Course of Study

Engineering Chemistry

SH 453

Theory : 3
Year : I
Tutorial : 1
Part : I/II
Practical : 3

Course objectives: To develop the basic concepts of Physical chemistry, Inorganic chemistry and Organic chemistry relevant to problems in engineering.

1. **Electrochemistry and Buffer** **(6 hours)**
   - 1.1. Electrochemical cells
   - 1.2. Electrode potential and Standard electrode potential
   - 1.3. Measurement of electrode potential
   - 1.4. Nernst equation
   - 1.5. EMF of cell
   - 1.6. Application of electrochemical and electrolytic cells
   - 1.7. Electrochemical series and its applications
   - 1.8. Buffer: its type and mechanism
   - 1.9. Henderson's equation for pH of buffer and related problems
   - 1.10. Corrosion and its types
   - 1.11. Factors influencing corrosion
   - 1.12. Prevention of corrosion
2. **Catalyst** **(4 hours)**
   - 2.1. Introduction
   - 2.2. Acction of catalyst (Catalytic promoters and catalytic poisons)
   - 2.3. Characteristics of catalyst
   - 2.4. Types of catalyst
   - 2.5. Theories of catalysis
   - 2.6. Industrial applications of catalysts
3. **Environmental chemistry** **(5 hours)**
   - 3.1. Air pollution
   - 3.2. Air pollutants i) gases; Sox, NOx, CO, CO2, O3 and hydrocarbons ii) Particulates dust, smoke and fly ash
   - 3.3. Effects of air pollutants on human beings and their possible remedies
   - 3.4. Ozone depletion and its photochemistry

Contents

Chapter

1

Electrochemistry

Electrochemistry

Introduction

The branch of science which deals with the inter-conversion of electrical energy into chemical energy and vice-versa is known as electrochemistry. Electrochemical cells are the main consequences of electrochemistry.

Any devices for converting either electrical energy into chemical energy or chemical energy into electrical energy are known as electrochemical cells. Accordingly, the two kinds of electrochemical cells are as follows,

1. Electrolytic cells and
2. Galvanic cells

1. Electrolytic cells:

The electrochemical cells in which chemical change in a solution is brought by passing electric current through it are known as electrolytic cells.

Construction: In electrolytic cell, the two electrodes are dipped in an electrolytic solution. The two electrodes are directly connected to a source of electricity (say battery). The electrode which is connected to the positive terminal of battery is called anode and electrode which is connected to the negative terminal of battery is called cathode.

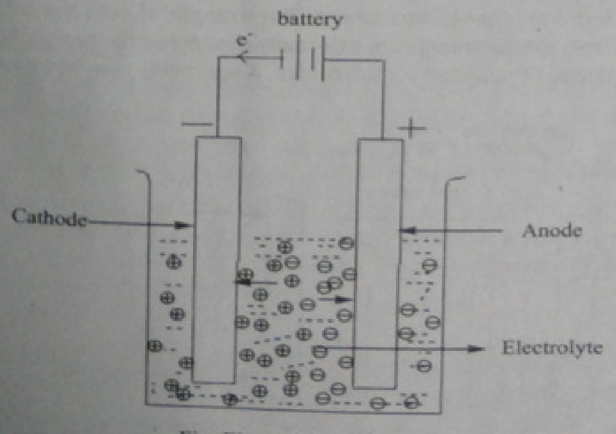


Fig: Electrolytic cell

When electric current is supplied into the solution through electrodes, the cations move toward cathode and they are reduced there by gaining electrons. On the other hand, the anions move toward anode and are oxidized there. **Therefore, cathode is the electrode where reduction of cations takes place and anode is the electrode where oxidation takes place.**

Let us take an example, the electrolysis of HCl. In aqueous solution, HCl ionizes as follows,

$$HCl \rightarrow H^+ + Cl^-$$

When electric current is supplied,

At cathode, (reduction)

$$H^+ + e^- \rightarrow H$$
$$H + H \rightarrow H_2(g)$$

At anode, (oxidation)

$$Cl^- \rightarrow Cl + e^-$$
$$Cl + Cl \rightarrow Cl_2(g)$$

Hence, the overall redox reaction is,

$$2HCl \rightarrow H_2(g) + Cl_2(g)$$

2. Galvanic cells

The electrochemical cells in which electricity is generated by the process of chemical change in solution are called galvanic cells. These are also called Voltaic cells.

Construction: A galvanic cell is constructed by utilizing a redox reaction such that oxidation half reaction occurs in one compartment (known as anodic compartment) and the reduction half reaction occurs in another compartment (known as cathodic compartment). The two half cells are physically separated but they are internally connected via salt bridge and externally connected by means of a conducting wire with a voltmeter. Once this arrangement is set up, the deflection in voltmeter is observed confirming the generation of electricity.

A typical galvanic cell is Daniell cell. In Daniell cell, the zinc electrode is dipped in the solution of its ions forms one compartment and copper electrode dipped in the solution of its ions forms another compartment. The strength of both the solutions is unit molarity. The two compartments are externally connected by means of a conducting wire and internally connected via salt bridge. A voltmeter may be inserted in the circuit of wire.

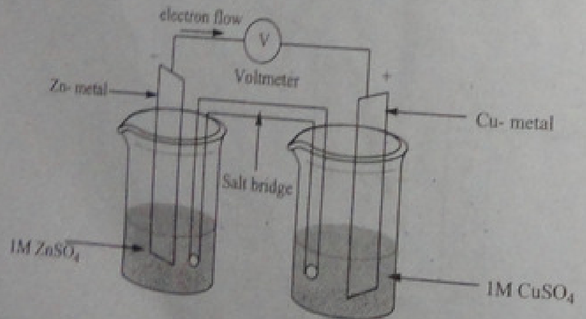


Fig: Daniell Cell

The initial voltage of this set up is found to be 1.10V. Following observations are also noted as the cell is working.

- Mass of zinc is gradually decreased and the concentration of Zn^{2+} ion in the solution is increasing gradually.

- Mass of copper electrode is gradually increased and the concentration of Cu^{2+} ions in the solution is decreasing gradually.
- The charge balance (electro neutrality) in both the compartment is maintained by the migration of ions through the salt bridge.

These observations confirm the following chemical changes,

Anode reaction: $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (oxidation)

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

Net reaction: $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

The emf of cell is 1.10V.

Thus the zinc electrode is anode but it acquires negative charge and copper electrode is cathode but it acquires positive charge. This polarity is opposite to the case of electrolytic cells.

Salt bridge

Two electrolyte solutions at different concentration of a galvanic cell form a heterogeneous system such that the cations and anions diffuse with different speed, then a potential difference is set up at the junction of two electrolyte solutions called liquid junction potential. It is necessary to avoid, eliminate or minimize the liquid junction potential as it interferes in the accurate determination of electromotive force of the cell (emf).

An inverted U-shaped tube used to physically connect the two half-cells of a galvanic cell is known as salt bridge. It is a device to minimize or eliminate the liquid junction potential. Saturated solution of salts like KCl, KNO_3, NH_4Cl and NH_4NO_3 etc. in agar-agar gel is used in salt bridge.

Role of salt bridge

Salt bridge contains high concentration of ions viz., K^+ and NO_3^- at the junction of electrolyte solution. Thus salt bridge carries whole of the current across the boundary; where the K^+ and NO_3^- ions have same speed or transport number. Hence, the salt bridge with uniform and same mobility of cations and anions minimize the liquid junction potential.

Potassium chloride in salt bridge cannot be used in presence of electrolyte solution of silver, mercurous or thallus salt as it may cause precipitation of corresponding chloride. A porous partition may also be used in place of the salt bridge. This permits the flow of ions without allowing the two solutions to mix.

Cell notations: A general convention is made for representing the galvanic cells; this is known as cell notation. Following general rules are used in cell notations,

- A vertical line represents the electrode electrolyte interface. In anode half, solid metal is written first followed by its electrolyte e.g., M/M^{n+}. It is reverse in cathode half e.g., M^{n+}/M.
- The molar concentration of electrolyte is written in bracket.
- In case of gaseous electrode, the pressure is expressed within the bracket. For example, the hydrogen electrode as a cathode is represented as,

$$H^{+}(1M)/H_2(1atm), Pt$$

Whereas hydrogen electrode as anode is represented as,

$$Pt, H_2(1atm)/ H^{+}(1M)$$

- A double vertical line between anodic and cathodic half represents the salt bridge.
- It is universally adopted that the anode is written on left and cathode on the right.

Thus the cell notation of the **Daniell cell** is,

$$Zn/Zn^{2+}(1M)//Cu^{2+}(1M)/Cu$$

- Sometimes, the sign above anode and cathode is also written. This represents the direction of the flow of electrons. Anode has negative charge and cathode has positive i.e. the electrons flow from the anode to cathode.

$$^{\ominus}Zn/Zn^{2+}(1M)//Cu^{2+}(1M)/Cu^{\oplus}$$

Differences between Electrolytic and Galvanic cell:

S.N.	Electrolytic cell	Galvanic cell
1.	It converts electrical energy into chemical energy.	It converts chemical energy into electrical energy.
2.	Redox reaction is produced in the electrolytes by supplying electricity.	Electricity is produced by the redox reaction.
3.	The redox reaction is non-spontaneous.	The redox reaction is spontaneous.
4.	Single electrolytic solution is used.	Two different electrolytes are taken in two separate vessels.
5.	The electrodes taken may be of same or different materials.	The electrodes of different materials are used.
6.	The electrode which is connected to the negative terminal of the battery is called cathode, negative terminal and the electrode connected to the positive terminal of the battery is called anode, positive terminal.	The electrode on which oxidation takes place is called anode, negative pole and the electrode on which reduction takes place is called the cathode or positive pole.
7.	No salt bridge is used.	A salt bridge is used.

Applications of electrochemical cells:

- Galvanic cells are widely used to produce electricity. In practical importance, the galvanic cells are broadly classified into three groups;
  i. Primary cells- E.g. Dry cell, Bottom cell etc
  ii. Secondary cells or Rechargeable cells. These cells are galvanic cells during the discharge but are electrolytic cells during recharging. E.g. Lead storage cell or lead acid cell, Ni-Cd cell etc. and
  iii. Fuel cells- E.g. Hydrogen-Oxygen cell. These are the cells in which the reactants are continuously supplied as fuels. They have been used to produce electric

power on some space missions.

- Electrolytic cells are famous for electroplating of precious metals. It is very important for decorating purpose and protecting the metals from corrosion.
- Electrolytic cells are also common in the field of electrometallurgy. It is the method to extract the metals in highest purity.
- Hydrogen and oxygen gas can be produced by the electrolysis of water.

Single Electrode Potential:

A potential difference is developed at the interface between the metal and the solution, when it is in contact with the solution of its ions. This is called single electrode potential.

In other word, Electrode potential is defined as the potential developed at the interface between the metal and the solution, when it is in contact with the solution of its ions. It is denoted by E. Electrode potential indicates a measure of the tendency of an electrode to gain electrons i.e., to undergo reduction.

Origin of electrode potential

When a metal is in contact with a solution of its own ions, two types of reactions are possible. The metal shows the tendency to go into the solution as metal ion by losing electrons.

$$M(s) \longrightarrow M^{n+}(aq) + ne^{-}$$

At the same time, metal ions in the solution show the tendency to get deposited as metal atoms.

$$M^{n+}(aq) + ne^{-} \longrightarrow M(s)$$

Depending upon the nature of the metal, either the dissolution of metal or the deposition of metal is faster in the beginning and the other one is slower. But as the reactions proceed, the faster reaction becomes slower and the slower reaction becomes faster and a state of equilibrium is reached after some time.

$$M(s) \rightleftharpoons M^{n+}(aq) + ne^{-}$$

Now, the number of metal atoms dissolving is equal to the number of atoms getting deposited. But the net charge at the equilibrium is dependent on the nature of the metal.

Case I:

If the dissolution reaction is faster than the deposition reaction, at equilibrium, the net change is observed with few metal atoms are oxidized and dissolved in the solution. These so liberated electrons accumulate on the electrode surface, making it negatively charged. The negatively charged electrode surface attracts a layer of positively charged ions at the interface, developing an electrical double layer at the metal –solution interface. It is shown in the figure as below,

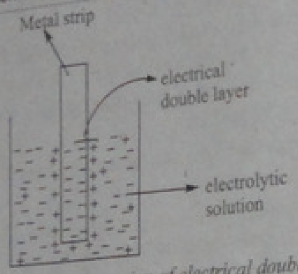


Fig: showing the formation of electrical double layer

Case II:

Similarly, if the deposition reaction is faster than dissolution, at equilibrium, the net change is found with the deposition of few metal ions as metal atoms by consuming electrons. As a result the electrode surface develops a layer of positive charges which attracts a layer of negatively charged ions at the interface again establishing an electrical double layer. It is shown in the figure below as,

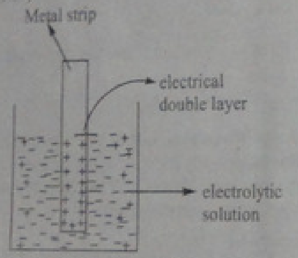


Fig: showing the formation of electrical double layer.

Formation of an electrical double layer gives rise to a potential difference across the layer. This potential difference between the metal and the solution at the interface is known as the single electrode potential.

A detail structural view of the electrical double layer is shown as below,

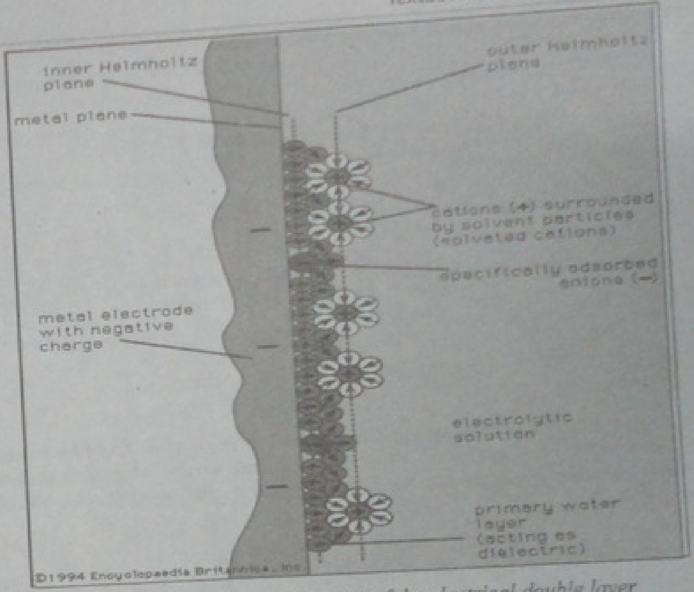


Fig: *showing the establishment of the electrical double layer when a metal rod is negatively charged when dipped into its salt solution.*

Standard Electrode Potential:

The electrode potential when a metal strip is immersed in its electrolytic solution of 1M concentration at 298K and 1atmospheric pressure is called standard electrode potential. It is denoted by E°. When the complete cell is made by combining two half cells in the standard state, the cell is said to be in the standard state.

The electrode potential of an electrode depends upon concentration of ions in solution in contact with metal. Simply, oxidation potential of an electrode is inversely proportional to the concentration of ions and reduction potential is directly proportional to the concentration of ions.

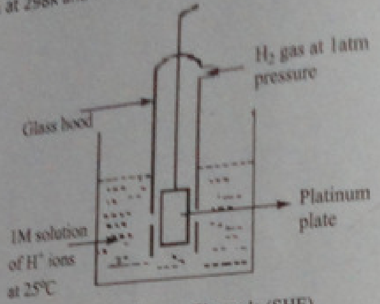
Measurement of electrode potential:

1. **Under the standard condition i.e. standard electrode potential-**

   The standard electrode potential E° enables one to assess the thermodynamic activity of various chemical substances. But there are no methods available by which we can measure the absolute value of single electrode potential. The electrode potential of an electrode is measured with respect to a primary reference electrode known as Standard Hydrogen Electrode (SHE) or Normal Hydrogen Electrode (NHE).

Standard Hydrogen Electrode (SHE):

Standard hydrogen electrode contains hydrogen gas in contact with H^+ ions of 1M concentration at 298K and at 1 atmospheric pressure.



Standard Hydrogen Electrode (SHE)

In hydrogen electrode, hydrogen gas is bubbled through solution of hydrogen ions. The inert metal, often platinum (Pt) acts as a source or sink of electrons, but takes no other part in the reactions other than acting as a catalyst for it. This electrode is denoted as,

$Pt, H_2(g)/H^+(aq)$ when anode and

$H^+(aq)/H_2, Pt$ when cathode.

The hydrogen electrode may act as either a cathode or an anode, depending on the other electrode in the cell and the spontaneous direction of the overall reaction. When the electrode is acting as cathode, the reaction is,

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

When the hydrogen electode is acting as anode,

$$H_2(g) \rightarrow 2H^+(aq) + 2e^-$$

For determining the electrode potential of the given electrode, the electrode is coupled with SHE. The emf of the cell is then determined with the help of a potentiometer. The electrode potential of SHE is arbitrarily taken as zero. Thus, the emf of cell gives the value of electrode potential of the given electrode. For example,

Measurement of standard electrode potential of zinc:

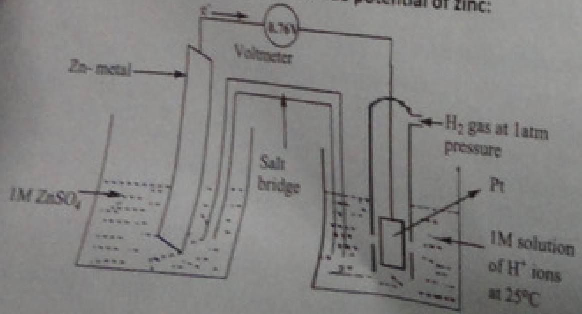


Fig.: Zinc electrode coupled with Standard Hydrogen Electrode

When zinc electrode is dipped into its ionic solution of 1M concentration and coupled with SHE as shown in figure above, oxidation takes place at the zinc electrode. Then, the cell representation is given by,

$$Zn/Zn^{2+}(1M)//H^+(1M)/H_2(g, 1atm), Pt$$

The emf of the cell is found to be 0.76V.i.e,

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$0.76 \quad = E^\circ_{H+/H2} - E^\circ_{Zn2+/Zn}$$

Since the standard hydrogen electrode potential is set arbitrarily zero,

$$0.76 \quad = 0 - E^\circ_{Zn2+/Zn}$$

Therefore, $E^\circ_{Zn2+/Zn} = -0.76$ V

For any particular electrode, **oxidation potential = – reduction potential**

Thus, $E_{Zn/Zn2+} = -E^\circ_{Zn^{2+}/Zn} = -(-0.76)V = +0.76V$

Hence, the standard reduction potential of zinc is found to be –0.76V and the oxidation potential of zinc electrode is taken as +0.76 V.

Similarly, when copper electrode is coupled with SHE, reduction takes place at copper electrode and the cell representation is given by,

$$^{\ominus}Pt, H_2(g, 1atm)/H^+(1M)// Cu^{2+}(1M)/Cu^{\oplus}$$

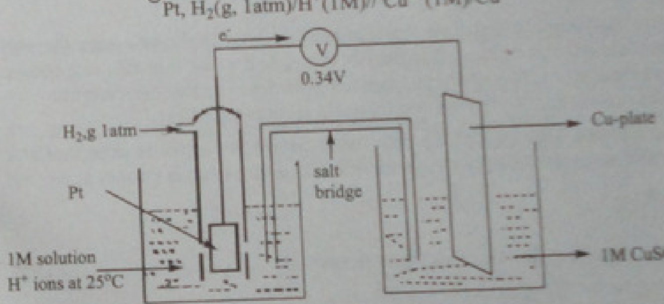


Fig.: Cu electrode coupled with Standard Hydrogen Electrode

The emf of cell is found to be 0.34V.i.e,

$$E^\circ_{cell} \quad = E^\circ_{cathode} - E^\circ_{anode}$$
$$0.34 \quad = E^\circ_{Cu2+/Cu} - E^\circ_{H+/H2}$$

Since the standard hydrogen electrode potential is set arbitrarily zero,

$$0.34 \quad = E^\circ_{Cu2+/Cu}$$

Therefore, $E^\circ_{Cu^{2+}/Cu} = 0.34$ V

Hence, the standard reduction potential of copper is found to be +0.34V and the oxidation potential of copper electrode is taken as –0.34 V.

Calculation of the emf of the cell under standard condition:

The standard emf of a galvanic cell (E°_{cell}) is consequently the sum of the standard oxidation potential (anodic potential) and the standard reduction potential (cathodic potential). Thus, E°_{cell} of the cell can be calculated from the given standard electrode potentials of anodic and cathodic half cells. It can be done in following ways;

- When anodic potential is the standard oxidation potential and cathodic potential is the standard reduction potential. Then the sum of them gives the standard emf of the cell. That is,

$$E^\circ_{cell} = E^\circ_{ox(anode)} + E^\circ_{red(cathode)}$$

- When both the anodic and cathodic potentials are the respective standard reduction potentials. We have,

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

- When both the anodic and cathodic potentials are the respective oxidation potentials. We have,

$$E^\circ_{cell} = E^\circ_{anode} - E^\circ_{cathode}$$

2. Measurement of electrode potential and cell potential under non-standard conditions- NERNST EQUATION

Now it is known that how to determine the electrode potential and hence the cell potential under standard condition. But they also depend upon the concentrations, pressure and temperature. The electrode potential and hence the cell potential under non-standard condition is determined by using Nernst equation.

In 1989, Nernst derived a quantitative relationship between electrode potential and concentration of the electrolyte species involved. This expression is known as Nernst equation.

Derivation of Nernst's equation for the electrode potential

Consider the following reversible electrode reaction:

$$M(s) \rightleftharpoons M^{n+}(aq) + ne^-$$

By convention, the electrode reaction is written with reduction in the forward direction, as electrode potential is the measure of reduction tendency.

The decrease in free energy, ΔG, accompanying the process is given by the well known thermodynamic equation,

$$\Delta G = \Delta G^\circ + RT\ln k \text{..........} (1)$$

Where ΔG° = free energy change accompanying the same process when the reactants and products of the reaction are in their standard states of unit activity,

ΔG = free energy change involved at any other condition and

K = reaction quotient of the activities of the products and reactants at any given stage of the reaction.

Substituting the value of K, we have,

$$K = \frac{a_{M^{n+}}}{a_M} \text{..........} (2)$$

As an approximation, substituting molar concentration for activities,

$$K = \frac{[m^{n+}]}{[M]}$$

If E is the electrode potential of the electrode in volts and the electrode reaction involves transfer of 'n' number of electrons, i.e., nF coulombs, the electrical work available from the electrode is nFE volt coulomb of joules. Hence free energy decreases of the system, ΔG is given by the expression.

$$-\Delta G = nFE \text{......................} (4)$$

Hence, from equations (1) and (4), we get

$$-nFE = -nFE^\circ + RT\ln \frac{[m^{n+}]}{[M]}$$

Since the concentration of solid species is unity i.e. [M] = 1, we get

$$E = E^\circ - \frac{RT}{nF}\ln [M^{n+}] \text{......................} (5)$$

or, $$E = E^\circ - 2.303\frac{RT}{nF}\log [M^{n+}]$$

The equation (5) is the Nernst's equation for the electrode potential. The equation can be used to calculate the electrode potential of an electrode if the concentration is known. At 298K, when the values of R, T and F are substituted, the equation reduces to,

or, $$E = E^\circ - \frac{0.0591}{n}\log [M^{n+}]$$

The Nernst equation can also be applied for the calculation of emf of a cell. Consider the cell reaction,

$$aA + bB \rightleftharpoons cC + dD$$

The Nernst equation for the emf of the cell 'E_{cell}' is given by,

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln \frac{(C)^c(D)^d}{[A]^a[B]^b}$$

or, $$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF}\log \frac{(C)^c(D)^d}{[A]^a[B]^b}$$

Where, n = number of electrons transferred during the cell reaction and

E°_{cell} = standard emf of the cell.

Above is the Nernst's equation for calculating the emf of the cell under non-standard conditions.

At 25°C, this equation is obtained as below by substituting the value of constants,

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

Example:

Calculate the emf of the following cell at 25°C.

$Zn/Zn^{2+}(0.01M)//Cu^{2+}(0.5M)/Cu$

$E^\circ_{(Zn^{2+}/Zn)} = -0.76V$ and

$E^\circ_{(Cu^{2+}/Cu)} = +0.34V$

Solutions,

I. Using the method of individual electrode potentials:

Anodic reaction,

$$Zn \longrightarrow Zn^{2+} + 2e^- \quad E^\circ_{Zn/Zn^{2+}} = +0.76V$$

Here, n = 2

Then, Nernst equation for electrode potential is given by,

$$\text{or, } E_{Zn/Zn^{2+}} = E^\circ_{Zn/Zn^{2+}} - \frac{0.0591}{n}\log\frac{[Zn^{2+}]}{1}$$

$$\text{or, } E_{Zn/Zn^{2+}} = 0.76 - \frac{0.0591}{2}\log\frac{[0.01]}{1}$$

$$\text{or, } E_{Zn/Zn^{2+}} = 0.76 - \frac{0.0591}{2}(-2)$$

$$\text{or, } E_{Zn/Zn^{2+}} = 0.76 - (-0.0591)$$

$$\text{or, } E_{Zn/Zn^{2+}} = 0.819\ V$$

Similarly, the cathodic reaction,

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

$$E^\circ_{[Cu^{2+}/Cu]} = +0.34V$$

Then we have,

$$\text{or, } E_{Cu^{2+}/Cu} = E^\circ_{Cu^{2+}/Cu} - \frac{0.0591}{2}\log\frac{1}{[Cu^{2+}]}$$

$$\text{or, } E_{Cu^{2+}/Cu} = 0.34 - \frac{0.0591}{2}\log\frac{1}{[0.5]}$$

$$\text{or, } E_{Cu^{2+}/Cu} = 0.34 - \frac{0.0591}{2}(0.301)$$

$$\text{or, } E_{Cu^{2+}/Cu} = 0.34 - (0.0089)$$

$$\text{or, } E_{Cu^{2+}/Cu} = 0.331\ V$$

Then, the emf of cell is given by,

$$E_{cell} = E_{Zn/Zn^{2+}} + E_{Cu^{2+}/Cu} = 0.819 + 0.331$$

$$= 1.15\ V$$

II. Alternative method:

The net cell reaction is given by,

$$\begin{array}{ll} Zn \longrightarrow Zn^{2+} + 2e^- & E^\circ_{Zn/Zn2+} = +0.76\ V \\ Cu^{2+} + 2e^- \longrightarrow Cu & E^\circ_{Cu2+/Cu} = +0.34\ V \\ \hline Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu & E^\circ cell = 1.10\ V \end{array}$$

The Nernst equation is given by,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Zn^{2+}][Cu]}{[Zn][Cu^{2+}]}$$

$$\text{or, } E_{cell} = 1.10 - \frac{0.0591}{2}\log\frac{0.01\times 1}{1\times 0.5}$$

$$\text{or, } E_{cell} = 1.10 - (-0.05)$$

$$\text{or, } E_{cell} = 1.15\ V$$

Electrochemical series:

The standard potential of an electrode can be measured with reference to standard hydrogen electrode, whose potential is arbitrarily assigned to zero volts. These electrodes can be arranged in order of their increasing reduction potentials. ***A series of electrodes according to the increasing value of their standard reduction potential is known as electrochemical series. This is also known as the emf series or activity series.***

Reduction half reaction of electrode	E°(V)
$Li^+ + e^- \rightarrow Li$	−3.05
$Na^+ + e^- \rightarrow Na$	−2.71
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$Cr^{3+} + 3e^- \rightarrow Cr$	−0.74
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.31
$Co^{2+} + 2e^- \rightarrow Co$	−0.28
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.25
$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$2H^+ + 2e^- \rightarrow H_2$	0.00
$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77
$Ag^+ + e^- \rightarrow Ag$	0.80
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09
$O_2^+ + 4H^+ + 4e^- \rightarrow H_2O$	1.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36
$Au^{3+} + 3e^- \rightarrow Au$	1.50

The values reported in table for standard electrode potential corresponds to the half cell reaction in which reduction is taking place. Therefore E values are also known as standard reduction potentials.

Important features of electrochemical series

i. Metals near the top of the series are strongly electropositive (or weakly electronegative). They lose electrons readily to give cations.

ii. Lower the position of metal in the series, greater is its tendency to be reduced. Thus metals having higher position in the series are strong reducing agents and their ions are stable. On the other hand, those near the bottom of the series are stable metals and their ions are easily reduced to the metals. Accordingly, any metal will reduce any cation below it in the electrochemical series, if one molar solution is used.

iii. Weakly electronegative metals in the upper part can displace more electronegative metals below them from their salts. For example, iron displaces copper from $CuSO_4$ solution, Cu displaces silver from silver salt solution, and silver displaces gold form gold salt solution as in photography during gold toning process.

iv. Metals above hydrogen can displace hydrogen from dilute acids.

v. An oxidizing agent with a higher reduction potential will oxidize any reducing agent with a lower reduction potential e.g., silver (standard reduction potential +0.80V) will be deposited from its solution when treated with copper metal (reduction potential +0.34V).

vi. A reducing agent with a lower reduction potential will reduce any oxidizing agent with a higher reduction potential e.g., Li^+/Li has the lowest reduction potential. This means that all ions below it can be reduced by lithium.

vii. Metals which are above hydrogen in ECS are easily rusted and those situated below are not rusted.

Importance of electrochemical series

1. **Prediction of anode and cathode:** Since the standard electrode potential of a metal represents its oxidizing tendency, one can easily predict anode and cathode in a cell made by coupling any two metals in electrochemical series. A metal with higher oxidation potential (or lower reduction potential) is anode and the metal with lower oxidation potential (or higher reduction potential) is cathode. In general, the metal electrode lower in the electrochemical series acts as cathode to the one above it. For e.g., in Zn-Ag cell, the standard reduction potential of Zn is –0.76V and that of Ag electrode is +0.80V. Thus, zinc electrode acts as anode and silver acts as cathode.
2. **Predicting the displacement of one metal by other metal from its salt solution:** the metals lying higher up in electrochemical series are easily oxidized and those lying lower in the series are easily reduced. Thus when zinc is placed in $CuSO_4$ solution, Cu metal gets precipitated by the oxidation reaction of zinc.

$$Zn \longrightarrow Zn^{2+} + 2e^-$$

$$\underline{Cu^{2+} + 2e^- \longrightarrow Cu}$$

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

Therefore, a metal lying high in the electrochemical series can precipitate the lower one in the series. Silver cannot precipitate copper from its salt solution.

3. **Predicting whether a metal will displace hydrogen from dilute acid solution or not:**

A metal system occurring above hydrogen electrode displaces H_2 gas from dilute acids. A metal system occurring below H_2 does not displace H_2 from dilute acids, water or steam does not get tarnished.

4. **Calculation of standard Emf of cell (E°_{cell}):**

In order to calculate the standard Emf of the cell, the electrochemical reaction is to be set into two half reactions, viz.,

   a. Oxidation half reaction and
   b. Reduction half reaction

According to the cell representation, the oxidation half is written at left hand side followed by reduction half at right hand side. Then, standard emf of the cell(E°_{cell}) = $E^\circ_{cathode} - E^\circ_{anode}$

For e.g.,

$$Zn/Zn^{2+}(aq, 1M)//Cu^{2+}(aq, 1M)/Cu$$

From electrochemical series, we have,

$$E^\circ_{(Zn^{2+}/Zn)} = -0.76V \text{ and}$$
$$E^\circ_{(Cu^{2+}/Cu)} = +0.34V$$

Then,
$$\begin{aligned} E^\circ_{cell} &= E^\circ_{right} - E^\circ_{left} \\ &= E^\circ_{(Cu^{2+}/Cu)} - E^\circ_{(Zn^{2+}/Zn)} \\ &= 0.34 - (-0.76)V \\ &= 1.10V \end{aligned}$$

5. **Predicting the feasibility of cell reaction:**

   The feasibility of redox reaction can be predicted with the help of electrochemical series. Since the net emf of the cell can be determined by using the relation,

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

   In general, if the net emf of the cell is positive the redox reaction is spontaneous otherwise not.

6. **Determination of standard free energy change of a reaction:**

   The standard free energy change (ΔG°) of a cell reaction is related to its standard emf as,

$$\Delta G^\circ = -nFE^\circ$$

   Thus, knowing the standard emf of a cell one can calculate the standard free energy change (ΔG°) of the cell reaction.

7. **Determination of equilibrium constant(K) of the cell reaction:** Using the emf of the cell, standard free energy change of the cell reaction can be determined and standard free energy change(ΔG°) of the cell reaction and its equilibrium constant are related as,

$$\Delta G^\circ = -RT\ln K$$

Where, R = universal gaseous constant
T = Temperature in Kelvin scale
K = equilibrium constant of the reaction.

Numericals based on Electrochemical cells:

1. Calculate the emf of the following cell at 25°C giving electrode reactions and cell reaction.

   $Cd(s)/Cd^{++}(0.01M)//Cu^{++}(0.5M)/Cu(s)$, $E^\circ_{Cd^{++}/Cd} = -0.140V$ and $E^\circ_{Cu^{++}/Cu} = 0.34V$

Solution:

Given,
$$E^\circ_{Cd^{++}/Cd} = -0.140V, [Cd^{2+}] = 0.01M$$
$$E^\circ_{Cu^{++}/Cu} = 0.34V, [Cu^{2+}] = 0.5M$$

Since the standard reduction potential of Cd is less than that of Cu i.e. $E^\circ_{Cd^{++}/Cd} < E^\circ_{Cu^{++}/}$

Cd acts as anode and Cu acts as cathode. Then, we have,

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

or, $E^\circ_{cell} = E^\circ_{Cu^{2+}/Cu} - E^\circ_{Cd^{2+}/Cd}$

or, $E^\circ_{cell} = 0.34 - (-0.140)\ V$

or, $E^\circ_{cell} = 0.48\ V$

Now, Electrodic reactions,

Anodic reaction: $Cd \longrightarrow Cd^{2+} + 2e^-$

Cathodic reaction: $Cu^{2+} + 2e^- \longrightarrow Cu$

Net cell reaction: $Cd + Cu^{2+} \longrightarrow Cd^{2+} + Cu$

So, the no. of electrons involved (n) = 2.

Then, we have,

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF}\ln\frac{[Cd^{2+}]}{[Cu^{2+}]}$$

At 25°C, $E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Cd^{2+}]}{[Cu^{2+}]}$

Substituting for the respective values, we get,

$E_{cell} = 0.48 - \frac{0.0591}{2}\log$ [illegible]

$E_{cell} = 0.48 - (-0.05)\ V$

or, $E_{cell} = 0.53\ V$

Hence the emf of the cell is found to be 0.53 V.

2. Calculate the emf of the galvanic cell made by coupling two half cells viz. Cr/Cr^{3+}(0.5M) and Fe/Fe^{2+}(0.2M). Given that $E^\circ_{Cr/Cr^{3+}} = 0.75V$ and $E^\circ_{Fe^{2+}/Fe} = -0.44$ V. also write the cell notation, cell reaction and spontaneity of the reaction.

Solution:

Given, $E^\circ_{Cr/Cr^{3+}} = 0.75V$ i.e. $E^\circ_{Cr^{3+}/Cr} = -0.75V$

$E^\circ_{Fe^{2+}/Fe} = -0.44\ V$

Since the standard reduction potential of Cr is less than that of Fe i.e. $E^\circ_{Cr^{3+}/Cr} < E^\circ_{Fe^{2+}/Fe}$ Cr acts as anode and Fe acts as cathode. So, the cell notation is,

Cr/Cr^{3+}(0.5M)//Fe^{2+}(0.2M)/Fe

Now, we have,

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

or, $E^\circ_{cell} = E^\circ_{Fe^{2+}/Fe} - E^\circ_{Cr^{3+}/Cr}$

or, $E^\circ_{cell} = -0.44 - (-0.75)\ V$

or, $E^\circ_{cell} = 0.31\ V$

Now, Electrodic reactions,

Anodic reaction: $Cr \longrightarrow Cr^{3+} + 3e^-] \times 2$

Cathodic reaction: $Fe^{2+} + 2e^- \longrightarrow Fe] \times 3$

Net cell reaction: $2Cr + 3Fe^{2+} \longrightarrow 2Cr^{3+} + 3Fe$

No. of electrons involved (n) = 6

Then, emf of the cell at 25°C is given by Nernst's equation as,

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[Cr^{3+}]^2}{[Fe^{2+}]^3}$$

Substituting for the respective values, we get,

$E_{cell} = 0.31 - \frac{0.0591}{6}\log\frac{0.5^2}{0.2^3}$

or, $E_{cell} = 0.31 - 0.0078$

or, $E_{cell} = 0.302\ V$

Since the emf is positive, the cell reaction is spontaneous to generate the above potential.

3. Calculate the emf of the cell at 25°C made by coupling electrodes; Cr/Cr^{++} and Au/Au^{+++}. Given that the concentration of Cr^{2+} and Au^{+3} are 0.5 M and 0.08 M respectively.

