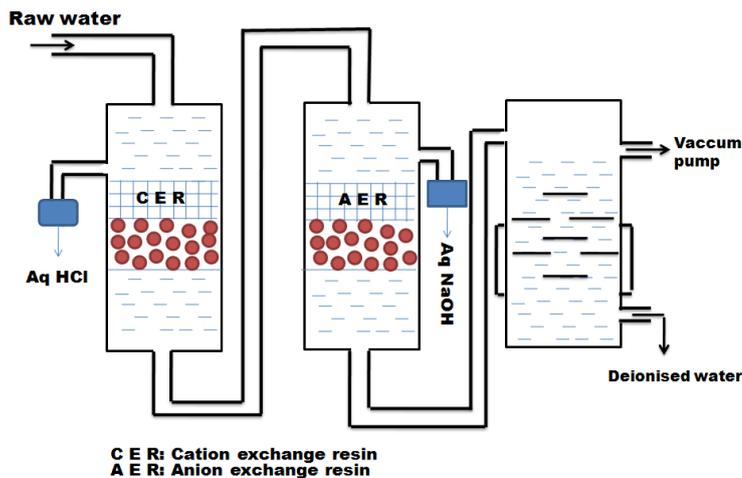


### Anion Exchange Resins:

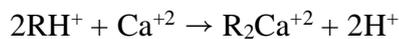
1. These are mainly poly-styrene polymers which contain basic functional groups.
2. The basic functional group is capable of exchanging its  $OH^-$  ions with anions present in water.



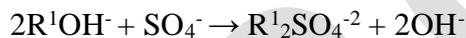
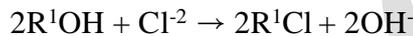
Process:



### Cation Exchange Resins

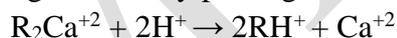


### Anion Exchange Resins

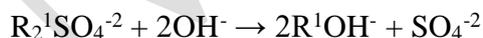


### Regeneration:

When cation exchanger losses capacity of producing  $H^+$  ions and anion exchanger losses capacity of producing  $OH^-$  ions, they are said to be exhausted. The exhausted cation exchanger is regenerated by passing it through dilute sulphuric acid.



The exhausted anion exchanger is regenerated by passing a dilute solution of NaOH.



### Merits of Ion-exchange process:

1. This process can be used to soften highly acidic or alkaline water.
2. It produces water of very low hardness (2ppm). So it is very good for treating water for use in high-pressure boilers.
3. The operational expenses are less because the resins can be regenerated.

### Demerits of Ion-exchange process:

1. The equipment is costly and more expensive chemicals are needed.
2. If water contains turbidity, the output of the process is reduced. The turbidity must be below 10 ppm; else it has to be removed by coagulation and filtration.

**POTABLE WATER:**

The water which is used for drinking is called potable water.

**Specification of potable water/drinking water:**

1. It should be sparkling clear and odourless.
2. It should be pleasant in taste.
3. It should be perfectly cool.
4. Its turbidity should not exceed 10ppm.
5. It should be free from objectionable dissolved gases like hydrogen sulphide.
6. It should be free from minerals such as lead, arsenic, chromium and manganese salts.
7. Its alkalinity should not be high.
8. Its pH should be about 8.0.
9. It should be reasonably soft.
10. Its total dissolved solids should be less than 500 ppm.
11. It should be free from disease-producing micro-organisms.
12. Chloride, fluoride and sulphide contents should be less than 250ppm, 1.5ppm and 250ppm respectively.

**Steps involved in treatment of potable water:****Disinfection of surface water / Removal of micro-organisms in water:****Disinfection:**

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

Disinfectants:

The chemicals or substances which are added to water for killing the bacteria are called disinfectants.

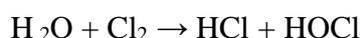
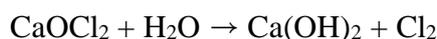
The disinfection of water can be carried out by following methods:

**a). Boiling:**

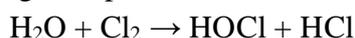
When water is boiled for 10-15 minutes, all the disease-producing bacteria are killed and water becomes safe for use.

**b) By using Bleaching power:**

Bleaching powder contains 80% chlorine. 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 disinfecting action, kills germs and purifies the drinking water effectively.

**c) By using Chlorine:**

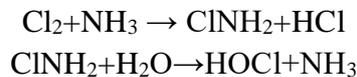
Chlorination is the process of purifying the drinking water by producing a powerful germicide like hypochlorous acid. When this chlorine is mixed with water it produces hypochlorous acid which kills the germs present in water.



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.

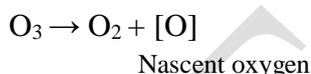
**d) By using chloramines:**

Chlorine is mixed with ammonia in 2:1 ratio by volume to produce a stable compound chloramines which generates hypochlorous acid which is a powerful disinfectant.



**e) Ozonisation:**

Ozone is a 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.



The nascent oxygen is very powerful oxidizing agent and kills all the bacteria's as well as oxidizes the organic matter present in water. For carrying out the disinfection by ozone, ozone is released/injected into the water and the two are allowed to come in contact in sterilizing tank. The disinfected water is removed from the top. The contact period is about minutes and the usual dose strength is 2-3 ppm.

**Advantages:**

Disinfection by ozone is costlier than chlorine, but it simultaneously removes colour, odour and taste without giving any residue. Its excess is not harmful, since it is unstable and decomposes into oxygen.

**Disadvantages:**

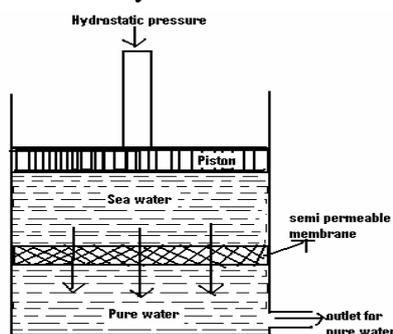
This method is quite expensive and hence, not employed for disinfection of municipal water supply.

**Desalination of Brackish water:**

The process of removing common salt from the water, is known as desalination. Water containing high concentration of dissolved solids with peculiar salty or brackish taste is called brackish water. Sea water is an example for brackish water as it contains about 3.5% of dissolved salts.

Commonly used methods for the desalination of brackish water is:

1. Reverse Osmosis
2. Electrodialysis



**Reverse Osmosis:**

When two solutions of unequal concentrations are separated by a semi permeable membrane, flow of solvent takes place from dilute to concentrated sides, due to osmosis. If, however, a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the solvent flow is reversed, i.e. solvent is forced to move from concentrated side to dilute side across the membrane. This is the principle of reverse osmosis. This membrane filtration is also called 'super-filtration' or 'hyper – filtration. The membrane consists of very thin films of cellulose acetate, affixed to either side of a perforated tube. However, more recently superior membranes made of polymethacrylate and polyamide polymers have come into use.

**Method of purification:** The reverse osmosis cell consists of a chamber fitted with a semi permeable membrane, above which sea water / impure water is taken and a pressure of 15 to 40 kg/cm<sup>2</sup> is applied on the sea water / impure water. The pure water is forced through the semi-permeable membrane which is made of very thin films of cellulose acetate.

**Advantages:**

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

# UNIT - IV : ORGANIC REACTIONS

## Organic Reactions

**Introductions:** Organic reactions are chemical reactions involving organic compounds. The basic organic chemistry reaction types are addition reactions, elimination reactions, substitution reactions, pericyclic reactions, rearrangement reactions, photochemical reactions and redox reactions. In organic synthesis, organic reactions are used in the construction of new organic molecules. The production of many man-made chemicals such as drugs, plastics, food additives, fabrics depend on organic reactions.

### Few Organic Terms:

**Substrate:** one which is being attacked is called substrate.

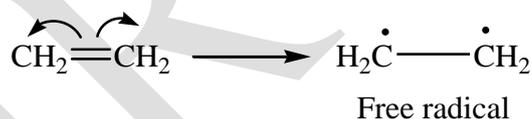
**Reagent:** The substance which attacks the substrate is called reagent.



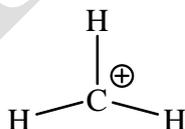
The step by step description of a chemical reaction is called mechanism



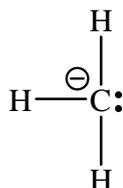
**Free radicals:** The atom or group of atoms which contain unpaired electrons is called free radical.



**Carbonium ions (carbocations):** The organic ions in which carbon carries positive charge is called carbocation.



**Carbanions:** The organic ions in which carbon carries negative charge is called carbanion.



**Transition state:** A imaginary state which cannot be isolated is called transition state. On the other hand an intermediate is a stable species and can be isolated.

## Organic reactions Categorizes with their Functional groups

Organic reactions can be categorized based on the type of functional group involved in the reaction as a reactant and the functional group that is formed as a result of this reaction. For example, in the Fries rearrangement the reactant is an ester and the reaction product an alcohol. Examples:

Alcohol (R-OH), Aldehydes (R-CHO), Acid amides (R-CONH<sub>2</sub>-R), Alkanes (R-CH<sub>3</sub>), Alkenes (R-C=C-R), Alkynes (R-C≡C-R), Amides (R-NH<sub>2</sub>), Carboxylic acids (R-COOH), Esters R-COO-R), Ethers (R-O-R), Phenols (R-C<sub>6</sub>H<sub>4</sub>-OH), Ketones (R-CO-R), Nitriles (R-CN) etc...

### Types of Organic Reactions:

Organic reactions are of following types:

1. Addition
2. Elimination
3. Substitution
4. Oxidation
5. Reduction

- An **addition reaction** occurs when two or more reactants combine to form a single product. This product will contain *all* the atoms that were present in the reactants. Addition reactions occur with **unsaturated** compounds.
- An **elimination reaction** occurs when a reactant is broken up into two products. Elimination reactions occur with **saturated** compounds.
- A **substitution reaction** occurs when an exchange of elements in the reactants takes place. The initial reactants are transformed or replaced *to* give a final product.
- An **oxidation reaction** occurs when oxygen added and hydrogen removed from organic compound. (or) loosing of electrons.
- A **reduction reaction** occurs when hydrogen added and oxygen removed from the organic compounds. (or) gaining of electrons.

### Nucleophiles:

A reagent which can donate an electron pair in a reaction is called nucleophiles.

The name nucleophile means nucleus loving

Nucleophiles are electron rich.

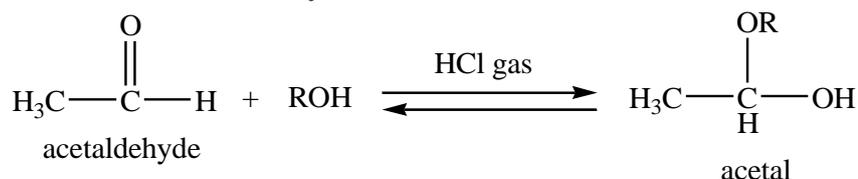
They may be negative ions including carbanions or neutral molecules with free electron pair.

A nucleophile can be represented by a general symbol Nu:<sup>-</sup>

Examples are: Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, CN<sup>-</sup>, OH<sup>-</sup>, RCH<sub>2</sub><sup>-</sup>, NH<sub>3</sub>, RNH<sub>2</sub>, H<sub>2</sub>O, ROH.

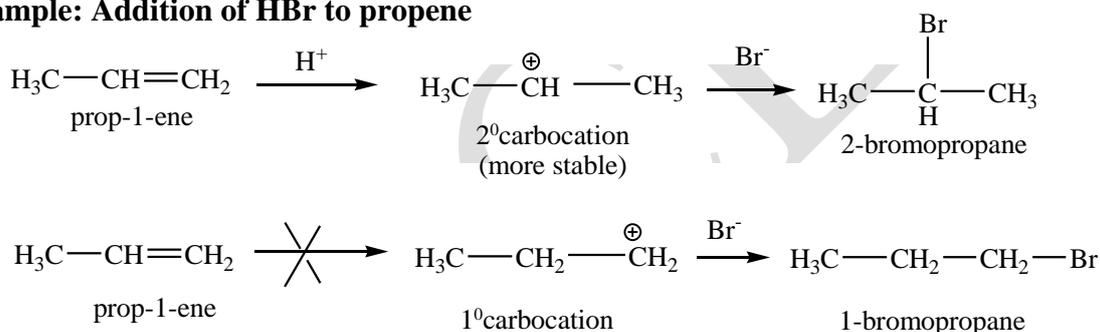




**(b) Addition of Alcohol on Aldehyde:****(c) Markownikoff's Addition:**

The addition of HX to a symmetrical olefins gives only one product, but the addition of HX to an unsymmetrical olefins gives two products, the stability of the two products are governed by **Markownikoff's rule**. On the basis of extensive studies on the addition of unsymmetrical reagents (like HCl, HBr, HI, H<sub>2</sub>SO<sub>4</sub>, HOCl ) to unsymmetrical alkenes, formulated an empirical rule known as Markownikoff's rule .

According to this rule, the negative end of the reagent goes to the carbon atom containing lesser number of hydrogen atoms.

**Example: Addition of HBr to propene**

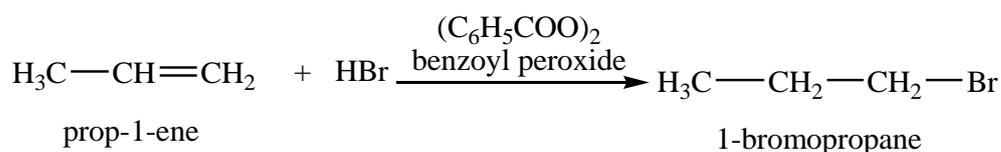
Markownikoff's rule can be explained on the basis of relative stabilities of the intermediate carbocations. The addition of H<sup>+</sup> to propene may give rise to the formation of either primary or secondary carbocation. As the secondary carbocation is more stable ,it will be exclusively formed,resulting in the formation of 2-bromo propane.

**Anti-Markownikoff's rule (Anti-Markownikoff addition) or Peroxide Effect:**

The addition of halogen acids to unsymmetrical alkenes give Markownikoff's product.

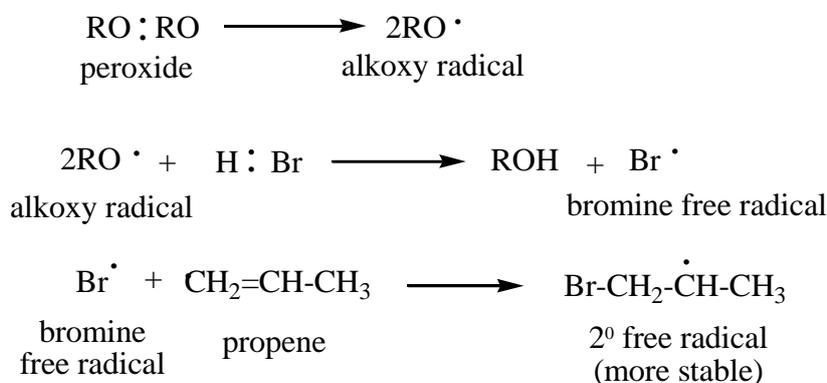
However, this is not always the case. The addition of HBr to unsymmetrical alkenes in the presence of a peroxide gives a product which is different from the Markownikoff's product. In the presence of a peroxide this effect is reversed . This is called as Anti- Markownikoff's rule or peroxide effect.

Thus, the addition of HBr to propene in the presence of peroxides gives 1- bromopropane rather than 2- bromo propane according to Anti-Markownikoff's rule.

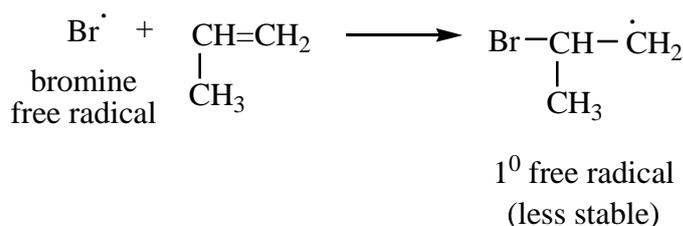


The formation of Anti-Markownikoff's addition product is explained by the free radical mechanism compared to the formation of carbocation intermediate for Markownikoff's addition product.