$Cr^{+++} + 3e^- \rightarrow Cr$, $E^\circ = 0.50\ V$

$Cr^{+++} + e^- \rightarrow Cr^{++}$, $E^\circ = -0.41\ V$ and

$Au \rightarrow Au^{+++} + 3e^-$, $E^\circ = -1.42\ V$

Solution:

Here,

$Cr^{+++} + 3e^- \rightarrow Cr$, $E^\circ = 0.50\ V$

$Cr^{+++} + e^- \rightarrow Cr^{++}$, $E^\circ = -0.41\ V$

Subtracting 2nd from 1st reaction, we get

$Cr^{+++} + 3e^- \rightarrow Cr$, $E^\circ = 0.50\ V$

$Cr^{+++} + e^- \rightarrow Cr^{++}$, $E^\circ = -0.41\ V$

$- \quad - \quad - \quad -$

$2e^- \rightarrow Cr - Cr^{++}$, $E^\circ = 0.50-(-0.41)V = 0.91V$

or, $Cr^{++} + 2e^- \rightarrow Cr$, $E^\circ = 0.91V$

So, $E^\circ_{Cr^{2+}/Cr} = 0.91V$ and $E^\circ_{Au/Au^{3+}} = -1.42$ V or $E^\circ_{Au^{3+}/Au} = 1.42$ V.

Since the standard reduction potential of Cr is smaller than that of Au, Cr acts as anode.

Then, $E^\circ_{cell} = E^\circ_{Cathode} - E^\circ_{anode}$

$= 1.42 - 0.91$

= 0.51 V

Now,

Anodic reaction: $Cr \rightarrow Cr^{++} + 2e^-] \times 3$

Cathodic reaction: $Au^{+++} + 3e^- \rightarrow Au] \times 2$

Net reaction: $3Cr + 2Au^{+++} \rightarrow 3Cr^{++} + 2Au$

So, no. of electrons involved (n) = 6

Then, emf of the cell at 25°C is given by Nernst's equation as,

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

Substituting for the respective values, we get,

$E_{cell} = 0.51 - \frac{0.0591}{6} \log$ [illegible]

or, $E_{cell} = 0.51 - 0.0265$

or, $E_{cell} = 0.483$ V

Corrosion

The International Union of Pure and Applied Chemistry (IUPAC) defines corrosion as **"an irreversible interfacial reaction of materials (metallic, ceramic or polymer) with their environment which results in the destruction of materials".** This is a very broad definition that includes the corrosion of not only metallic substances but also any other materials used for engineering purposes.

In recent years, the definition of corrosion is restricted to the metals that **the destruction of metals or alloys due to their electrochemical reactions with the environment is known as corrosion.** ***Rusting is a common example of corrosion.***

Rusting is the corrosion of iron by which metallic iron is changed into hydrated form of ferric oxide ($Fe_2O_3.xH_2O$), which is called rust. Various theories are put forward regarding the rusting of iron. Among them, electrochemical theory of corrosion is the most accepted one. According to this theory, iron is non–homogeneous due to non-uniform distribution of impurities and strain in the iron crystal where by some portion of iron acts as anode that the oxidation of iron into ferrous ion takes place.

$Fe \rightarrow Fe^{2+} + 2e^-$ ....(1)

The electrons so liberated are migrated into the portion of iron having high potential that acts as cathode. The reduction of oxygen or other ions takes place.

$12 O_2 + H_2O + 2e^- \rightarrow 2OH^-$ .... (2)

$2H^+ + 2e^- \rightarrow H_2$ .... (3)

The H^+ ion necessary for reaction-3 is produced by self dissociation of water or by the interaction of CO_2 of air in water.

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

$CO_2 + H_2O \rightarrow H_2CO_3$

$H_2CO_3 \rightarrow H^+ + HCO_3^-$

In neutral medium, the reduction of oxygen is mostly occurred while in acidic medium, the reduction of H^+ ions is common.

The anodic and cathodic products now combine to form $Fe(OH)_2$.

$$Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$$

$Fe(OH)_2$ is rapidly oxidized to ferric hydroxide in the moist air,

$$2Fe(OH)_2 + \frac{1}{2}O_2 + H_2O \rightarrow 2Fe(OH)_3$$

Ferric hydroxide is unstable and changes into ferric oxide losing water molecule.

$$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$$

Ferric oxide absorbs moisture from air and forms a brown hydrated ferric oxide, called rust.

$$Fe_2O_3 + xH_2O \rightarrow \underset{\text{Rust}}{Fe_2O_3.xH_2O}$$

Importance of Corrosion Science and Engineering

Corrosion is an unavoidable process. The study of corrosion science is of central importance in many areas of engineering, science and technology. Corrosion is a major scientific and industrial problem whose effects are felt by many engineering, scientific and industrial processes. New chemical processes that look very attractive on paper are sometimes of no real value in practice because of the problem of corrosion. For example, if the equipment has to be replaced frequently due to corrosion damage, the system is not likely to be of industrial interest. Therefore all the sectors where the chemical or electrochemical or metallurgical processes are involved, the knowledge of corrosion scientists and engineers is essential to the success of the over all process for a long time. Corrosion experts are highly familiar with the dangers of different aggressive ion coming into contact with certain metals or alloys.

The lack of corrosion behavior of the engineering materials will be cause of wastage of much money, labor as well as degradation in quality of such materials in the short time. Therefore, the works of engineering and technology become unreliable without the testimony of corrosion properties of the materials by scientists. Early in the past, engineers did not take into consideration the importance of corrosion science during the initial designing of the materials with the thought that the problems arising from corrosion could be avoided by additional surface treatments. Whenever novel materials are developed, the industrial application for them depends on their corrosion behavior over extended period of services. The corrosion problems should be considered at an appropriate stage of the material development. Hence, corrosion research should be a part of engineering. In general, two things are to be significantly taken in mind before the engineering materials are subjected for application. Firstly, under what conditions it is used and secondly, how it is processed.

Corrosion research and engineering are closely linked with the development of a new technology. Corrosion scientists are concerned with the study of corrosion mechanisms through which a better understanding the causes of corrosion is obtained and the available means for preventing or minimizing corrosion damage. On the other hand, engineers apply accumulated scientific knowledge to control of corrosion damage by practical and economical means. Nowadays, it is apparent that corrosion is not only of interest to corrosion scientists and engineers but also to the industrialists, because material degradation is the problem that influences all areas of modern technology.

It is believed that the cost of corrosion is about 3-4% of the Gross National Products of the most industrialized countries. Moreover, it is assumed that about 40% of this GNP loss can be avoided by improving corrosion properties of engineering materials.

Types of Corrosion

By the mechanism of corrosion, it may be of two types.

i. Chemical or dry corrosion and
ii. Electrochemical or wet corrosion

i. Chemical or dry corrosion:

When a metal surface is exposed into atmospheric gases or anhydrous liquid, a direct chemical reaction between the two leads to chemical corrosion. It may be of following three types.

a. **Oxidation corrosion**- it is the corrosion by oxygen gas. It generally takes place in absence of moisture via

$$2M + nO_2 \rightarrow \underset{\text{Metal ion}}{2M^{n+}} + \underset{\text{oxide ion}}{2nO^{2-}} \rightarrow \underset{\text{metal oxide}}{M_2O_n}$$

b. **Corrosion by other gases**- the gases such as Cl_2, H_2S etc exert different extent of corrosive effect. Examples,

➢ $2Ag + Cl_2 \rightarrow 2AgCl$

AgCl film is protective and thus protects the metal from further attack of chlorine on silver.

➢ $Sn + 2Cl_2 \rightarrow SnCl_4$

$SnCl_4$ film is volatile and hence Sn undergoes excessive corrosion.

c. **Liquid metal corrosion**- It occurs when liquid metal is allowed to flow over solid metal at high temperature. It leads to weakening of the solid metal due to i) its dissolution in liquid metal or ii) penetration of liquid metal into solid metal. For example, sodium metal leads to corrosion to cadmium in nuclear reactor.

ii. Electrochemical or Wet corrosion:

There are mainly seven types of electrochemical corrosion on the basis of outward appearance of physical properties of the corroded materials.

1. Uniform or general corrosion

This type of corrosion is characterized by corrosive attack proceeding evenly over the entire surface area and general thinning takes place until failure. Schematic representation of uniform corrosion is shown below,

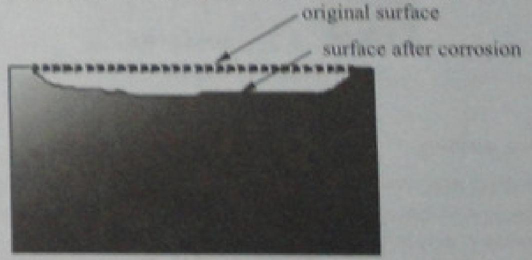


Fig: Uniform corrosion

2. Pitting corrosion

The corrosion which is localized into a particular point and leads to the formation of pits is called pitting corrosion. It is considered to be more dangerous than uniform corrosion because it is difficult to detect and causes unexpected failure. A small and narrow pit with minimum loss of metal can lead to the failure of an entire engineering system.

Fig: Pitting Corrosion

3. **Galvanic corrosion**

The corrosion which occurs when dissimilar metals are brought into contact in the presence of an electrolyte is known as galvanic corrosion. The metal which acts as anode undergoes dissolution (corrosion). Here, an electrochemical corrosion cell is said to be set up.

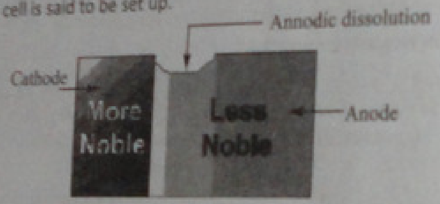


Fig: Galvanic Corrosion

4. **Selective leaching**

The selective removal of one element or phase from alloy by corrosion reaction leaving a porous material is known as selective leaching. Dezincification is a common example of selective leaching.

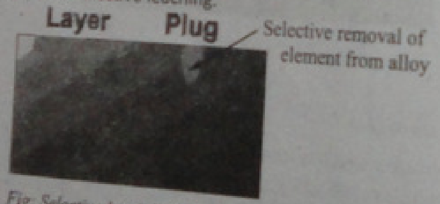


Fig: Selective leaching (dealloying)

5. **Intergranular corrosion**

Microscopic study of metals and alloys shows that these are made up of grains and are separated by grain boundaries. The corrosion which is localized along the grain boundaries is known as intergranular corrosion.

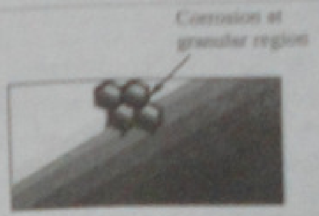


Fig: Intergranular corrosion

6. **Environmental cracking**

Environmental cracking (EC) is a very acute form of localized corrosion. Stress corrosion cracking (SCC), fatigue corrosion (FC) and hydrogen embrittlement (HE) are main three types of environmental cracking (EC). Description of all its types is beyond the scope of the course specified.

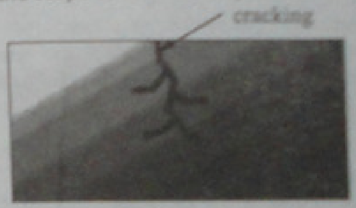


Fig: Stress corrosion cracking

7. **Crevice corrosion**

Crevice corrosion is a localized form of corrosion associated with a stagnant solution on the micro-environmental level. Such stagnant microenvironment occurs in the crevice region (e.g. Metallic joints, fastener heads).

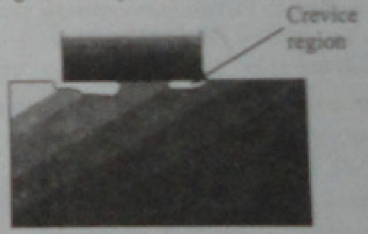


Fig: Crevice corrosion

Factors influencing corrosion

1. **Nature of the metal:** The nature of the metal is described in following several characteristics.
    i. **Position in galvanic series:** A series of metals or alloys according to their extent of corrosion in a given environment like sea-water is known as galvanic series. A part of galvanic series is shown as,

$\longrightarrow$

Mg, Mg alloys, Zn, Al, Cd, Al alloys, Mild steel, Cu, Ni, Au, Pt

When two metals or alloys are in electrical contact, the one higher up in the series suffers corrosion.

ii. **Overvoltage:** The reduction in overvoltage of the corroding metal/alloy accelerates the corrosion rate. Because of high overvoltage (0.70V), the effective electrode potential of zinc is reduced to a small value, that the rate of corrosion is slow. But if few drops of $CusO_4$ are added, the corrosion rate of zinc is accelerated because some copper gets deposited on the zinc surface forming minute cathodes, where the hydrogen overvoltage is only 0.33V.

iii. **Relative area of anodic and cathodic part:** Corrosion is more rapid and severe if the anodic region is small. The corrosion here is highly localized because the current density at a smaller anodic area is much greater and the demand for electrons can be met by smaller anodic areas undergoing severe corrosion.

iv. **Purity of metal:** Heterogeneity of the metal cause the formation of tiny electrochemical cells that anodic part gets corroded. The rate and extent of corrosion increases with the increasing exposure and extent of impurities. Therefore the corrosion resistance of a metal may be improved by increasing the purity.

v. **Physical state of metal:** The rate of corrosion is influenced by physical state of the metal such as grain size, orientation of crystal etc. The smaller the grain size greater is its solubility and hence corrosion. Further, the region of the metals under stress tends to be anodic and cause corrosion.

vi. **Nature of surface film:** If the surface film formed earlier by the oxidation reaction of metal/alloy is more passive and insoluble, this act as a barrier for further reaction. Thus the rate of corrosion is dramatically reduced. This is known as passivation.

vii. **Passive character of metal:** It is too very important character of the metal to determine its life span into the environmental exposure. Metals like Al, Tl, Ni and Co are passive and they exhibit high corrosion resistance than expected from galvanic series due to the formation of highly passive film on the metal surface.

viii. **Volatility of corrosion products:** If the product of corrosion is more volatile, it leaves the surface fresh to react with the environment and continues the corrosion. E.g., MoO_3 is volatile.

2. **Nature of corroding environment:** This may explained in terms of the several factors.

i. **Temperature:** With increase in the temperature of environment, the reaction as well as diffusion rate increase, thereby increasing the corrosion rate.

ii. **Humidity of air:** It is important factor in deciding atmospheric corrosion. Critical humidity is defined as the relative humidity above which the atmospheric corrosion rate of metal increases sharply. Since more humid air forms a medium between anodic and cathodic parts of the metals/alloys that makes process faster.

iii. **Presence of impurities in atmosphere:** The impurities in the atmosphere such as excess of CO_2, NO_x, SO_2 etc causes acid rain. The acid rain is more reactive to

the metals that it can readily damage the metallic parts exposed into the atmosphere.

iv. **Presence of suspended particle in atmosphere:** If the suspended particles in air are chemically active like NaCl, $(NH_4)_2SO_4$, they absorb moisture and acts as strong electrolyte thereby enhancing the corrosion.

v. **Influence of pH:** It depends on the characteristics of metal that it can be studied well from potential-pH diagram of metals. The metals highly corroded in low pH may be protected at high pH or vice versa. In general acidic media are more corrosive than neutral and alkaline media. However, the metals like Al, Pb, Cd etc dissolve in alkaline solutions as complex ions.

vi. **Nature of ions present:** Presence of anions like silicate leads to the formation of insoluble reaction products which reduces further corrosion. While some other ions like SO_4^{-}, Cl^- ions enhance the corrosion.

vii. **Conductance of the corroding medium:** In the corrosion of underground structures, the conductance of the medium is of prime importance. More corrosion is found in the good conducting medium (clayey and mineral soil).

viii. **Formation of oxygen concentration cell:** The more supply of oxygen/air into the moist metal surface, more sever the corrosion becomes as it enhances the cathodic reaction and there by pushing anodic dissolution.

$$2H_2O + O_2 + 2e^- \rightarrow 4OH^-$$

Electrons are supplied from anodic dissolution and

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

ix. **Polarization of electrodes**- The potential difference between the anode and cathode is the driving force of an electrochemical corrosion process, but the corrosion rate is controlled by the current flowing in the circuit.

Corrosion control

Since the cost of corrosion is so high that it becomes necessary for the development of the effective ways to prevent and control the corrosion. The commonly adopted methods to control the corrosion are mentioned as below.

1. Proper designing is the foremost thing to be considered when a metal that has to be used even if it has low corrosion resistance. The early damage and failure of the materials can be controlled by designing materials such that the anodic part has larger surface area and making it in contact with substances (materials) close potential so that the rate of corrosion will be controlled.
2. Using the pure metal as far as possible so that homogeneity of pure metal is maintained.
3. **Using metal alloys:** The corrosion resistance of the most metals is best increased by alloying them with suitable elements with high corrosion resistance. However, the alloys should be made much homogeneous as much as possible.
4. **Cathodic protection:** It is a widely used method to protect the large metallic substances under the ground. It is done by supplying electron currents into the material

so as to form cathode instead of anodic dissolution. This is carried out by two methods.

a. **Sacrificial anodic protection:** In this method, the metal to be protected is connected with the more electropositive metal both in the same medium, so that the next metal is corroded in order to protect another. Thus the method is called sacrificial anodic protection.

b. **Impressed current cathodic protection:** In this method, current is made to supply from external source by making a complete source using an inert electrode in the same medium. Where the metal to be protected is made cathode to prevent anodic dissolution.

5. **Application of protective coatings:**

a. Anodic coatings; e.g., galvanization.

b. Cathodic coatings: the coating with the inert and noble metal and prevent the metal to be exposed into the corroding medium.

c. Organic coatings such as paints are commonly applied to control corrosion of the metals as it prevents the metallic surface being directly exposed into the atmosphere.

6. **Use of inhibitors:** Any chemical substances that inhibit the anodic or cathodic reaction rate and so control the corrosion rate are known as corrosion inhibitors.

➢ **Anodic inhibitors like** chromates, phosphates, tungstates or other ions of transition element with high oxygen content. They react with the ions of the anode and produce insoluble precipitates. The precipitate so formed is absorbed on the metal surface, forming a protective film or barrier, thereby reducing the corrosion rate.

➢ **Cathodic inhibitors; any substances** which are capable of being adsorbed at the metal surface and slow down the cathodic reactions thereby reducing the corrosion rate. Antimony and arsenic oxides are cathodic inhibitors.

➢ **Vapour phase inhibitors are organic inhibitors** which readily sublime and form a protective layer on the metal surface. An example, dicyclohexylammonium nitrite is used for the protection of machineries and sophisticated equipments.

Practice Questions:

1. Define electrochemical cells. Distinguish its types.
2. How does electrode potential originate? Define standard electrode potential. Write the cell notation and cell reaction for Zn-Cu cell.[2+1+2] [IOE-'67]
3. What do you mean by single electrode potential? How do you measure standard potential of an electrode?
4. What is normal hydrogen electrode? Describe with its construction.
5. What is electrochemical series? Mention its applications.
6. What is Nernst's equation? Write its significance.
7. Construct a galvanic cell using the following metal electrodes,
   $E^\circ_{Ag^+/Ag} = 1.8V$ and $E^\circ_{Fe/Fe^{2+}} = 0.44V$
   Write the cell notation and cell reaction. Also calculate the emf of cell.
8. Calculate the emf of the following cell at 20°C. **[PU-2004, Fall]**
   $Zn/Zn^{++}(a=0.01)//Cu^{++}(a=0.1)/Cu$
   Given, $R = 8.314\ JK^{-1}mol^{-1}$ and $F = 96487\ Cmol^{-1}$.
   $Zn^{++} + 2e^- \rightarrow Zn\ (E^\circ = -0.763\ V)$
   $Cu^{++} + 2e^- \rightarrow Cu\ (E^\circ = +0.337\ V)$
9. Calculate the molarity of Fe^{2+} ion in the cell when iron electrode is coupled with standard AgCl/Ag, Cl^- electrode having emf 0.57 V of the cell. Given, $E^\circ_{AgCl,\ Cl^-} = 0.22V$ $E^\circ_{Fe/Fe^{2+}} = 0.44V$
10. From the given electrode couple, $E^\circ_{Fe^{2+}/Fe^{3+}} = -0.77V$, $E^\circ_{Cu^{2+}/Cu} = 0.34V$, calculate the emf of cell if the concentration of Fe^{2+}, Fe^{3+} and Cu^{2+} are 0.2M, 1M and 0.1M respectively. Also indicate the cell notation.
11. What is meant by Normal Hydrogen Electrode? Calculate the emf of the following cell at 25°C, $Mg/Mg{+}{+}(0.1M)//Ag{+}(1M)/Ag$.
    Given $E^\circ_{Mg^{2+}/Mg} = -2.37V$ and $E^\circ_{Ag/Ag^+} = -0.80V$. **[IOE-'68]**
12. Give electrochemical mechanism of corrosion. What are the important measures to control corrosion?
13. What is standard electrode potential? How would you measure the EMF of copper where it functions as cathode? Calculate the emf of a galvanic cell prepared by dipping metallic zinc plate into 0.1 M zinc nitrate solution and lead plate into 0.02 M lead nitrate solution at 25oC and connected externally by means of a wire and internally by means of the salt bridge. Given;
    $E^\circ_{Zn^{++}/Zn} = -0.76\ V$, $E^\circ_{Pb^{++}/Pb} = -0.13\ V$, $R = 8.314\ JK^{-1}mol^{-1}$ and $F = 96487\ Cmol^{-1}$.
    [PU-2004, Fall]

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Chapter

2

Ionic Equilibria & Buffer Solutions

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Strong and weak electrolytes

Any materials which are ionized in water and can conduct electricity through their aqueous solution are known as electrolytes and those which aren't ionized in solution and the solution cannot conduct electricity are known as non-electrolytes. The electrolytes are categorized into two groups according to the extent of dissociation in any volume of solution.

i. Strong electrolytes and
ii. Weak electrolytes

Strong electrolytes are those electrolytes which are completely ionized in any volume of solution. All inorganic salts, mineral acids and alkalies are the common example of strong electrolytes.

Strong acids:	HCl, HBr, HI, HNO_3, H_2SO_4 etc
Strong alkalies:	LiOH, NaOH, KOH, $Ca(OH)_2$ etc
Salts:	NaCl, KCl, KNO_3, K_2SO_4, Na_2SO_4, $CaCl_2$ etc

Weak electrolytes are those which are only feebly or partially ionized in a certain volume of solution. Generally, most organic acids are weak electrolytes.

Weak acids:	HCOOH, CH_3COOH, HCN etc
Weak alkalies:	NH_4OH, $Al(OH)_3$, $Fe(OH)_3$ etc

Auto ionization of water and its ionic product

Water is also a very weak electrolyte and it just slightly ionizes as,

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

Since the hydrogen ion is readily combined with the water molecule, the ionization of water molecule is better represented as,

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

According to the law of mass action,
Equilibrium constant is given by, $K = [H3O+]\ [OH-][H2O]2$
$\text{or, } K \times [H_2O]^2 = [H_3O^+][OH^-]$

Since water is in excess its concentration can be considered as constant. So, the product of equilibrium constant and concentration of water is also a constant, say K_w. That means, $K_w = K \times [H_2O]^2$, this is known as the ionic product of water. Now, ionic product of water is given by,

$$K_w = [H_3O^+]\,[OH^-]$$

Experiments have shown that, pure water consists equal number of OH^- and H_3O^+ ions. At 25°C, this is found as,

$$[H_3O^+] = [OH^-] = 1.7 \times 10^{-7} \text{ mole/litre}$$

Thus from the equation of ionic product of water,

$$\begin{aligned} K_w &= (1.0 \times 10^{-7})(1.0 \times 10^{-7}) \\ &= 1.0 \times 10^{-14} \end{aligned}$$

Ostwald's dilution law

This law deals with the change in degree of ionization of electrolytes in different dilution. This is the application of the law of mass action to the ionic equilibrium.

Let us consider the ionization of a binary electrolyte AB in the solution of concentration C mole/litre. Suppose the degree of ionization of electrolyte is α.

$$\begin{array}{lccc} & AB & \rightleftharpoons & A^+ + B^- \\ \textit{Initially C moles/l} & & 0 & 0 \\ \textit{At equilibrium,} & C - C\alpha & C\alpha & C\alpha \end{array}$$

Thus, the concentration of AB, A^+ and B^- in the solution at equilibrium is,

$$[AB] = C - C\alpha,\ [A^+] = C\alpha \text{ and } [B^-] = C\alpha$$

Applying law of mass action to the equilibrium, the equilibrium constant of the electrolyte is given by,

$$K = \frac{[A^+][B^-]}{[AB]} \text{ .... (1)}$$

Substituting their concentration, $K = \dfrac{C\alpha C\alpha}{C(1-\alpha)}$

$$\text{Or, } K = \frac{C\alpha^2}{(1-\alpha)} \text{ .... (2)}$$

This equation represents the variation of degree of ionization of an electrolyte with the change in its concentration. This is known as Ostwald's dilution law.

For weak electrolytes, the value of α is very small as compared to 1 and hence it can be neglected. That is, $1-\alpha \approx 1$. Thus, equation (2) becomes,

$$K = C\alpha^2$$

$$\text{Or, } \alpha^2 = \frac{K}{C}$$

$$\text{Or, } \alpha\ \alpha \frac{1}{\sqrt{c}} \text{ ....(3)}$$

Thus, the degree of ionization of weak electrolyte is inversely proportional to square root of its concentration. That means the degree of ionization of weak electrolytes increases with the decrease of its concentration and vice–versa. In other word, the degree of ionization of weak electrolyte increases with the increase of its dilution.

For strong electrolytes, α is significantly large and cannot be neglected comparing to one.

Limitations of Ostwald's dilution law

The value of dissociation constant K for a particular weak electrolyte is always constant as given by Ostwald's dilution law. That is, every weak acid or base has a fixed value of K disregarding the concentration of the solution. The degree of ionization (α) of weak electrolytes increases with the increase of dilution but dissociation constant K remains constant. **Experimental study of the dissociation of electrolytes at different dilution shows that the weak electrolytes obey this law fairly well but the strong electrolytes do not.** This is because the strong electrolytes are fully ionized at all dilution and hence α is equal to one. Then, the value of K does not remain constant at all dilution but falls rapidly with the dilution.

pH and pH scale

pH is a term introduced by Sorenson (1909) in order to define the acidity or alkalinity of the solution. Mathematically, it is defined as the negative logarithm of the molar concentration of H^+ or H_3O^+ ions in the aqueous solution. i.e.

$$pH = -\log_{10}[H^+]$$

Thus, the indication p stands for the negative logarithm of the symbol. So,

$$pOH = -\log_{10}[OH^-]$$

Similarly,
$$pK_a = -\log K_a \quad \text{and}$$
$$pK_b = -\log_{10} K_b$$

Relation between pH and pOH:

From the auto ionization of water, we have, at 25°C

$$[H^+][OH^-] = 1.0 \times 10^{-14}$$

Taking $\log_{10}$ on both sides, we get,

$$\log_{10}[H^+] + \log_{10}[OH^-] = \log_{10}[1.0 \times 10^{-14}]$$

Reversing the sign,

$$-\log_{10}[H^+] - \log_{10}[OH^-] = -\log_{10}[1.0 \times 10^{-14}]$$

Thus, using the indication p for $-\log_{10}$, we get,

$$pH + pOH = 14$$

This shows that an aqueous solution can have maximum of pH or pOH just 14. Hence, in terms of the pH value of solutions, the solutions are categorized as,

Neutral solutions: $[H^+] = [OH^-] = 1.0 \times 10^{-7}$ M i.e. pH = pOH = 7

Acidic solutions: $[H^+] > 1.0 \times 10^{-7}$ M i.e. pH < 7

Alkaline solutions: $[H^+] < 1.0 \times 10^{-7}$ M i.e. pH > 7

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pH scale: As the pH value of an aqueous solution can vary from 0 (i.e. 1M concentration of H^+ ion, as in 1M HCl) to 14 (i.e. 10^{-14}M concentration of H^+ ion, as in 1M NaOH). A scale designed by computing the pH values from 0 to 14 is known as pH scale. This is shown in the figure as below,

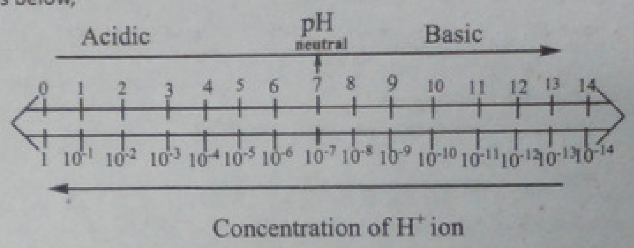


Fig: pH scale

Thus, acidic or basic strength of the solutions are defined in terms of their respective pH values as,

Solutions	Strongly acidic	Moderately acidic	Weakly acidic	Neutral	Weakly alkaline	Moderately alkaline	Strongly alkaline
pH values	0 – 2	2 – 4	4 – 7	7	7 – 10	10 – 12	12 – 14

Determination of pH value:

pH value of a solution can be determined by using a pH meter or by using the indicator method. By using a pH meter, one can get exact pH value of the solution but by using universal indicator, one can just obtain the approximate pH of the solution since it is determined by the method of best match of colour between a solution of unknown pH and one that of the series of solutions of known pH. Equal number of drops of universal indicator is used in each of the solutions used.

Universal indicator is a mixture of several acid-base indicators that can show several colour changes over a wide range of pH values.

Numericals:

1. **Calculate the pH of 0.05N H_2SO_4 solution assuming that it ionizes completely in the solution.**

Solution:

Here

$[H_2SO_4]$ = 0.05 N = 0.05 M

This is ionized in the solution as follows,

$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{--}$$

initially, 0.025 M $\quad 0 \quad 0$

finally, $0 \quad 2 \times 0.025$ M $\quad 0.025$ M

Therefore, $[H^+] = 2 \times 0.025 \text{ M} = 0.05 \text{ M}$

Then, we have, $pH = -\log_{10}[H^+] = -\log_{10}[0.05]$

$= 1.301$

In actual, H_2SO_4 ionizes in two steps as,

1st $\quad H_2SO_4 \longrightarrow H^+ + HSO_4^-$

2nd $\quad HSO_4^- \rightleftharpoons H^+ + SO_4^{--}$

2. What would be the pH of 0.2 M formic acid? Given that Ka = 1.74×10^{-5} at 25°C.

Solution:

Here

$[HCOOH] = 0.2$ M

Since it is a weak acid and its dissociation may be shown as,

$$HCOOH \rightleftharpoons H^+ + HCOO^-$$

Initially, 0.2 M $\quad 0 \quad 0$

Finally, $0.2 - 0.2\alpha \quad 0.2\alpha \quad 0.2\alpha$

Thus, α has to be determined to obtain the exact concentration of H^+ ion in the solution.

Using Ostwald's dilution law,

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.74 \text{x} 10^{-5}}{0.2}} = 9.3 \times 10^{-3}$$

So, $[H^+] = 0.2\alpha = 0.2 \times 9.3 \times 10^{-3} = 1.86 \times 10^{-3}$ M

Then, $pH = -\log_{10}[H^+] = -\log_{10}[1.86 \times 10^{-3}]$

$= 2.73$

Common ion effect in ionic equilibria:

The suppression of the degree of ionization of weak electrolytes due to the presence of a strong electrolyte having a common ion is known as common ion effect. This effect works

on the basis of Le-Chatelier's principle.

Let us take a weak base, NH_4OH that feebly ionizes in the solution as,

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Suppose, a strong electrolyte having a common ion to above is NH4Cl and it is added into above solution. It is ionized as follow,

$$NH_4Cl \longrightarrow NH_4^+ + Cl^-$$

In the above solution, a common ion from both the electrolytes is NH_4^+. Now, due to the large concentration of NH_4^+ ions from NH_4Cl, the equilibrium shifts to the left forming unionized NH_4OH molecules. Thus, the ionization of NH_4OH is reduced to a certain extent by the presence of a common ion from next strong electrolyte. This is known as common ion effect.

This may be illustrated by the following example.

- **Find the degree of ionization of 0.2 M acetic acid alone and in the presence of 0.3 M sodium acetate. Given Ka = 1.8×10^{-5}.**

1st case,

Concentration of acetic acid (C) = 0.2 M

Dissociation constant of acid (K_a) = 1.8 × 10–5

Using Ostwald's dilution law, degree of ionization $(\alpha) = \sqrt{\frac{K_a}{C}}$

$= \sqrt{\frac{1.8 \text{x} 10^{-5}}{0.2}}$

$= 9.48 \times 10^{-3}$

$= 0.95\%$

2nd case,

Sodium acetate is completely ionized as,

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+$$

initially, 0.4 M $\quad 0 \quad 0$

finally, $0 \quad 0.4$ M $\quad 0.4$ M

And the acetic acid is ionized as,

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

initially, 0.2 M $\quad 0 \quad 0$

0.2α 0.2α

Finally, $0.2-0.2\alpha$

Now, we have

$$\text{Equilibrium constant } (K_a) = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{(0.4+0.2\alpha)(0.2\alpha)}{0.2(1-\alpha)}$$

Since α is very small in comparison to one, i.e. $\alpha <<< 1$, $1-\alpha \approx 1$ and α^2 is negligible, then $K_a = 0.4\,\alpha$

$$1.8 \times 10^{-5} = 0.4\,\alpha$$

$$\text{or,}\quad \alpha = \frac{1.8\text{x}10^{-5}}{0.4} = 4.5 \times 10^{-5} = 0.0045\%$$

This clearly shows that the degree of ionization of acetic acid is reduced to 0.0045% from 0.95% by the presence of a strong electrolyte (CH_3COONa) having a common ion, CH_3COO^-.

Buffer solution

Introduction

In general the pH of a solution alters by the addition of small amount of acids or bases into it. In most of the laboratory and industrial experiments, it becomes necessary to carry out the chemical reactions at almost constant pH. This is made possible by the use of buffer solution.

A solution that can resist the change in pH and tends to maintain its pH almost to a constant value even after the addition of small amount of acid or base is known as buffer solution.

According to the composition, buffer solutions are the equimolar mixture of weak acid and its ionic salt or weak base and its ionic salt.

Sea water and blood are the natural buffers. Human blood has pH value about 7.40. Blood plasma in the living system resists the change in its pH value even by the intake of acidic or basic foods. The pH of blood is maintained by buffer action of carbonic acid (H_2CO_3), salts of bicarbonate ion (HCO_3^-) and carbon dioxide.

Sea water has a pH of about 8.2 and it is maintained by the complex buffer action of various salts and weak bases present in the sea water.

Depending on the pH values, buffer solutions are divided into two classes.

i. Acidic buffer

ii. Basic buffer

i. **Acidic buffer:** The buffer solution made by mixing equimolar concentrations of weak acid and its strong salt solution is known as acidic buffer. It has the pH below 7. For example,

- The mixture of acetic acid and sodium acetate solutions

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad \text{(partially ionized)}$$
$$CH_3COONa \longrightarrow CH_3COO^- + Na^+ \quad \text{(completely ionized)}$$

- The mixture of formic acid and sodium formate solutions etc.

$$HCOOH \rightleftharpoons HCOO^- + H^+ \quad \text{(partially ionized)}$$
$$HCOONa \longrightarrow HCOO^- + Na^+ \quad \text{(completely ionized)}$$

ii. **Basic buffer:** The buffer solution made by mixing equimolar concentrations of weak base and its strong salt solution is known as basic buffer. For example,

- The mixture of ammonium hydroxide and ammonium chloride solutions

$$NH_4OH \rightleftharpoons NH_4^+ + OH^- \quad \text{(partially ionized)}$$
$$NH_4Cl \longrightarrow NH_4^+ + Cl^- \quad \text{(completely ionized)}$$

- The mixture of methyl amine and methyl ammonium chloride.

Mechanism of buffer action:

The ability of a buffer solution to resist the change in pH on addition of small amount of acid or base is called **buffer action**. The buffer works in effect of common ion (common ion effect) as required by Le-Chatelier's principle.

Let us take an example of acidic buffer, a mixture of acetic acid and sodium acetate solution having acetate ion (CH3COO⁻) as a common ion. Individually, these are ionized in the solution as follows,

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad \text{(partially ionized)}$$
$$CH_3COONa \longrightarrow CH_3COO^- + Na^+ \quad \text{(completely ionized)}$$

Addition of strong acid solution:

When a few drops of HCl are added to this buffer solution, it provides H+ ions as it dissociates completely in the solution as follows,

$$HCl \longrightarrow H^+ + Cl^-$$

These H^+ ions combine with the acetate ions to form unionized acetic acid shifting the equilibrium to the left as required by the Le-Chatelier's principle, thus maintaining the pH almost constant.

$$CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$$

However owing to the increased concentration of unionized CH_3COOH, the equilibrium shifts slightly to the right to increase H^+ ions. This causes the marginal increase of pH of the buffer on addition of HCl.

Addition of strong alkali solution:
When a few drops of NaOH are added to this buffer solution, it releases OH^- ions as it is dissociated completely in the solution as follows,

$$NaOH \longrightarrow Na^+ + OH^-$$

These OH^- ions combine with the H^+ ions of buffer to form unionized water molecules. This causes the greater ionization of CH_3COOH in order to restore the concentration of H^+ ions to its initial level thus shifting the equilibrium to the right as required by the Le-Chatelier's principle. Therefore, the pH value remains almost unchanged.