Peroxide dissociates into two free radicals called as alkoxy radicals. These in turn attack HBr to form bromine free radical.

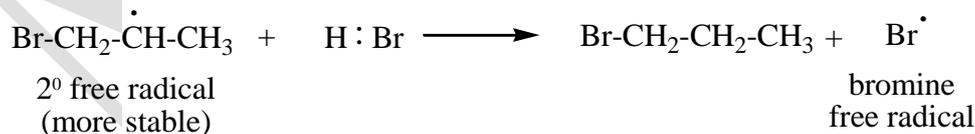


The bromine free radical attacks the alkene molecule to give two possible alkyl free radicals.



Since secondary free radical is more stable than the primary free radical, product is formed from secondary free radical.

The secondary free radical being more stable reacts with HBr forming anti- Markownikoff addition product and another bromine free radical is formed ,which turn propogates the chain.



## 2. Substitution Reactions:

The reactions in which one functional group is replaced by another functional group is known as substitution reaction.

Substitution reactions are of two types.

1. Nucleophilic substitution reaction
2. Electrophilic substitution reaction

**Nucleophilic substitution reaction:**

The reactions in which a substrate is initially attacked by a nucleophilic reagent which gives substitution product is known as nucleophilic substitution reaction

The nucleophilic substitution reactions are carried out into two ways.

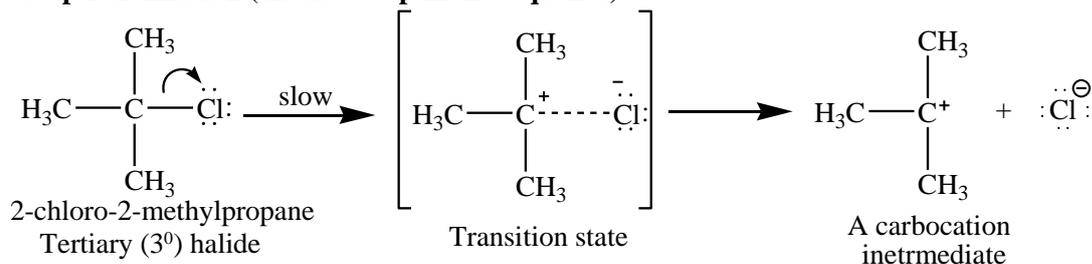
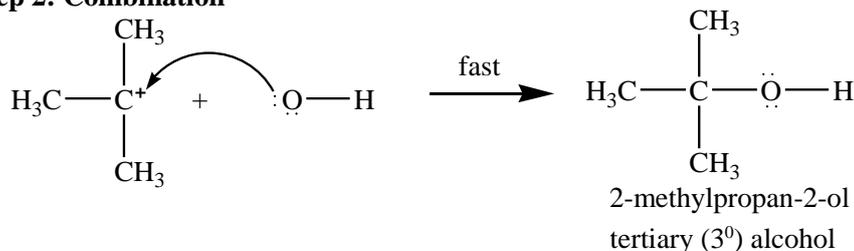
- Unimolecular Substitution reactions (or)  $S_N1$  reaction
- Bimolecular Substitution reactions (or)  $S_N2$  reaction

**Unimolecular Nucleophilic Substitution or  $S_N1$ :**

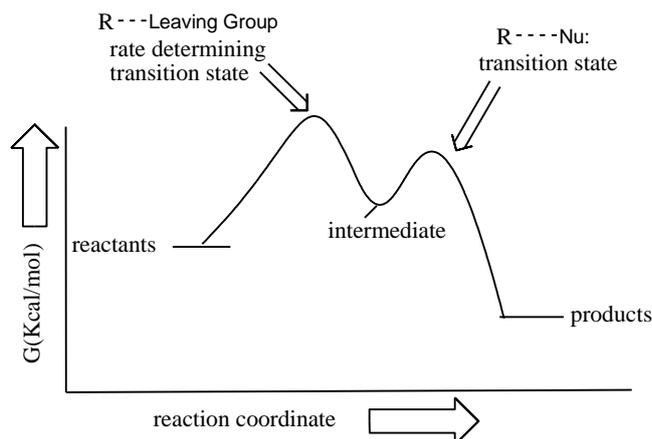
- In  $S_N1$ , S means substitution, N means nucleophilic and 1 means unimolecular reaction.
- $S_N1$  follows first order kinetics, so the rate of the reaction depends only on the concentration of the substrate.  
 $\therefore \text{Rate} \propto [\text{substrate}]$
- It is a two step process.
- Polar protic solvents (MeOH and  $H_2O$ ) favours  $S_N1$  reaction.
- Electronic factors play vital role in  $S_N1$  reaction, but steric factors are not important for  $S_N1$  reaction.
- The hydrolysis of tertiary butyl bromide is an example of  $S_N1$  reaction.

**Mechanism of  $S_N1$  reaction**

The mechanism of  $S_N1$  occurs in two steps. In the first step heterolytic cleavage of t-butyl bromide takes place and t-butyl carbocation is formed. The reaction is unimolecular because first step is slow step and it is also rate determining step. In the second step t-butyl carbocation combines with nucleophile to form t-butyl alcohol.

**Step 1: Ionization (the slow step in the sequence)****Step 2: Combination**

### Energy Diagram of S<sub>N</sub>1



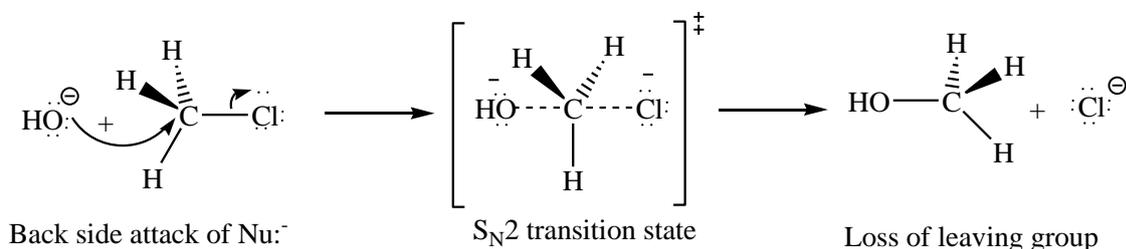
### Bimolecular Substitution reactions or S<sub>N</sub>2:

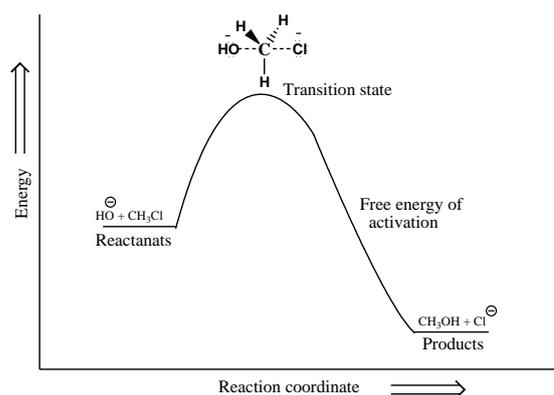
1. In S<sub>N</sub>2, S means substitution, N means nucleophilic and 2 means bi-molecular reaction.
2. S<sub>N</sub>2 follows second order kinetics, so the rate of the reaction depends on the concentration of the substrate and nucleophile.  
∴ Rate ∝ [substrate][nucleophile]
3. It is a one step process.
4. Polar aprotic solvents (Acetone and DMF) favours S<sub>N</sub>2 reaction.
5. Steric factors play vital role in S<sub>N</sub>2 reaction.
6. The hydrolysis of methyl bromide is an example of S<sub>N</sub>2 reaction.