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

However, the pH of buffer is slightly increased because the concentration of CH_3COOH and hence the H^+ ions is slightly lower in the buffer by the addition of NaOH.
Diagrammatically, the mechanism of action of acidic buffer may be shown as,

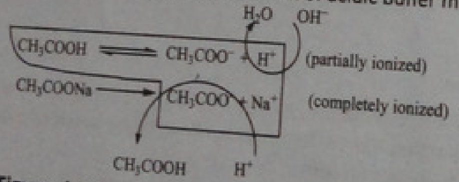


Fig: mechanism of the action of acidic buffer

In basic buffer, let us take the equimolar mixture of ammonium chloride and ammonium hydroxide. These are ionized in the solution as follows,

$$NH_4OH \rightleftharpoons NH_4^+ + OH^- \quad \text{(partially ionized)}$$
$$NH_4Cl \longrightarrow NH_4^+ + Cl^- \quad \text{(completely ionized)}$$

Addition of strong acid solution:
When a few drops of HCl are added, the added concentration of H+ ions are neutralized by OH– ions in buffer forming neutral unionized water molecules.

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

The so reduced concentration of OH^- ions is restored by the further ionization of NH_4OH thus shifting the equilibrium to the right as required by Le-Chatelier's principle. Therefore, the pH of the solution remains almost unchanged. In actual, the pH of buffer is slightly decreased because of slightly lowered concentration of NH_4OH and hence the OH^- ions.

Addition of strong alkali solution:
If few drops of NaOH are added, the added concentration of OH^- ions combine with NH_4^+ ions to form unionized NH_4OH molecules shifting the equilibrium to the left as required by Le-Chatelier's principle. Thus the pH of the solution remains approximately constant.

$$NH_4^+ + OH^- \rightleftharpoons NH_4OH$$

But in real, the pH of buffer is slightly increased because of the increased concentration of NH_4OH by the addition of NaOH and hence the slightly higher concentration of OH^- ions.
Diagrammatically, the mechanism of the action of basic buffer may be shown as,

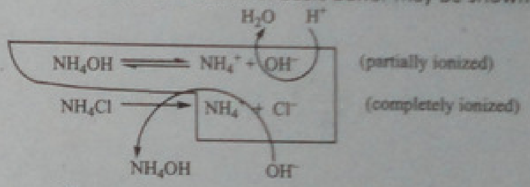


Fig: mechanism of the action of basic buffer

Calculation of pH of the buffer solutions:
The pH of buffer solution is more easily calculated by using **Henderson's equation.**
Henderson's equation for acidic buffer is derived as follows,
Let us consider an acidic buffer containing the weak acid HA and its ionic salt NaA. These are ionized in the solution as given by,

$$HA \overset{K_a}{\rightleftharpoons} H^+ + A^- \quad \text{(partially ionized)}$$
$$NaA \longrightarrow Na^+ + A^- \quad \text{(completely ionized)}$$

Where, K_a is the dissociation constant of weak acid. It is given by,

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$\text{or,} \quad [H^+] = K_a \frac{[HA]}{[A^-]} \quad \text{.....................} (1)$$

Taking logarithm of base 10 on both sides,

$$\log[H^+] = \log K_a + \log \frac{[HA]}{[A^-]}$$

Reversing the sign, we get

$$-\log[H^+] = -\log K_a - \log \frac{[HA]}{[A^-]} \text{ .... (2)}$$

But we know,

$$-\log[H^+] = pH \text{ and } -\log Ka = pK_a$$

Then equation (2) can be written as,

$$pH = pK_a - \log \frac{[HA]}{[A^-]}$$

$$\text{or,} \quad pH = pK_a + \log \frac{[A^-]}{[HA]}$$

Since, the acid is weak, $[A^-]$ is almost equal to the concentration of salt, [NaA], then, we get,

$$pH = pK_a + \log \frac{[salt]}{[acid]} \text{ .... (3)}$$

This is the required Henderson-Hasselbalch equation or more commonly called Henderson's equation for acidic buffer.

Henderson's equation for basic buffer is derived as follows,

Let us consider a basic buffer containing the weak base BOH and its ionic salt BCl. These are ionized in the solution as given by,

$$BOH \overset{K_b}{\rightleftharpoons} B^+ + OH^- \quad \text{(partially ionized)}$$

$$BCl \longrightarrow B^+ + Cl^- \quad \text{(completely ionized)}$$

Where, K_b is the dissociation constant of weak base. It is given by,

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

$$\text{or,} \quad [OH^-] = K_b \frac{[BOH]}{[B^+]} \text{ .... (1)}$$

Taking logarithm of base 10 on both sides,

$$\log[OH^-] = \log K_b + \log \frac{[BOH]}{[B^+]}$$

Reversing the sign, we get

$$-\log[OH^-] = -\log K_b - \log \frac{[BOH]}{[B^+]} \text{ .... (2)}$$

But we know,

$$-\log[OH^-] = pOH \text{ and } -\log K_b = pK_b$$

Then equation (2) can be written as,

$$pOH = pK_b - \log \frac{[BOH]}{[B^+]}$$

$$\text{or,} \quad pOH = pK_b + \log \frac{[B^+]}{[BOH]}$$

Since, the base is weak, $[B^+]$ is almost equal to the concentration of salt, [BCl], then, we get,

$$pOH = pK_b + \log \frac{[salt]}{[base]} \text{ .... (3)}$$

This is the required Henderson–Hasselbalch equation or more commonly called Henderson's equation for basic buffer. Then, pH of basic buffer is given by,

$$pH = 14 - pOH$$

Significances of Henderson's equation:

1. The pH of a buffer solution can be calculated from the initial concentration of the weak acid and the salt provided the dissociation constant of acid, K_a. However, the Henderson's equation of basic buffer will give pOH and then pH = 14– pOH.
2. The dissociation constant of weak acid (or base) can be determined by measuring the pH of a buffer solution containing equimolar concentration of the acid (or base) and the salt.

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

Since [acid] = [salt], then

$$\text{or,}\quad pH = pK_a + \log 1$$

$$\text{or,}\quad pH = pK_a$$

The measurement of pH therefore gives the value of pK_a of acid which ultimately gives the dissociation constant of acid. Similarly, the pK_b of weak base can also be obtained taking equimolar mixture of weak base and salt.

3. A buffer solution of desired pH can be prepared by adjusting the concentration of the salt and the acid added for the buffer.

Numerical problems based on Henderson's equation:

Problem 1. Calculate the pH of a buffer consisting 0.3M CH_3COOH and 0.5M CH_3COONa. Ka = $1.8x10^{-5}$

Solution:

Here,

$[CH_3COOH]$ = 0.3M

$[CH_3COONa]$ = 0.5M

Dissociation constant of acetic acid, Ka = $1.8x10^{-5}$

Now we know that, $pK_a = -\log K_a$

$= -\log (1.8x10^{-5})$

$= 4.74$

Then, we have,

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

$$\text{or,}\quad pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$

$$\text{or,}\quad pH = 4.74 + \log\frac{[0.5]}{[0.3]}$$

$$\text{or,}\quad pH = 4.74 + 0.22$$

$$\text{or,}\quad pH = 4.96$$

Hence, the pH of buffer is found to be 4.96.

Problem 2. 100 ml of 0.2M acetic acid solution is mixed with 300ml of 0.3M sodium acetate solution. Calculate the pH of resulting mixture. pK_a = 4.74

Solution:

Here,

Volume of 0.2M acetic acid mixed = 100 ml

Volume of 0.3M sodium acetate mixed = 300 ml

So, the total volume of the mixture = 100 ml + 300 ml

= 400 ml

Now, the concentration of acetic acid in mixture is given by,

$$[CH_3COOH] = \frac{100x0.2}{400}$$

$$= 0.05M$$

$$\text{Similarly,}\quad [CH_3COONa] = \frac{300x0.3}{400}$$

$$= 0.225M$$

Then, we have,

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

$$\text{or,}\quad pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$

$$\text{or,}\quad pH = 4.74 + \log\frac{[0.225]}{[0.05]}$$

$$\text{or,}\quad pH = 4.74 + 0.65$$

$$\text{or,}\quad pH = 5.39$$

Hence, the pH of the resulting mixture is 5.39.

Problem 3. Calculate the concentration of ammonium chloride required to produce the pH of resulting mixture 10 with 0.2M ammonium hydroxide. $K_b = 1.8 \times 10^{-5}$

Solution:

Here,

$$[NH_4OH] = 0.2M$$
$$\text{pH of resulting buffer} = 10$$
$$\text{Dissociation constant of } NH_4OH,\ K_b = 1.8 \times 10^{-5}$$
$$[NH_4Cl] = ?$$

Now, $pK_b = -\log K_b$

$= -\log(1.8 \times 10^{-5})$

$= 4.74$

We have, $pH + pOH = 14$

or, $pOH = 14 - pH$

so, $pOH = 14 - 10 = 4$

Then, from Henderson's equation,

$$pOH = pK_b + \log\frac{[salt]}{[base]}$$

$$\text{or, } pOH = pK_b + \log\frac{[NH_4Cl]}{[NH_4OH]}$$

$$\text{or, } 4 = 4.74 + \log\frac{[NH_4Cl]}{[0.2]}$$

$$\text{or, } \log\frac{[NH_4Cl]}{[0.2]} = 4 - 4.74 = -0.74$$

$$\text{or, } \frac{[NH_4Cl]}{[0.2]} = \text{antilog}(-0.74) = 0.182$$

$$\text{or, } [NH_4Cl] = 0.182 \times 0.2 = 0.0364M$$

Hence, the required concentration of ammonium chloride is 0.0364M.

Problem 4. The pH of a buffer solution containing 0.2 mole/litre of CH_3COOH and 0.2 mole/litre of CH_3COONa has been found to be 4.74. What will be the pH of this solution when 0.1 ml of 0.1 M HCl is added into it? Assume that the volume is unchanged. $pK_a = 4.74$

Solution:

Since acetic acid is weakly ionized and sodium acetate is completely ionized, the concentration of acetate ion is almost equal to the concentration of sodium acetate.

The added concentration of acid (i.e. H^+) is consumed by acetate ion.

$$HCl + CH_3COONa \rightleftharpoons CH_3COOH + NaCl$$

Initially, 0.1M 0.2M 0.2M

Finally, 0 (0.2 − 0.1)M (0.2 + 0.1)M

Therefore, the concentration CH_3COOH and CH_3COONa in the new equilibrium are found as,

$$[CH_3COOH] = (0.2 + 0.1)M = 0.3M$$
$$[CH_3COONa] = (0.2 - 0.1)M = 0.1M$$

Then, the pH of buffer is corresponded by these concentration terms.

We have,

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

$$\text{or, } pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$

$$\text{or, } pH = 4.74 + \log\frac{[0.1]}{[0.3]}$$

$$\text{or, } pH = 4.74 + (-0.47)$$

$$\text{or, } pH = 4.26$$

Hence, the pH of buffer after the addition of acid is reduced to 4.26.

Problem 5. Calculate the pH of a solution made by adding 100 ml of 0.05M HCl into 100 ml of 0.2 N ammonia solution. $K_b = 1.75 \times 10^{-5}$.

Solution:

Here, dissociation constant of ammonia solution, $K_b = 1.75 \times 10^{-5}$

So, $pK_b = -\log K_b = -\log(1.75 \times 10^{-5}) = 4.75$

In the mixture, total volume = 100 ml + 100ml = 200ml

$$\text{Then, } [HCl] = \frac{100 \times 0.05}{200} M = 0.025M$$

$$[NH_4OH] = \frac{100 \times 0.2}{200} M = 0.1M$$

Now, as soon as the acid is added into the ammonia solution, following reaction occurs,

	HCl	+ NH_4OH	→ $NH_4Cl + H_2O$
Initially,	0.025M	0.1M	0
Finally,	0	(0.1 − 0.025)M	0.025M

Therefore, after the reaction, concentration of NH4OH and NH4Cl are found as,

$[NH_4OH] = (0.1 - 0.025)M = 0.075M$

$[NH_4Cl] = 0.025M$

Then, we have,

$$
\begin{aligned}
pOH &= pK_b + \log\frac{[salt]}{[base]}\\
\text{or,}\quad pOH &= pK_b + \log\frac{[NH_4Cl]}{[NH_4OH]}\\
\text{or,}\quad pOH &= 4.75 + \log\frac{[0.025]}{[0.075]}\\
\text{or,}\quad pOH &= 4.75 + (-0.477)\\
\text{or,}\quad pOH &= 4.27\\
\text{Therefore,}\quad pH &= 14 - pOH\\
&= 14 - 4.27 = 9.72
\end{aligned}
$$

Hence the pH of the resultant mixture is 9.72.

Problem 6. What would be the pH of 100 ml solution made by dissolving 0.5 mole of sodium acetate and 0.2 mole of acetic acid? Calculate the pH of solution if 1 ml of 0.5 M HCl is added into it neglecting the volume change by addition of HCl. pKa = 4.74.

Solution:

Here,

no. of moles of CH_3COONa = 0.5 mole

No. of moles of CH_3COOH = 0.2 mole

Volume of the solution = 100ml

Then, molar concentration of acetic acid, $[CH_3COONa] = \frac{\text{no. of moles}}{\text{vol. in liter}}$

$$= \frac{0.5}{100/1000}\,M$$

$$= 5\,M$$

Similarly, $[CH_3COOH] = \frac{0.2}{100/1000}\,M = 2\,M$

Then, we have,

$$
\begin{aligned}
pH &= pK_a + \log\frac{[salt]}{[acid]}\\
\text{or,}\quad pH &= pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}\\
\text{or,}\quad pH &= 4.74 + \log\frac{[5]}{[2]}\\
\text{or,}\quad pH &= 4.74 + (0.397)\\
\text{or,}\quad pH &= 5.138
\end{aligned}
$$

When 1 ml of 0.5 M HCl is added into the solution assuming no change in total volume, the concentration of acetate ion is reduced and concentration of acetic acid is increased because of the following reaction.

Molar concentration of HCl in the mixture = $\frac{0.5x1}{100}$ M = 0.005 M

	H^+	+ CH_3COO^-	→ CH_3COOH
Initially,	0.005M	5M	2M
Finally,	0	(5-0.005)M	(2+0.005)M

So, the concentrations of the salt and acid in the new equilibrium are found as,

$[CH_3COONa] = (5-0.005)M = 4.995\,M$

$[CH_3COOH] = (2+0.005)M = 2.005\,M$

Then pH of the solution is given by,

$$
\begin{aligned}
pH &= pK_a + \log\frac{[salt]}{[acid]}\\
\text{or,}\quad pH &= pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}\\
\text{or,}\quad pH &= 4.74 + \log\frac{[4.995]}{[2.005]}\\
\text{or,}\quad pH &= 4.74 + (0.396)\\
\text{or,}\quad pH &= 5.136
\end{aligned}
$$

Hence, by the addition of 1 ml of 0.5 M HCl into the buffer solution the pH is reduced to 5.136.

Problem 7. Calculate the pH of a solution resulted by adding 0.1 gm of NaOH into 100 ml of 0.1M acetic acid solution. Given that the pKa for acid is 4.74.

Solution:

Here,

$$\text{weight of NaOH added} = 0.1\text{gm}$$

$$\text{So, no. of moles of NaOH added} = \frac{\text{weight of NaOH}}{\text{mol.Wt.of NaOH}}$$

$$= \frac{0.1}{40}$$

$$= 0.0025 \text{ moles}$$

$$\text{Then, molar concentration of NaOH, [NaOH]} = \frac{0.0025}{100/1000}\text{ M}$$

$$= 0.025\text{M}$$

Now, as soon as NaOH is added into the solution of acetic acid, it reacts as follows.

$$\underset{0.025M}{NaOH} + \underset{0.025M}{CH_3COOH} \rightarrow \underset{0.025M}{CH_3COONa} + H_2O$$

Therefore, finally the concentration of acetic acid is reduced by 0.025M and same concentration of sodium acetate is formed. This is given by,

$[CH_3COOH] = (0.1 - 0.025)M = 0.075M$

$[CH_3COONa] = 0.025M$

Then, we have,

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

$$\text{or,}\quad pH = pK_a + \log\frac{[CH_3COONa]}{[CH_3COOH]}$$

$$\text{or,}\quad pH = 4.74 + \log\frac{[0.025]}{[0.075]}$$

$$\text{or,}\quad pH = 4.74 + (-0.477)$$

$$\text{or,}\quad pH = 4.26$$

Hence, the pH of resultant solution is 4.26.

Problem 8. Calculate the pH of resulting solution when 0.005 mole of KOH is added to 200ml of 0.1N formic acid solution. Given Ka = 1.75×10^{-5}.

Solution:

it is same as previous.

Problem 9. What would be the change in pH of buffer solution made by mixing 100 ml of 0.4M formic acid and 200 ml of 0.2M sodium formate after the addition of 5 ml of 0.2M of HCl. Ka = $1.75\text{x}10^{-5}$.

Solution:

Here,

Case I, Total volume of the mixture = 100 + 200 ml = 300 ml

$$\text{So,}\quad [HCOOH] = \frac{100\text{x}0.4}{300}\text{ M} = 0.133\text{ M}$$

$$[HCOONa] = \frac{200\text{x}0.2}{300}\text{ M} = 0.133\text{ M}$$

$K_a = 1.75\text{x}10^{-5}$, then $pK_a = -\log K_a = -\log 1.75 \times 10^{-5} = 4.75$

Now, we have,

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

$$\text{or,}\quad pH = pK_a + \log\frac{[HCOONa]}{[HCOOH]}$$

$$\text{or,}\quad pH = 4.75 + \log\frac{[0.133]}{[0.133]}$$

$$\text{or,}\quad pH = 4.75$$

Case II,

When 5 ml of 0.03M HCl is added into the solution, the total volume of the solution is given by,

$$= 300 + 5\text{ ml} = 305\text{ ml}$$

$$\text{Then,}\quad [HCOOH] = \frac{100\text{x}0.4}{305}\text{ M} = 0.131\text{ M}$$

$$[HCOONa] = \frac{200 \times 0.2}{305} M = 0.131\ M$$

$$[HCl] = \frac{5 \times 0.2}{305} M = 0.0032\ M$$

Now, the concentration of salt and acid are changed as follows,

	HCl	+	HCOONa	→	HCOOH	+	NaCl
Initially,	0.0032M		0.131M		0.131M		
Finally,	0		(0.131 – 0.0032)M		(0.131 + 0.0032)M		

Therefore, $[HCOONa] = (0.131-0.0032)M = 0.1278M$

$[HCOOH] = (0.131+0.0032)M = 0.1342M$

Then the pH of the solution is given by,

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

$$\text{or,}\quad pH = pK_a + \log\frac{[HCOONa]}{[HCOOH]}$$

$$\text{or,}\quad pH = 4.75 + \log\frac{[0.1278]}{[0.1342]}$$

$$\text{or,}\quad pH = 4.75 + (-0.0212)$$

$$\text{or,}\quad pH = 4.728$$

Now, the change in pH of the buffer solution by the addition of 5 ml of 0.2M HCl is given by,

$= 4.728 - 4.75$

$= -0.0212$

Hence, the pH change of buffer by the addition of acid is – 0.0212.

Practice Questions

1. What do you mean by Ostwald's dilution law? Discuss its limitations.
2. Define pH and buffer solution. Calculate the pH of a solution made by mixing 500 ml of 0.2 N HCl with 500 ml of 0.1 N NaOH solutions. **[PU–2004, Fall]**
3. Define and derive Ostwald's dilution law for the ionization of a weak electrolyte. A buffer solution is made by adding 500 ml of 0.3 M acetic acid in 400 ml of 0.5 M sodium acetate. Calculate the pH of resulting solution and pK_a for acetic acid = 4.74. **[PU-2006, Spring]**
4. What is buffer capacity of a buffer solution? Give the mechanism of buffer action taking a suitable example of basic buffer. **[PU-2006, Spring]**
5. State and explain Ostwald's dilution law for weak electrolytes. Why is this law no applicable for strong electrolyte? **[PU-2006, Spring]**
6. What is buffer solution? Describe the mechanism of buffer action taking a suitable example. **[IOE-'68]**
7. What is buffer solution? Calculate the pH of resulting solution when 0.005 mole of KOH is added to 200ml of 0.1N acetic acid solution. ($pK_a = 4.74$) **[IOE-'67]**
8. 1.64 g of anhydrous sodium acetate is added to 200 ml of 0.2 M acetic acid. What is the pH of buffer? Calculate the degree of ionization of the acid in the solution. (K_a of acid = 1.8×10^{-5}) **[IOE-'67]**
9. How does an acidic buffer solution reserve its pH value on the addition of strong acid or strong base? 100 ml of 0.2 M CH_3COONa is mixed with 200 ml of 0.3 M CH_3COOH, which is 2.1% ionized in dilute solution. Find out the pH of the resulting solution. **[IOE-'68]**
10. What do you mean by buffer range and buffer capacity?
11. Derive Henderson's equation to determine the pH of basic buffer. Also write the significances of this equation.
12. Calculate the pH change of a buffer solution of 100 cc of semi molar CH_3COOH and 400 cc of N/10 CH_3COONa in which 10ml of 0.2N HCl is added. $K_a = 1.8 \times 10^{-5}$.

◆ ◆ ◆

Chapter

3

Catalysis

Catalysis

Introduction:

In 1835, J. J. Berzelius introduced the term catalysis (Greek *kata = wholly, lein = to loosen*) since he realized that there are substances which increase the rate of a reaction without themselves being consumed. Initially, it was thought a catalyst is a substance to increase the rate of reaction. But now it has got a broad definition that, **'a catalyst is a substance which alters (increase/decrease) the rate of a chemical reaction but itself remains unchanged in mass and composition at the end of the reaction'**. The phenomenon is called catalysis. The catalyst does not appear in the net chemical equation for the reaction, although its presence may be indicated above the arrow in the chemical equation.

Types of catalysts:

Now from the definition of the catalyst, a catalyst may increase or decrease the rate of a reaction. Accordingly, there are two types of catalysts;

1. Positive catalysts
2. Negative catalysts

1. **Positive catalyst:** A catalyst which increases the rate of a reaction is called positive catalyst and the phenomenon is called *positive catalysis*. Some examples of positive catalysis are as follows;
   i. Haber's synthesis of ammonia in the presence of finely divided iron as catalyst

$$N_2(g) + H_2(g) \xrightarrow[500atm.]{Fe} 2NH_3(g)$$

   ii. Decomposition of potassium chlorate in the presence of MnO2 as catalyst

$$2KClO_3(s) \xrightarrow{MnO_2} 2KCl(s) + 3O_2(g)$$

2. **Negative catalyst:** A catalyst which decreases the rate of a reaction is called

negative catalyst (inhibitor) and the phenomenon involved is called *negative catalysis (or inhibition)*. Some examples of negative catalysis are as follows;

i. Small amount of ethanol in the chloroform slows down its oxidation by air. Therefore the ethanol is an inhibitor for the oxidation of chloroform.

$$2CHCl_3 + O_2(g) \xrightarrow{C_2H_5OH} 2COCl_2 + 2HCl$$

Carbonyl chloride

ii. Decomposition of Hydrogen peroxide is slowed down by the presence of acetanilide or dilute acids or glycerol in small amount.

$$2H_2O_2 \xrightarrow{\text{glycerol}} 2H_2O + O_2$$

iii. When tetraethyl lead, $Pb(C_2H_5)_4$, is added to the petrol, it controls the very rapid or explosive combustion of the petrol in the combustion chamber. This is responsible for knocking of the engine.

Applications of negative catalysts:

Unstable chemicals are preserved by negative catalyst e.g. sodium benzoate is used as a food preservative. An important type of negative catalyst is classed as anti-oxidants. Aromatic amines are used as antioxidants for prolonging the life of rubber. n-propyl gallate, butoxy anisole etc. are added to vanaspati butter and some oils to retard the onset of rancidity.

Mechanisms of negative catalysis are different for different reactions.

i. **By poisoning a catalyst:** A negative catalyst may function by contaminating the catalyst already present in the reaction mixture that reduces the activity of the catalyst. For e.g., a small amount of alkali present in the container of hydrogen peroxide enhance the rate of its decomposition. But the addition of small amount of acid destroys the alkali catalyst and thus prevents the decomposition.

ii. **By breaking the chain reaction:** *In chain reactions, the negative catalysts perform their effect by breaking the chain of reactions. For e.g., nitrogen trichloride (NCl_3) inhibits the combination of H_2 and Cl_2, which proceeds via chain reaction.*

$$Cl_2 \longrightarrow Cl^{\cdot} + Cl^{\cdot}$$
$$H_2 + Cl^{\cdot} \longrightarrow HCl + H^{\cdot}$$
$$H^{\cdot} + Cl_2 \longrightarrow HCl + Cl^{\cdot}$$

NCl_3 breaks the chain reactions by reacting with the propagating species, chloride radical, $Cl^{\cdot}$, and there will be no further reaction.

$$NCl_3 + Cl^{\cdot} \longrightarrow 1/2N_2 + 2Cl_2$$

Auto catalysis

Some reactions proceed with gradually increasing rapidity due to the formation of a catalyst (a product) as a result of the chemical reaction. Such reactions are called autocatalytic reactions and the phenomenon is called autocatalysis. For e.g., decolorization of permanganate by oxalic acid, which is initially a very slow reaction but after sometime goes on fairly rapidly due to the formation of Mn^{2+} ions, which catalyzes the reaction.

$$2MnO_4^- + 16H^+ + 5C_2O_4^{-2} \longrightarrow 2Mn^{+2} + 8H_2O + 10CO_2$$

Thus when one of the products of a reaction itself acts as a catalyst for that reaction, the phenomenon is called autocatalysis.

Other examples of autocatalysis are given as,

a. Hydrolysis of an ester: Acetic acid and ethanol are the products formed during the hydrolysis of ethyl acetate. Of these, acetic acid acts as catalyst for the reaction.

$$CH_3COOC_2H_5 + H_2O \longrightarrow \underset{\text{catalyst}}{CH_3COOH} + C_2H_5OH$$

b. Decomposition of Arsine: The free arsenic produced by the decomposition of arsine, auto catalyses the reaction.

$$\underset{\text{arsine}}{2AsH_3} \longrightarrow \underset{\text{catalyst}}{2As} + 3H_2$$

Action of catalyst

The action of a catalyst in a chemical reaction is to either increase or decrease the reaction rate. This is also called **catalytic activity**. However, it is also found that the catalytic activity of a catalyst for a chemical reaction is affected by other chemical substances added into the reaction mixture along with the catalyst. Accordingly, such substances are categorized into two groups:

i. Catalytic promoters
ii. Catalytic poisons

i. Catalytic promoters

The chemical substance which increases the activity of the catalyst, though itself is not a catalyst is called **catalytic promoter.** For e.g., in the Haber's synthesis of ammonia, the activity of iron catalyst is greatly increased by the molybdenum, Mo or aluminum oxide (Al_2O_3).

$$N_2(g) + 3H_2(g) \xrightleftharpoons[Mo]{Fe} 2NH_3(g)$$

So, Mo or Al_2O_3 in this reaction is known as catalytic promoter.

In some of the reactions, the mixture of catalysts is used to obtain the maximum efficiency of catalyst. For e.g., a mixture of zinc and chromium oxide is used as catalyst for the synthesis of methanol from carbon monoxide and hydrogen.

$$CO + 2H_2 \xrightarrow[Cr_2O_3]{ZnO} CH_3OH$$

Mechanism of the promotion of catalytic activity is mainly assumed to be due to following processes; however it is not clearly understood.

a. By changing the lattice spacing
b. By altering the surface of catalyst

a. **Change of lattice spacing:** The lattice spacing of the solid catalyst is changed due to the occupation of general lattice sites of the catalyst atoms by the atoms of the promoter. In general, the space between the catalyst atoms is increased because of the larger atomic size of the promoter. Thus the bonds of adsorbed molecules of the reactant are more weakened and broken easily. This causes the reaction to be faster than that of single catalytic action. This may be clearly understood from the following example.

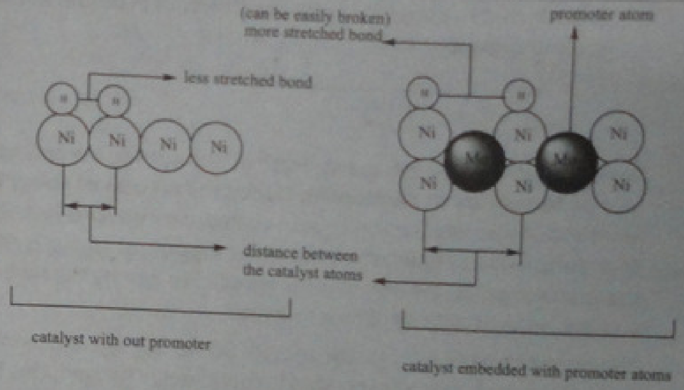


Fig: showing the change of crystal lattice spacing of catalyst makes the reaction faster.

b. **Promotion action due to increase of peaks and cracks on the surface of the catalyst (Altering the surface of catalyst):** The presence of the promoter increases the peaks and cracks on the surface of catalyst thereby increasing the number of active centres. This causes the reactant molecules to accumulate at a site that causes the reaction to be faster.

ii. Catalytic Poisoning

A substance which reduces the efficiency of the catalyst to accelerate a reaction is called catalytic poison and the phenomenon is called catalytic poisoning. A small amount of poison is sufficient to retard the rate of reaction. This effect is commonly observed in heterogeneous catalysis. Some examples of catalytic poisoning are given as,

a) Haber's synthesis of ammonia using iron as a catalyst is poisoned by the presence of small amount of H_2S.

$$N_2(g) + 3H_2(g) \xrightarrow[\substack{\text{poisoned by} \\ H_2S}]{Fe} 2NH_3(g)$$

b) Oxidation of hydrogen using platinum catalyst is found poisoned by Carbon monoxide.

$$2H_2 + O_2 \xrightarrow[\substack{\text{poisoned by} \\ CO}]{Pt} 2H_2O$$

c) Arsenic oxide inhibits the catalytic activity of platinum in oxidation of sulphur dioxide.

$$SO_2 + O_2 \xrightarrow[\text{poisoned by } As_2O_3]{Pt} 2SO_3$$

Depending on the extent and strength of absorption, the catalytic poisoning may be **temporary or permanent.** During the process of Haber's synthesis of ammonia, water vapour and O_2 act as temporary poisons by combining with Fe to form oxide of iron. When the water vapours or O_2 gas is removed from the reactant gases, the iron oxide is reduced to iron by the hydrogen present and the catalytic activity of Fe is restored.

The catalytic action of Pt in oxidation of SO_2 to SO_3 is permanently poisoned by As_2O_3. In such cases the catalyst is completely changed, this however can be brought into original form by suitable chemical treatment.

Mechanism of catalytic poisoning is explained in following assumptions.

1) The poison is adsorbed preferentially on the surface of catalyst than the reactants. Even a monomolecular layer adsorption of catalytic poisons on the catalyst's surface causes unavailability of the surface of catalyst for the reactant molecules and hence retards the rate of reaction. The catalytic poisoning by carbon monoxide appears as follows.

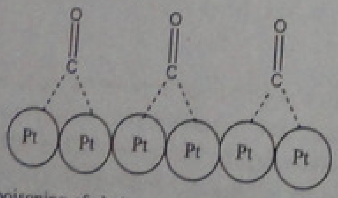


fig:poisoning of platinum catalyst by carbonmonoxide

2) *By the chemical combination of the catalyst with impurity. The poisoning of the iron catalyst by H_2S during Haber's synthesis of ammonia falls in this mechanism. The presence of hydrogen sulphide changes the pure iron into iron sulphide as,*

$$Fe + H_2S \rightarrow FeS + H_2$$

Thus due to the unavailability of pure iron, the rate of reaction is retarded.

Types of catalysis

The phenomenon of catalysis is categorized into two classes depending on the state of catalyst corresponding to the bulk state of reactants.

1. Homogeneous catalysis
2. Heterogeneous catalysis

1. Homogeneous catalysis

If the reactants and catalyst are in the same phase and hence distributed throughout, the catalysis is said to be homogeneous catalysis. This type of catalysis occurs either in the gas phase or in the liquid (solution) phase.

Some examples of the **gas phase homogeneous catalysis** are as follows;

i. Nitric oxide (NO) gas acts as a catalyst in the combination of moist sulphur dioxide and oxygen in the lead chamber process for the manufacture of sulphuric acid.

$$2SO_2(g) + O_2(g) \xrightarrow{NO(g)} 2SO_3(g)$$

ii. NO gas also acts as a catalyst in the combination of CO with oxygen.

$$2CO(g) + O_2(g) \xrightarrow{NO(g)} 2CO_2(g)$$

iii. Decomposition of acetaldehyde occurs readily in the presence of iodine.

$$\underset{\text{vapour}}{CH_3CHO} \xrightarrow{I_2 \text{ vapour}} \underset{\text{gas}}{CH_4} + \underset{\text{gas}}{CO}$$

Some examples of the **liquid (solution) phase homogeneous catalysis** are as follows;

i. Hydrolysis of cane sugar in aqueous solution in the presence of mineral acid as catalyst.

$$\underset{\text{sugar}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{H^+(aq)} \underset{\text{glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{fructose}}{C_6H_{12}O_6(aq)}$$

ii. Hydrolysis of an ester occurs rapidly in the presence of acid or alkali.

$$CH_3COOC_2H_5(aq) + H_2O \xrightarrow{H^+/OH^-(aq)} CH_3COOH(aq) + C_2H_5OH(aq)$$

iii. Decomposition of hydrogen peroxide in the presence of iodide ion as catalyst.

$$2H_2O_2(aq) \xrightarrow{I^-(aq)} 2H_2O + O_2(g)$$

2. **Heterogeneous Catalysis**

If the catalyst is present in a phase different from that of the reactants, then the catalysis is said to be heterogeneous catalysis. The most common type of heterogeneous catalysis is a solid catalyst either as such or supported on an inert solid such as asbestos, while the reactants are either liquids or gaseous. The process is also called contact catalysis. In contact catalysis, generally the catalyst is used in a finely divided form. This form of catalysis has great industrial importance that several chemical reactions in the industrial processes are carried out by heterogeneous catalysis.

Some examples:

1. Heterogeneous catalysis with gaseous reactants (contact catalysis)
   i. Finely divided platinum or vanadium pentoxide (V_2O_5) acts as a catalyst for the oxidation of sulphur dioxide.

$$2SO_2(g) + O_2(g) \xrightarrow{Pt,\ solid} 2SO_3(g)$$

ii. Haber's synthesis of ammonia is also an example of contact catalysis.

$$N_2(g) + H_2(g) \xrightarrow{Fe(s)} 2NH_3(g)$$

iii. In the manufacture of hydrogen gas from the water gas by the Bosch process, solid ferric oxide is used as catalyst.

$$CO(g) + H_2O(g) \xrightarrow[673\text{-}723K]{Fe_2O_3(s)} CO_2(g) + H_2(g)$$

iv. Methanol is manufactured from CO and Hydrogen gas by using solid zinc oxide as catalyst and Cr_2O_3 as a promoter.

$$CO(g) + H_2(g) \xrightarrow[Cr_2O_3]{ZnO(s)} CH_3OH(l)$$

v. Hydrogenation of unsaturated organic compound is catalyzed by finely divided nickel.

$$CH_2{=}CH_2 + H_2 \xrightarrow{Ni,\ solid} CH_3\text{-}CH_3$$

When hydrogen is passed through the vegetable oils in the presence of nickel, the carbon-carbon double bonds are hydrogenated to yield solid fats (Vanaspati ghee).

2. Heterogeneous catalysis with liquid reactants
   i. The decomposition of hydrogen peroxide solution is catalyzed by manganese dioxide or platinum in colloidal form.

$$2H_2O_2 \xrightarrow{Pt\text{ (solid)}} 2H_2O + O_2$$

ii. Benzene and ethanoyl chloride react in the presence of anhydrous aluminum chloride to form phenyl methyl ketone.

$$\underset{\text{liquid}}{C_6H_6} + \underset{\text{liquid}}{CH_3COCl} \xrightarrow{AlCl_3\text{ (solid)}} C_6H_5COCH_3 + HCl$$

3. Heterogeneous catalysis with solid reactants

The decomposition of potassium chlorate is catalyzed by manganese dioxide (MnO_2).

$$2KClO_3(s) \xrightarrow{MnO_2\text{(solid)}} 2KCl(s) + 3O_2(g)$$

Characteristics of a catalyst:

A catalyst has the following characteristics, are often referred to as the criteria of catalysts.

a. **A small quantity of catalyst is generally enough to produce almost unlimited reaction.**

Small amount of catalyst is sufficient to effect on appreciable change in the velocity of a reaction. Usually a small amount of the catalyst can bring about a large amount of chemical changes. However, the rate of reactions in some reactions is directly proportional to the concentration of catalyst especially in the case of homogeneous catalytic reaction in which catalyst reacts with the reactants to form the intermediate compounds. For e.g., in the hydrolysis of ester,

$$RCOOR + H_2O \xrightarrow{H^+ \text{ or } OH^-} R\text{-}COOH + R\text{-}OH$$

For acid and alkaline hydrolysis of an ester, the rate of reaction is proportional to the concentration of acid or base which acts as catalyst.