### Mechanism of S<sub>N</sub>1 reaction:

The mechanism of S<sub>N</sub>2 occur in one step. Initially methyl bromide is attacked by OH<sup>-</sup> nucleophile from the opposite of the bromine atom, transition state results in which both OH<sup>-</sup> and Cl<sup>-</sup> are partially bonded to the carbon atom. It is highly unstable and readily bromine leaves the molecule as bromide ion and OH<sup>-</sup> form a covalent bond with the carbon giving alcohol as a reaction product. In this reaction the configuration of the carbon atom is inverted and hence it is known as Walden inversion.

### S<sub>N</sub>2 Mechanism, Backside Attack with Inversion



Energy Diagram of S<sub>N</sub>2Differentiate between S<sub>N</sub>1 and S<sub>N</sub>2

S <sub>N</sub> 1	S <sub>N</sub> 2
<ol style="list-style-type: none"> <li>Two step reaction.</li> <li>Rate of reaction = <math>K [R-L]</math></li> <li>It is a first order reaction.</li> <li>Carbocation intermediate is formed. rearrangement of carbocation is possible.</li> <li>Rate is dependent on concentration of substrate</li> <li>Rate of reaction also depends on stability of carbocation.</li> <li>Polar Protic Solvent favors S<sub>N</sub>1 reaction.</li> <li>Steric crowding not play vital role in S<sub>N</sub>1 reaction.</li> </ol>	<ol style="list-style-type: none"> <li>Single step reaction.</li> <li>Rate of reaction = <math>K [R-L] [Nu(:)]</math></li> <li>It is a second order reaction.</li> <li>No carbocation intermediate formation.</li> <li>Rate is dependent on concentration of substrate and the strength of Nucleophile.</li> <li>Transition state is formed which is sp<sup>2</sup> hybridized, planar structure.</li> <li>Polar Aprotic Solvent like DMSO, DMF, DMA favours S<sub>N</sub>2 reactions.</li> <li>Steric crowding play an important role in S<sub>N</sub>2 reaction.</li> </ol>

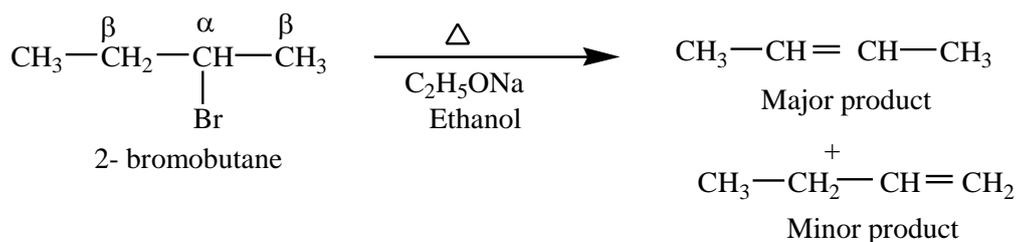
## 3. Elimination Reactions:

The reactions in which two atoms (or) two groups eliminated from either same carbon atom of the substrate or adjacent carbon atom of the substrate is known as elimination reaction.

Dehydrohalogenation and dehalogenations are the best examples of elimination reaction.

**DEHYDROGENATION OF ALKYL HALIDES – SAYTZEFF RULE :**

Dehydrohalogenation of unsymmetrical alkyl halides gives two products. The stability of the two products are governed by Saytzeff rule. According to this rule, β-hydrogen atom is eliminated preferentially from carbon atom which has lesser number of hydrogen atoms and gives highly substituted alkene as the major product.



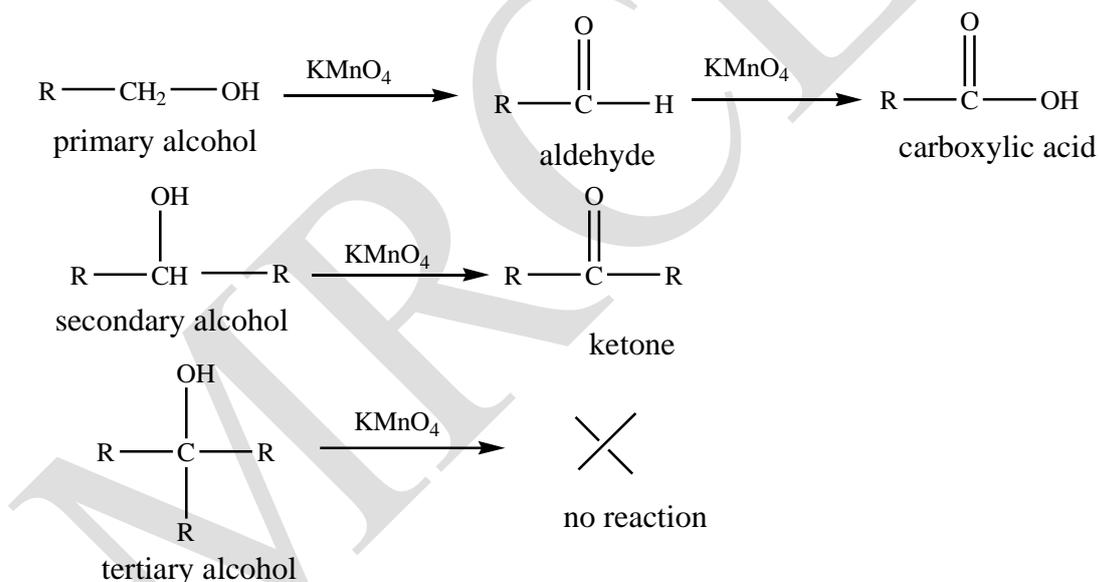
#### 4. Oxidation Reaction:

An oxidation reaction is defined as addition of oxygen to an organic compound removal of hydrogen or removal of an electron. Most commonly used oxidizing agents are  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{H}_2\text{CrO}_4$

Oxidation reaction by using  $\text{KMnO}_4$  &  $\text{K}_2\text{Cr}_2\text{O}_7$  (as oxidizing agent).

##### (i) Oxidation of Alcohol by Using $\text{KMnO}_4$ :

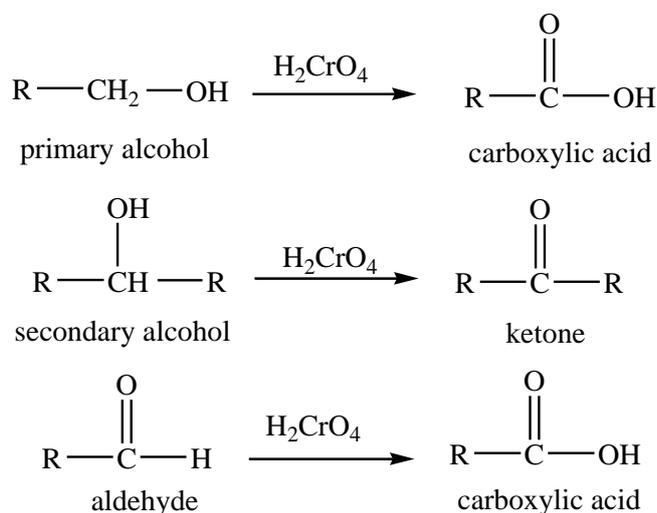
Potassium permanganate ( $\text{KMnO}_4$ ) is a very strong oxidizing agent to react with many functional groups, such as primary alcohols, secondary alcohols, 1,2-diols, aldehydes, alkenes, oximes, sulfides and thiols. Under controlled conditions,  $\text{KMnO}_4$  oxidizes primary alcohols to carboxylic acids very efficiently.



##### (ii) Oxidation of Alcohol by Using Chromic Acid:

Chromic acid,  $\text{H}_2\text{CrO}_4$ , is a strong acid and is a reagent for oxidizing alcohols to ketones and carboxylic acids. 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 ketones.