In the conversion of sugar into glucose and fructose, acid acts as a catalyst.

$$\underset{\text{Sugar}}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{H^+(aq)} \underset{\text{glucose}}{C_6H_{12}O_6(aq)} + \underset{\text{fructose}}{C_6H_{12}O_6(aq)}$$

However, there are catalysts which need to be present in relatively large amount to function effectively. For e.g., in Friedel-Crafts reaction,

$$C_6H_6 + C_2H_5Cl \xrightarrow{AlCl_3} C_6H_5C_2H_5 + HCl$$

b. **A catalyst remains unchanged in mass and chemical composition at the end of the reaction.**

A catalyst can take part in the reaction but is never consumed. The mass and chemical composition remains unchanged but the change in its physical state may be possible. Granular MnO_2 which is added to accelerate the thermal decomposition of potassium chlorate is found to change into fine powder.

$$2KClO_3(s) \xrightarrow{MnO_2} 2KCl(s) + 3O_2(g)$$

c. **The catalyst does not influence the position of equilibrium but it shortens the time required to establish the equilibrium.**

The use of catalyst can help to achieve the equilibrium in lesser time as the forward and the backward reactions are effected to the same extent by the catalysis. Therefore, the equilibrium constant remains unchanged.

The effect of a catalyst on shortening the time required to establish the equilibrium for a reaction is illustrated as,

$$A + B \rightleftharpoons C + D$$

Initially, the rate of forward reaction is maximum and it decreases with the time till the equilibrium is established. For the reverse reaction, initially the concentration of C and D are zero and the rate of reaction is the lowest. As the time passes, the rate of reaction increases gradually till the equilibrium is established. Similar trend is observed for the reactions with catalyst but just the time to attain equilibrium is shorter because the rates of forward and backward reaction are equally altered. Graphically, it is shown as below,

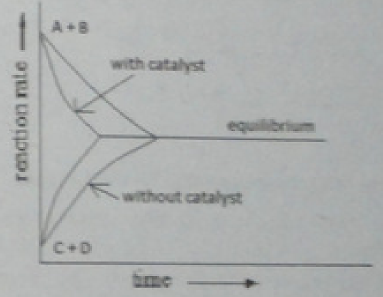


Fig: The effect of a catalyst on the time required for the equilibrium to be established.

d. **A catalyst, in general, cannot start a reaction, but it will affect the rate.**

In most cases, a catalyst can only accelerate a reaction which is already in progress and does not initiate the reaction. But in some reactions, catalyst also plays a role to initiate the reaction. For example, a mixture of hydrogen and oxygen remains unchanged almost indefinitely at room temperature, which can be brought to reaction by the platinum (catalyst) in a few seconds.

$$H_2 + O_2 \xrightarrow{\text{room temp.}} \text{no reaction}$$

$$2H_2 + O_2 \xrightarrow{\text{Pt black}} 2H_2O$$

Therefore it is now considered that the catalyst can also initiate a reaction.

e. **It is highly specific in its action.**

A catalyst can affect the rate of a particular reaction but it can not be used in all reaction. For e.g. the presence of MnO_2 accelerates the rate of decomposition of potassium chlorate on the other hand it is unable to influence the rate of decomposition of $KClO_4$. Similarly the mechanism and the nature of the products formed in a catalyzed reaction depend largely on the nature of the catalyst used. For example, ethanol vapors when heated on nickel surface to about 350°C get dehydrogenated but it undergoes dehydration on alumina.

$$CH_3CH_2OH \xrightarrow{Ni} CH_3CHO + H_2$$

$$CH_3CH_2OH \xrightarrow{Al_2O_3} CH_2{=}CH_2 + H_2O$$

$$HCOOH \xrightarrow{Al_2O_3} CO + H_2O$$

$$HCOOH \xrightarrow{Cu} H_2 + CO_2$$

f. **A catalyst is more effective when it is finely divided.**

In heterogeneous catalysis, the solid catalyst is more effective when in a state of finely divided than in its bulk size. Thus, a lump of platinum will have much less catalytic activity than colloidal or platinized asbestos. Finely divided nickel is a better catalyst than its lump solid. This is because the higher surface area for the reaction to take place in the finely powdered catalyst than at its lump.

g. **Effect of temperature on catalyzed reaction:**

The effect of temperature change on reversible reaction is explained as required by Le-Chatelier's principle. Now for a catalytic reaction, the temperature has two opposing effects.

- Rate of reaction is increased with the increase of the temperature.
- Decrease the rate of catalytic reaction as the catalytic activity is decreased with increasing temperature; there is an optimum temperature at which the efficiency of the catalyst is a maximum. This is particularly true with the colloidal solution where the rise in temperature cause the coagulation of catalyst

In such case, the rate of catalytic reaction increases upto certain point and then gradually decreases.

Theories of Catalysis

Fundamentally, catalyst often acts by providing a reaction path that has considerably low energy of activation than that of the uncatalyzed path of reaction. There are two theories which can better explain the mechanism of catalytic reactions;

1. Intermediate Compound formation theory or theory of homogeneous catalysis
2. Adsorption theory of catalysis or theory of heterogeneous catalysis

In general, the intermediate compound formation theory better explains the homogeneous catalysis and the adsorption theory is found best fit for the heterogeneous or contact catalysis.

1. Intermediate Compound Formation Theory

This theory was put forward by Desormes in 1806. This theory explains catalytic phenomena as due to the formation of unstable intermediate compounds of greater activity than the reactants. This unstable intermediate reacts suddenly with other reactants to give the products regenerating the catalyst. According to this theory, a catalytic reaction occurs in two steps as follows.

i. The catalyst, first forms an intermediate compound with one of the reactant. The formation of this compound needs lesser amount of energy than that of the actual reaction.

$$A + X \xrightleftharpoons[K_2]{K_1} [AX]^*$$

Where, A = reactant, X = Catalyst and [AX]* = intermediate compound

ii. The highly reactive intermediate compound then reacts with another reactant B to form the product and releasing the catalyst.

$$AX + B \xrightarrow{K_3} AB + X$$

This reaction is slow and rate determining. The catalyst regenerated can be further utilized to form more and more products.

Illustrations:

a. Decomposition of $KClO_3$

$$2KClO_3 + \underset{\text{catalyst}}{MnO_2} \longrightarrow [K_2MnO_4] + Cl_2 + 2O_2$$

$$[K_2MnO_4] + Cl_2 \longrightarrow 2KCl + MnO_2 + O_2$$

$$2KClO_3 + MnO_2 \longrightarrow 2KCl + 3O_2 + \underset{\text{(regenerated catalyst)}}{MnO_2}$$

b. Manufacture of sulfuric acid by lead chamber process in the presence of nitric oxide as catalyst

$$2SO_2 + O_2 + \underset{\text{catalyst}}{NO} + 2H_2O \longrightarrow [2H_2SO_4 NO]$$

$$[2H_2SO_4 NO] \longrightarrow 2H_2SO_4 + \underset{\text{catalyst regenerated}}{2NO}$$

c. Decomposition of hydrogen peroxide in the presence of iodide ion as catalyst

$$H_2O_2 + \underset{\text{catalyst}}{I^-} \longrightarrow H_2O + [IO^-]$$

$$[IO^-] + H_2O_2 \longrightarrow H_2O + O_2 + \underset{\text{catalyst regenerated}}{I^-}$$

Limitations of Intermediate compound formation theory:

a. This theory fails to explain the action of catalytic promoters and poisons.

b. This theory is only applicable to the homogeneous catalysis. In heterogeneous catalysis where the catalyst is a solid and reactants are gases, the formation of intermediate compound is not possible.

2. **Adsorption theory or Theory of heterogeneous catalysis**

This theory was put forward by Faraday in 1883 and it is based upon the phenomenon of adsorption. The action of the catalyst is due to the presence of free valencies on its surface. These free valencies after an opportunity to the reactant molecules to undergo chemical reactions on the surface of the catalyst. An atom within the body of a catalyst is joined to the surrounding almost and hence it's all valencies are satisfied. The atom present on the surface of the catalyst possesses a free valency directed outward. According to Langmuir, the heterogeneous catalysis involves the following steps.

Generally, five steps can be put forward for a completion of heterogeneous catalysis. Now, for a general reaction,

$$A(g) + B(g) + catalyst \;\square\; C(g) + D(g)$$

i. **Diffusion:** The reactant molecules from the gaseous or liquid phase undergo diffusion on the surface of the catalyst.

ii. **Adsorption of reactant molecules:**

The reactant molecules are adsorbed on the catalyst surface either by physical adsorption or by chemical adsorption to form layer of unimolecular thickness which leads to higher concentrations of the reactants on the surface of catalyst. Adsorption causes stretching and weakening of bonds necessary for subsequent reaction. Further, adsorption being an exothermic process, it decreases the energy of activation.

iii. **Formation of activated complex:** The reactants molecules form an activated complex on the catalyst's surface. This is highly unstable and exists only for a short time.

iv. **Decomposition of activated complex:** As soon as the activated complex is formed, it starts its decomposition to give the products; C and D. The separated particles of the products hold to the catalyst surface by partial chemical bonds.

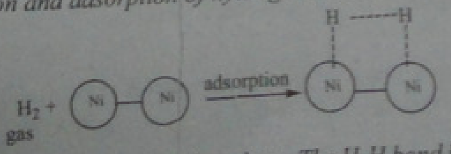
v. **Diffusion of product:** The molecules of the product diffused away slowly from the surface of the catalyst.

Illustration:

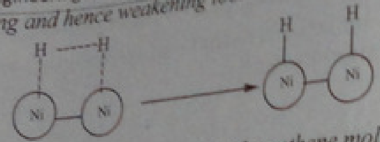
Hydrogenation of ethene in presence of nickel is an example of adsorption theory of catalysis.

The catalyst here is supposed to operate by the following steps.

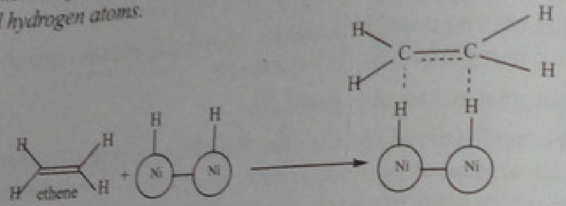
Step I. *Diffusion and adsorption of hydrogen molecules on the surface of nickel.*



Step II. *Breaking of H-H bonds takes place. The H-H bond is smaller than the Ni-Ni bond. Therefore the adsorption of hydrogen molecules on nickel surface cause the* *bond stretching and hence weakening too.*

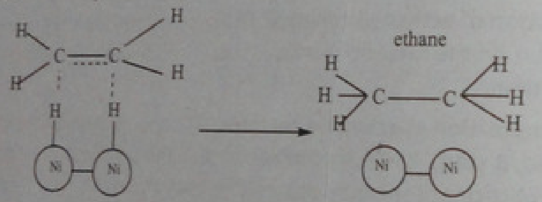


Step III. *Formation of activated complex when ethene molecule gets combined with the adsorbed hydrogen atoms.*



Activated complex

Step IV. *Decomposition of the activated complex and diffusion of the ethane molecules away from the surface.*



The freed catalyst surface is now available for carrying out for further reactions.

Industrial applications of catalysis

Modern chemical industry depends upon the development, selection and application of the catalyst. The phenomenon of catalysis is of great significance in the efficient manufacturing of many practical substances such as polythene, vanaspati ghee etc. some of the prominent applications of catalysts in the industrial processes are as follows.

i. The wide application of polythene was made possible by the development of a catalyst for the synthesis of polythene by the polymerization reaction of ethene, which is catalyzed by Ziegler- Natta's catalyst, $TiCl_4$(titanium chloride).

ii. Finely divided nickel is used for the hydrogenation of vegetable oils such as groundnut oil or cotton-seed oil etc to a semisolid product popularly known as Vanaspati-ghee.

iii. A feasible method of synthesizing ammonia in industrial scale was made possible by the discovery of iron as catalyst for breaking of N-N bond, which is must for the formation of ammonia from hydrogen and nitrogen gases. The activity of catalyst is improved by using Molybdenum as a promoter.

iv. Manganese dioxide is used for the preparation of oxygen gas in commercial scale by decomposing the potassium chlorate.

v. Platinum is used as catalyst for oxidizing sulphur dioxide into sulphur trioxide, which is the important primary step for the production of sulphuric acid, an important chemical for several purposes.

vi. Fe_2O_3 and Cr_2O_3 are used as catalyst in the Bosch process for the manufacture of the Hydrogen gas.

vii. To prepare methanol from H_2 and CO, $(ZnO + Cr_2O_3)$ is used as catalyst.

viii. Acetaldehyde is prepared from acetylene using $HgSO_4$ as catalyst and to convert acetaldehyde into acetic acid V_2O_5 is the catalyst.

ix. In cracking of heavy petroleum fractions, silica and alumina gel are used as catalyst.

x. Pt gauze is used as a catalyst for the oxidation of NH3 and NO in the manufacture of HNO3 by Ostwald's process.

xi. $Al_2(SiO_3)_3$ Zeolites is used in cracking of petroleum.

$C_{10}H_{22}$ □□ $C_5O_{12} + C_5H_{10}$

Criteria for choosing catalyst for industrial applications

A variety of substances have been used as catalyst for various chemical processes. The criteria for choosing catalyst for industrial applications are as follows.

i. It should be more selective to produce the desired product as a major product.

ii. It should have sufficiently maximum activity for the proper yield of the desired product.

iii. There should be easy method for its regeneration and reactivation while using.

iv. It should be cheap and available abundantly.

v. It should be stable at normal conditions.

Practice Questions

1. Define catalyst. Explain the characteristics of catalyst.
2. Describe the types of catalyst with suitable examples.
3. Define catalyst and catalysis. Describe the adsorption theory of heterogeneous catalysis with a suitable example. [IOE-'68]
4. Explain the intermediate compound theory of catalysis. Also write a suitable example.
5. Explain the adsorption theory of catalysis with an example. How does a poison paralyze the activity of catalyst? Give any two industrial applications of catalysts. [IOE-'67]
6. What do you mean by catalytic poisoning? Illustrate this with a suitable mechanism.
7. What is meant by homogeneous catalysis? Describe the intermediate compound formation theory of catalysis with suitable example. List the criteria for choosing a catalyst for industrial application. [1+3+1] [IOE-'67]
8. What is catalytic promoter? Describe the activity in enhancing the reaction rate.
9. Mention the criteria of choosing catalyst in industrial process. And list out the important industrial applications of catalysis.

Chapter

4

Engineering Polymers

Engineering Polymers

Introduction:

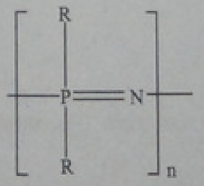
The word polymer is derived from the classical Greek word *poly* meaning 'many' and *mers* meaning 'parts'. Simply stated, a polymer is a high molecular weight compound which is formed by large number of small repeating units. The repeating units are of low molecular weight compounds refer to as monomers. For example, polyethylene is a polymer formed by linking together of a large number of ethene molecule.

$$\underset{\text{Ethene (monomer)}}{nCH_2{=}CH_2} \longrightarrow \underset{\text{polyethene (polymer)}}{-[CH_2-CH_2]_n-}$$

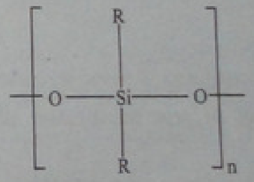
Depending on their origin, polymers can be grouped as natural or synthetic. Certain polymers such as proteins, cellulose, silk etc. are found in nature are called natural polymers. Whereas a number of polymers are produced by synthetic routes are called synthetic polymers. Synthetic polymers are man-made polymer. Synthetic polymers are divided in two parts- **Inorganic polymers** and **organic polymers**

1. Inorganic polymers

Inorganic polymers are the macromolecules composed of atoms other than carbon in backbone chain. These atoms are linked together mainly by covalent bonds .e.g.



Polyphosphazines



Silicones

General properties of inorganic polymers

i. Inorganic polymers have high density of covalent bonds if cross linking is considerable, they become much stiffer than organic polymers.

ii. Inorganic polymers can usually be obtained in pure amorphous or pure crystalline forms. Organic polymers on the other hand have structures which are partly crystalline and partly amorphous.

iii. Generally, inorganic polymers do not burn (except sulphur containing polymers). At high temperature they soften (or melt).

iv. Inorganic polymers do not allow intercalation of solvent molecules because chain segments between cross links in polymers are usually short and stiff.

v. Inorganic polymers cannot be extended much as compared to organic polymers. They are much less ductile.

vi. These are stronger but harder and more brittle than organic polymers.

Among the wide variety of inorganic polymers the frequently known polymers are discussed below in details.

1. Silicon based polymers - e.g. polysiloxanes (silicones)
2. Phosphorus based polymers - e.g. Polyphosphazines
3. Sulphur based polymers -e.g. polymeric sulphur, polymeric sulphur nitride, chalcogen glass etc

1. Silicon based polymers - Silicones (Polysiloxanes)

Silicones are organo-silicon polymers containing Si-O-Si linkage. It can be categorized both as organic as well as inorganic polymers. These polymers resemble inorganic polymers in having high percentage of ionic character of silicone-oxygen bond and backbone chain contains atoms other than carbon. They resemble organic polymers in having organic groups on silicon atoms. Silicones may be cyclic silicones, chain silicones and cross-linked silicones.

Preparation of silicones:

Preparation of silicones involves following three steps.

1. **Preparation of alkyl or aryl substituted silicon Chloride (Preparation of chlorosilanes)**

Preparation of R_3SiCl, R_2SiCl_2 and $R_3SiCl$where R is alkyl or aryl groups can be done by following method.

i. By the action of Grignard reagent with Silicon Chloride, we get a mixture

of chlorosilanes.

$$RMgCl + SiCl_4 \longrightarrow RSiCl_3 + MgCl_2$$
$$2RMgCl + SiCl_4 \longrightarrow R_2SiCl_2 + 2MgCl_2$$
$$3RMgCl + SiCl_4 \longrightarrow R_3SiCl + 3MgCl_2$$

Mixture can be separated by careful fractional distillation.

ii. By heating Chloroalkane or Chlorobenzene with Silicon in presence of Cu as a catalyst at a temperature of 300°C, we get a mixture of Chlorosilanes.

$$RCl + Si \longrightarrow R_3SiCl + R_2SiCl_2 + R_3SiCl$$
$$CH_3Cl + Si \longrightarrow CH_3SiCl_3 + (CH_3)_2SiCl_2 + (CH_3)_3SiCl$$

The mixture can be separated by careful fractional distillation since they have different boiling points. For example, above chlorosilanes have different boiling points as,

CH_3SiCl_3 (**b.p = 66.9°C**), $(CH_3)_2SiCl_2$(**b.p = 69.6°C**) and $(CH_3)_3SiCl$(**b.p = 87.7° C**).

2. **Hydrolysis of alkyl or aryl substituted silicon Chloride (preparation of silicols or Silanols or Silandiols).**

Preparation of Silanols can be done by treating alkyl or aryl substituted silicon chloride with water. Hydrolysis of different intermediates under controlled conditions yield different products. Since these intermediates are very reactive and inflammable, they are preserved under dry inert gases such as nitrogen.

$$RSiCl_3 + 3H_2O \longrightarrow RSi(OH)_3 + 3HCl$$
$$R_2SiCl_2 + 2H_2O \longrightarrow R_2Si(OH)_2 + 2HCl$$
$$R_3SiCl + H_2O \longrightarrow R_3Si(OH) + HCl$$

The general equation representing the hydrolysis reaction can be written as,

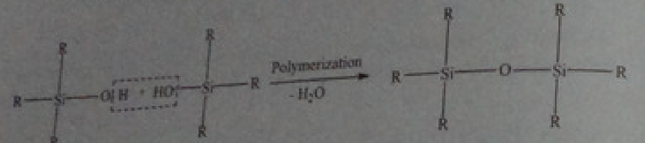
$$\text{Chlorosilanes} + \text{water} \longrightarrow \text{Hydrolysis} \quad \text{Silanols} + HCl$$

3. Polymerization of Silicols:

Silicones are obtained by condensation polymerization of Silicols. Types of the polymers depend upon the nature of R and the way in which hydroxyl derivative undergo polymerization.

a. Polymerization of R_3SiOH:

The polymerization of R_3SiOH gives a dimer.



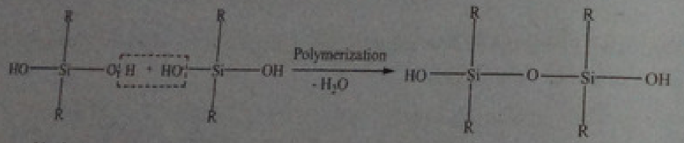
Where, R may be alkyl or aryl group

(Dimer) hexa alkyl or aryl disiloxane

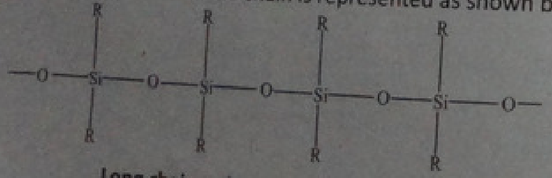
Since this compound has no hydroxyl groups left, it cannot polymerize any further.

b. Polymerization of $R_2Si(OH)_2$:

When many molecules of $R_2Si(OH)_2$ polymerize, we get a long straight chain polymer.



Hydroxyl group is present at each end of the chain hence polymerization continues and the chain length increases continuously producing a long chain polymer. Therefore the chain is represented as shown below.

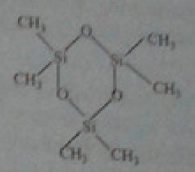


Long chain polymer

The length of the chain can be limited by adding calculated amount of R_3SiCl before hydrolysis.

Cyclic polymers can also be formed by the polymerization of $R_2Si(OH)_2$

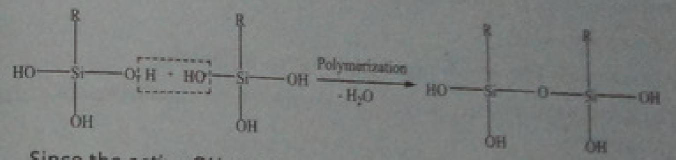
Hydrolysis under carefully controlled conditions can produce cyclic structures with rings containing three, four five or six Si-atoms.



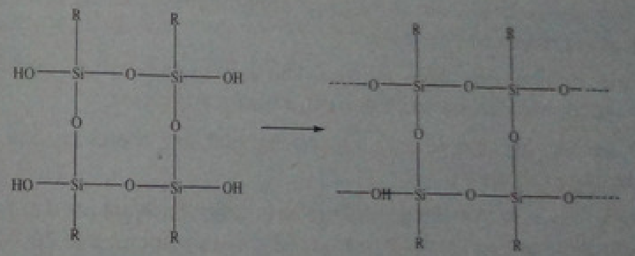
Triscyclodimethyl Siloxane

c. Polymerization of $RSi(OH)_3$:

Polymerization of $RSi(OH)_3$ gives rise to a complex cross-linked silicones.



Since the active OH-groups are present at each end of the chain hence polymerization continues to produce a complex cross-linked polymer. The reaction may be represented as shown below.



Complex cross-linked polymer

Properties of Silicones:

Silicones exhibit a number of unusual but desirable properties. The physical properties are depending upon the kind and number of organic groups attached to the silicon backbone whereas the chemical properties are governed by Si-O-Si bonds in siloxanes. Silicones can be obtained in the form of oils, viscous-liquid, resins or rubber like solids. Some of the characteristic properties of silicones are:

1. Silicone resins are highly water repellent since silicone chain is surrounded by organic groups. High content of hydrocarbon is responsible for this property.
2. Silicones are resistance to oxidation: Siloxanes are quite resistant to attack by oxygen. The presences of aromatic group on silicones increase the stability towards the oxygen.
3. Resistance to chemical attack: Polysiloxanes are unaffected by the majority of mild chemical reagents such as weak acids and alkalis. However due to the polar nature of Si-0 bond and the ability of silicone to expand its valency due to the presence of vacant orbitals makes it susceptible to attack by several reagents.
4. High thermal stability: Silicones have high thermal stability because of stable silica like arrangement of Si-O-Si bond. Moreover Si-O bond has very high bond energy. The Si-O-Si bond in siloxanes has some ionic character or partial double bond character which confers stability to the bond.
5. They do not freeze at low temperature and do not melt at high temperature.
6. They are non-toxic.
7. Silicon oil are highly stable non –volatile even on heating.
8. The boiling point and viscosity of the silicones increase with increase in the chain length.

Uses of Silicones

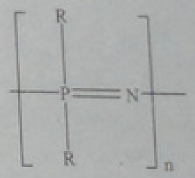
Silicones are highly used inorganic polymers. These are found having wide engineering applications. Some of the major applications of silicones in the present day context are mentioned as below.

1. Silicones oils are very stable and non-volatile even on heating. Therefore they are used for high temperature oil bath, vacuum pumps etc.
2. They do not become viscous on cooling and are therefore use for low temperature lubricants.
3. They are also used in making Vaseline like grease, which are used as lubricants in airplane since they do not freeze at -40^{0}C and do not melt at 200^{0}C.
4. Silicones resins are highly water repellent therefore they are used for making water proof clothes and papers.
5. Silicones fluids are mixed with paints, enamels to resist to the effect of high temperature, sunlight, chemical and damp.
6. They are used for making nonstick pans.
7. Silicones rubbers are used for making artificial heart valves, transfusion tubing and in transplant surgery.

8. They are used for making insulating materials for electric motor and other electric appliances since they can withstand high temperature without charring.

1. **Phosphorous based polymers: Polyphosphazines**

Nitrogen and phosphorus have little tendency on their own to undergo catenation. However nitrogen and phosphorus catenate together resulting in a very extensive chemistry of polymeric compounds known as Polyphosphazines. Simply polyphosphazines are inorganic polymers containing phosphorous atoms. Their general formula is



$$\left[-\overset{R}{\underset{R}{P}}=N- \right]_n$$

Polyphosphazines

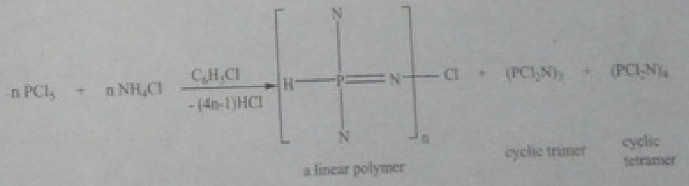
Where,

R = -Cl in polyphosphonitrilic chlorides

R = -OCH$_3$ in polydimethoxy phosphazines

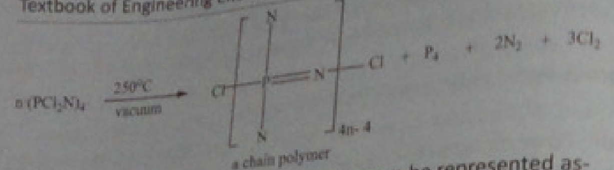
R = -OC$_2$H$_5$ in polydiethoxy phosphazines

Preparation of polyphosphonitrilic chlorides: Polyphosphonitrilic can be prepared by the reaction between phosphorus pentachloride and ammonium chloride in presence of C$_6$H$_5$Cl or by heating PCl$_5$ with NH$_4$Cl at 120-150°c.



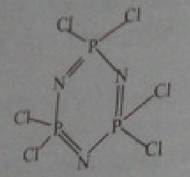
$$n\,PCl_5 + n\,NH_4Cl \xrightarrow[-(4n-1)HCl]{C_6H_5Cl} H\left[-\overset{N}{\underset{N}{P}}=N- \right]_n Cl + (PCl_2N)_3 + (PCl_2N)_4$$

The trimeric or tetrameric compounds are easily separated by distillation method. The cyclic tetramer when heated in vacuum at 250°C, changes in to a chain polymer.



a chain polymer

Structurally cyclic phosphonitrilic chlorides can be represented as-



Trimer

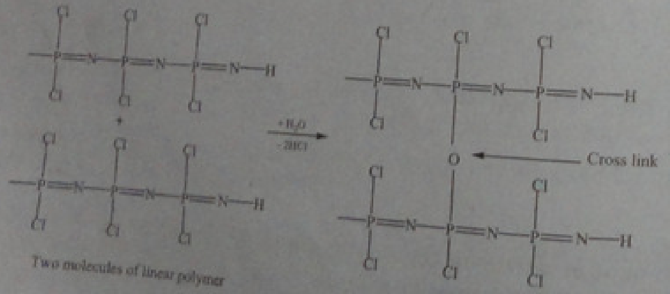
Properties:

Some important and interesting characteristics of Polyphosphonitrilic chlorides *are listed as below.*

i. These polymers exhibits high elasticity and can be stretched many times reversibly hence, also called inorganic rubbers.

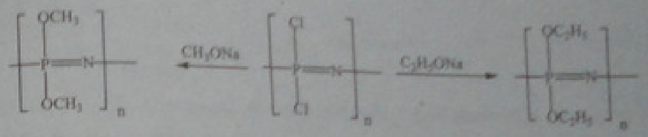
ii. Freshly prepared samples are soluble in chloroform, but not in petroleum ether. However, when their solutions are allowed to stand, they slowly form gel and get cross-linked.

iii. Their storage in the absence of air does not cause any change in elastic properties, but it becomes brittle due to the storage in the moist air. This is because the action of moisture (of air) forming oxygen bridges from chain-to-chain, there by leading to reduction in the average length of chain segments.



Preparation of polydimethoxyphosphazines and polydiethoxyphosphazines

Polydimethoxyphosphazines and polydiethoxyphosphazines are prepared by treating phosphonitrilic choloride with sodium methoxide (CH_3ONa) and sodium ethoxide (C_2H_5ONa) respectively as:



Polydimethoxyphosphazines

polydiethoxyphosphazines

Properties:

1. They are colorless, transparent and film thermoplastics.
2. On heating above 100°C, they slowly form cyclic polymers.

Uses:

There are many uses of Polyphosphazines as they have mechanical properties comparable to those of rubber. Some of the important uses are listed below.

1. They are used as rigid plastics, expanded foam and fibers.
2. They form flexible plastics which are useful for fuel **hoses** (flexible tube for flowing fuel) and gaskets.
3. Certain type polymers show water repellent properties and are used to make water proof thermoplasts.

1. Sulphur based inorganic polymers:

Sulphur because of its ability for catenation though much less than that of carbon, forms open and cyclic S_n species. A large number of sulphur based polymers are known. They fall under two categories.

i. Linear chain polymers which includes polymeric sulphur and sulphur nitrides.

ii. Network polymers which includes chalcogenide glasses

a. Polymeric sulphur (PS):

Polymeric sulphur is prepared by melting the rhombic S_8 at 165-168°C. When this molten sulphur is poured into ice water; the so called plastic sulphur is obtained. The rhombic structure of the sulphur (S_8) opens up to produce the free radical which combines with others S_8 to produce long chains.

$$S_8 \xrightleftharpoons{165\text{-}168^\circ C} \dot{S}-S_6-\dot{S}$$

$$\dot{S}-S_6-\dot{S} + S_8 \rightleftharpoons \dot{S}-S_{14}-\dot{S} \quad \text{and so on.}$$

The solid product is then purified by washing with carbon disulphide (to remove traces of S_8).To remove S_8 is a must because in presence of S_8 in polymer, the transition of polymeric sulphur to S_8 is facilitated.

Polymeric sulphur is unstable below the boiling point of sulphur i.e. 114°C. Below these temperatures, sulphur is unstable and reverts back to rhombic sulphur.

Uses of polymeric sulphur (PS):

Polymeric sulphur has very good applications in the flame proofing fabrics, as plasticizers. They are also used as catalyst in the manufacture of silicones.

b. Polymeric sulphur nitride $(SN)_n$:

Sulphur and nitrogen have similar electronegativities and strong tendencies to form single and multiple covalent bonds. Among the best known sulphur nitrogen compounds, tetrasulphur tetranitride (S_4N_4) is studied the most. S_4N_4 is obtained as diamagnetic orange solid by passing ammonia into a warm solution of disulphur dichloride in dry CCl_4.

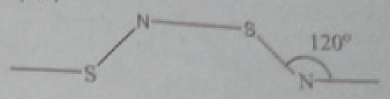
$$6S_2Cl_2 + 16NH_3 \longrightarrow S_4N_4 + 12NH_4Cl + 8S$$

S_4N_4 is a source compound for the preparation of $(SN)_n$. If S_4N_4 is vaporized under reduced pressure and passed through silver wool then disulphur dinitride is formed.

$$S_4N_4 + 4Ag \longrightarrow S_2N_2 + 2Ag_2S + N_2$$

Slow polymerization of S_2N_2 gives polythiazyl $(SN)_n$.

The structure of the polymeric nitride $(SN)_n$ can be represented approximately as,



Properties:

1. It is soft and malleable.
2. Polymeric sulphur nitride, $(SN)_n$ is golden bronze in colour.
3. It is slowly attacked by moisture when exposed to it for several months.
4. One of the remarkable properties of polymeric sulphur nitride is that; the material possesses metallic conductivity. It becomes superconductor at 0.26 K. Polymeric sulphur nitride is the first example of a nonmetallic super conductor.

Uses of polymeric sulphur nitride $(SN)_n$

It is used to make digital circuit, digital computer, electric power transition, transformer, power storage devices, electric motors etc.

a. Net work polymers:

Sulphur based network polymers are cross-linked polymers formed by reacting polyvalent element such as silicone antimony, arsenic, bismuth, germanium, indium etc with chalcogens (S,Se,Te).The resulting binary compounds are of great variety and complexity is known as chalcogenide glasses (or chalconide glasses). The nature of the products depends on the ratios of reactants, the temperature of reaction and other conditions. Chalcogenide polymers are generally prepared by the fusion of the element under conditions selected for minimizing oxidation and loss of volatilization of the components. Examples include, $(SiS_2)_n$, $(As_2S_3)_n$ etc.$(As_2S_3)_n$ is the best known chalcogenide containing two elements. The structure of common chalcogenide glass is given below.

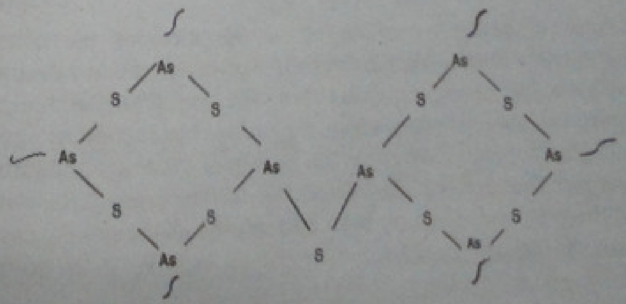


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Fig: Structure of $(As_2S_3)_n$

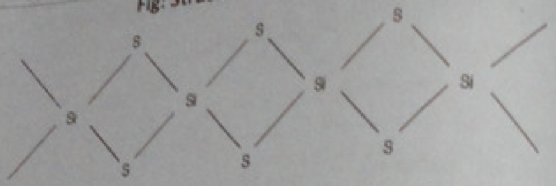


Fig: Structure of $(SiS_2)_n$

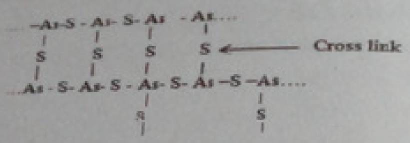


Fig: Structure of $(As_2S_3)_n$

Properties:

These polymers resemble organic polymers as well as glasses. Some of the properties of network polymers are listed below.

1. These polymers have lower softening points and lower tensile strengths as compared to other inorganic polymers such as borophosphate glasses.
2. These are stable to acids but are attacked by concentrated alkalies.
3. A remarkable property of these polymers is that, these can be distilled in vacuum without decomposition. Actually dissociation of polymeric network into small fragments in vapour phase in vacuum takes place. As the vapour condense, the small fragments recombine spontaneously forming the polymer network again.
4. Chalcogenide glasses are deeply coloured.
5. Unique property of network polymer of sulphur includes the changes conductivity reversible from low conductivity to high conductivity state under the applied voltage. This phenomenon is called switching. After the threshold voltage is applied the low conducting polymer becomes highly conducting with a thousand fold greater conductivity than the state prior to voltage application. It is due to the fact that under high voltage, the current causes dissociation of the bonds, there by a conducting path through the chalcogenide glass is produced when the voltage gradient becomes high enough. There are two modes of switching phenomenon.

---

i. **Threshold switching action:** The resistance of chalcogenide glass is high, until certain threshold voltage gradient (approx. 10^4 Vcm^{-1}) is reached. When this voltage gradient is reached, then the chalcogenide glass abruptly changes into a low resistance state. At this state conductivity is thousand times greater than that of state prior to the application of threshold voltage. The high conductivity state of the chalcogenide glass remains unaltered as long as certain specific current is maintained.

ii. **Memory switching action:** The chalcogenide glass maintains high resistivity below a certain threshold voltage gradient. Above the threshold gradient, the chalcogenide glass abruptly changes into high conductivity state even after the current is switched off. However, it can return to the low conductivity state when a short pulse exceeding the original threshold voltage passes.

Uses:

1. Chalcogenide glasses are used in ultrasonic delay lines, high energy particle detector, memory devices for computers.
2. These are also used for infrared transmitting windows because most of them are good infrared transmitting materials. They are used for fabrication of IR windows for army and civil optical devices.