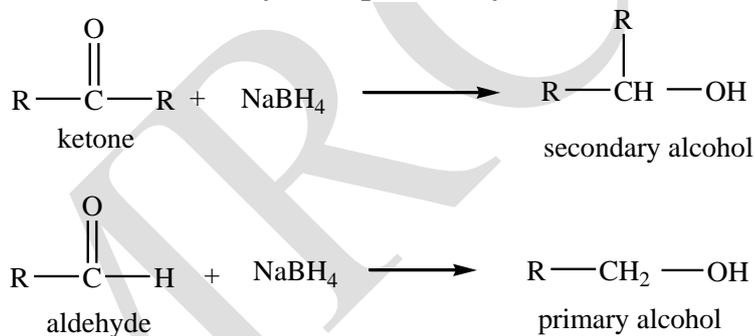
### 5. Reduction Reaction:

An increase in hydrogen content or a decrease in oxygen content of an organic compound is usually described as its reduction.

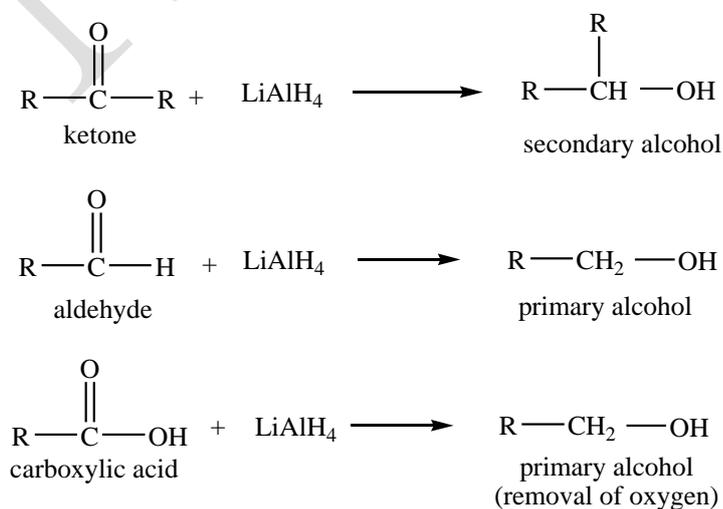
Or

Removal of oxygen and addition of hydrogen from chemical compounds is called reduction. There are so many reducing agents but most commonly used reducing agents are  $\text{NaBH}_4$  and  $\text{LiAlH}_4$ .

#### (i) Reduction of Carbonyl Compounds By $\text{NaBH}_4$



#### (ii) Reduction of Carbonyl Compounds By $\text{LiAlH}_4$



# UNIT - V : ENERGY SOURCES

## Introduction:

In recent years the dependency on energy by mankind has tremendously increased because of increase in standard of living and rapid technological advances. The energy needed today is derived from fossil fuels such as petroleum, coal and natural gas. Owing to the growing demands of these fuels, a proper knowledge of various fuels, their utilization and conservation is necessary.

## Fuel:

A fuel can be defined as a combustible substance containing carbon as the major constituent which is capable of releasing a large amount of heat that can be used for domestic and industrial needs. The main sources of fuel are coal and petroleum oils. For example, coal is used in locomotives and as reducing agent in blast furnaces. Petrol is used in internal combustion engines and for doing mechanical work.

Combustion is the process of chemical reaction between fuel and oxygen. During combustion heat and products of combustion are released. The combustion process is an exothermic chemical reaction.



Heating value of a fuel is the amount of energy or heat released per unit mass during combustion of that fuel. The main elements of combustion are carbon, hydrogen, sulphur, oxygen and nitrogen.

## CLASSIFICATION OF FUELS:

Fuels can be classified into 2 types

- a) On the basis of their occurrence
- b) On the basis of physical state of aggregation

### On the basis of occurrence:

- 1) **Natural or primary fuels**, which are found in nature such as e.g., wood, peat, coal, petroleum, natural gas etc.
- 2). **Artificial or secondary fuels** are those which are prepared from the primary fuels. For example, charcoal, coke, kerosene, diesel, petrol, coal gas, oil gas, producer gas, blast furnace gas, etc.

**On the basis of physical state of aggregation:**

a) Solid fuels; b) Liquid fuels, and c) Gaseous fuel

Type of fuel	Natural or primary	Artificial or secondary
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.

**Characteristics of a good fuel:**

While selecting an ideal fuel for domestic or industrial purpose we should keep in mind that the fuel selected must possess the following characteristic properties.

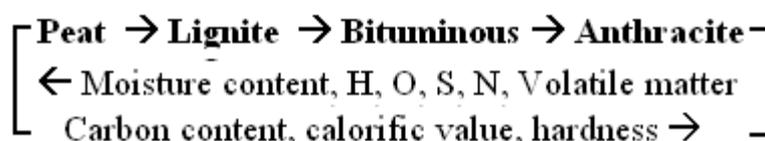
1. It should possess high calorific value.
2. It should have proper ignition temperature. The ignition temperature of the fuel should neither be too low nor too high.
3. It should not produce poisonous products during combustion. In other words, it should not cause pollution on combustion.
4. It should have moderate rate of combustion.
5. Combustion should be easily controllable i.e., combustion of fuel should be easy to start or stop as and when required.
6. It should not leave behind much ash on combustion.
7. It should be easily available in plenty.
8. It should have low moisture and volatile content.
9. It should be cheap.
10. It should be easy to handle and transport.

**COAL:**

It is highly carbonaceous matter and is regarded as a fossil fuel produced from large accumulations of vegetable debris and alternation of vegetable matter like plants etc. under certain favorable conditions by the action of heat and pressure over millions of years. Coal is mainly composed of carbon, oxygen, hydrogen and nitrogen.

Coal has been classified in several ways. The most common method of classification is on the basis of rank. From the origin of coal it is clear the wood, after a long interval of time and under certain conditions was converted into coal. The successive stages in the transformation of vegetable matter into coal are wood, peat, lignite, bituminous coal and anthracite coal.

Coal is classified based on the carbon content. The following is sequence of conversion.



## Analysis of Coal

Two types of analysis: Proximate and Ultimate

### 1. Proximate Analysis of Coal

Proximate analysis is the study or analysis of coal sample in which

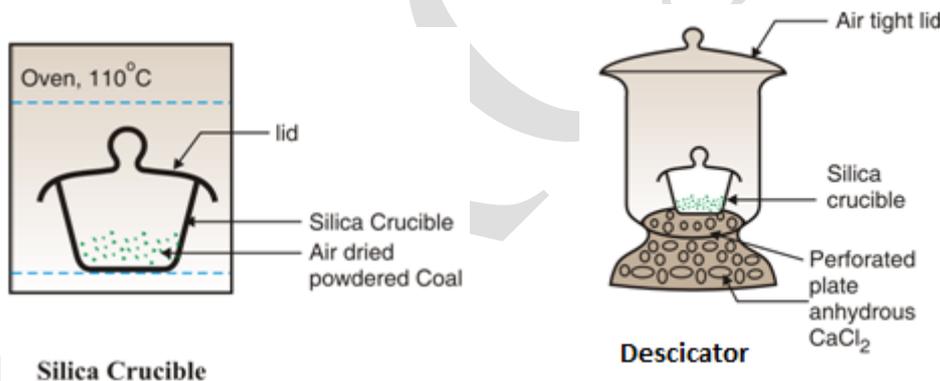
(i) moisture %                      (ii) volatile matter %                      (iii) ash %                      (iv) fixed carbon %, are found out.

#### (i) Moisture %

(a) Principle : All moisture in coal escapes on heating coal at 110°C for 1 hour.

(b) Method : A known weight of powdered and air dried coal sample is taken in a crucible and it is placed in an oven for 1 hour at 110°C. Then the coal is cooled in a desiccator and weighed out. If the initial weight of the coal is  $m$  gms and final weight is  $m_1$  gms. The loss in weight ( $m - m_1$ ) corresponds to moisture in coal.

$$\text{Moisture \%} = \frac{\text{Loss in weight}}{\text{Weight of coal sample}} \times 100 = \frac{m - m_1}{m} \times 100$$



#### (ii) Volatile Matter (V.M.) %

(a) Principle : At 925°C, coal molecules undergo thermal degradation to produce volatile matter.

(b) Method : Moisture free coal left in the crucible in first experiment ( $m_1$ ) is covered with a lid loosely. Then it is heated at 925°C in a muffle furnace for 7 minutes. The crucible is taken out and cooled in a desiccator. Then it is weighed ( $m_2$  gms). The loss in weight ( $m_1 - m_2$ ) is due to loss of volatile matter in the  $m$  gms of the coal sample. (Volatile matter is the thermally decomposed coal during burning of coal, that escapes without combustion, in the form of smoke).

$$\text{Volatile matter \%} = \frac{\text{Weight of volatile matter}}{\text{Weight of air dried coal}} \times 100 = \frac{m_1 - m_2}{m} \times 100$$

The volatile matter % can also be determined by taking the fresh weight of the air dried coal but the loss in weight at 925°C, will be due to loss of moisture and volatile matter. If  $w$  is the weight of air dried coal and  $w_1$  is the mass of coal left at 925°C heating, then

### (iii) Ash %

(a) Principle : Inorganic matter in the coal gets oxidised to form metal oxides and silica, which is non-combustible and left as ash.

(b) Method : The residual coal in the above experiments is heated and burnt in a open crucible at above 750°C for half hour. The coal gets burnt. The ash left in crucible is cooled in a desiccator and weighed ( $m_3$  gm).

$$\text{Ash \%} = \frac{\text{Weight of ash}}{\text{Weight of coal}} \times 100 = \frac{m_2}{m} \times 100$$

### (iv) Fixed carbon %

$$\text{Fixed carbon \%} = 100 - (\% \text{ Moisture} + \% \text{ V. M.} + \% \text{ ash})$$

### Significance or Importance of Proximate Analysis:

- (i) Moisture content: High percentage of moisture is undesirable because it reduces the calorific value of coal.
- (ii) Volatile matter: High percentage of volatile matter is undesirable because high volatile matter burns with long flame with high smoke and reduces the calorific value of fuel.
- (iii) Ash content: High percentage of ash content is undesirable because it causes hindrance to heat flow as well as produces clinkers which blocks the air supply through fuel and reduces the calorific value of fuel.
- (iv) Fixed carbon: High percentage of fixed carbon is desirable because higher the percentage of fixed carbon in a coal, greater is its calorific value.

## 1. Ultimate Analysis of Coal

Definition : The analysis of coal in which percentages of C, H, N, S and O elements are found out, is known as ultimate analysis.

### (i) Carbon and Hydrogen:

(a) Method for determination :

- A known weight of powdered and air dried coal sample is burnt in the presence of pure oxygen, in a combustion apparatus. C and H are converted to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  vapours respectively.



**(iii) Nitrogen****Principle :**

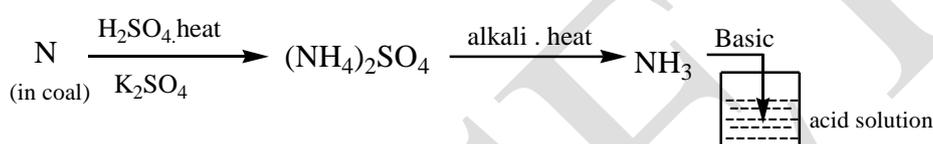
N in coal gets converted to ammonium sulphate, by action of hot concentrated  $\text{H}_2\text{SO}_4$  and then on treatment with alkali solution, equivalent amount of  $\text{NH}_3$  is liberated.

**Method :**

A known weight of powdered and air dried coal is heated with concentrated  $\text{H}_2\text{SO}_4$  along with  $\text{K}_2\text{SO}_4$  catalyst in a long necked Kjeldahl flask.

After the contents become clear, it is treated with alkali solution in a round bottom flask. The ammonia (basic gas) liberated is passed in known volume of standard acid solution.

The unused acid is determined by back titration with  $\text{NaOH}$  solution.



i) Mass of coal = m gm.

ii)  $V_2$  ml = (Blank titration reading).

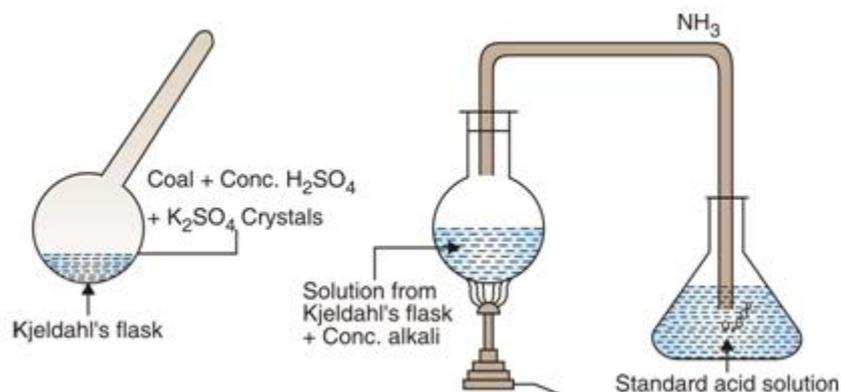
iii)  $V_1$  ml = (Back titration reading, after passing  $\text{NH}_3$ )

iv) Volume of the acid consumed by  $\text{NH}_3 = (V_2 - V_1)$  ml.

$$\text{N \%} = \frac{\text{Volume of acid consumed} \times \text{normality of NaOH} \times 1.4}{\text{Weight of coal sample}}$$

OR

$$\text{N \%} = \frac{\text{Volume of acid} \times \text{change in normality of acid} \times 1.4}{\text{Weight of coal sample}}$$



Estimation of nitrogen in coal

**(iv) Oxygen:**

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

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

**Significance or Importance of Ultimate analysis:**

- (i) Carbon and Hydrogen contents: Higher the percentage of carbon and hydrogen, better is the quality of coal and higher is its calorific value. Higher percentage of carbon in coal reduces the size of combustion chamber required.
- (ii) Nitrogen content: Nitrogen does not have any calorific and its presence in coal is undesirable. Good quality coal should have very little nitrogen content.
- (iii) Sulphur: Its presence in coal is undesirable because the combustion products of sulphur i.e.  $\text{SO}_2$  and  $\text{SO}_3$  are harmful and have corrosion effects on equipments.
- (iv) Oxygen content: Lower the percentage of oxygen higher is its calorific value. As the oxygen content increases its moisture holding capacity increases and the calorific value of the fuel reduces.

**PETROLEUM:**

- The crude oil or petroleum also known as rock oil or mineral oil is a dark colored liquid found well deep in the earth.
- It is mainly composed of hydrocarbons which may be solids, liquids or gases.
- Some optical active compounds having S and N also present.
- On average the composition of petroleum is
 

C = 79.5-87.1%	H = 11.5-14.8%
S = 0.1-3.5%	N and O = 0.1-0.5%

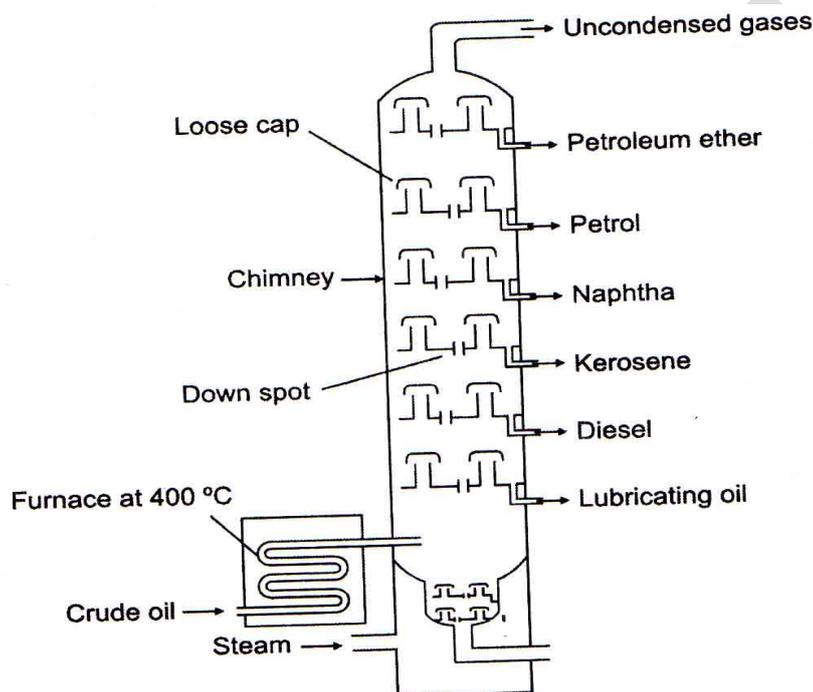
**Refining of Petroleum:**

Crude oil obtained from the mines contains lot of soluble and insoluble impurities which must be removed. Refining can be defined as the process by which crude oil is separated into various useful fractions by fractional distillation and finally converted into desired specific products. The industry where the refining of crude oil takes place is called oil refinery.