Organic Polymers:

A polymer whose backbone chain is essentially made of carbon atoms is called organic polymer. The atoms attached to the side valencies of the backbone carbon atoms are usually hydrogen, oxygen, nitrogen etc. The majority of synthetic polymers are organic polymers. If the polymer is formed by identical monomer the polymer is known as homopolymer. If the polymer is formed by more than one type of monomers then it a is called copolymer.

Polymerization:

The reaction by which monomers are converted in to a polymer is called polymerization. There are two types of polymerization.

1. Addition polymerization
2. Condensation polymerization

1. Addition polymerization:

(Chain Growth Polymerization or Chain Polymerization)

Addition polymerization is a reaction that yields a products, which is exactly multiply of original monomeric molecule.This polymer is formed from the monomers without loss of any simple molecules. Addition polymers are obtained from unsaturated monomer. Therfore this type of polymerization also called vinyl polymerization. During the polymerisation pi-bond is broken and new sigma bond is formed and the reaction is usually catalyzed by acids or peroxides. Application of energy in the form of heat, light, pressure or presence of a catalyst, is usually necessary for initating the chain polymerization.

Mechanism of addition polymerisation:

Mechanisum of additiom polymerisation depend upon reagent that used. If organic peroxide is used free radical mechnism is occurred and if acids like H_2SO_4, HF is used ionic mechanism takes place.

Free radical mechanism:

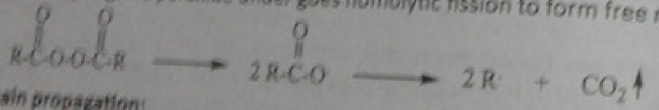
$$n\,CH_2{=}CH_2 \longrightarrow -\!\!\left[CH_2{-}CH_2\right]\!\!-_n$$

In free radical mechanism following steps are involved.

1. *Chain initiation*
2. *Chain propagation*
3. *Chain termination*

1. ***Chain initiation:***

In this step organic peroxide under goes homolytic fission to form free radical.



$$R{-}\overset{O}{\overset{\|}{C}}{-}O{-}O{-}\overset{O}{\overset{\|}{C}}{-}R \longrightarrow 2\,R{-}\overset{O}{\overset{\|}{C}}{-}\dot{O} \longrightarrow 2\,R^{\cdot} + CO_2\uparrow$$

2. ***Chain propagation:***

Free radical from the first step adds to the ethylene monomer to form new free radicals. The new free radicals again attack to another alkene and so on.

$$R^{\cdot} + CH_2{=}CH_2 \longrightarrow R{-}CH_2{-}\dot{C}H_2$$

$$R{-}CH_2{-}\dot{C}H_2 + n\,CH_2{=}CH_2 \longrightarrow R{-}CH_2\!\left[CH_2{-}CH_2\right]_n\!\dot{C}H_2$$

3. ***Chain termination:***

Chain termination takes place when two free radical combines.

$$R{-}CH_2\!\left[CH_2{-}CH_2\right]_n\!\dot{C}H_2 + R{-}CH_2\!\left[CH_2{-}CH_2\right]_n\!\dot{C}H_2$$

$$\downarrow$$

$$R{-}CH_2\!\left[CH_2{-}CH_2\right]_n\!CH_2{-}CH_2\!\left[CH_2{-}CH_2\right]_n\!CH_2{-}R$$

Polyethene

Ionic mechanism:

In ionic polymerization, reaction is initiated by acids such as H_2SO_4, HF, BF3/H2O. Following steps are involved.

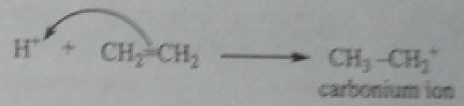
1. Chain initiation
2. Chain propagation
3. Chain termination

Cationic mechanism:

1. **Chain initiation:**

Proton from acid adds to the ethylene monomer to give the carbonium ion.

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$



$$H^+ + CH_2{=}CH_2 \longrightarrow \underset{\text{carbonium ion}}{CH_3{-}CH_2^+}$$

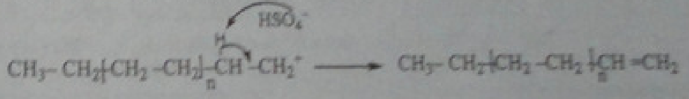
2. **Chain propagation:**

The carbonium ion adds to another ethylene molecule to produce new carbonium ion and so on.

$$CH_3{-}CH_2^+ + CH_2{=}CH_2 \longrightarrow CH_3{-}CH_2\!\left[CH_2{-}CH_2\right]_n\!CH_2{-}CH_2^+$$

3. **Chain termination:**

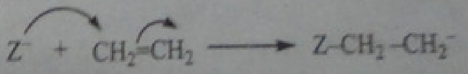
Chain termination takes place by combination with anion or loss of proton.



$$CH_3{-}CH_2\!\left[CH_2{-}CH_2\right]_n\!\overset{H}{C}H{-}CH_2^+ \xrightarrow{} CH_3{-}CH_2\!\left[CH_2{-}CH_2\right]_n\!CH{=}CH_2 \qquad HSO_4^-$$

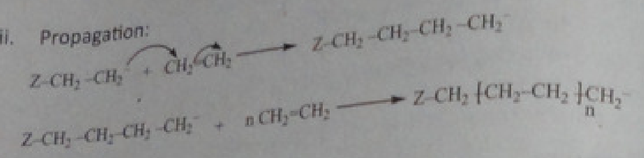
Anionic mechanism:

i. Chain initiation:



$$Z^- + CH_2{=}CH_2 \longrightarrow Z{-}CH_2{-}CH_2^-$$

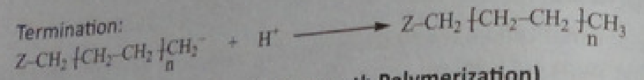
ii. Propagation:



$$Z\text{-}CH_2\text{-}CH_2^- + CH_2{=}CH_2 \longrightarrow Z\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2^-$$

$$Z\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2^- + n\,CH_2{=}CH_2 \longrightarrow Z\text{-}CH_2\left[CH_2\text{-}CH_2\right]_n CH_2^-$$

iii. Termination:



$$Z\text{-}CH_2\left[CH_2\text{-}CH_2\right]_n CH_2^- + H^+ \longrightarrow Z\text{-}CH_2\left[CH_2\text{-}CH_2\right]_n CH_3$$

2. Condensation Polymerization: (Step-Growth Polymerization)

Condensation polymerization has been defined as that reaction between functional molecules leading to the formation of a polymer with elimination of some small molecules like H_2O or HCl. e.g. Hexamethylene diamine and adipic acid condenses to form a polymer nylon-6, 6 (polyamide) or condensation between phenol and formaldehyde formed Bakelite

Differences between addition and condensation polymerization

The table below explains the difference between addition and condensation polymerization with respect to some selected points.

Points	Addition polymerization	Condensation polymerization
Type of molecules involved.	Unsaturated molecules	Saturated molecules
By-product	No by product	Always yield a byproduct along with a polymer
Action between two polymer	If two growing polymer chain undergo addition reaction, terminating of polymerization results	If two growing polymer chains react, the reaction propagates instead of termination.
Number of units	Number of units decreases steadily throughout the reaction.	Monomer disappears early in the reaction.
molecular mass	High molecular mass polymer is formed at once.	Polymer molecular mass rises steadily through the reaction.

On the basis of polymerisation, polymers are of two types.

1. ***Addition polymer:*** *Polymers which is formed by addition polymerisation is called addition polymer.e.g. PVC, teflon etc*
2. ***Condensation polymers:*** *Polymers which is formed by condensation polymerisation is called condensation polymer.eg Bakelite, Nylon-6, 6 etc.*

On the basis of moulding and nonmoulding point of view plastics polymers are divided into two main groups.

i. Thermosetting polymer

Thermosetting polymers are those polymers which upon heating, change irreversibly into hard and rigid materials.. If the set article is again heated, after cooling, it will not soften again. The thermosetting polymer during moulding acquires three dimensional cross-linked structures with predominantly covalent bonds which retain their strength even on heating. Thus the three dimensional network structure joined by strong covalent bonds, make the thermosetting resins harder, stronger and more brittle than thermoplastic resins. .If heating of a thermoset resin is prolonged; they undergo change in chemical composition to give hard, infusible and insoluble mass. E.g. bakelite, epoxy resins etc.

ii. Thermoplastics polymer

Thermoplastics polymers are those, which can be softened on heating and harden on cooling reversibly. Thus, they soften on heating and remain soft as long as they are hot. On cooling they regain their original rigidity and hardness. Repeated heating and cooling do not alter the chemical nature of these materials because the changes involved are purely of physical nature. Only the secondary bonds between the individual molecular chains are broken on heating which results in their softening. On cooling secondary bonds are again formed and hence they become hard. e.g. Polyethylene, polystyrene, polyvinylchloride etc..

Difference between thermoplastics polymer and thermosetting polymer

Thermoplastics polymer	Thermosetting polymer
They are formed by addition polymerization.	They are formed by condensation polymerization.
They consist of long chain linear polymers with negligible cross- liked.	They have three dimensional network structures.
They soften on heating readily, because secondary forces between the individual chains can break easily by heat or pressure or both.	They cross-links and bonded retain their strength on heating and hence, they do not soften on heating. On prolonged heating however charring of polymers is caused.
By reheating to a suitable temperature they can be softened reshaped and thus reused.	They retain their shape and structure even on heating. Hence they cannot be reshaped and reused.

They are usually soft, weak and less brittle.	They are usually hard, strong and more brittle.
These can be reclaimed from wastes.	They cannot be reclaimed from wastes.
They are usually soluble in some organic solvents.	Due to strong bonds and cross-links they are insoluble in almost all organic solvents.

Some Examples of Addition polymers

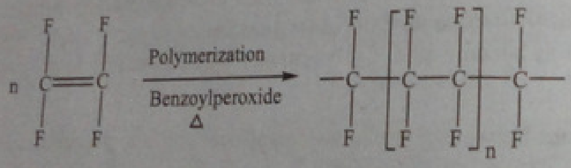
a) Teflon:- Polytetrafluoroethylene, Fluon(PTFE)

It is obtained by polymerization of water emulsion of tetrafluoroethylene, under pressure in presence of benzoylperoxide as catalyst. Tetrafluoroethylene is obtained from chloroform as below.

$$CHCl_3 + 2HF \longrightarrow CHClF_2 + 2HCl$$

$$2CHClF_2 \xrightarrow{900^\circ C} CF_2{=}CF_2 + 2HCl$$

Tetrafluoroethylene



Tetrafluoroethylene **Polytetrafluoroethylene**

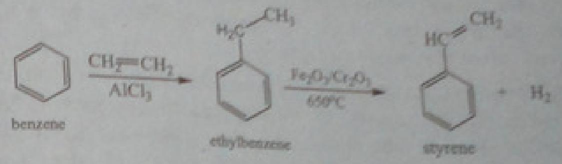
Uses:

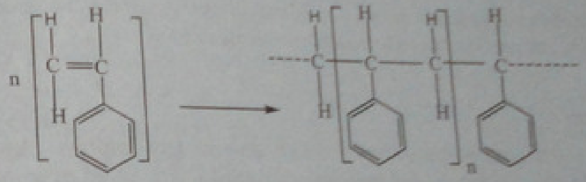
- As insulating materials (for motors, transformers, cables, wires and gaskets),
- for coating and impregnating glass fibers, asbestos fibers and cloths,
- in non-sticking stopcocks (for burettes), in non-stick frying pans, and
- Manufacture of gasket and valves etc.

b) Polystyrene (polyvinyl benzene)

Polystyrene is also known as polyvinyl benzene. It is isotactic polymer (if the side groups of the monomers lie on the same side of the chain, it is called an isotactic polymer). The monomer styrene is produced from the reaction

of ethylene and benzene. When ethylene is passed into benzene in presence of $AlCl_3$ catalyst, ethyl benzene is formed, which on passing over iron oxide catalyst at high temperature, it is converted in to styrene. The polymerization of styrene gives polystyrene.





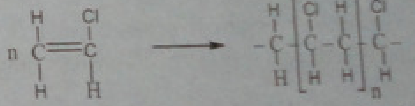
styrene Polystyrene

Uses:

In the manufacture of food containers, cosmetic bottles, television cabinets, plastic cups, packaging, toys, combs, buttons etc.

c) Polyvinyl chloride (PVC)

PVC is obtained by heating a water emulsion of vinyl chloride in presence of a small amount of benzoylperoxide or hydrogen peroxide in an autoclave under pressure.



Vinyl chloride Polyvinyl chloride

Vinyl chloride is generally prepared by treating acetylene at 1 to 1.5 atmospheres with hydrogen chloride at 60-80°C, in presence of metal chloride as catalyst.

$$\underset{\text{Acetylene}}{HC{\equiv}CH} + HCl \xrightarrow{HgCl_2} \underset{\text{Vinylchloride}}{CH_2{=}CHCl}$$

Uses:

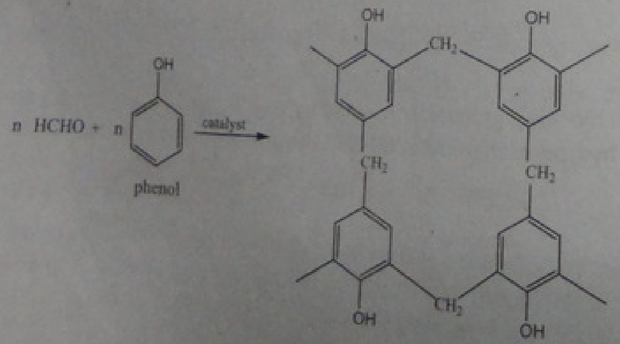
- Rigid PVC or unplasticied PVC have superior chemical resistance and high rigidity but brittle. It is used for making sheets, which are employed for tank linings, safety helmets, refrigerator components, tires, and cycle and motorcycle mud guards. It is also extruded in strip and tube form to use in place of nonferrous metals.
- Plasticized PVC (i.e. obtained by adding plasticizers such as dibutylphthalate, dioctylphthalate) is used for making insulating materials. Employed for packing rain-coats, table cloths and curtains, electrical insulation like coverings of electric cable, injection moulding of article like toys tool, handles, toilet goods, radio-components, plastic coated cloth, chemical containers, thermal insulation foam (used in buildings, cinemas and aircrafts).

Plasticizers:

Plasticizers are organic compounds which are used to improve plasticity and flexibility of the plastics. The plasticizer properties are believed to be mainly due to neutralization of intermolecular force of attraction in the plastic molecule.

Some of the examples of condensation polymer are discussed below.

a) **Phenol formaldehyde resin (bakelite):** It is prepared by condensing phenol with formaldehyde in the presence of catalyst. The nature of product depends on the nature of the catalyst (acid or base) and upon the proportion of the reactants. In the presence of acid catalysts and with the mole ratio of phenol to formaldehyde greater than one (i.e. P/F > 1) gives bakelite. The initial step results in the formation of o- and p-hydroxymethyl phenol, which condenses with phenol to form linear polymer known as Novolac. Further heating of novolac in the presence of hexamethylenetetramine (it produces HCHO) as curing agent produces three dimensional crosslinked network polymer which is known as bakelite.



Bakelite

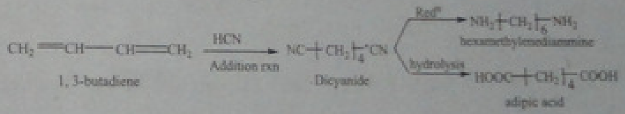
Note: As–OH group is ortho and para director, the electron density is always rich in orho and para positions and hence substitution takes place at these positions.

In presence of alkaline catalyst and when P/F < 1, instead of novolac, a linear polymer resoles is formed which on heating converted into a cross link structure called resite.

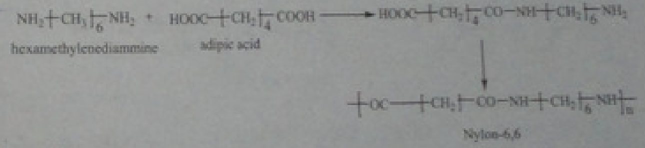
Uses:

- In making electric insulator parts like switches plugs, switch boards, heater handles etc.
- for making moulding articles like telephone parts, cabinets for radio and television,
- for impregnating fabrics wood and paper,
- as adhesives (binder) for grinding wheels, in paints, as hydrogen exchanger resins, in rolling mills and paper industry.

b) **[Nylon-6, 6]:** It is the most important polyamide polymer. It can be obtained by heating adipic acid with hexamethylene diamine at 200°C. Nylon-6, 6 derives its name from its starting materials, adipic acid and hexamethylene, both of which have six carbons. The hexamethylene diamine and adipic acid both can be prepared by 1, 3- butadiene.



Reaction:

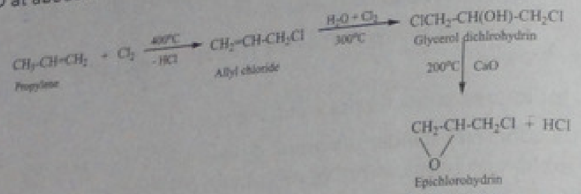


Uses:

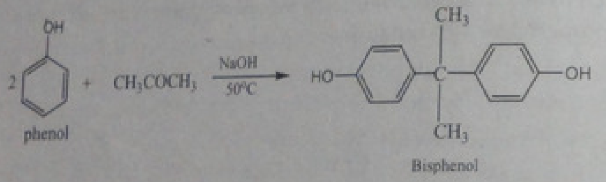
- Nylon-6,6 is primarily used for fibers, which find used in making socks ladies shoes ,under garments dresses, carpets, ropes etc.
- Nylon 6, 6 being a tough plastic, is used as a substitute for metals in gears and bearings etc.

c) **Epoxy Resins:** *The epoxy resins are basically polyether, but they are given this name due to the fact that their starting material is epichlorohydrin and the polymer before cross linking contains epoxy groups. Epoxy resins are prepared by the condensation of bisphenol and excess of epichlorohydrin.*

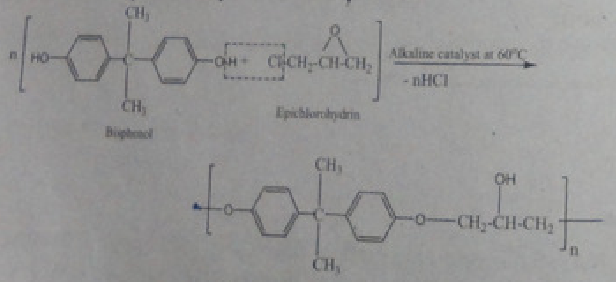
Preparation of epichlorohydrin: Propylene reacts with chlorine at 400°C to give allyl chloride, which on reacting with the mixture of water and chlorine at 300°C gives glycerol dichlorohydrin. On heating glycerol dichlorohydrin with CaO at about 200°C gives epichlorohydrin.



Preparation of bisphenol: It is prepared by reacting phenol with acetone in the presence of NaOH at 50°C.



Condensation of epichlorohydrin with bisphenol:



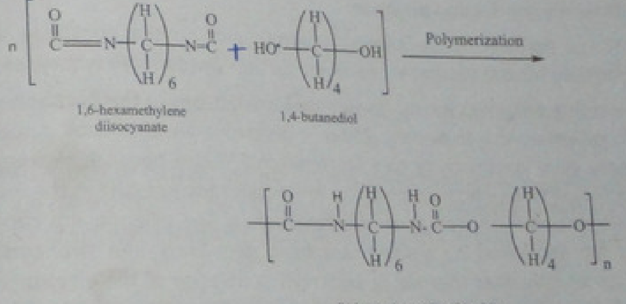
Epoxy resin

The reactive epoxide and hydroxyl groups give a three – dimensional cross-linked structure and the value of n ranges from 1 to 20.

Uses:

- As surface coating, adhesives like araldite (for glass, metal)
- For skid-resistance surfaces for highways.
- Epoxy resins are applied over cotton rayon to impart crease resistance and shrinkage control.
- As laminating materials, used in electrical equipment.

d) **Polyurethanes:** Polyurethanes are obtained by rearrangement polymerization commercially, by treating diisocyanate and diol.



Polyurethane (Perlon-U)

Uses:

- Polyurethanes are used as coatings, film, foam and elastomers.
- They find as a leather substitute.
- They are used to make mattress and pillow.
- They are also used to cast to produce gaskets and seals

Conducting polymers:

Most of the polymeric materials are poor conductor of electricity, because of the non-availability of large number of free electrons in the conduction process. Within the past several years; polymeric material has been synthesized which possess electrical conductivities on par with metals conductors. A polymer which can conduct electricity is termed as conducting polymer. The phenomenon of conduction is observed in a number of polymers such as polyacetylene, polypyrolle, polyaniline etc. Conducting polymers are classified as follows;

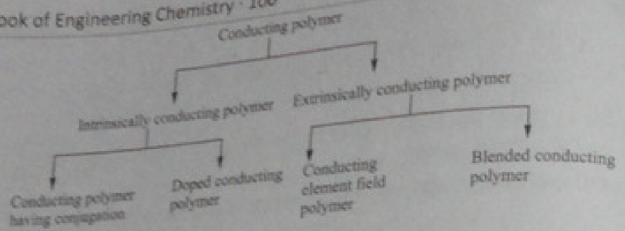


Fig: Classification of conducting polymers

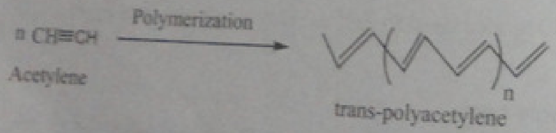
1. **Intrinsically conducting polymer:**

These polymers have extensive conjugation in the backbone which is responsible for conductance. These are further divided into two types;

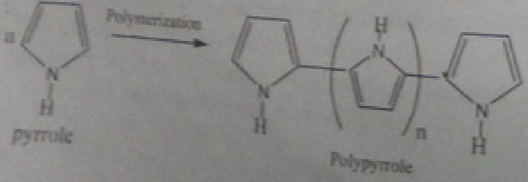
a. **Conducting polymers having conjugated π-electrons in the backbone:** Such polymers contain conjugated π-electrons in the back bone which increase their conductivity to a large extent. This is because overlapping of the conjugated π- electrons over the entire backbone results in the formation of valance bonds as well as conduction bands. The valence and conduction bands are separated by a significant band gap. Thus, electrical conduction could occur only after thermal or photolytic activation of the electrons to give them sufficient energy to jump the band gap and reach into the lower level of conduction band.

In an electric field, conjugated π-electrons of the polymer get excited thereby can be easily made mobile in conduction band and their mobility is responsible for conductivity. E.g. polypyrrole, polyacetylene etc.

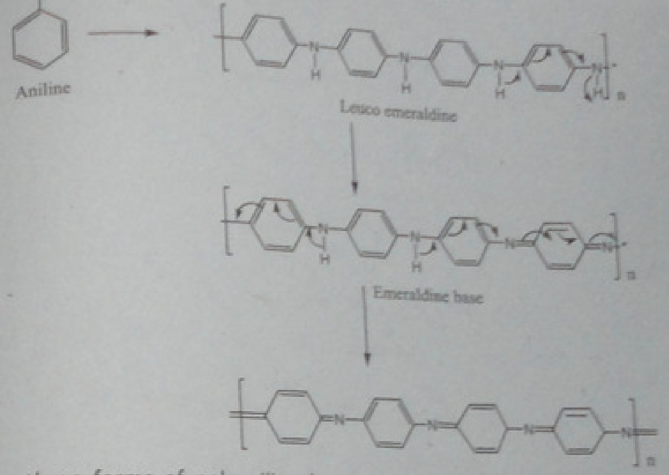
Polymerization of acetylene:



Polymerization of pyrrole:



Polymerization of aniline:



All the three forms of polyaniline have the conductivity of the orders of 10^{-10} $ohm^{-1}cm^{-1}$. Conductivity of these polymers having conjugated π-electrons in the backbone is not sufficient for their use in different applications.

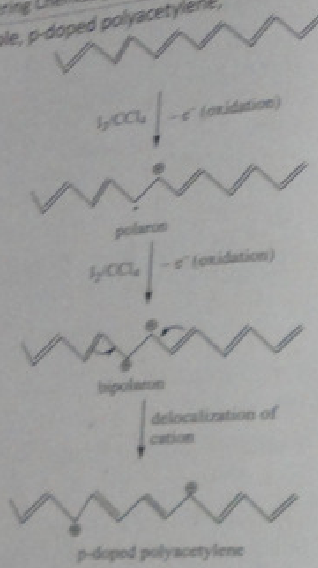
b✓ **Doped conducting polymers:** The process of transforming a polymer into its conductive form via chemical oxidation or reduction is called doping by analogy to somewhat related doping of semiconductors. The conductivity of the polymers having conjugated pi-electrons in the backbone can be increased by process of doping which can be carried out by two processes.

i. **p-doping (oxidative doping):** In p-doping, conducting polymer is partially oxidized by using a suitable oxidizing agent (that is why it is also called oxidative doping). This oxidation process (i.e. removal of electron from the polymer π-backbone) leads to the formation of delocalized radical ion called polaron. A second oxidation of this polaron, followed by radical recombination yields two positive charges on each chain which are mobile. Thus, these positive charges are current carriers for conduction. The oxidation is generally carried out by treated with Lewis acids such as I_2, Br_2, AsF_5 etc.

$$\text{Polymer} + X\ (\text{Lewis acid}) = (\text{Polymer})^{n+} + X^{n-}$$

$$\underset{\text{polymer}}{(CH)_x} + \underset{\text{lewis acid}}{X} \rightleftharpoons \underset{\text{p-doped polymer}}{(CH)_x^{\oplus} X^{\ominus}} \quad (\text{oxidation})$$

For example, p-doped polyacetylene,



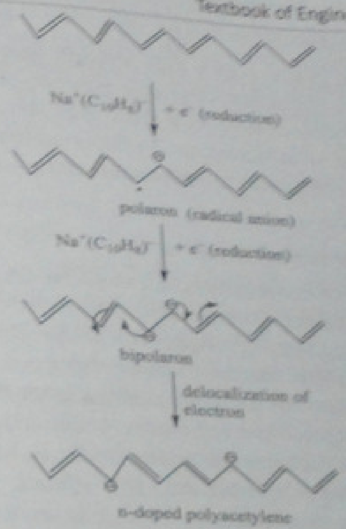
n-doping (reductive doping): It is done by reduction process (i.e. by adding electron to the polymer backbone). This type of conducting polymer can be prepared by treating it with Lewis base e.g. sodium naphthalide.

In this type of doping some electrons are introduced into the polymer backbone using a reducing agent like sodium naphthalide, leads to the formation of polaron and bipolaron, which contain two negative charges on the polymer chain and delocalization of these negative charges on the entire polymer chain is responsible for the conduction.

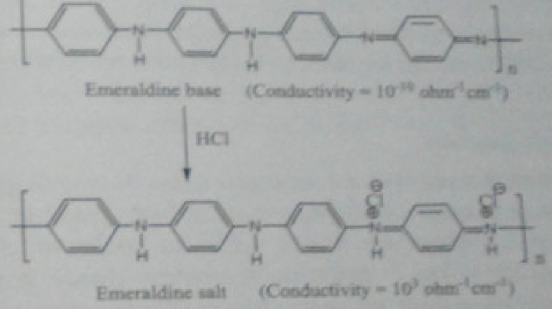
$$\text{Polymer} + \text{M (Lewis base)} = (\text{Polymer})^{n-} + \text{M}^{n+}$$

$$\underset{\text{polymer}}{(CH)_x} + \underset{\text{lewis base}}{B} \rightleftharpoons \underset{\text{n-doped polymer}}{(CH)_x^{\ominus} B^{\oplus}} \quad \text{(reduction)}$$

For example, n-doped polyacetylene,



Protonic doping: Addition of proton to the backbone of the polymer. Emeraldine salt (polyaniline salt) is also known as synthetic metal. It has conductivity and luster same that of the metals.



Applications:

- In rechargeable light weight batteries,
- In analytical sensors, sensors for pH, NH_3, NO_x, SO_2 etc.
- In making ion-exchangers, photovoltaic devices, telecommunication system,
- In electronics (electron beam lithography),
- In wiring in aircrafts and aerospace company,
- In solar cells, electronic display, variable transmission windows (optical filters)
- In drug delivery system for human body.

Fiber reinforced plastics

Reinforcing a plastic matrix with a high- strength fibre material result in the formation of what is called fiber-reinforced polymer. Glass, graphite, alumina, carbon, boron are the main reinforcing fibers used. Natural fibres such as sisal, asbestos are also used for reinforcement. The nature of fibres used determines the properties of the final reinforced composite desired.

Characteristics of fiber reinforced plastics

Glass fibre is the most extensively used and it continues to be the work-horse of the FRP industry. Low coefficient of thermal expansion, high dimensional stability, low cost of production, good tensile strength, non-flammability, corrosion resistance, chemical resistance easy to fabricate, neither shrink nor stretch are the most attractive features of glass fiber reinforced plastics. Carbon fibers have much higher specific modulus than glass fibers and possess better resistance to temperature and corrosive chemicals, high strength to weight ratio. However, carbon fibers are more expensive and have only limited short fiber utilization. The other fibers are used mainly when some specific added advantage or service conditions are to be fulfilled. They are generally costlier than the glass fibres.

Application

Fiber-reinforced polymer find extensive use in spacecraft, wall panel and window frames, boat hulls, acid storage tanks, motor cars and bathroom units, pipes etc.

Biodegradable polymers

Notwithstanding that polymers are reasonably stable. They undergo degradation due to exposure to oxygen, moisture, and ozone, heat, hydrolytic, enzymatic or bacteriological. The degradation may be due to the breakdown of the polymer structure resulting in loss in toughness or strength, change in chemical and electrical properties or there may be structural modification such as cross linking. Degradable polymers may be broadly divided in two basic categories.

1. **Photo degradable polymers:** In this type of polymer, light, particularly the higher energy part of the sun light spectra, can initiate reactions leading to degradation of the polymer.
2. **Biodegradable polymers:** Biodegradable polymer is a degradable polymer in which the degradation results from the action of biological enzymes or naturally occurring microorganisms such as bacteria, fungi and algae or biodegradable polymers are such polymers in which degradation is mediated at least partially by a biological system. A Biodegradable Polymer has the ability to break down, safely, reliably, and relatively quickly, by biological means, into raw materials

of nature and disappear into nature. Biodegradable polymers may be naturally occurring or they may be synthesized by chemical means. Cellulose, starch etc. are natural occurring biodegradable polymers. Polylatide, polyamide esters, polyglycoide etc. are synthesized biodegradable polymer.

Applications of biodegradable polymers:

Biodegradable polymers have captured tremendous public attention in recent years. Some of their applications are given below.

1. **Application in agriculture:** Time controlled biodegradable polyolefins are used in agriculture for mulching, netting etc. They have yield considerable economic dividends in increasing crops yields.
2. **Waste management application:** Polymer waste account for about 15% of the total wastes. Polymer waste management requires sound complementary practices of conservation, recycling, incineration, biodegradation. Since biodegradation is potentially the most environmentally friendly of all these practices. Therefore biodegradable polymers are receiving greater attention particularly for the use of packaging materials.

Non-biodegradable polymer:

A polymer whose degradation is not possible by the action of biological enzymes or naturally occurring microorganism such as bacteria, fungi and algae is called non-biodegradable polymer. Such type of polymers do not have the ability to break down, safely, reliably, and relatively quickly by biological means, into raw materials of nature and disappear into nature. E.g. polyurethanes, Epoxy resins etc.

Practice Questions

1. Write the preparation and uses of polymers formed by the polymerization of tetrafluoroethylene and vinyl chloride.
2. What are the differences between condensation and addition polymerization? Explain with examples of each.
3. Define the terms thermosetting and thermoplastics polymers with example. Write the preparation and uses of Bakelite and nylon-6,6.
4. Differentiate thermoplastic and thermosetting polymer with suitable examples. Describe the preparation and uses of polyurethane and epoxy resins.
5. Describe the preparation and uses of Polyphosphazines and polymeric sulphur $(PS)_n$. **[IOE-'67]**
6. Define the terms biodegradable and non-biodegradable polymers with suitable example.
7. What are the general characteristics of inorganic polymer? What do you mean by cross linked polymer? What are the engineering uses of chalcogenide polymer? **[IOE-'68]**
8. What are fibers –reinforced plastics? Write down the characteristics and its applications.
9. What are silicones? Write the application and uses of silicones.
10. What are chalcogenide glasses? Give an account of preparation and uses of network polymers of sulphur.
11. Write short notes on the following:
    a. Polyphosphazines
    b. Chalcogenide glasses
12. Show your acquaintance with long chain polymer of silicon.
13. What are silicones? How are they prepared?
14. Write down the preparation and uses of different types of sulphur based inorganic polymers.

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Chapter

5

Transition Elements & their applications

Transition Elements & their applications

Introduction:

The elements in which the last electron enters into the d-orbital are called d-block elements. These are also called transition elements because of their position in the periodic table, which lie between s- and p-block elements. They exhibit the transitional behavior between the highly reactive metallic elements of the s-block, which form ionic compounds and the p-block elements which form covalent compound on the other side. In the s- and p-blocks, electrons are added to the outer orbital of the atom. In the d-block elements, electrons are added to the penultimate shell expanding it from 8 to 18 electrons. Therefore the general valence shell electronic configuration of transition elements is **$(n-1) d^{1-10} ns^{1-2}$**.

According to the definition, transition elements have incompletely filled d-orbital i.e. typical transition elements have incompletely filled d-orbital. The elements of Cu-group (Cu, Ag, Au) and Zn-group (e.g. Zn, Cd, Hg) have d^{10} configuration and since the d-shell is complete, the compounds of these elements are different from that of other transition elements. Therefore, these elements are called non-typical transition elements. Overall, the transition elements comprise 3d, 4d, 5d and 6d- series.

i. First transition series (3d-series) include the elements from Sc (Z=21) to Zn (Z=30). These elements lie in the 4th period of the periodic table.
ii. Second transition series (4d-series) include the elements from Y (Z=39) to Cd (Z=48). These elements lie in the 5th period of the periodic table.
iii. Third transition series (5d-series) include the elements La (Z=57), and from Hf (Z=72) to Hg (Z=80). These elements lie in the 6th period of the periodic table.
iv. Fourth transition series (6d-series) include the elements Ac (Z=89) and beyond Lr (Z=104). These elements lie in the 7th period and this period is incomplete.

General characteristics of transition elements:

i. All they are metals. They are very hard, good conductor of heat and electricity.
ii. They have high melting and boiling points with few exceptions.

iii. They have high specific gravity.

iv. They exhibit variable oxidation state except zinc.

v. They form complex compounds.

vi. They form alloys with one another or with other elements.

vii. They dissolve in mineral acids with few exceptions.

viii. They form coloured compounds.

ix. They and their compounds are generally paramagnetic.

x. They and their compounds are used as a catalytic agent.

The general properties of the transition elements of any given period are not so much different from one another because of the electronic configuration that differs only in the number of electrons in penultimate d-subshell in the (n-1)th shell and the number of electrons in the outermost shell, ns is invariably 1 or 2. Some of the important properties of the transition elements are explained as follows. These properties are more focused for the 3d transition series as required by our syllabus. Almost similar trend is observed in other transition series.

1. Electronic Configuration:

The general valence shell electronic configuration of the d-block elements is $(n-1)d^{1-10}ns^{1-2}$. The electronic configuration of 3d-series elements are shown below.

S.N.	Elements	Atomic no. (Z)	Electronic Configuration
1.	Scandium (Sc)	21	$[Ar]_{18}\ 3d^1\ 4s^2$
2.	Titanium (Ti)	22	$[Ar]_{18}\ 3d^2\ 4s^2$
3.	Vanadium (V)	23	$[Ar]_{18}\ 3d^3\ 4s^2$
4.	Chromium (Cr)	24	$[Ar]_{18}\ 3d^5\ 4s^1$
5.	Manganese (Mn)	25	$[Ar]_{18}\ 3d^5\ 4s^2$
6.	Iron (Fe)	26	$[Ar]_{18}\ 3d^6\ 4s^2$
7.	Cobalt (Co)	27	$[Ar]_{18}\ 3d^7\ 4s^2$
8.	Nickel (Ni)	28	$[Ar]_{18}\ 3d^8\ 4s^2$
9.	Copper (Cu)	29	$[Ar]_{18}\ 3d^{10}\ 4s^1$
10.	Zinc (Zn)	30	$[Ar]_{18}\ 3d^{10}\ 4s^2$

The above configurations of the transition elements show the following features.

a. Atoms of all the transition elements consist of inner core of electrons having noble gas configuration.

b. The half-filled and completely filled d-orbitals gain extrastability by gaining such favourable configuration whenever possible.

2. Metallic character:

All the transition elements are metals. They are therefore good conductors of heat and electricity have metallic luster and are hard, malleable and ductile. They also form alloys with other metals.

The metallic character of transition elements is mainly attributed to their low value of ionization energies, so that they can easily lose outer ns-electrons to form M^+ or M^{2+} cations.

They have high melting points, boiling points and heat of vapourization. The high melting and boiling points indicate the existence of strong metallic bonding between the atoms. It has been predicted that the unpaired electrons in the inner d-orbital take part in bonding. This is evident from the graph of the variation of melting and boiling points in 3d-series shown below. Zinc has the lowest m.p. and b.p. This suggests that all the d-electrons in zinc are paired and play a little part in metallic bond formation. Hence, zinc is soft.