**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.
- d. **Fractional distillation:** Heating of crude oil around  $400^{\circ}\text{C}$  in an iron retort, produces hot vapours 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 vapours go up they get cooled gradually and fractional condensation takes place. Higher boiling fractions condenses first later the lower boiling fractions



Name of Fraction	Boiling range	Approx- composition in terms of hydrocarbon atoms 'C'	Uses
(1) Uncondensed gas	Below 30 <sup>0</sup> C	C <sub>1</sub> toC <sub>4</sub>	A domestic or industrial fuel.
(2) Petroleum ether	30 <sup>0</sup> -70 <sup>0</sup> C	C <sub>5</sub> -C <sub>7</sub>	As a solvent.
(3) Gasoline or petrol	40 <sup>0</sup> -120 <sup>0</sup> C	C <sub>5</sub> -C <sub>9</sub>	As motor fuel, solvent, in dry cleaning
(4) Naphtha or solvent spirit	120-180 <sup>0</sup> C	C <sub>9</sub> -C <sub>10</sub>	As solvent, in dry cleaning
(5) Kerosene	180 <sup>0</sup> C-250 <sup>0</sup> C	C <sub>10</sub> -C <sub>16</sub>	As an illuminant ,Engine fuel
(6) Diesel oil	250-320 <sup>0</sup> C	C <sub>10</sub> -C <sub>18</sub>	Diesel engine fuel
(7) Heavy oil on refraction	320-400 <sup>0</sup> C	C <sub>17</sub> -C <sub>30</sub>	Gasoline by cracking
(a) Lubricating oil	---	.....	As lubricant
(b) petroleum jelly	-----	.....	As lubricant and in cosmetics and ointments
c) Paraffin wax			In candles, boot polishes
d) Greases			As lubricant
8) Residue (asphalt, petroleum coke)			Used for making tar roads, water proof roofing

### Knocking-Petrol Knock :

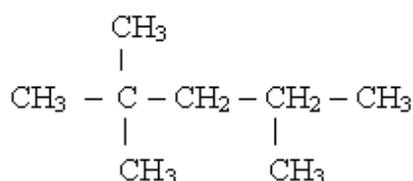
1. In internal combustion engine, diesel or gasoline mixed with air is used as fuel
2. The power output and efficiency of internal combustion engine depends on a factor called compression ratio
3. CR is the ratio of volume of gases at the end of suction stroke to the volume of gases at the end of compression stroke:  $C.R = V_{s.s}/V_{c.s}$
4. The efficiency of engine increases with increase in CR ratio which depends on the constituents present in petrol
5. Due to higher compression ratio fuel air mixture is heated to higher temperatures; the fuel ignites even before the regular spark occurs. This pre-ignition is called knocking
6. Some constituents of petrol, the rate of CR raises fast so that the last drops of the fuel air mixture gets instantaneously ignited producing a loud noise.
7. This rattling noise produced in the internal combustion engine is known as knocking.

**Octane number:**

1. The performance of gasoline in internal combustion has been rated on the basis of octane number
2. The higher the octane number, lower is knocking and better is its performance
3. The knocking is maximum for n-heptane and has lowest antiknock value and its octane number is assigned as zero
4. Knocking is minimum for iso-octane (2,2,4-trimethyl pentane), has highest anti-knocking value and its octane number is given as 100.
5. Octane number of gasoline is the percentage of iso-octane in the mixture of isooctane and n-heptane which has same knocking as the gasoline itself
6. The higher the octane number, lower is knocking
7. The octane number of poor fuels can be raised by the addition of extremely poisonous materials such as tetraethyl lead  $(C_2H_5)_4Pb$  and diethyl-telluride  $(C_2H_4)_2Te$
8. The tendency of knocking is based on the chemical structure of hydrocarbons

n-paraffins > isoparaffins > Olefins > cycloparaffins > naphthalenes > aromatics

Decreasing order of knocking



2,2,4 trimethyl pentane

(isooctane) octane number 100 (good fuel)



n-heptane

octane number zero (bad fuel)

**Diesel Knock:****Cetane Number:**

1. The quality or rating of diesel is expressed by cetane number. Cetane is n- Hexadecane  $(C_{16}H_{34})$
2. Diesel knock is due to post-ignition (delayed ignition) of fuel air mixture with the application of heat and pressure but not by spark as in petrol I.C engine
3. n-Hexadecane has a short ignition lag as compared to any commercial diesel fuel. Its cetane number is 100
4.  $\alpha$ -methyl naphthalene has very long ignition lag as compared to any commercial diesel oil. Its cetane number is taken as zero
5. *Cetane Number is the percentage of n-hexadecane in a mixture of n- hexadecane and  $\alpha$ -methyl naphthalene which has the same ignition characteristics as that of the sample under test.*
6. The order of cetane number for the following is given as:

7. n-alkanes > naphthalenes > alkenes > branched alkanes > aromatics
8. n-alkanes have good anti-knock value and aromatics have least anti-knock value

**2-methyl naphthalene**

Cetane number = 0 (bad fuel)

**n-hexadecane**

Cetane number = 100 (good fuel)

**Petrol knocking is defined as the rattling sound produced in petrol engine due to pre-ignition of fuel air mixture**

**Diesel knocking is defined as the rattling sound produced in diesel engine due to ignition lag of fuel air mixture**

- Knocking is due to improper ignition of fuel –air mixture.
- Knocking decreases the efficiency of engine.
- Petrol Knock is maximum in open chain straight paraffins and least in aromatics
- For internal combustion engine a fuel is said to be a good fuel if it has least knocking

S. No	Petrol Knocking	Diesel Knocking
1	Petrol knocking is due to pre-ignition of the fuel	Diesel knocking is due to post-ignition (ignition–lag) of the fuel
2.	Octane number is the rating of petrol knock	Cetane number is the rating of diesel knock
3	Straight chain hydrocarbons causes maximum petrol knock where as aromatics causes least knock	Aromatic hydrocarbons causes maximum diesel knock where as straight chain hydrocarbons causes least knock
4	To improve anti-knock value TEL, and diethyl telluride are added	To improve antiknock value pre-ignition dopes like ethyl nitrite, isoamyl nitrite and acetone peroxide are added

**Knocking can be prevented by using:**

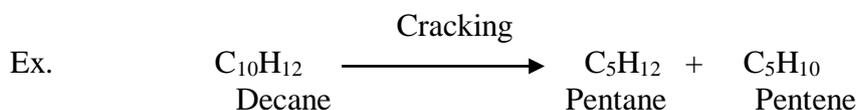
- i) Good quality fuel with higher octane number
- ii) By adding anti-knocking agents like tetraethyl lead, diethyl telluride etc.
- iii) By retarding spark plug ignition

**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 PbBr<sub>2</sub> and eliminated through exhaust. Presence of any sulphur compounds reduces the efficiency of TEL. However lead bromide is harmful to environment

**Prevention of Knocking:** To improve the antiknock value of the petrol sample, Tetraethyl lead (TEL) and diethyl telluride [(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>Te] are added

## Cracking of Petrol:

The quality and yield of petrol produced by the fractionation of petroleum is low. Hence, the middle oil and heavy oil fractions are cracked to give petrol. Cracking is defined as the “decomposition of bigger hydrocarbon molecules into simpler, low boiling hydrocarbons of low molecular weight”.