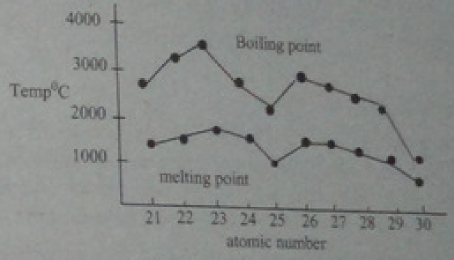

Fig: Melting and boiling points of 3d-series

3. Atomic radii:

In 3d-transition series moving from left to right, the atomic radii first decrease till the middle, becomes almost constant and increase from Ni to Zn. This is shown in the following table;

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic radii (A⁰)	1.44	1.32	1.22	1.17	1.17	1.17	1.16	1.15	1.17	1.25

Initial decrease in atomic radii is attributed to the increase in nuclear charge. However, the increased nuclear charge is partly cancelled by the increased screening effect of electrons in the penultimate d-orbital. When the increased nuclear charge and screening effect balance each other, the atomic radii become almost constant. Increase in atomic radii toward the end may be attributed to the electron-electron repulsions. Since the pairing of electrons in d-orbital occurs after d^5-configuration. The repulsive interactions between the paired electrons in the d-orbital become very dominant towards the end of period therefore the electron cloud expansion and hence results increasing atomic radii.

4. **Ionization energies:**

The ionization energies of d-block elements lie between that of s- and p-block elements. They are higher than those of s-block and are lesser than those of p-block elements. The ionization energy gradually increases with increase in atomic number along a given transition series. It is due to the increased nuclear charge with increase in atomic number which reduces the size of the atom making the removal of outer electron difficult. In a given series, the difference in ionization energies between two elements is very much less than s- and p-block elements. It is due to the screening effect of d-electron to the outer s-electrons. Thus the effect of increased nuclear charge and addition of d-electrons oppose each other. This is due to their counter effect that the ionization energies show a little variation on moving along a period. The value for zinc is appreciably higher due to the increase in atomic size.

Ionization energies of 3d-series (in KJ/mole)

Elements	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Ionization energy (KJ/mol)	631	656	650	652	717	762	758	736	745	905

5. **Variable Oxidation States:**

One of the striking features of the transition elements is that the elements usually exhibit variable oxidation states. The large numbers of oxidation states of the transition elements are related with their electronic configurations. Oxidation states of the 3d-series of the elements are illustrated in the table below.

Table: *The outer electronic configuration and the possible oxidation states of the 3d-transition elements*

Elements	Outer electronic configuration	Oxidation states
Sc	$3d^1 4s^2$	+2, +3
Ti	$3d^2 4s^2$	+2, +3, +4
V	$3d^3 4s^2$	+2, +3, +4, +5
Cr	$3d^5 4s^1$	+1,+2, +3, (+4), (+5), +6
Mn	$3d^5 4s^2$	+2, +3, +4, (+5), +6, +7
Fe	$3d^6 4s^2$	+2, +3, (+4), (+5), (+6)
Co	$3d^7 4s^2$	+2, +3, (+4)
Ni	$3d^8 4s^2$	+2, +3, +4
Cu	$3d^{10} 4s^1$	+1,+2, (+3)
Zn	$3d^{10} 4s^2$	+2

Note: *The unstable oxidation states are kept inside the bracket.*

The variable oxidation of the transition elements is mainly attributed to the following two reasons:

i. Participation of outer ns- and penultimate (n-1)d-electrons in bonding since these orbitals have almost equivalent energies. The most common oxidation state shown by the elements of 3d-series is +2. The highest oxidation states are observed when the atoms are combined with the most electronegative anions such as fluorides and oxides.

ii. After removing ns-electron(s), the remainder is called core. In the case of d-block elements, the core is usually unstable and hence loses one or more electrons. The removal of one or more electrons from the unstable core gives several oxidation states to transition metals.

Illustrations:

- The **Sc** could have an oxidation number **II** if both the s-electrons are used for bonding and **III** if two s- and one d-electron are involved. The most stable oxidation state of Sc is **III**.
- In a similar way, the oxidation states **II**, **III** and **IV** are possible for Titanium. The possible oxidation states for vanadium are **II**, **III**, **IV** and **V**.
- In the case of Chromium, by using a single s-electron, the oxidation number is **I** and then by varying number of d-electrons, possible oxidation states are **II**, **III**, **IV**, **V** and **VI**. Manganese has oxidation states **II**, **III**, **IV**, **V**, **VI** and **VII**.

Once the d^5-configuration is exceeded, the tendency of all the d-electrons to participate in bonding decreases due to more effective nuclear charge. Therefore the oxidation states start decreasing after Mn. Hence, Fe has maximum oxidation state **VI** due to the participation of outer s-electrons and unpaired d-electrons. Similarly, Co and Ni have maximum oxidation state **IV** and Cu and Zn have **II**.

Transition metals also form compounds in low oxidation states such as +1 and zero. For example, Ni in $[Ni(CO)_4]$ has zero oxidation state.

The relative stability of various oxidation states of the element can be explained on the basis of stability of d^0, d^5 and d^{10} orbitals.

6. **Complex forming tendencies:**

The transition elements have unusual tendency to form complex compounds with electron pair donars. Such electron pair donars are called ligands.

The transition elements are good at forming complexes because of the following factors:

- Transition metal atoms or cations have small size and they have high positive charge density. This high positive charge density makes the atoms or cations to strongly attract the lone pairs of electrons from the ligands.

- The transition metal cations or atoms have vacant d-orbitals in which they can accommodate the lone pairs of electrons donated by ligands and thus can form L→M co-ordinate bonds. The detail of complex compounds is given in the next chapter.
- The transition metals are capable of showing several oxidation states. At several oxidation states, they form stable complexes.

Relative stability of the complexes:

i. The stability of complex compounds decreases with increase in atomic number of the central metal atom.

ii. Complexes where the metal has higher oxidation state are generally more stable than those where the metal is in lower oxidation state.

7. Alloys formation:

It is known that the atoms of many transition elements have very much comparable (almost same) size and hence the atoms of one metal can be replaced by the atoms of other metal. This replacement gives rise to the formation of alloys. Thus when Mn is dissolved in molten iron and the solution is cooled; manganese-iron alloy is obtained. Such alloys are hard, have high melting point and are more resistant to corrosion than the parent metals.

8. Catalytic activity:

Many transition metals (Fe, Ni, Pt), alloys (Fe/Mo) and their compounds (V_2O_5, MnO_2) act as catalyst in many chemical reactions. It is due to the following reasons.

a. Since the transition metals have vacant d-orbitals and show variable oxidation states, these elements can form unstable intermediate compounds with suitable reactants. These intermediate compounds give reaction paths for lower activation energy and therefore increase the rate of reaction. The intermediate compounds decompose readily to give the final products and original substance (catalyst).

$$\begin{tikzcd}
\text{Reactants + Transition metals or compounds} \arrow[r] & \text{unstable intermediate compound} \arrow[d, "\text{decompositon}"] \\
& \text{products + Transition metals or compounds}
\end{tikzcd}$$

b. In some cases, the transition metals and their compounds provide large surface area on which the reactants may be absorbed and therefore come closer to each other for the reaction. For the example, see in the chapter-catalysis.

9. *Colour formation:*

Many ionic and covalent compounds of transition elements are coloured while that of the s- and p- block elements are almost always white or colourless.

Causes of Colour appearance-

When white light passes through a material the transmitted radiations are deprived of those wavelengths that are absorbed. If the absorption occurs in the visible region of the spectrum, the transmitted light has complementary colour to the colour of the light radiation absorbed. Absorption in the visible region of the spectrum is caused by changes in the electronic energy. Thus the spectra are sometimes called electronic spectra. The electronic changes are accompanied by vibration and rotational changes. Usually the electronic jumps require much energy and the absorption occurs in the uv-region. However, some special circumstances cause the smaller electronic jumps and absorption occurs in the visible region. This is the instance at which the substance appears colourful.

The compounds of the typical transition metals are usually colourful. This is because of the incompletely filled d-orbital. In a free isolated gaseous ion, the five d-orbitals are degenerate (i.e. have equal energy) but in the solution state or compound state the energy of the d-orbitals is perturbed/changed cause splitting into different energy d-orbitals. This is known as crystal field splitting. The energy differences between splitted orbitals lie in the visible range. Now the electronic transition between low energy d- to high energy d-orbital of the same sub shell is called d-d transition is possible by the absorption of visible radiation. This is the reason why the solution or complexes of the transition metal ions are usually colourful.

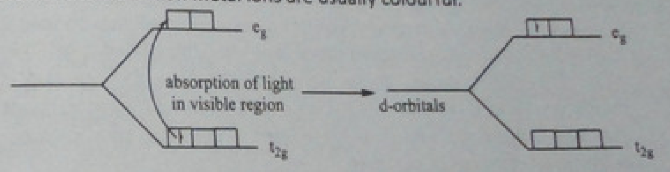

fig: showing d-d transition in a complex $[M(H_2O)_6]^{n+}$ when it has one unpaired electron in the central metal atom(M).

The colours of some common hexa hydrated transition metal complex ions $[M(H_2O)_6]^{n+}$ are given below,

Table: The colour of the hexa hydrated octahedral complexes of the 3d-transition metals.

Ions	Complexes	Outer electronic configuration	No. of unpaired electrons(n)	Colour of the Ions
Ti^{3+}	$[Ti(H_2O)_6]^{3+}$	$3d^1$	1	Violet(almost purple)
V^{3+}	$[V(H_2O)_6]^{3+}$	$3d^2$	2	Green
V^{2+}, Cr^{3+}	$[Cr(H_2O)_6]^{3+}$	$3d^3$	3	Violet
Cr^{2+}	$[Cr(H_2O)_6]^{2+}$	$3d^4$	4	Blue

Mn^{2+}	$[Mn(H_2O)_6]^{2+}$	$3d^5$	5	Pink
Fe^{2+}	$[Fe(H_2O)_6]^{2+}$	$3d^6$	4	Green
Co^{2+}	$[Co(H_2O)_6]^{2+}$	$3d^7$	3	Pink
Ni^{2+}	$[Ni(H_2O)_6]^{2+}$	$3d^8$	2	Blue-green
Cu^{2+}	$[Cu(H_2O)_6]^{2+}$	$3d^9$	1	Blue
Zn^{2+}	$[Zn(H_2O)_6]^{2+}$	$3d^{10}$	0	Colourless

The energy associated with the wavelength of the radiation absorbed by the complex ion can be calculated. Suppose $[M(H_2O)_6]^{n+}$ ion absorbs the radiation of wavelength λA°. The frequency in wave number (cm^{-1}) is given by,

$$\bar{\upsilon} = 1/\lambda \text{ in A}^\circ = 1/\lambda x 10^{-8}\text{cm} \quad [1\text{ A}^\circ = 10^{-8}\text{cm}]$$
$$= 10^8/\lambda \text{ cm}^{-1}$$

This frequency is associated with the energy as, $350 cm^{-1} = 1 Kcalmol^{-1}$

$$83.7 cm^{-1} = 1 KJmol^{-1}$$

It may be noted that transition metal ions containing filled d-orbitals (d^{10}) such as Zn2+, Cd2+, Hg2+ etc are white. Similarly, Sc3+, Ti4+, V5+ are also white because they have empty d-orbitals (d^0). In such cases, the d→d transition is not possible and hence no light of any colour or wavelength is absorbed by such ions resulting the transmitted radiation to be white.

Illustration: $[Ti(H_2O)_6]^{3+}$ has purple colour.

In this ion, the oxidation state of Ti atom is +3 i.e. Ti^{3+} and it can exist in the aqueous solution in the form of Ti^{3+} and it has d^1 configuration. The single electron in the complex will occupy the lowest energy orbital i.e. one of the t_{2g} orbitals (d_{xy}, d_{yz}, d_{xz}) while e_g orbitals (d_{x2-y2}, d_{z2}) remain completely vacant. The energy difference of t_{2g} and e_g orbitals lie in the visible range and the absorption of visible radiation lead to electronic transition from t_{2g} to e_g. In the case of this complex, the absorption of green radiation takes place so that the ion has complementary color, which is purple. This type of transition is called d-d transition and the above transition may be represented as,

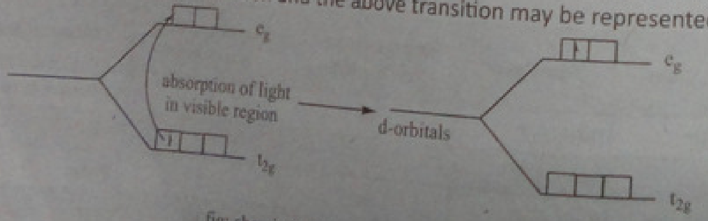

fig: showing d-d transition in Ti^{3+} complex

In the similar way, the colour of different complex compounds can be explained. $[Cu(H_2O)_6]^{2+}$ appears blue-green.

Some compounds of transition metals are white and colourless, for example $ZnSO_4$ and TiO_2. In these compounds, d-d transition is not possible. In $ZnSO_4$, Zn^{2+} has d^{10} configuration i.e. the d-orbital is fully filled and there is no possibility of electron transition. In TiO_2, Ti^{4+} has d^0 configuration and there are no d-electrons for d-d transition. Therefore the compounds where there is no possibility of d-d transition are colourless.

The s and p-block elements don't have partially filled d-shell so there cannot be any d-d transitions. The energy to promote an s or p-electron to a higher energy level is much greater and corresponds to uv-region of light being absorbed. Thus the compounds of s and p-block elements are colourless.

Illustrations:

V_2O_5 is colourless while VO_2 is purple in colour. This can also be explained on the basis of d-d transition. In V_2O_5, the oxidation state of vanadium is +5 and V^{+5} has d^0 configuration. Thus there is no possibility of d-d transition and hence it has no typical colour. But in VO_2, the oxidation state of vanadium is +4 and V^{+4} has d^1 configuration and d-d transition is possible at the absorption of green radiation. Therefore the transmittance of complementary colour causes it to appear purple in colour.

TiO_2 is white but $TiCl_3$ is violet. This is because in TiO_2, the oxidation state of Ti is +4 and Ti^{4+} has d^0 configuration. Then there is no possibility of d-d transition and hence it is white in appearance. But in $TiCl_3$, the oxidation state of Ti is +3 and Ti^{3+} has d^1 configuration. That is, there is one unpaired electron and its d-d transition takes place by the absorption of red and yellow radiations, the complementary of which is violet.

10. Magnetic properties:

In general all the materials are associated with the magnetic properties. When a substance is placed in a magnetic field of strength H, the intensity of magnetic field in the substance may be greater or less than H. if the field in the substance is greater than H, a substance is paramagnetic where as if the field in the substance is less than H, the substance is diamagnetic.

Most of the transition elements and their compounds show paramagnetism. Paramagnetism arises by the presence of unpaired electrons in atoms, ions or complexes or molecules. The spin and orbital motion of an electron (a charged particle) creates a magnetic field. Thus each electron is regarded as micro magnet having a definite value of magnetic moment. Then the total magnetic moment of a substance is the resultant of the magnetic moments of all the individual electrons. The magnetic moment is related to the number of unpaired electrons by the following relation,

Magnetic moment (μ) = $\sqrt{n(n+2)}$ BM (Bohr Magnetron)

Where, n = number of unpaired electrons.

$$1\ BM = \frac{eh}{4\pi mc} = 9.27 \times 10^{-21}\ \text{erg/gauss}$$

Where, e = electronic charge, h = Planck's constant, m = mass of electron and c= velocity of light.

The total magnetic moment is the sum of spin magnetic moment (μ_s) and orbital magnetic moment (μ_l).

$$\mu = \mu_s + \mu_l$$

The orbital magnetic moment is given by,

$$\mu_l = \sqrt{l(l+1)}\ BM$$

Where, l = orbital angular momentum.
The spin magnetic moment is given by,

$$\mu_s = 2\sqrt{s(s+1)}\ BM$$

Then, $$\mu = \left(\sqrt{l(l+1)} + 2\sqrt{s(s+1)}\right) BM$$

$$= \left(\sqrt{l(l+1)} + 2\sqrt{s(s+1)}\right) \frac{eh}{4\pi mc}$$

In case of transition metal ions, the crystal field effect (i.e. the ligands surrounding the metal ions) restrict the moment of electron round the nucleus of the orbit. Hence orbital magnetic moment is quenched and hence,

$$\sqrt{l(l+1)} = 0$$

Thus the magnetic moment of the electron is given by,

$$\mu = 2\sqrt{s(s+1)}\ BM$$

If there is one unpaired electron, the value of $s = +\frac{1}{2}$ or $-\frac{1}{2}$. Then, the magnetic moment (μ) is given by, For electron, s = 12

So, $$\mu_s = 2\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)} = 2\sqrt{\frac{1}{2} \times \frac{3}{2}} = \sqrt{3}\ BM$$

In the transition series, paramagnetism first increases and then decreases. The maximum paramagnetism is observed around the middle of the series because of the large number of unpaired electrons. After that, the electrons undergo pairing and hence the magnetic moment decreases. The atoms or ions having paired electrons are diamagnetic because the magnetic moment due to one electron is opposite in direction to that of the next and it is cancelled out so that the resultant magnetic moment is zero.

Uses of magnetic moment

The experimentally determined magnetic moment of a complex can be used to deter-

mine the total number of unpaired electrons occupying the d-orbitals of the central metal atom/ion. The number of unpaired electrons provides the informations such as,

- Whether the 4-coordinated complex compound is square planar or tetrahedral.
- Whether the given 6-coordinated complex compound is inner octahedral or outer octahedral complex

Applications of 3d-transition elements:

1. Sc^{3+} is smaller than that of other ions of this sub-group. It has greater tendency to form complexes e.g., $[ScF_4]^-$, $[ScF_5]^{2-}$, $[ScF_6]^{3-}$ etc.
2. Due to the strength, lightness, corrosion resistance and low thermal expansion of Ti, it is used in high speed air craft, military projects and in chemical industry.
3. Ti is used to remove traces of gases like O_2, H_2 and N_2 from evacuated vessels.
4. $TiCl_4$ is a Ziegler-Natta catalyst used in the polymerization of alkenes.
5. Alloys of Ti are used as deoxidizers and in construction of tanks, automobiles and ships. Ferro-titanium which is an alloy of titanium with iron is obtained in electric furnace by reducing ilmenite ore ($FeTiO_3$) with carbon or aluminum is used in steel industry as a scavenger to remove absorbed O_2, H_2 and N_2 and hence as cleansing and deoxidizing agent.
6. Alloy of Ti with Cr, Fe and Mn are used for making rails, gears, propellers, car wheels etc.
7. TiO_2 is used in the manufacture of paints and pigments. Mixed with $BaSO_4$, it is sold under the trade name 'titanox'.
8. Titanium dioxide can also be used in making non-greasable paper, in the manufacture of arc lamp electrodes and for the preparation of glazes.
9. $TiCl_4$ is used in making smoke screens while the dichloride and oxalate are used in dyeing and mordanting.
10. About 90% of vanadium is used for making ferro-vanadium alloy which is used in the manufacture of steel and as a scavenger (removal of N_2 and O_2). Addition of 0.1-0.3% vanadium to steel increases toughness, tensile strength. The resulting special steel is much used in the construction of motor cars. Alumino-vanadium alloy is used in the manufacture of air-crafts. Vanadium is an essential constituent of high speed tool.
11. V_2O_5 is used as a catalyst in the manufacture of sulphuric acid by contact process and oxidation of naphthalene. Vanadium compounds find applications in the manufacture of ink, in dyeing, as accelerators in drying paints and varnish, in insecticides, photographic chemicals, medicine and in glass industry.
12. Chromium is used mostly for chrome plating and making alloys (stellite is an alloy containing Cr, 20-35%, Co 40-80%, Ni 0.25%, C 0.75-2.5% , W (tungsten) remaining part is employed for making surgical instruments.
13. Cr_2O_3 dissolved in glacial acetic acid is used as an oxidizing agent and as a disinfectant to wash foul ulcers and sores.

14. $K_2Cr_2O_7$ is used as a lab reagent, indicator.
15. A mixture of potassium dichromate and conc. Sulphuric acid known as chromic acid has strong oxidizing properties and is used as a cleansing agent for glass wares etc. It is also used in leather industry (chrome tanning).
16. A number of alloy and manganese are of very good importance. Ferro-manganese; 70-80% Fe and 12% Mn is very hard and resistant to wear and is used for making rock crushers, rail road, and armor plate.
17. $KMnO_4$ is used as a disinfectant, oxidizing agent, in volumetric reagent and is used for the estimation of ferrous salts.
18. MnO_2 is used as an oxidizing agent.
19. Iron is used in construction of building, bridge, making magnets, steel. Alloy steels are used in industry.
20. Cobalt is used in electroplating and in the formation of alloys. Cobalt-chrome is an alloy of 60% Co, 15% Cr, and 25% Fe and it is used for making resistance wire similar to nickel-chrome, stellite is used for making surgical instruments.
21. Ni finds use in making crucibles, dishes and other chemical wares due to high melting point, greater resistance to corrosion in acids and alkalies.
22. Finely divided Ni is used as a catalyst in the hydrogenation of oils.
23. Invar is an alloy containing 35% Ni with Fe and C is used for making meter scale, measuring instruments and clock pendulum.
24. Copper is extensively employed for making electrical wires, for making vacuum pans, heating utensils, calorimeters and conductor coils, for making coins and in electroplating and electrotyping. Compounds of Cu are used as insecticides and colouring materials.
25. Zinc is used for the galvanization of iron to prevent from rusting. Zn is used for making alloys e.g. brass. Granulated zinc is used in lab for the preparation of hydrogen gas. Zn is used in metallurgy of silver and gold, as reductant, for the manufacture of dyes, drugs and perfumes.

Practice Questions

1. What are transition elements? Why are they called so? Show with their general outer electronic configuration. [IOE-'66]
2. Explain why transition metals (i) show variable oxidation states and (ii) form large number of complexes. [IOE-'66]
3. Discuss the properties of transition elements with reference to
    i. complex formation
    ii. variable oxidation states
    iii. Magnetic properties [IOE-'67]
    [IOE-'67]
4. $[Ti(H_2O)_6]^{3+}$ has purple colour. Explain with the phenomenon of d-d transition.
5. Why does the presence of unpaired electrons make a substance paramagnetic in nature?
6. Give reasons for the following.
    i. Transition elements have variable valency.
    ii. Transition element complexes are coloured. [IOE-'66]
    iii. Transition elements are suitable for complex formation. [IOE-'66]
    iv. Transition element compounds are paramagnetic. [IOE-'66]
    v. V_2O_5 is a colourless compound but VO_2 is blue in colour.
    vi. All the d-block elements are not transition elements.
    vii. D-block elements except Zn form coloured compounds.
7. Show your acquaintance with application of 3-d transition elements. [IOE-'67]

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Chapter

6

Coordination Chemistry

Coordination Chemistry

Coordination chemistry is a branch of chemistry which deals with the study of the formation, geometry, stability and the characteristics associated with the coordination compounds. This is an important dimension of chemistry that has significant contributions to human society to come to this stage.

Background: We know that a neutral salt is produced by the reaction between acid and base. For e.g.

$$HCl + NaOH \rightarrow NaCl + H_2O$$

The simple salts produce their individual ions on dissolving into the solvent.

$$NaCl \rightarrow Na^+ + Cl^-$$

However, depending on the extent of neutralization, the salts may be normal, acidic or basic salts.

When the solutions of two or more simple salts are mixed in the ratio of their molecular weights and the solution is allowed to crystallize, a new compound separates out. Such compounds are known as addition compounds and the nature of such addition compounds is found mainly of two types.

i. Double salts or Lattice compounds
ii. Complex salts or Coordination compounds

Double salts

The compounds which exist only in the crystal state but break down into their constituents when dissolved in water are called double salts. They dissociate into the individuals like the ions released by the dissolution of simple salts. For e.g., Mohr's salt – $FeSO_4(NH_4)_2SO_4.6H_2O$

Potash alum (Fidkiri) – $K_2SO_4Al_2(SO_4)_3.24H_2O$

Carnallite – $KCl.MgCl_2.6H_2O$ etc.

The formation and dissociation of them may be shown as follows,

$$KCl + MgCl_2 + 6H_2O \rightarrow \underset{\text{carnallite}}{KClMgCl_2.6H_2O} \leftrightarrow K^+ + Mg^{2+} + 3Cl^-$$

$$K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \rightarrow \underset{\text{Potash alum}}{K_2SO_4Al_2(SO_4)_3.24H_2O} \leftrightarrow 2K^+ + 2Al^{3+} + 4SO_4^{2-}$$

$$FeSO_4 + (NH_4)_2SO_4 + 6H_2O \rightarrow \underset{\text{Mohr's salt}}{FeSO_4(NH_4)_2SO_4.6H_2O} \leftrightarrow Fe^{2+} + 2\,NH_4^+ + 2\,SO_4^{2-}$$

Co-ordination compound

The compounds which retain their identities even in the solution state as they are not dissociated into their individual ions in the solution are called coordination compounds. For e.g., when ammonium hydroxide solution is added into a copper sulphate solution, an intense blue coloured solution is formed.

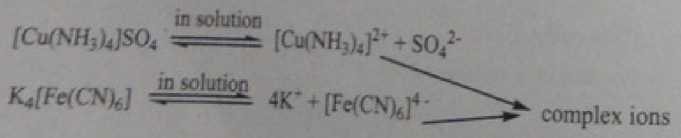
$$CuSO_4 + 4NH_4OH \longrightarrow CuSO_4.4NH_3 \quad \text{or} \quad \underset{\substack{\text{tetraammine copper sulphate}\\ \text{(intense blue)}}}{[Cu(NH_3)_4]SO_4}$$

Now the solution does not give cu^{2+} ion test since it forms a complex ion in association with ammonia. This ion is called complex ion. Similarly, when the solution of $Fe(CN)_2$ and KCN are mixed together, one gets,

$$Fe(CN)_2 + 4KCN \longrightarrow Fe(CN)_2.4KCN \quad \text{or} \quad \underset{\text{Potassium hexacyanoferrate (II)}}{K_4[Fe(CN)_6]}$$

The solution of this salt does not give free Fe^{2+} ion or CN^- ion test, confirms that a complex ion is formed.

These compounds dissociate in the solution as follows;



$$[Cu(NH_3)_4]SO_4 \xrightleftharpoons{\text{in solution}} [Cu(NH_3)_4]^{2+} + SO_4^{2-}$$

$$K_4[Fe(CN)_6] \xrightleftharpoons{\text{in solution}} 4K^+ + [Fe(CN)_6]^{4-}$$

Differences between Double salts and Complex salts

S.N.	Double Salts	Complex Salts
1.	These salts are the combination of two simple salts in equimolar ratio.	These salts may or may not contain the simple salts in equimolar ratio.
2.	They retain their identity only in solid state but loses as soon as they are dissolved.	They retain their identity both in solid as well as solution state.
3.	They are dissociated into their individual ions in the solution. For e.g., K^+, Mg^{2+}, NH_4^+ etc.	They are not dissociated into their individual ions in the solution but they give complex ions in the solution. For e.g., $[Fe(CN)_6]^{4-}$
4.	No coordinate bonds are present.	The ligands are attached to the central metal atom/ion through co-ordinate bonds.
5.	In double salts, metal ions show their normal valencies.	In complex salts, metal ions exhibit primary valencies i.e. oxidation state and secondary valencies i.e. coordination number.

Important terms related to co-ordination compounds:

Co-ordination compound

A compound in which a metal atom or ion is coordinated to anions or neutral molecule which retains its identity in the solid as well as in the solution is called coordination compound. It is not completely dissociated into individual ions instead it releases complex ion when dissolves in the solution. Some examples are as follows,

Tetra ammine copper (II) sulphate, $[Cu(NH_3)_4]SO_4$ gives complex ion, $[Cu(NH_3)_4]^{2+}$

Hexa ammine cobalt (III) chloride, $[Co(NH_3)_6]Cl_3$ gives complex ion, $[Co(NH_3)_6]^{3+}$

Potassium hexacyanoferrate (II), $K_4[Fe(CN)_6]$ gives complex ion, $[Fe(CN)_6]^{4-}$ etc.

Complex ion: An electrically charged ion which consists of a central metal atom or ion surrounded by a group of ions or neutral molecules is called complex ion. The complex ion carrying a positive charge is called cationic complex and that carrying negative charge is called anionic complex. For e.g., $[Cu(NH_3)_4]^{2+}$, $[Co(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{4-}$ etc.

Cationic complex: A complex ion having a net positive charge is known as cationic complex. For e.g., $[Cu(NH_3)_4]^{2+}$.

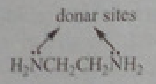
Anionic complex: A complex ion having a net negative charge is known as anionic complex. For e.g., $[Fe(CN)_6]^{4-}$.

Central atom or ion: The metal atom or ion to which two or more ions or neutral molecules are attached is called central atom or ion. For e.g., Cu^{2+} ion is a central ion in $[Cu(NH_3)_4]^{2+}$ complex ion.

Ligands: The molecular or ionic species which get attached directly to the central metal atom or ion during the formation of complex compound is called ligand. The ligands are attached to the central atom or ion through co-ordinate bonds and hence they are also called coordinating groups. They are the electron pair donars to form the coordinate bonds with the metal atom or ion and it is represented as L→M. The atom through which a ligand donates electron pair to vacant orbitals of metal atom or ion is called electron donors atom. Ligands are of several types depending on the number of donors sites (the atoms through which the ligands are attached to the central atom or ion).

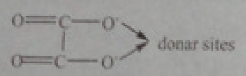
1. **Monodentate ligands:** The ligands having only one donor site are known as monodentate ligands. They donate only a single pair of electron to form a single coordinate bond to metal atom or ion. For e.g., H_2O, NH_3, Cl^-, CN^- etc.
2. **Bidentate ligands:** The ligands having two donor sites are called bidentate ligands. They donate double pairs of electrons to form two coordinate bonds. For e.g.,

Ethylenediamine - binding via nitrogen,



$H_2\ddot{N}CH_2CH_2\ddot{N}H_2$

Oxalato - $C_2O_4^{2-}$, binding via oxygen



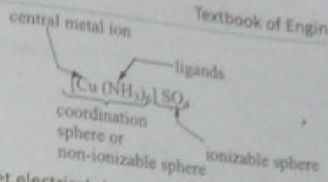
3. **Polydentate ligands:** The ligands having more than two donor sites are called polydentate ligands. These ligands can form more than two coordinate bonds to the same central metal atom/ion. For e.g.,

   Diethylenetriamine, $NH(CH_2CH_2NH_2)_2$,

   $EDTA^{4-}$, (sexidentate or hexadentate, binding via nitrogen and oxygen)

Co-ordination number (CN): The total number of lone pairs through which the ligands are directly connected to the central metal atom or ion in a complex is called co-ordination number of the central metal atom/ion. For e.g., the C.N. of Ag^+ in $[Ag(CN)_2]^-$ is 2.

Co-ordination sphere: In co-ordination compounds, the central metal ion along with the non-ionizable ligands attached to it is always expressed in a square bracket. This part of the complex is called a co-ordination sphere or non-ionizable sphere. The portion present outside the square bracket is called ionization sphere or outer sphere. For e.g.,

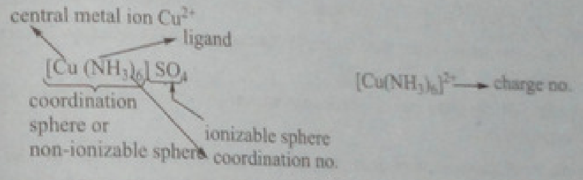


Charge number: The net electrical charge on a complex ion is called the charge number. It is determined by calculating the sum of the charges carried by central metal ion and the ligands.

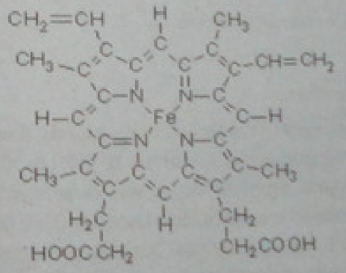
In $[Fe(CN)_6]^{4-}$, the charge number is calculated as,

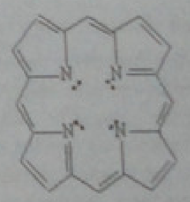
The charge on iron ion is 2+ and the charge on each ligand (CN^-) is -1, so $6CN^-$ = -6. Therefore the charge number of the above ion is given by, +2+ (-6) = -4.

Thus in summary, all the terms are diagrammatically shown as,



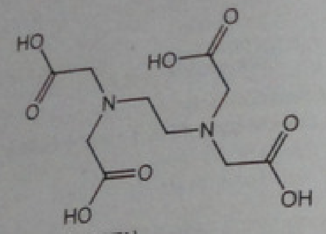
Chelating ligands and Chelates: The bidentate or polydentate ligands when attached to the same central metal ion through their all donor sites form a ring structure like that 'a prey is captured by many legs of scorpion'. The so formed ring shaped structure is more stable than normal expectation. Such ring shaped complex is called chelate and the ligands involved are called chelating ligands. For e.g.





Porphyrin macrocycle

Heme



Ethylene Diammine Tetraacetic acid (EDTA)

Applications of chelates:

Some important applications of the formation of chelated complexes are given below.

1. Metal chelates are good reagents in quantitative analysis. Examples are:
   - Separation of Co^{2+} ion from Ni^{2+} ion.
   - Estimation of Mg^{2+} and Ca^{2+} ions by Ethylene Diammine Tetraaceticacid (EDTA).
   - Ag^{+} ions can be separated by precipitating with EDTA solution from the mixture of Fe^{3+}, Cu^{2+}, Pb^{2+}, Bi^{3+} and Ag^{+}.
2. Formation of chelates has a good application in softening the hard water by ion exchange method.
3. Formation of chelates has also very good application in removing the poisonous metals from the body. Example, Removal of lead from the body. When Ca-EDTA chelate is injected into the patient, it reacts with Pb in the body to form Pb-EDTA chelate as it is more stable than Ca-EDTA chelate and goes out of the body in urine.
4. Metal chelates have important roles in living systems. Example,
   - Role of haemoglobins
   - Role of chlorophyll in plants
   - Function of trace metals in human body etc.

Development of Coordination chemistry:

Backing to the history of the development of the complex compounds, it was an accidental discovery of hexaamminecobalt (III) chloride, $CoCl_3.6NH_3$ by Tassaert in 1878. He obtained it by mixing the solution of $CoCl_3$ and aqueous NH_3. It was surprising that two stable compounds such as $CoCl_3$ and NH_3 could combine to form another stable compound. Many theories were put forward to explain the chemistry of coordination complexes from time to time. Among them, Werner's theory of co-ordination compound is the most accepted one.

Werner's theory of coordination compounds:

Alfred Werner (1893), regarded as the father of coordination chemistry, put forward his well known Werner's theory of coordination. By recognizing his contribution, he was awarded the Nobel Prize in chemistry in 1913. The important postulates of this theory are as follows:

1. In co-ordination compounds, the metal atoms exhibit two types of valencies; primary valency and secondary valency.

   The primary valency is ionizable that it represents the oxidation state of the metal and it is also known as principal valency. Whereas the secondary valency is non-ionizable that it represents the co-ordination number of metal and it is also known as auxiliary valency.
2. Every metal atom has a fixed number of secondary valencies.
3. The primary valencies of the metal atom are satisfied by negative ions but secondary valencies may be satisfied by negative ions or neutral molecules.
4. The secondary valencies are directional in character where as primary valencies are non-directional. Therefore, secondary valencies determine the geometry of the complex compounds.
5. The net charge on the complex is the algebraic sum of the charge borne by the central atom and the ligands. For example $[Fe(CN)_6]^{3-}$ carries -3 charge because Fe^{3+} ion carries +3 charge and $6CN^-$ carries -6 charge hence net charge is $+3+(-6) = -3$.
6. The secondary valencies attribute to the isomerism in coordination compounds.
7. The attachment of the species satisfying the primary valency of the metal atom/ion are shown by dotted line (------), whereas that satisfying secondary valency are shown by solid line (   ).

   Werner's theory is mainly applied to give the structures of Co (III) ammines; the complexes of cobalt with ammonia. This may be illustrated as follows.

   Werner illustrated his theory taking four complexes of cobalt (III) chloride with ammonia, he discovered. The compounds were named according to their colour:

Complex	Colour	Early name
$CoCl_3.6NH_3$	Yellow	*Luteocobaltic chloride*
$CoCl_3.5NH_3$	Purple	*Purpureocobaltic chloride*
$CoCl_3.4NH_3$	Green	*Praseocobaltic chloride*
$CoCl_3.3NH_3$	Violet	*Violeocobaltic chloride*

In all compounds the coordination number of cobalt is 6 and exhibits primary valency of 3 but these differ from each other in respect of the ions or neutral molecules present in the coordination sphere.

a. **Luteo Cobaltic chloride, $CoCl_3.6NH_3$**
   i. It is an orange yellow crystalline solid.
   ii. On treatment with $AgNO_3$, all the three chlorine atoms are precipitated as AgCl. This indicates that all the three chlorine atoms are attached to the metal with

an ionic bond.

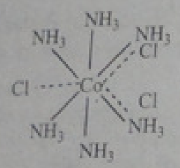
$$\mathrm{COCl_3.6NH_3} \longrightarrow [\mathrm{Co6NH_3}]^{3+} + 3\mathrm{Cl}^-$$
$$3\mathrm{AgNO_3} + 3\mathrm{Cl}^- \longrightarrow 3\mathrm{AgCl}\downarrow + 3\mathrm{NO_3}^-$$

White ppt

iii. On treatment with conc. H_2SO_4, it gives $Co_2(SO_4)_3$ and all the three chlorine atoms are lost as HCl. This indicates that all the six ammonia molecules are attached to the metal with strong bonds.

iv. The conductivity measurement shows the presence of four ions.

On the basis of the above facts, the structure of the complex $[Co(NH_3)_6]Cl_3$ may be given as shown in fig.



Werner's representation of compound $CoCl_3.6NH_3$

The primary valencies are represented by dotted lines (------) and secondary valencies are represented by thick lines.

b. **Purpureo cobaltic chloride, $CoCl_3.5NH_3$**

i. It is violet crystalline solid.

On treatment with $AgNO_3$, only two chlorine atoms are precipitated as AgCl. This indicates that only two chlorine atoms are attached to the metal with an ionic bond and one Cl atom satisfies both primary and secondary valencies of the metal, so it is denoted by both solid and dotted lines together as (⩦).

$$\mathrm{COCl_3.5NH_3} \longrightarrow [\mathrm{CoCl.5NH_3}]^{3+} + 2\mathrm{Cl}^-$$
$$2\mathrm{AgNO_3} + 2\mathrm{Cl}^- \longrightarrow 2\mathrm{AgCl}\downarrow + 2\mathrm{NO_3}^-$$

White ppt

ii. On treatment with conc. H_2SO_4, it gives $CoCl(SO_4).5NH_3$ and two chlorine atoms are lost as HCl. This compound does not give any precipitate with $AgNO_3$. This indicates that all the five ammonia molecules and one chlorine atom are attached to the metal with strong bond.

iii. The conductivity measurement shows the presence of three ions. On the basis of above facts, the structure of the complex $[Co(NH_3)_5Cl]Cl_2$, may be given as shown in figure...

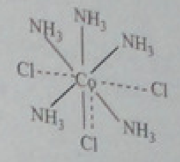


Fig.: *Werner's representation of compound $CoCl_3.5NH_3$*

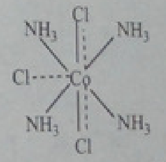
c. **Praseo cobaltic chloride, $CoCl_3.4NH_3$**

On treatment with $AgNO_3$, only one chlorine atom is precipitated as AgCl. This indicates that only one chlorine atom is attached to the metal with an ionic bond and two Cl atoms satisfy both primary and secondary valencies of the metal, so it is denoted by both solid and dotted lines together as (⩦).

$$\mathrm{COCl_3.4NH_3} \longrightarrow [\mathrm{CoCl_2.4NH_3}]^{3+} + \mathrm{Cl}^-$$
$$\mathrm{AgNO_3} + \mathrm{Cl}^- \longrightarrow \mathrm{AgCl}\downarrow + \mathrm{NO_3}^-$$

White ppt

i. The conductivity measurement shows the presence of two ions. On the basis of above facts, the structure of the complex $[Co(NH_3)Cl_2]Cl$, may be given as shown in figure as,



No. of Cl^- ions precipitated = 1

Total no. of ions = 2

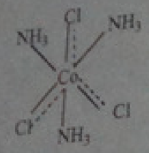
Fig.: *Werner's representation of* **$COCl_3.4NH_3$**

d. **Violeo cobaltic chloride, $CoCl_3.3NH_3$**

i. On treatment with $AgNO_3$, no precipitation of AgCl takes place. This indicates that no ionizable chlorine atoms are present in this complex. Thus, all the three chlorine atoms satisfy both the primary and secondary valencies and it is denoted by both solid and dotted lines together as (- - - -).

$$CoCl_3.3NH_3 \rightarrow [CoCl_3.3NH_3]$$

ii. The conductivity measurement shows the presence of only one type of ion. On the basis of above facts, the structure of the complex $[Co(NH_3)Cl_3]$, may be given as shown in figure as,



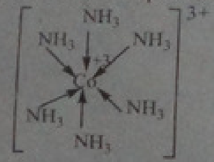
No. of Cl^- ions precipitated = 0

Total no. of ions = 0

Fig.: *Werner's representation of* $CoCl_3.3NH_3$

Sidgwick's electronic concept of coordinate bond in complex compounds:

In 1916, Lewis introduced a concept of two electron covalent bond between two atoms in a molecule. Sidgwick (1927) extended this Lewis concept and introduced a new concept of coordinate bond which is also sometimes called polar or dative bond. According to the Sidgwick's concept the ligands donate the electron pair to the central metal atom/ion and thus form a coordinate bond, L → M which indicates that the ligand, L (donor) has donated an electron pair to the metal ion, M(acceptor). This concept is based on the fact that all the ligands contain at least one lone pair of electrons. Thus according to the Sidgwick's concept, the structure of the complex ion, $[Co(NH_3)_6]^{3+}$



Sidgwick's representation of hexaammine cobalt (III) ion

Thus the formation of ligands-metal ion bonds occurs through the N-atom of each ligand. In all, twelve electrons are donated by six ligands to Co^{3+} ion forming six coordinate bonds. The donation of electron pair is represented as L→M.

Limitations of Sidgwick's concept of coordinate bond:

The donation of electron pair from each ligand to the central metal atom/ion accumulates

negative charge on the central metal ion which is most unlikely. For e.g., in $[Co(NH_3)_6]^{3+}$, six NH_3 molecules donate 12-electrons, then half share of electrons (i.e. 6 electrons) to Co^{3+} ion and thus +3 charge on cobalt atom is reduced to -3 (+3 - 6= -3). Such an accumulation of negative charge on the central atom is unlikely as it makes the complex compounds unstable. This defect is removed by Pauling on the basis of electroneutrality theory.

Effective Atomic Number (EAN)-rule:

The number of secondary valencies in the Werner's theory is now called the coordination number of the central metal in the complex. Simply this represents the number of ligand atoms bonded to the central metal ion. Each ligand donates an electron pair to the metal ion, thus forming coordinate bond. The electronic arrangement of the noble gases is known to be very stable. **Sidgwick (1927)** suggested the stability of complex compounds in terms of the Effective Atomic Number (EAN) rule. It states that electron pairs from ligands are added until the central metal acquires number of electrons as the next noble gas. Hence, this rule is also known as noble gas rule. He pointed out that if the EAN of the central metal atom/ion in a given complex compound is equal to the atomic number of the nearest inert gas, such complex compound is stable and diamagnetic, if not equal such complexes are unstable and paramagnetic.

Calculation of EAN: Effective Atomic Number of the central metal atom is calculated as follows:

- Deduce the number of electrons lost by central metal atom while changing into ion.
- Add the number of electrons gained by central metal ion during coordination.

Therefore,

EAN = Atomic number of central metal atom(Z) − no. of e^- lost during ion formation(x) + no. of e^- gained through coordination(y)

= Z − x + y

For e.g., the EAN of Co (III) in $[Co(NH_3)_6]^{3+}$ may be calculated as;

At. no. of Co(Z) = 27

No. of e^- lost during ion formation (x) = 3

No. of e^- gained through coordination (y) = 2x6 = 12

Therefore, EAN = Z − x + y

= 27 − 3 + 12

= 36, it is the atomic no. of next inert gas element, Krypton (Kr).

Exceptions to EAN-rule:

This rule is found perfectly obeyed by many of the complexes. However, some irregularities are observed in some of the complexes. These are taken as exceptions to the EAN rule.

If the original metal ion has odd number of electrons, adding of electrons gained through coordination cannot result in a next noble gas atomic number. For e.g., complexes of Fe (III) having coordination number 4, $[FeCl_4]^-$ or C.N. = 6, $[Fe(CN)_6]^{3-}$ never obey the Sidgwick's EAN-rule. For $[FeCl_4]^-$,

$$\begin{aligned} EAN &= N - x + y \\ &= 26 - 3 + 2 \times 4 \\ &= 31, \text{ this is not atomic no. of next noble gas element.} \end{aligned}$$

The complexes of Ni^{2+}, Co^{2+} and Ag^+ never obey the EAN rule.

Applications of EAN rule:

i. *The EAN rule correctly predicts the number of ligands in many complexes.*
ii. *This supports the more stability of the complex compounds.*
iii. *It illustrates the electronic interpretation of coordination bonds in complex compounds.*
iv. *By using this rule to metal carbonyls it is possible to predict whether a given carbonyl is a monomer.*
v. *It determines the magnetic properties of the complexes.*

Nomenclature of co-ordination compounds:

In 1976, the International Union of Pure and Applied Chemistry (IUPAC) published rules for the systematic nomenclature for coordination compounds. The important rules of systematic naming of the co-ordination compounds are as follows:

1. *The cation is named first followed by the anion. For example,*

$$K_4[Fe(CN)_6] \overset{\text{in solution}}{\rightleftharpoons} 4K^+ + [Fe(CN)_6]^{4-}$$

Here, K^+ is named first and then anion $[Fe(CN)_6]^{4-}$

2. *If the complex compound is non-ionic or neutral or molecular, the name of the complex is written as one word. For example,* $[Cr(NH_3)_3Cl.CN.(NO_2)]^0$ is written as one *word.*
3. *In the complex ion or coordination sphere, the ligand is named first then followed by the central metal atom/ion.*
4. *If there are different types of ligands, these are named in alphabetical order.*
5. *If there are more than one simple ligands of same kind, these are prefixed by di (for 2), tri (for 3), tetra (for 4), penta (for 5), hexa (for 6) and so on.*

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6. If the ligands are complex one, generally the organic neutral ligands and which have already di, tri, tetra in their names, these are prefixed by bis (for 2), tris (for 3), tetrakis (for 4), pentakis (for 5), hexakis (for 6) and so on and the name of such ligand is written inside the bracket. For example,
   [Cr(en)3]Cl3 where, en = ethylenediammine is named as Tris (ethylenediammine) chromium (III) chloride.
7. Naming of ligands: Different types of ligands are named differently as follows.
   i. If the name of negative ligands ends in 'ide' it is changed to 'o'. For e.g., chloride to chloro, cyanide to cyano, bromide to bromo, hydroxide to hydroxo etc. and if the name ends in 'ate' or 'ite' the 'e' is changed to 'o'. For eg. nitrate to nitrato, nitrite to nitrito, sulphate to sulphato, sulphite to sulphito etc.
   ii. For neutral inorganic ligands, it is not systematic. For eg. water is changed to aqua, ammonia to ammine and carbon monoxide to carbonyl. Other neutral groups are named as, NO is nitrosyl, NS is thionitrosyl and CS is thiocarbonyl.
   iii. Positive ligands (which are very few) end in –ium, e.g., $NH_2NH_3^+$ (hydrazinium), NO^+ (nitrosonium), NO_2+(nitronium).
   iv. For organic ligands, they are given their own names such as, CH_3- methyl, C_6H_5 – phenyl, $NH_2CH_2CH_2NH_2$ – ethylenediamine (en) etc.
8. When the central metal ion is attached to different atoms of a particular ligand, then ligands are distinguished by writing the names in different ways. For e.g., a ligand thiocyanide SCN is attached to metal ion as, M-SCN, the ligand is known as thiocyanato-S or simply thiocyanato while if SCN is attached to metal ion as M-NCS, the ligand is known as thiocyanato-N or simply isothiocyanato. The name of the ligand NO_2^- is nitro or nitrito depending on whether the linkage to metal ion is through Nitrogen ($-NO_2$) or through oxygen atom (-ONO).

$[Co(NO_2)_3(NH_3)_3]$: *Trinitrotriamminecobalt (III)*
$[Co(ONO)(NH_3)_5]SO_4$: *Nitritopentaamminecobalt (III) sulphate*
$[Co(CNS)(NH_3)_5]Cl_2$: *Isothiocyanatopentaamminecobalt (III) chloride*

9. The ligands so named are followed by the name of the central metal atom/ion. The oxidation state of the metal ion is always indicated by the Roman numerals written within the brackets followed by the name of the central metal ion.
10. The metal ion is referred by its usual name if the complex ion is cationic. On the other hand, the metal ion is referred by the name from which their symbol is derived and is made to end in 'ate' if the complex is anionic. For e.g., iron is named ferrate in $[Fe(CN)_6]^{3-}$.

Nomenclatures of some of the important complex compounds are listed as below.

i. $[Fe(H_2O)_6]SO_4$: Hexaaquairon (II) sulphate
ii. $K_4[Fe(CN)_6]$: Potassium hexacyano ferrate (II)

iii. $[Pt(NH_3)_4Cl_2]Cl_2$: Tetraamminedichloro platinum (IV) chloride
iv. $[Pt(py)_4][PtCl_4]$: Tetrakis(pyridine) platinum (II) tetrachloro palatinate (II)
v. $[Cr(NH_3)_6][Co(CN)_6]$: Hexaammine chromium (III) hexacyano cobaltate (III)
vi. $[Cr(en)_3]Br_3$: Tris(ethylenediammine) chromium (III) bromide
vii. $[Cr(H_2O)_5Cl]Cl_2$: Pentaaquachloro chromium (III) chloride
viii. $K_3[AlF_6]$: Potassium hexafluoro aluminate (III)
ix. $[Co(NH_3)_4SO_4]NO_3$: Tetraamminesulphato cobalt (III) nitrate
x. $Na_3[Co(NO_2)_6]$: Sodium hexanitrito cobalt (III)
xi. $Na_3[Al(C_2O_4)_3]$: Sodium trioxalato aluminate (III)
xii. $[Pb(OH)_4]^{2-}$: Tetrahydroxo plumbate (II) ion
xiii. $[PtCl(NO_2)(NH_3)_2]$: Diamminechloronitrito platinum (II)
xiv. $K_3[Co(CN)_5Cl]$: Potassium chloropentacyano cobalt (III)
xv. $[Zn(NCS)_4]^{2-}$: Tetrathiocyanato-N-zincate (II) ion
xvi. $[Zn(SCN)_4]^{2-}$: Tetrathiocyanato-S-zincate (II) ion
xvii. $Na_2[Cr(CH_3COO)_4en]$: Sodium tetraacetato (ethylenediammine) chromate (II)
xviii. $[Cr(C_6H_6)_2]$: Bis(benzene) chromium (0)
xix. $[Ni(NH_3)_4]^{2+}$: Tetraammine nickel (II) ion.

Theories of Bonding in complex compounds:

Valence Bond Theory:

This theory was developed by Pauling in 1935. It deals with the electronic structure of the central metal atom/ion in its ground state, type of bonding, geometry and magnetic properties of the complexes. The main assumptions of this theory are as follows.

1. The central metal atom/ion makes available a number of empty s, p and d atomic orbitals equal to its coordination number for accommodating electrons donated by the ligands.
2. These vacant orbitals hybridize together to form hybrid orbitals which are the same in number as the atomic orbitals hybridizing together. These hybrid orbitals are vacant, equivalent in energy and have definite geometry.
3. The ligands have at least one σ-orbital containing a lone pair of electrons.
4. Vacant hybrid orbitals of the metal atom/ion overlap with the filled σ-orbital of the ligands to form ligand → metal σ-bond (L→M). This bond is generally known as coordinate bond.
5. The strong ligands such as CN^-, NO_3^-, NH_3, CO, NO and organic ligands have tendency to pair up the unpaired electron in (n-1)d orbital of the metal atom i.e. cause back pairing of electrons. But the weak ligands such as F^-, Cl^-, Br^-, I^-, H_2O etc cannot cause the back pairing of electrons in the (n-1)d orbital of the metal ion.

6. The non-bonding electrons of the metal atom/ion are then rearranged in the (n-1)d orbitals of metal which do not participate in forming the hybrid orbitals. The rearrangement of non-bonding electrons takes place according to Hund's rule of maximum multiplicity.
7. The d-orbitals involved in the hybridization may be inner (n-1)d-orbitals or outer nd-orbitals. The complexes so formed by these two ways are respectively referred to as low spin and high spin complexes.
8. If the complex contains unpaired electrons, it is paramagnetic in nature while if it does not contain unpaired electrons, the complex is diamagnetic.
9. The number of unpaired electrons in the complex indicates its geometry and vice-versa. In practice, the number of unpaired electrons in a complex is found.

Applications of VBT: VBT is used to predict the geometry and magnetic properties of complex compounds.

1. **VBT as applied to octahedral complexes (coordination number = 6)**

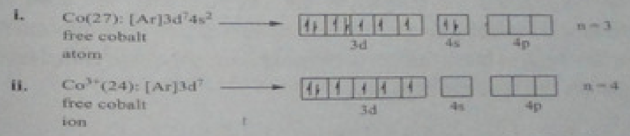
According to valence bond theory, octahedral complexes are of two types.

i. Inner orbital octahedral complexes
ii. Outer orbital octahedral complexes

Inner orbital octahedral complexes:

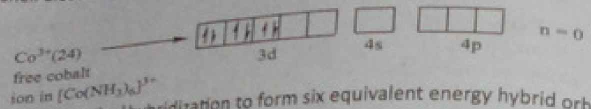
The complexes in which central metal atom/ion has coordination number 6 and formed by d^2sp^3 hybridization are called inner orbital octahedral complexes. These are generally formed by strong field ligands such as CN^-, NH_3, NO_2^-, H_2O etc. This may be illustrated by taking an example, $[Co(NH_3)_6]^{3+}$.

In this complex, the central metal atom Co (27) is present as Co^{3+} (24) ion. The valence shell electronic configuration of the free cobalt atom and ion are represented as shown below.



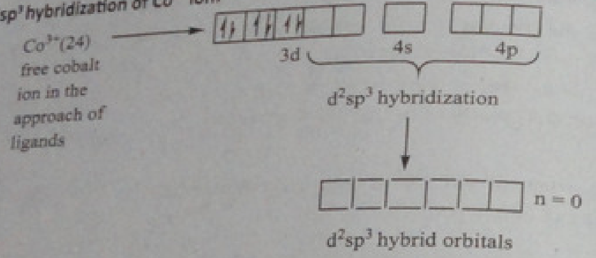
iii. Back pairing of electrons due to the approach of NH_3 ligands:

The measurement of the magnetic moment (μ) of $[Co(NH_3)_6]^{3+}$ ion has shown that μ=0 i.e. this complex ion has no unpaired electrons (i.e. all electrons are paired). The electrons in 3d-orbitals are forced to pair up against Hund's rule of maximum multiplicity due to the presence of six NH_3 ligands. This is called back pairing of electrons due to the strong field ligands. Thus after pairing up against Hund's rule, the valence shell electronic configuration of Co^{3+} ion becomes,



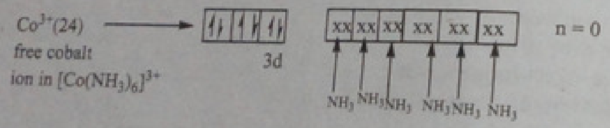
Now the Co^{3+} undergoes d^2sp^3 hybridization to form six equivalent energy hybrid orbitals.

iv. **d^2sp^3 hybridization of Co^{3+} ion:**

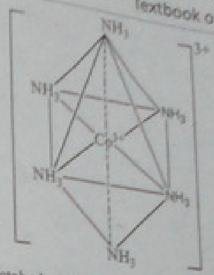


The formation of complex takes place by the donation of electron pairs from each NH_3 molecule into each vacant hybrid orbitals of Co^{3+} ion to form ligand → metal (L→M) coordinate bond.

v. **Formation of complex, $[Co(NH_3)_6]^{3+}$:**



This complex is formed by d^2sp^3 hybridization, thus the complex has octahedral geometry. Evidently, there are no unpaired electrons left in $[Co(NH_3)_6]^{3+}$ ion and the complex is diamagnetic. In the formation of this complex, as the inner d-orbitals are used in hybridization, it is the inner orbital complex. Since these complexes usually have maximum number of paired electrons and no or less number of unpaired electrons, these complexes are also known as low spin or spin paired complexes.



Octahedral geometry of $[Co(NH_3)_6]^{3+}$

The following complexes can be explained in the similar way using VBT.

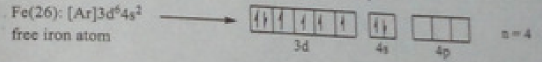
Paramagnetic:

$[Ti(H_2O)_6]^{3+}(n=1)$ $[Cr(NH_3)_6]^{3+}(n=3)$
$[Mn(CN)_6]^{4-}(n=1)$ $[Mn(CN)_6]^{3-}(n=2)$
$[Fe(CN)_6]^{3-}(n=1)$ $[Co(CN)_6]^{4-}(n=1)$
$[Cr(H_2O)_6]^{3+}(n=3)$ $[Cr(NO_3)_6]^{3-}(n=3)$ etc.

Diamagnetic:

$[Pt(NH_3)_6]^{4+}(n=0)$ $[Co(CN)_6]^{3+}(n=0)$
$[Fe(CN)_6]^{4-}(n=0)$ etc.

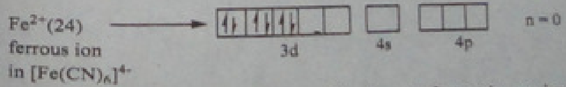
Formation of $[Fe(CN)_6]^{4-}$: In this complex, the central metal atom Fe (26) is present as Fe^{2+} (24) ion. The valence shell electronic configuration of the free iron atom and ion are represented as shown below.

i. 

ii. 

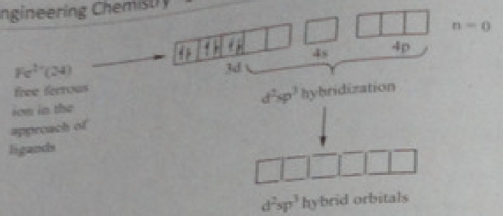
iii. **Back pairing of electrons:**

The measurement of the magnetic moment (μ) of $[Fe(CN)_6]^{4-}$ ion has shown that μ=0 i.e. this complex ion has no unpaired electrons (i.e. all electrons are paired). The electrons in 3d-orbitals are forced to pair up against Hund's rule of maximum multiplicity due to the presence of six CN^- ligands. This is called back pairing of electrons due to the strong field ligands. Thus after pairing up against Hund's rule, the valence shell electronic configuration of Fe^{2+} ion becomes,



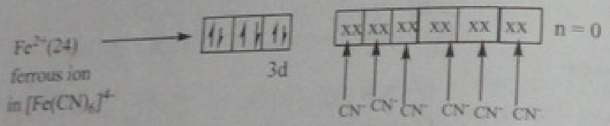
Now the Fe^{2+} ion undergoes d^2sp^3 hybridization to form six equivalent energy hybrid orbitals.

iv. **d^2sp^3 hybridization of Fe^{2+} ion:**

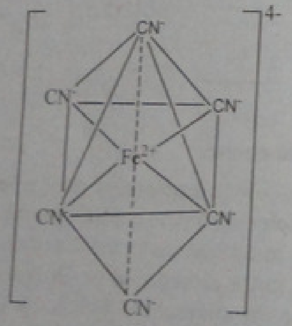


The formation of complex takes place by the donation of electron pairs from each CN$^-$ ions into each vacant hybrid orbitals of Fe^{2+} ion to form ligand → metal (L→M) coordinate bond.

v. **Formation of complex, [Fe(CN)$_6$]$^{4-}$:**



This complex is also formed by d^{2}sp^3 hybridization, thus the complex has octahedral geometry. Since, no unpaired electrons are left in the complex it is also diamagnetic complex. The geometry of the so formed complex is shown as below.



Octahedral geometry of [Fe(CN)$_6$]$^{4-}$

Outer orbital octahedral complexes:

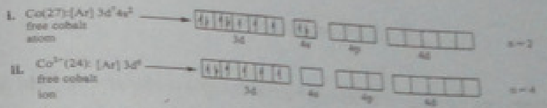
The complexes in which central metal atom/ion has coordination number 6 and formed by sp^{3}d^2 hybridization are called outer orbital octahedral complexes. These are generally formed by weak field ligands such as F$^-$, Cl$^-$ etc. Sometimes these are also formed by strong field ligands in the case when the central metal atom/ion has such electronic configuration in (n-1)d-orbital that it is impossible to create the required number of vacant (n-1)d-orbitals.

Illustration:

1. **Formation of outer orbital octahedral complex by weak field ligands.**

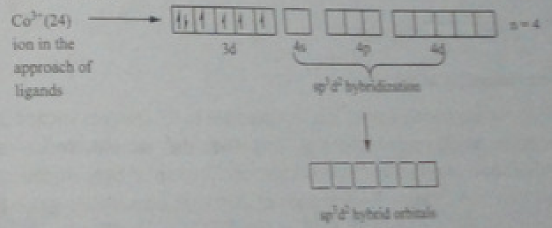
Let us take an example,[CoF$_6$]$^{3-}$.

In this complex, the central metal atom Co (Z=27) is present as Co^{3+} ion. The valence shell electronic configuration of the free cobalt atom and ion are represented as shown below.

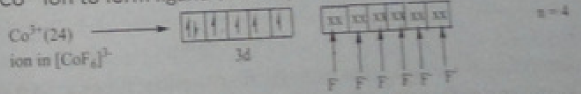


The measurement of the magnetic moment (μ) of [CoF$_6$]$^{3-}$ ion has shown that Co^{3+} ion has four unpaired electrons. That is, no back pairing of electrons takes place. Hence, outer d-orbitals are involved in hybridization. Thus, Co^{3+} ion undergoes sp^{3}d^2 hybridization so that forming six sp^{3}d^2 hybrid orbitals to accommodate six lone pairs of electrons donated from each F$^-$ ligand.

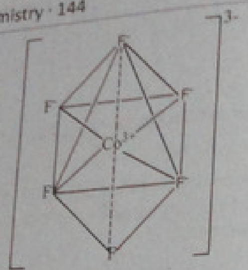
a. **sp^{3}d^2 hybridization:**



b. **Formation of complex, [CoF$_6$]$^{3-}$:** The formation of complex takes place by the donation of electron pairs from each F$^-$ ligand into each vacant hybrid orbitals of Co^{3+} ion to form ligand→metal (L→M) coordinate bond.



This complex is formed by sp^{3}d^2 hybridization, hence it has octahedral geometry. Since outer 4d-orbitals are involved in hybridization the complex is known as outer orbital octahedral complex. Due to the presence of unpaired electrons in it, the complex is paramagnetic. Furthermore, since these complexes involve no back pairing of electrons and the electrons are generally left unpaired. These complexes are also known as high spin or spin free complexes. The geometry of this complex is shown in the figure as below.

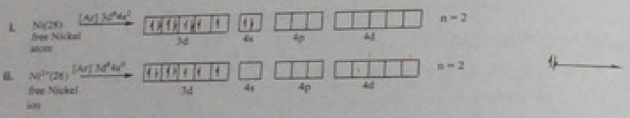


Octahedral geometry of $[CoF_6]^{3-}$

II. Formation of outer orbital octahedral complexes by strong field ligands:

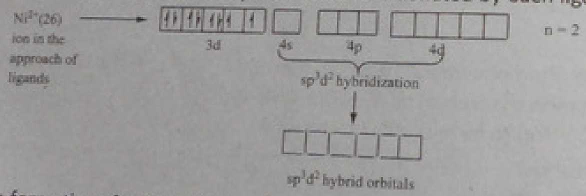
Let us take an example, $[Ni(NH_3)_6]^{2+}$,

In this complex, the central metal atom Ni(28) is present as Ni^{2+}(26) ion. The valence shell electronic configuration of the free Ni atom and ion are respectively represented as shown below.



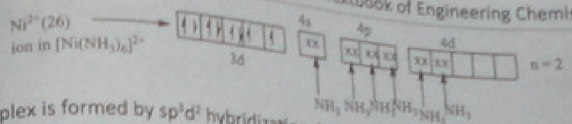
ii. **sp^3d^2 hybridization in Ni^{2+} ion:**

Though ammonia is a strong ligand, it is not possible to create two vacant 3d-orbitals due to such electronic configuration of the Ni^{2+} ion. Then the two electrons are left unpaired d outer 4d-orbitals are involved in hybridization. Thus sp^3d^2 hybridization takes place in metal ion to accommodate six lone pairs of electrons donated by each ligand.

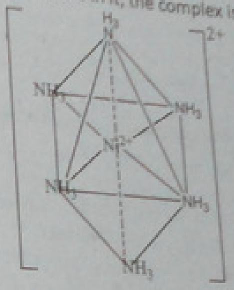


Then the formation of complex takes place by the donation of electron pairs from each NH_3 ligand into each vacant hybrid orbitals of Ni^{2+} ion to form ligand → metal (L → M) coordinate bond.

iii. Formation of complex, $[Ni(NH_3)_6]^{2+}$:



This complex is formed by sp^3d^2 hybridization, hence it has octahedral geometry and due to the presence of two unpaired electrons in it, the complex is paramagnetic.



Octahedral geometry of $[Ni(NH_3)_6]^{2+}$

The following complexes can be explained in the similar way using VBT.

$[Fe(H_2O)_6]^{2+}$(n=4) $[Fe(H_2O)_6]^{3+}$(n = 3) $[Fe(NH_3)_6]^{2+}$(n=4) $[FeF_6]^{4-}$(n=4)

$[Co(NH_3)_6]^{2+}$(n = 3) $[Cu(NH_3)_6]^{+}$(n = 0) $[Cu(NH_3)_6]^{2+}$(n = 1) $[FeF_6]^{3-}$(n=5)

$[CoF_6]^{3-}$ (n=4) $[Zn(NH_3)_6]^{+2}$(n=0) $[Ni(NH_3)_6]^{2+}$(n = 2) etc.

Differences between inner and outer orbital octahedral complexes

S.N.	Inner Orbital Octahedral Complexes	Outer Orbital Octahedral Complexes
1.	These complexes are formed by the d^2sp^3 hybridization i.e. two inner or (n-1)d-orbitals are involved in hybridization.	These complexes are formed by sp^3d^2 hybridization of central metal ion i.e. two outer or nd-orbitals are involved in hybridization.
2.	Back-pairing of electrons takes place in (n-1) d-orbitals during the formation of these complexes.	No back-pairing of electrons takes place in (n-1)d-orbitals during the formation of these complexes.
3.	These are generally formed by the strong field ligands since they cause the effective back pairing of electrons.	These are generally formed by weak field ligands since they do not cause the back pairing of electrons and outer d-orbitals need to be involved to accommodate the donated pair of electrons.

4.	In general, these complexes are diamagnetic and only a few are known to be paramagnetic.	Just reverse, these complexes are generally paramagnetic and only a few are known to be diamagnetic.
5.	These complexes are also called low spin or spin-paired complexes because these have comparatively less number of unpaired electrons in the central metal ion.	These complexes are also called high spin or spin-free complexes because these have comparatively larger number of unpaired electrons in the central metal ion.

iv. VBT as applied to tetrahedral complexes (coordination no. 4).

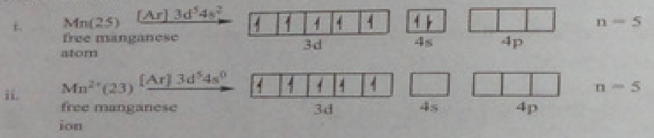
The complexes formed by sp^3 hybridization of the central metal atom/ion are called tetrahedral complexes. These complexes are usually formed by the weak ligands with the central metal atom/ion of coordination number-4. When the central metal atom/ion has the electronic configuration like (n-1) d^{9-10}, even the strong ligands have no use to create a vacant (n-1)d-orbital, as a result tetrahedral complexes are formed. For example, $[Zn(NH_3)_4]^{2+}$, $[MnCl_4]^{2-}$ etc.

Illustration:

I. Formation of tetrahedral complex by weak field ligands:

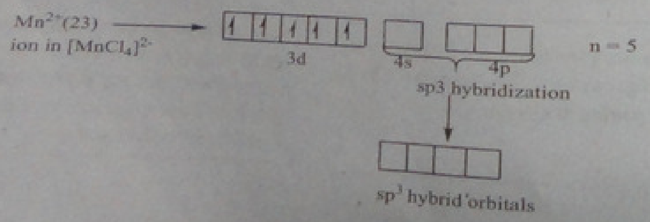
Let us take an example, $[MnCl_4]^{2-}$

In this complex, the central metal atom Mn(25) is present as Mn^{2+}(23) ion. The valence shell electronic configuration of the free Mn atom and ion are represented as shown below.



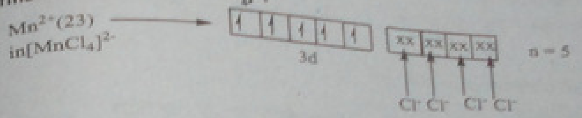
Sp³ hybridization of Mn²⁺ ion:

The measurement of the magnetic moment (μ) of $[MnCl_4]^{2-}$ ion has shown that Mn^{2+} ion has five unpaired electrons. Since Cl^- ion is a weak field ligand, no back pairing of electrons takes place. So Mn^{2+} ion undergoes sp^3 hybridization by mixing one s- and three p-orbitals to form four sp^3 hybrid orbitals. These hybrid orbitals accommodate four lone pairs of electrons donated from each Cl^- ligand.

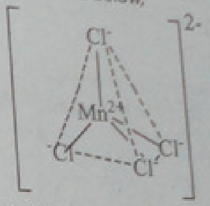


The formation of complex takes place by the donation of electron pairs into each vacant hybrid orbitals to form ligand→metal (L→M) coordinate bond.

iv. Formation of complex, [MnCl₄]²⁻:



The complex $[MnCl_4]^{2-}$ has tetrahedral geometry because of the sp^3 hybridization of Mn^{2+} ion and the structure is shown as below,

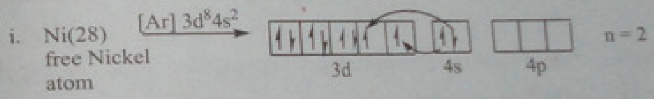


Tetrahedral geometry of $[MnCl_4]^{2-}$

Since there are five unpaired electrons in d-orbital, the complex is highly paramagnetic.

Similarly, the geometry and magnetic behavior of $[Ni(CO)_4]$ can be explained as below.

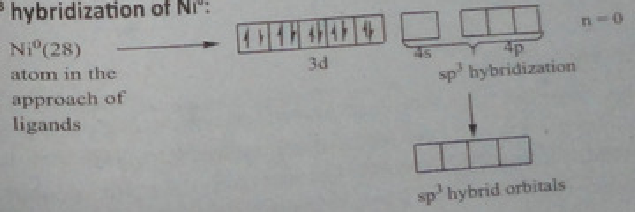
In this complex, the central metal atom Ni(28) has zero oxidation state and co-ordination number is four. The valence shell electronic configuration of the free Ni atom is as shown below.



Since 'CO' is strong ligand, as soon as the ligands come closer to the Ni atom, they force the two 4s-electrons undergo back pairing into the 3d-orbital and make all electrons in 3d-orbital paired and 4s-orbital vacant.

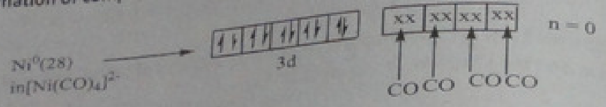
Then one s- and three p-orbitals are involved in sp^3 hybridization to form four sp^3 hybrid orbitals.

sp³ hybridization of Ni⁰:

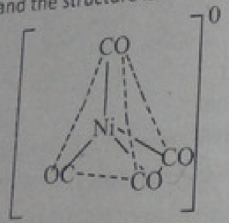


The four electron pairs donated by four ligands are accommodated into these hybrid orbitals to form four coordinate bonds. Thus, the valence shell electronic configuration of the complex is

Formation of complex, $[Ni(CO)_4]$:



Thus, the complex $[Ni(CO)_4]$ has tetrahedral geometry because of the sp^3 hybridization of Ni atom and the structure is shown as below,



Tetrahedral geometry of $[Ni(CO)_4]^0$

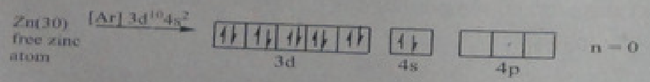
Since there are no unpaired electrons in the d-orbital, the complex is diamagnetic.

II. Formation of tetrahedral complex by strong field ligands

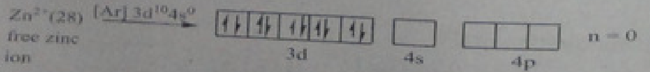
Let us take an example of $[Zn(NH_3)_4]^{2+}$

In this complex, the central metal atom Zn (Z=30) is present as Zn^{2+}(28) ion. The valence shell electronic configuration of the free Zn atom and ion are respectively represented as shown below.

i.

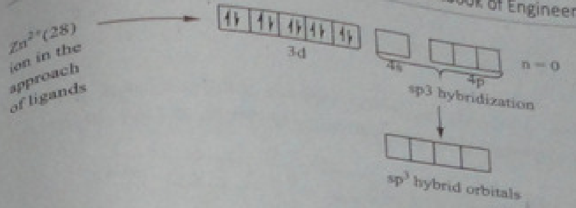


ii.