### Advantages

- The yield of petrol is higher.
- The quality of petrol produced is better.
- No external fuel is necessary for cracking.
- Cracking can be easily controlled, so we can get desired products.
- Evolution of by-product gases can be minimized.
- Product contains very less quantity of undesirable sulphur content. So it is very useful.

### Objectives:

A product from crude oil, gasoline has greater demand as motor fuel. But yield is only upto 20%, more over fractional distillation have high content of sulphur. To overcome these problems middle and heavy oil fractions are cracked to get petrol. The main objective of cracking is to get desired products. Petrol made by cracking as good characteristics than straight run petrol

### Cracking is mainly two types:

1. **Thermal cracking:** In this process, heavier hydrocarbon molecules are converted into lighter hydrocarbon molecules at high temperatures and pressures. Thermal cracking is carried out in two ways. The cracked products are then separated by fractional distillation. Generally, the yield is from 7 to 30%. It is of two types:

- 1) Liquid phase thermal cracking
- 2) Vapour phase thermal cracking

### 2. Catalytic Cracking:

In this type of cracking catalysts are used. The suitable catalysts used are  $\text{Al}_2\text{O}_3$  and  $\text{Al}_2(\text{SiO}_3)$ . This process completes at lower temperatures and low pressures compared to thermal cracking (300-450°C; 1-5kg/cm<sup>2</sup> pressure). The petrol sample produced contains higher content of aromatics, hence quality of petrol with better antiknock properties. The petrol sample contains less percentage of sulphur, hence less corrosive.

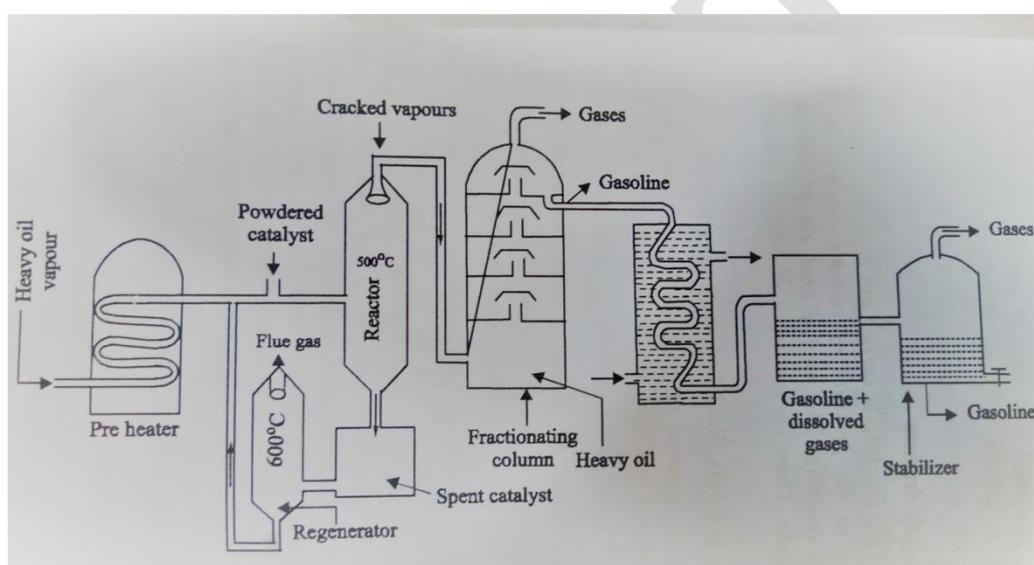
Catalytic cracking may be:

- 1) Fixed bed catalytic cracking
- 2) Fluid bed catalytic cracking or moving bed catalytic cracking

**Fluid bed catalytic cracking or moving bed catalytic cracking:**

In fluidized-bed catalytic cracking, the finely divided catalyst is kept agitated by gas streams (feed stock vapour) so that it can be handled like a fluid system i.e., it can be pumped as a true liquid. The advantage of fluidized-bed cracking process is that a high degree of mixing is achieved and consequently a good contact is established between the catalyst and the feed stock vapours. This results in a higher yield. The regeneration of the inactive catalyst can be carried out continuously without interrupting the production of gasoline unlike in fixed-bed cracking method.

**Process:** The finely divided catalyst bed ( $\text{Al}_2\text{O}_3 + \text{SiO}_2$ ) is fluidized by the upward passage of feed stock vapours (Heavy oil, gas oil, etc) in a cracking chamber (called Reactor) maintained at  $550^\circ\text{C}$ . Near the top of the reactor (Fig.3), there is a centrifugal



**Fluid Bed Catalytic Cracking**

separator (called cyclone), which allows only the cracked oil vapours to pass onto the fractionating column but retains the catalyst powder in the reactor itself. The catalyst powder gradually becomes heavier due to the deposition of carbon and settles to the bottom, from where it is forced by an air blast to the regenerator (maintained at  $600^\circ\text{C}$ ). After cracking, the products are fractionated into gases, gasoline, gas oils and residual oils (unconverted). The heavier oil fractions may be cracked in a second-stage cracking, thereby increasing the over all yield of the cracked products.

In regenerator, the spent catalyst is stripped of the adsorbed oil by passing steam and then decarbonized by a hot air blast, under controlled conditions. The heat liberated during this regeneration is used to raise steam and to preheat the catalyst.

**NATURAL GAS, LPG & CNG:****Natural Gas**

1. Natural gas is primary gaseous fuel. It is a fossil fuel
2. It is obtained from oil wells dug in the earth crust during mining of petroleum
3. It is mainly composed of methane and small quantities of ethane along with other hydrocarbons
4. It is also known as *methane gas or marsh gas* as it majorly contains methane
5. Composition of Natural gas:

$\text{CH}_4$  - 88.5%    $\text{C}_2\text{H}_6$  - 5.5%   Propane - 3.7%

Butane - 1.8%    $\text{H}_2$ , CO,  $\text{CO}_2$  - 0.5%

6. Calorific value varies from 12000-14000  $\text{Kg/m}^3$
7. It is used as a very good domestic fuel
8. It is used in the preparation of ammonia
9. It is used to prepare carbon black for rubber industry
10. It is used to prepare some synthetic proteins which are used as animal feed

**LPG (Liquified Petroleum Gas):****Characteristics**

1. LPG is obtained as byproduct during refining of crude oil or from natural gas
  2. It mainly contains n-butane, isobutane, butylene and propane
  3. It has high calorific value:  $27800 \text{ kcal/m}^3$
  4. It gives less CO and least un-burnt hydrocarbons. So it causes least pollution
  5. It gives moderate heat which is very useful for cooking
  6. It has a tendency to mix with air easily
  7. Even though it is toxic, on combustion it gives no toxic gases
  8. It neither gives ash or smoke content
  9. It is cheaper than gasoline. Hence used as motor fuel
  10. It is dangerous when leakage is there. It is highly knock resistant
  11. LPG is used as domestic fuel and as a fuel in internal combustion engines
  12. It is used as fuel in some industries
- LPG can be compressed under pressure in containers and sold under the trade name like Indane gas, Bharath gas etc.
  - Traces of smelling organic sulphides (mercaptans) are added to LPG for safety measures (to give warning of gas leakage)

**CNG (Compressed Natural Gas):**

1. Natural gas mainly contains  $\text{CH}_4$ . CNG is made by compressing natural gas to less than 1% of the volume it occupies at STP
2. It is stored in a cylinder made of steel at a pressure of 200-248  $\text{Kg/cm}^3$
3. It is odourless, non toxic gaseous mixture

4. Composition of CNG is  $\text{CH}_4$  (90%), other constituents are ethane, propane and gases like  $\text{N}_2$ , CO etc.
5. Calorific value of CNG is 900KJ/mole

**Advantages:**

1. Due to higher temperature of ignition, CNG is better fuel than petrol and diesel
2. Operating cost is less
3. It releases least pollutants like CO and unburnt hydrocarbons
4. It mixes with air easily and undergoes regular combustion
5. No anti-knocking agent is required as it has high octane number
6. It is used as fuel in automobiles like cars, trucks, buses etc.
7. It is also used as fuel for locomotive diesel generators to generate electricity that drive the motors of train

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