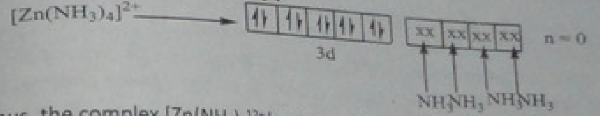
iii. sp^3 hybridization of Zn^{2+} ion:

The Zn^{2+} has completely fulfilled 3d-orbital where as on outer s- and three p-orbitals are vacant. Then, one s- and three p-orbitals are involved in hybridization to form four sp^3 hybrid orbitals and accommodate four lone pairs of electrons donated from each ligand.

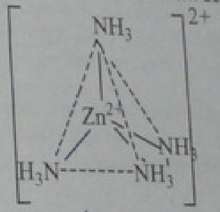


The formation of complex takes place by the donation of electron pairs from each NH_3 ligand into each vacant hybrid orbitals of Zn^{2+} ion to form ligand→metal (L→M) coordinate bond.

iv. Formation of complex, $[Zn(NH_3)_4]^{2+}$:



Thus, the complex $[Zn(NH_3)_4]^{2+}$ has tetrahedral geometry because of the sp^3 hybridization of Zn^{2+} ion and the structure is shown as below,



Tetrahedral geometry of $[Zn(NH_3)_4]^{2+}$

Since there are no unpaired electrons in the d-orbital, the complex is diamagnetic.

Examples of some other tetrahedral complexes are:

Paramagnetic:

$[NiCl_4]^{2-}$(n=2) $[CoCl_4]^{2-}$(n=3) $[FeCl_4]^{2-}$(n= 4)

$[MnBr_4]^{2-}$(n=5) $[FeCl_4]^-$ (n = 5) etc.

Diamagnetic:

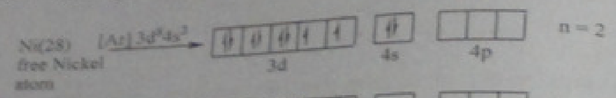
$[Cu(CN)_4]^{3-}$(n=0) $[Zn(NH_3)_4]^{2+}$(n=0) $[ZnCl_4]^{2-}$(n=0) etc.

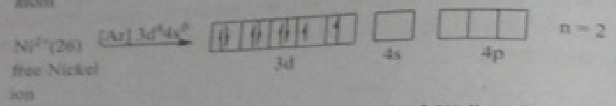
v. VBT as applied to square planar complexes (coordination no. 4).

The complexes formed by dsp^2 hybridization of the central metal atom/ion are called square planar complexes. These complexes are formed by strong field ligands such as CN^-, NH_3 etc.

This may be illustrated by taking an example, $[Ni(CN)_4]^{2-}$

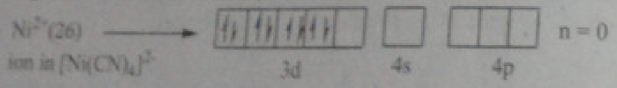
In this complex, the central metal atom Ni(28) is present as Ni^{2+} ion. The valence shell electronic configuration of the free Ni atom and ion are represented as shown below.

i.


ii.


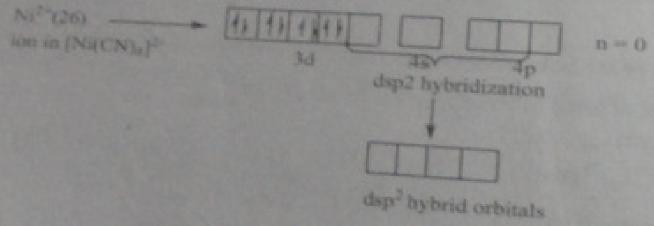
iii. **Back pairing of electrons in Ni^{2+} ion due to the approach of CN^- ligands.**

The measurement of the magnetic moment (μ) of $[Ni(CN)_4]^{2-}$ ion has shown that the complex ion has no unpaired electrons i.e. all electrons are paired. This pairing of electrons is due to the presence of four strong CN^- ligands. This is called back pairing of electrons due to the strong ligand field. Thus, the valence shell electronic configuration of Ni^{2+} in the complex is,



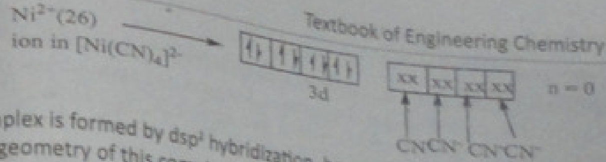
Now, Ni2+ ion undergoes dsp2 hybridization by mixing the vacant one d-, one s- and two p-orbitals to form four dsp^2 hybrid orbitals. These hybrid orbitals accommodate four electron pairs donated from each ligand.

iv. **dsp^2 hybridization of Ni^{2+} ion:**

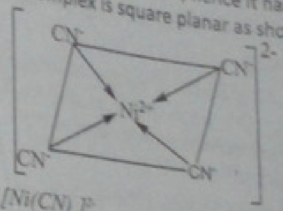


Thus, the formation of complex takes place by the donation of electron pairs into each vacant hybrid orbitals to form ligand→metal (L→M) coordinate bond.

vi. *Formation of complex, $[Ni(CN)_4]^{2-}$:*



This complex is formed by dsp^2 hybridization, hence it has square planar geometry and the geometry of this complex is square planar as shown below,



Square planar geometry of $[Ni(CN)_4]^{2-}$

Since there are no unpaired electrons in the complex, it is diamagnetic. Some examples of square planar complexes are given as:

$[Ni(NH_3)_4]^{2+}$ $[Co(CN)_4]^{2-}$ etc.

Note: Strong ligands cause back pairing of electrons rather than weak ligands. In general Ligands containing more electronegative atom are weak ligands. The strength of ligands are generally found in the order,

$$I^- < Br^- < S^{2-} < Cl^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NH_3 < en < NO_2^- < CN^-$$

Differences between tetrahedral and square planar complexes

	Tetrahedral complexes		Square planar complexes
1.	These complexes are formed by sp^3 hybridization of central metal ion.	1.	These complexes are formed by dsp^2 hybridization of the central metal ion.
2.	In general, these complexes are formed by weak field ligands.	2.	In general, these complexes are formed by strong field ligands.
3.	Generally these complexes are paramagnetic.	3.	Generally these complexes are diamagnetic.
4.	For example, $[NiCl_4]^{2-}$, $[MnCl_4]^{2-}$, $[Zn(NH_3)_4]^{2+}$ etc.	4.	For example, $[Ni(CN)_4]^{2-}$, $[Ni(NH_3)_4]^{2+}$ $[Co(CN)_4]^{2-}$ etc.

Limitations of Valence Bond Theory:

Although the Valence Bond Theory became successful to explain several characteristics of the coordination compounds such as their geometry and magnetic properties, it has suffered from following limitations.

1. VBT cannot account for the relative stabilities for different geometry and different coordination number in metal complexes. For example, it cannot explain satisfactorily as to why Co^{2+} forms both octahedral and tetrahedral complexes while Ni^{2+} rarely forms tetrahedral complexes.
2. It cannot explain why cu^{2+} forms only distorted octahedral complexes even when all the six ligands are identical.
3. VBT fails to explain the finer details of magnetic properties including the magnitude of the orbital contribution to the magnetic moments. For e.g., the tetrahedral and outer orbital octahedral complexes having same number of unpaired electrons have different magnetic moments.

   Tetrahedral complexes having 3 unpaired electrons have magnetic moments ranging from 4.4-4.8 Bohr Magneton(BM) while the outer orbital octahedral complexes having the same 3 unpaired electrons have magnetic moments from 4.7- 5.2 BM.
4. VBT cannot interpret the spectra or colour formation of the complexes.
5. VBT cannot explain the relative nature of the ligands such as strong field and weak field.
6. It also cannot explain the rates of the reaction and temperature dependent paramagnetism of the complexes.
7. It does not give quantitative interpretation of the thermodynamic or kinetic stabilities of the complexes.
8. The prediction of the magnetic behavior of the complex is not always right. For example, square planar complexes of Ni^{2+} (d^8 system) are diamagnetic and tetrahedral complexes of Ni^{2+} are paramagnetic. But X-ray study shows that Ni^{2+} (CN = 4) complex has shown both paramagnetic and diamagnetic forms.

Crystal Field Theory (CFT): This theory determines the effect of different electrostatic field caused by the different geometries of the complexes and different basic strength of ligands as the energies of the d-orbitals of the central metal ion. The theory and its explanation is beyond the scope of this book.

Application of complex compound

The discovery of complex compounds and the techniques of their formation brought a great change in the limited concept of chemistry and these are found of great use in various fields. Some of the important applications are mentioned as below,

1. **In qualitative analysis:** The complex formation techniques have proved to be of good use in qualitative analysis of the ions and their separation from the mixture.
2. **Estimation of hardness of water:** The hardness of water is estimated by complexometric titration. This involves the use of complexing agent, Ethylenediamminetetraacetic acid (EDTA) and complex forming metal-ion indicator, for eg, Eriochrome Black-T (EBT).

3. **In metallurgy:** It is more effective for the extraction of the metals from their ores. For example, the silver is extracted from its sulphide ore by making its cyano complex as,

$$Ag_2S + 4NaCN \rightarrow 2Na[Ag(CN)_2] + Na_2S$$

The metallic silver is obtained by treating the above complex with the zinc dust,

$$2Na[Ag(CN)_2] + Zn \rightarrow Na_2[Zn(CN)_4] + 2Ag$$

4. **Softening of hard water:** For the complete softening of hard water, permutit process is found more effective. It involves the complexation of calcium and magnesium ions with the zeolite ' a complex forming agent'.
5. **Electroplating:** The complexes are more beneficial to use in electroplating because; - they are stable to oxidation, reduction, hydrolysis and
   i. They give a controlled supply of metal ions to the cathode it is important for uniform and quality electroplating.

   $Na[Ag(CN)_2]$ and $Na[Au(CN)_2]$ are generally used in the electroplating of Ag and Au respectively.
6. **In catalysis:** some complex compounds are used as catalyst especially in organic synthesis. For eg, $Co_2(CO)_8$ i.e. cobalt carbonyl is used in the oxidation olefin into alcohol.
7. **In dyeing:** Since they have characteristic colour, they are very commonly used in dyeing industries.
8. **In the field of medicine:** Many complexes are found of great use in the medicinal treatment. For example, cis-$[Pt(NH_3)_2Cl_2]$ is used in treatment of cancer, chemotherapy.
9. **Natural uses:** Many important naturally occurring compounds are complex compounds. For e.g., haemoglobin is a complex of Fe^{2+} ion with porphyrin, Vitamin B_{12} is a complex of cobalt ion and chlorophyll is a complex of Mg^{+2} with porphyrin.

Practice Questions

1. What are double and complex salts? Describe in brief with suitable examples.
2. What are co-ordination compounds? State the postulates of Werner's theory of co-ordination compounds. **[IOE-'65,'66,'67]**
3. What are principal and auxillary valencies of the metal ion in complex compound? Illustrate them in $[Co(NH_3)_6]Cl_3$. **[IOE-'67]**
4. What are inner and outer orbital complexes? Explain why solution of $[Co(NH_3)_5Cl]Cl_2$ gives white precipitate with silver nitrate solution but $[Co(NH_3)_3Cl_3]$ does not give.
5. Explain the structure of $CoCl_3.6NH_3$, $CoCl_3.5NH_3$, $CoCl_3.4NH_3$ and $CoCl_3.3NH_3$ on the basis of Werner's theory, if 3, 2, 1 and 0 chloride ions are precipitated with AgCl from their aqueous solutions. **[IOE-'66]**
6. Show your familiarity with electronic interpretation of complexes. **[IOE-'67]**
7. State the postulates of Valence Bond Theory for the formation of co-ordination compounds. Explain why octahedral complexes of Ni^{2+} ion are outer orbital complex.
8. How the valence bond theory does explain the formation of tetrahedral complexes?
9. On the basis of VBT, explain the structure and hybridization involved in $[Ni(CN)_4]^{2-}$ and $[Ni(Cl)_4]^{2-}$ ions. **[IOE-'66]**
10. Explain why octahedral complexes of Ni2+ ion are outer orbital complex. **[IOE-'66]**
11. Explain the formation of $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ using valence bond approach.
12. $[FeF_6]^{3-}$ and $[Fe(CN)_6]^{3-}$, both are octahedral complexes. What is the difference between two? Explain on the basis of VBT. **[IOE-'66]**
13. Describe the structure of $[Co(NH_3)_6]^{3+}$ on the basis of Werner's postulates and calculate the EAN of the central metal ion of the compound.
14. How can valence bond theory explains the geometry of $[Ni(NH_3)_6]^{2+}$ and $[Ni(CO)_4]^0$.
15. Explain the following:
    - i. $[Fe(CN)_6]^{4-}$ ion is diamagnetic but $[Fe(CN)_6]^{3-}$ ion is paramagnetic.
    - ii. $[Ni(Cl)_4]^{2-}$ ion is tetrahedral and paramagnetic.
    - iii. The formation of inner orbital complexes of Ni2+ (CN=6) is not possible. **[IOE-'66]**
    - iv. $[Co(F)_6]^{3-}$ ion is paramagnetic but $[Co(NH_3)_6]^{3+}$ ion is diamagnetic.
    - v. $[Ni(CO)_4]^0$ is tetrahedral and diamagnetic.
16. Write IUPAC name of the following
    - i. $[Fe(H_2O)_6]SO_4$
    - ii. $K_4[Fe(CN)_6]$
    - iii. $[Pt(NH_3)_4Cl_2]Cl_2$
    - iv. $[Cr(en)_3]Br_3$
    - v. $[Cr(H_2O)_5Cl]Cl_2$
    - vi. $K_3[AlF_6]$
    - vii. $[Co(NH_3)_4SO_4]NO_3$
    - viii. $Na_3[Co(NO_2)_6]$

    - ix. $Na_3[Al(C_2O_4)_3]$
    - x. $[Pb(OH)_4]^{2-}$
    - xi. $[PtCl(NO_2)(NH_3)_2]$
    - xii. $K_3[Co(CN)_5Cl]$
17. What do you understand by principal and auxillary valency of the central ion in the complex compounds? Illustrate them in $K_4[Fe(CN)_6]$ and $[Co(NH_3)_6]Cl_3$. Calculate EAN of the central metal atom of these complexes also predict the stability and magnetic properties.
18. Write the differences of doubles salts and complex salts.
19. Describe the EAN concept of co-ordination compounds. Give the formula of the following compounds.
    - i. Tetra-aquadichlorochromium (III) chloride
    - ii. Potassium trioxalato aluminate (III)
    - iii. Diamminetetrachloroplatinum (IV)
    - iv. Potassium tetracyanonickelate (II)
    - v. Dibromotetraaquochromium (III) chloride
    - vi. Potassium hexacyanocobaltate (II)
    - vii. Tetrabromocuprate (II)
    - viii. Tetraamminedichlorocobalt (III)
    - ix. Hexacyanoferrate (III) ion
    - x. Sodium trioxalato aluminate (III)
20. Nickel having co-ordination number 4 in the following complexes show different geometries and magnetic properties. Explain.
21. What is hybridization? How the shape of octahedral molecules better does explained on the basis of hybridization.
22. Cr^{+3} (CN=6) always form inner orbital complexes. Give reason.

◆◆

Chapter

7

Environmental Chemistry

Environmental Chemistry

Introduction:

Environmental chemistry is the scientific study of the chemical and biochemical phenomena that occur in natural places. It can be defined as the study of the sources, reactions, transport, effects, and fates of chemical species in the air, soil, and water environments; and the effect of human activity on them. Thus, environmental chemistry is an interdisciplinary science that includes atmospheric, aquatic and soil chemistry, as well as heavily relying on analytical chemistry and being related to environmental and other areas of science.

Environmental chemistry involves first understanding how the uncontaminated environment works, which chemicals in what concentrations are present naturally, and with what effects. Without this it would be impossible to accurately study the effects humans have on the environment through the release of chemicals.

Environmental chemistry is an important aspect of engineering because almost all the environmental problems are manmade and mainly derived from the engineering processes. Therefore, it becomes foremost responsibility of all the engineers to think up that any engineering processes developed are whether environmental friendly or not.

Environmental pollution:

The modification of the environment by the addition of any undesirable substances which causes various harmful effects into the life processes is called environmental pollution. Environmental pollution is broadly classified as;

1. Air pollution
2. Water pollution
3. Soil pollution

1. Air Pollution

The addition of any undesirable substances in undesirable concentration into the atmosphere that may cause various harmful effects to the living beings is known as air pollution. These undesirable substances are known as air pollutants.

Air pollutants can be classified as either primary or secondary. **Primary pollutants** are any substances directly emitted from a process, such as ash from a volcanic eruption, the carbon monoxide gas from a motor vehicle exhaust or sulfur dioxide released from factories. **Secondary pollutants** are not emitted directly, rather they are formed in the atmosphere when primary pollutants react or interact. An important example of a secondary air pollutant is ground level ozone — one of the many secondary pollutants that make up photochemical smog. Other secondary pollutants are peroxy acetyl nitrate

(PAN), peroxy benzoyl nitrate (PBN) etc.

Note that some air pollutants may be both primary and secondary: that is, they are emitted directly from the source and formed from other primary pollutants as well.

A variety of air pollutants are released into atmosphere. The major sources of the air pollutants are; industries, automobiles, thermal power plants, nuclear power plants etc. the air pollutants are of different types according to their states as,

1. **Gaseous pollutants:**
   - Carbon compounds: CO_2 and CO; the former released by complete combustion of fossil fuels and the latter by automobiles.
   - Sulphur compounds: SO_2, H_2S, H_2SO_4 etc; mostly these are released from the industrial units and thermal power plants.
   - Nitrogen compounds: NO, NO_2 and HNO_3; mostly these are released from automobiles and industries.
   - Hydrocarbons: Benzene and methane are the hydrocarbons chiefly emitted from the industries and automobiles.
   - Ozone: Its level may rise in troposphere due to human activities.
2. **Particulate Matters (PM):** These are dust, fly ash, smoke and any other suspended particles such as metals, biotic particulates (e.g., pollengrains and spores).
3. **Radioactive pollutants:** These include all the radioactive elements released from the nuclear power plants and by nuclear experiments.

The major air pollutants and their adverse effects are discussed below:

i. **Carbon dioxide**

Major amount of carbon dioxide is released in the atmosphere from the burning of fossil fuel (coal, oil etc), fire woods etc.

Carbon dioxide gas in the atmosphere is essential for the process of photosynthesis in which the whole life processes depend. But the increased concentration of carbon dioxide in the atmosphere produces adverse effects such as green house effect and global warming.

Green house effect

The layer of carbon dioxide gas in the atmosphere plays a major role for heating up the atmosphere by trapping the radiations coming from the sun. This temperature increasing effect is known as green house effect. This is necessary for the evolution of life and the greening of earth only at the desirable extent. But its higher concentration increases the heating effect in undesirable extent.

The thick CO_2 layer functions like the glass panels of a green house. This allows the sunlight to filter through but preventing the heat radiations to go back into the space. The so trapped heat radiations (infra red radiations) give the heating effect to the earth surface and hence increase the temperature. This is called green house effect. The increasing CO_2 levels tend to warm the air in the lower layers of the atmosphere on a global scale. Every year the world-wide concentration of CO_2 is increasing by the rate of 0.75ppm and the temperature is rising at a rate of 0.05°C per year. Nearly 100 years ago the CO_2 level was 275 ppm. Today it is about 350 ppm and by the year 2035 and 2040 it is expected to reach 450 ppm. Imagine the earth's temperature. CO_2 increases the earth temperature by 50% while CFCs are responsible for another 20% increase. Thus global warming is the consequence of increasing green house effect, which can ultimately arise disastrous effects such as melting of polar ice caps forming glaciers and result in flooding in the sea, oceans. The change in climate, what is being realized these days is said to be the effect of **global warming.**

Other gases such as SO_2, NO, CH_4, chlorofluorocarbons (CFCs) etc also contribute for green house effect.

ii. **Carbon monoxide:**

It is released by the incomplete combustion of fuel in automobiles, industries and oil-refineries. It is very toxic and found more health hazardous to human beings. It causes difficulty in breathing, headache, and irritation of mucus membranes in the respiratory tract. Other than these, the most dangerous effect of CO in our body is, it causes great disturbance in the transportation of oxygen from lungs to body cells because CO is far (~210 times) more reactive to hemoglobin than oxygen. More number of carboxy hemoglobin is formed instead of oxyhaemoglobin, which drastically reduces the transportation of oxygen into the body parts.

$$\underset{\text{Haemoglobin}}{Hb} + O_2 \longrightarrow \underset{\text{oxyhaemoglobin}}{HbO_2} \longrightarrow \underset{\text{in cells}}{Hb + O_2}$$

$$Hb + CO \longrightarrow \underset{\text{Carboxy hemoglobin(Comparatively more stable)}}{COHb}$$

Thus it causes serious deficiency of oxygen in our body leading to headache and suffocation leading to death.

iii. **Sulfur oxides (SO_x)** - SO_2 is mainly produced by volcanoes and in various industrial processes. Since coal and petroleum often contain sulfur compounds, their combustion generates sulfur dioxide. Further oxidation of SO_2, usually in the presence of a catalyst such as NO_2, forms SO_3. This causes **acid rain (a global effect)**. This is one of the major concerns over the environmental impact of the use of these fuels as power sources.

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$SO_2 + \text{oxidizing agent} \longrightarrow SO_3$$
$$SO_3 + H_2O \longrightarrow H_2SO_4$$

The acid rain and its adverse effects are discussed at back.

The presence of this gas in the atmosphere causes eye irritation, throat problems, respiratory and heart diseases. Exposure to 1 ppm level of SO_2 level cause constriction of the air passage and causes significant broncho-constriction in asthmatics at even low (0.25-0.50 ppm) concentrations. Moist air and fog increase the SO_2 dangers due to formation of H_2SO_4 and sulphate ions; H_2SO_4 is strong irritant than SO_2. Furthermore, this also causes acid rain- an invisible threat to the human world.

iv. **Nitrogen oxides (NO_x)** - Especially nitric oxide and nitrogen dioxide are released into the atmosphere from explosive industry, automobiles etc. Nitric oxide (NO) does not harm us directly but forms the other harmful gases by its oxidation, so it is also called pivot compound. A number of chemical reactions serially convert a large amount of NO to more toxic NO_2 in the atmosphere.

NO is responsible for several photochemical reactions in the atmosphere, particularly in formation of several secondary pollutants like peroxy acetylnitrate (PAN), O_3, carbonyl compounds etc. in the presence of other organic substances.

Nitrogen dioxide (NO_2) is a reddish-brown toxic gas that has a characteristic sharp, biting odor. NO_2 is the only widely prevalent coloured pollutant in the atmosphere. The presence of this gas in the atmosphere causes respiratory illness, eyes irritation etc. The prolonged exposure causes lung inflammation; this may be followed by oedema and final death. NO_2 is highly injurious to plants. Their growth is suppressed when exposed to 0.3-0.5 ppm for 10-20 days. Sensitive plants show visible leaf injury when exposed to 4-8 ppm for 1-4 hours.

This gas is the chief constituent of photochemical smog in metropolitan areas. In the presence of sunlight, nitrogen dioxide and hydrocarbons interact to form smog. This smog has several harmful effects such as,

- Limits the visibility of road
- Causes eye irritation
- Causes difficulty in breathing and hence lung's asthma, bronchitis etc.

Acid rain: an invisible threat

The oxides of sulphur and nitrogen are chief air pollutants. These oxides are swept up into the atmosphere by the rain water. The longer they stay in the atmosphere, the more likely they are oxidized into acids. Sulphuric acid and nitric acid are the two main acids, which then dissolve in the rain water and fall on the earth as acid rain.

$$SO_2 + H_2O \longrightarrow H_2SO_3 \text{ (sulphurous acid)}$$
$$O_2 + 2\,SO_2 + 2H_2O \longrightarrow 2H_2SO_4$$
$$H_2O + NO_2 \longrightarrow HNO_2$$
$$4NO_2 + 2H_2O + O_2 \longrightarrow 4HNO_3$$

The acid rain is in fact a cocktail of H_2SO_4 and HNO_3 and the ratio of the two may vary depending on the relative quantities of oxides of sulphur and nitrogen emitted. In average, 60-70% of the acidity is ascribed to H_2SO_4 and 30-40% to HNO_3. The acid rain problem has dramatically increased due to industrialization.

The acid rains create complex problems and their impacts are far reaching. Some prime effects of acid rain are mentioned as follows:

a. It causes damage to buildings, rocks etc by causing faster weathering
b. It increases the rate of corrosion of the metals so that it can damage the architectural figures (monuments, statues, railings etc).
c. It causes irritation to eyes and mucus membrane
d. It increases the acidity of soil that drastically affects the fertility of soil.
e. It also affects the life of aquatic organisms.
f. Due to acidity, levels of heavy metals as aluminum, manganese, zinc, cadmium, lead and copper in water increases beyond the safe limits.

i. **Hydrocarbons:** These are emitted from the industries and automobiles. High concentration of hydrocarbons (5000-10000ppm) effects lungs and cause respiratory problems. It also affects the nervous system and induces cancer also.

ii. **Ozone:** ***It is the destroyer when it is in the troposphere.*** It is quite destructive to fabrics, rubber goods, crops etc. However, it is the protector when it is in the stratosphere. It protects us from the harmful uv-radiation by checking the entry these radiations.

The ozone near the earth's surface in the troposphere creates pollution problems. Ozone and the other oxidants such as peroxy acetylnitrate (PAN) and hydrogen peroxide are formed by photochemical reactions between NO_x and hydrocarbons. Ozone may also be formed by NO_2 under uv-radiations effect. These pollutants cause photochemical smog.

Increase in ozone concentration near the earth's surface significantly reduces crops yield. It also has adverse effects on human health.

Photochemistry of ozone

The formation and depletion of ozone gas in the stratospheric level of atmosphere takes place in the presence of uv-radiations. This is called photochemistry of ozone. It is described as follows.

Formation ozone: The high altitude ozone is formed by the action of ultraviolet light on O_2, as shown in equations (1) - (5).

1. $\square\square O_2 + hv \longrightarrow O + O$
2. $O + O_2 + M \longrightarrow O_3 + M^*$
3. $O_3 + hv \longrightarrow O_2 + O$

Then the reactions (2), (3), (2), (3) etc continues. These are propagation steps. In step (2) O_2 is converted into ozone and in step (3) ozone is converted back into O_2. It is this interconversion that has maintained the ozone concentration at a constant level. Here, M stands for third body such as O_2 or N_2 that carries away the excess energy of ozone molecule and stabilize it.

4. $O + O + M \longrightarrow O_2 + M^*$

or

5. $O + O_3 \longrightarrow O_2 + O_2$

These are chain terminating steps where the reactive particles are consumed but not generated.

Depletion of ozone layer:

The thinning of the ozone layer in the stratosphere due to the photochemical decomposition of ozone gas is called the depletion of ozone layer. It is caused by chlorofluorocarbons (CFCs or Freons), nitric oxide (NO) etc released by supersonic jets in the upper atmosphere and other sources. The photochemical reaction causing the depletion of ozone layer due to CFCs is shown as:

1. $CFCl_3 + uv \longrightarrow CFCl_2(g) + Cl(g)$
2. $Cl(g) + O_3(g) \longrightarrow ClO(g) + O_2\ (g)$
3. $ClO(g) + O(g) \longrightarrow Cl(g) + O_2\ (g)$

Then the reactions (2), (3), (2), (3) etc. continues. Thus, the destructive particle is chlorine radical that one chlorine radical can react with more than 10^5 molecules of ozone converting into oxygen. The chlorofluorocarbons viz. CF_2Cl_2, CF_3Cl all contribute equally to destroy the ozone molecules. Therefore use of CFCs is to be phased out by international agreement.

The most frightening aspect of the effect of CFCs is the **time lag**. CFCs rise very slowly up to the atmosphere where they are photolysed. Therefore, the ozone depletion so observed is only due to only small fraction of CFCs that had already released into the atmosphere in the past. The recently produced high concentration of CFCs is still waiting up above us like a time bomb even though its production is stopped now.

Also the emission of nitric oxide by supersonic jets is responsible for depletion of ozone layer.

$$NO\ (g) + ClO\ (g) \longrightarrow Cl\ (g) + NO_2\ (g)$$
$$Cl\ (g) + O_3\ (g) \longrightarrow ClO\ (g) + O_2\ (g)$$
$$NO\ (g) + O_3\ (g) \longrightarrow NO_2\ (g) + O_2\ (g)$$

Effects of ozone layer depletion: With the depletion of ozone layer, the extent of uv-radiation reaching over the earth's surface increases. These uv-radiations are harmful for human's life as;

- It causes skin cancer, sun burns, skin aging, leukemia, breast cancer, eye cataracts etc. A 10% decrease in stratospheric ozone appears likely to lead a 20-30% increase in skin cancer.
- It causes DNA breakage, alteration of DNA's replication and may result undesirable mutation and lead to death as well.
- Apart from the direct effects, there are also indirect effects. Under greenhouse effect conditions, plants exposed to uv-radiations showed 20-50% reduction in growth of chlorophyll content.
- Enhanced uv-radiation also impairs fish productivity.

Particulate matters (PM):

Particulates alternatively referred to as particulate matter (PM) are tiny particles of solid or liquid suspended in a gas. In contrast, aerosol refers to particles and the gas together. Some particulates occur naturally, originating from volcanoes, dust storms, forest and grassland fires, living vegetation, and sea spray. Human activities, such as the burning of fossil fuels in vehicles, power plants and various industrial processes also generate significant amounts of aerosols. Increased levels of fine particles in the air are linked to health hazards such as heart disease, altered lung function and lung cancer. Different types of particulates are:

- **Dust-** Its sources are: mines, quarries, furnaces, house cleanings, ceramic factory, agricultural, forest fires, natural winds, engine exhausts etc.

  Effects: allergic and respiratory diseases, it also causes corrosion.
- **Fly ash:** It is fine ash is mainly emitted from the burning coal in thermal power plant.
- **Smoke:** It is the cloud of fine particles of size smaller than 10µm. The major sources are; industries, open fires, diesel engines, furnaces etc.

  Effect: It is carcinogenic. It causes dull appearance of buildings and spoiling of the clothes. It also causes the imperfect combustion of the fuel and hence loses its fuel value.
- **Smog:** It is a mixture of smoke and fog in suspended droplet form. i.e. Smoke + fog = Smog.

  Classic smog results from large amounts of coal burning in an area caused by a mixture of smoke and sulfur dioxide. Modern smog does not usually come from coal but from vehicular and industrial emissions that are acted on in the atmosphere by sunlight to form secondary pollutants (PAN, PBN etc) that also combine with the primary emissions to form photochemical smog.

Effects: It causes irritation to eyes and lungs. It also affects the plant growth and visibility in the road track.

- **Asbestos:** It is the fibrous silicate mineral. It is used in industry for its high mechanical strength and heat resistance. Suspension of asbestos fibers in the atmosphere is found more health hazardous. Tiny asbestos fibers readily penetrate the lung tissues and the digestive tract and remain there permanently resulting asbestosis (a lung's disease) and cancer. The symptoms of its effects are not seen early.
- **Lead:** Tetraethyl lead is used as an antiknocking agent used for improving the performance of gasolines in automobiles. This may be released in to the atmosphere in its original state or elemental form; both are found harmful for our health. It may be inhaled and injected into the blood as Pb^{2+}. This has tendency to react with sulphydryl group (-SH) of the proteins.

$$\text{Protein-SH} + Pb^{2+} + \text{HS-Protein} \rightarrow \text{Protein-S-Pb-S-Protein} + 2H^+$$

It inhibits the biosynthesis of haemoglobin and results anemia. On the other hand, it also affects the central nervous system and impairs kidneys.

- **Mercury:** It is more dangerous in its vapour state. It causes irritation and destruction of lung's tissues. The Hg^{2+} ions concentrate chiefly in the liver and kidneys. Mercury poisoning can cause brain damage to unborn infants.
- **Cadmium:** It is mainly released from the industrial processes. It is toxic to living organism even in low concentration (<1ppm).

Control measures of air pollution:

Steps are to be taken to control pollution at source (prevention) as well as after the release of pollutants in the atmosphere. Ideally, the engineering designer's strategy with regard to control the air pollution should be to:

1. *Prevent the formation of the pollutants.*
2. *Reduce emission by the removal of the pollutant by modifying the industrial process.*
3. *Ensure efficient dispersion in the atmosphere.*

Some important methods of controlling air pollution are:

i. ***Smoke can be reduced or prevented by appropriate combustion of fuel:***
   - *Correct method of firing*
   - *Supplying correct quantities of air*
   - *Maintaining high temperature; at low temperature the combustion is incomplete and smoky.*
   - Feeding the fuel continuously

ii. **Ensuring well dispersion of industrial emission:** *The use of* ***tall stacks or chimneys*** *reduces the concentration of the air pollutants in the ground level.* The gases discharged from the industry get dispersed and diluted in the atmosphere. Thus the tall chimneys serve to ensure lower concentration of pollutants.

iii. **By using cyclone collector:** It is mostly used as pre-cleaner of air. It works on the principle of centrifuging. In this method, gas containing particles is allowed to flow into a tight circular spiral-fitted chamber. The centrifugal force exerts great inertial effect on the dispersed particulates, thereby forcing the particulates to move away from the gas and towards the wall of the chamber. Then they are settled due to the force of gravity. The particulates so collected at the bottom of the chamber are removed periodically. The schematic representation of this process is shown below:

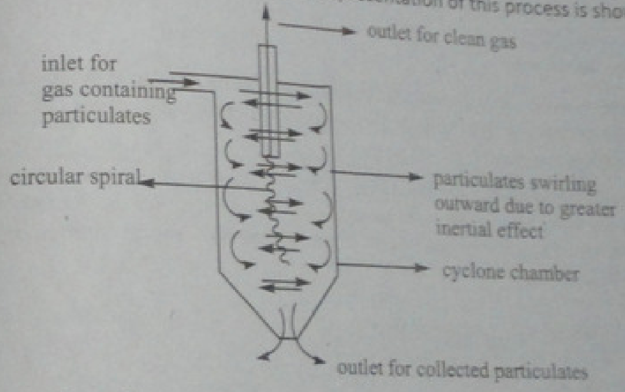


fig: cyclone collector showing removal of particulates from gas

This method of removing particulates is found better in the matter that; it is simple in construction and operation; it is low in cost as well. However, it suffers from early deterioration and it is less effective for settling the particles of size 5-10µm.

iv. **Control of vehicular emission:** The emission of air pollutants from automobiles and vehicles may be minimized by purifying the exhaust gases after combustion through the use of appropriate catalysts (i.e. using catalytic converters).

v. **By using Wet scrubbers:** Wet scrubbers remove pollutants by injecting liquid into the gas stream. Scrubbers built to remove particulates – such as dust scrubbers – the particulate is captured by the water droplets before it is discharged through the exhaust stack. This removes the gaseous pollutants by using adsorbents. The various types of scrubbers are developed such as centrifugal scrubbers, self-induced scrubber, venture scrubber etc.

   Chemical scrubbers are different: the liquid in question causes a chemical reaction that strips the chemical pollutant out of the waste stream.

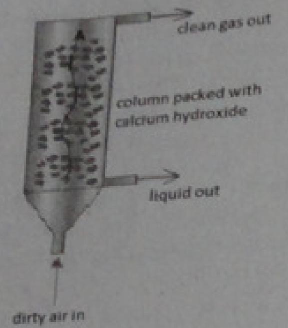


Fig: Wet Scrubber

Scrubbers offer a number of advantages; they can be used to remove gaseous as well as particulate pollutants, it also serves for cooling the machines as the liquid adsorbents are used.

vi. **By using gravity settlers**: Typical gravity settlers are used to collect fairly coarse dusts and may be used as pre-filters. In particular, the gravity settler works only for the large particles of size more than 50 µm. A simple schematic representation of gravity settler is shown below:

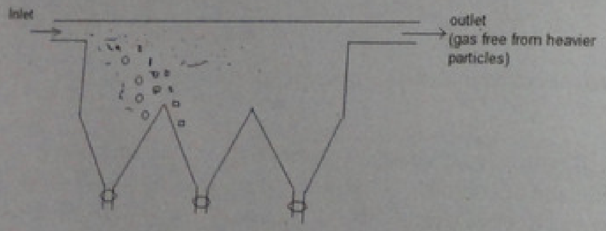


Fig: Gravity settler

vii. **Smoke may be reduced by using electrostatic precipitator (ESP):** An electrostatic precipitator is air pollution control device used to separate solid particulate matter from a contaminated air stream. Contaminated air flows into an ESP chamber and is ionized by electron emitting electrodes; also known as the corona chamber. The suspended particles are charged by the electron field and migrate to a collection plate. Accumulate particulate matter is removed from the collection plates at periodic intervals by rapping or hitting the plates with rappers (mallets type hammers). Heavy particles fall to the base of the ESP where hoppers hold the removed particles for disposal.

Smoke is a colloidal solution of negatively charged carbon particles in air. Before passing the smoke to chimney, it is sent through a chamber provided with a high potential of 30,000 volts or more. Under the influence of strong electric field, the smoke particles get robbed of their negative charge, there by the smoke particles precipitate out and settle at the bottom of the chamber.

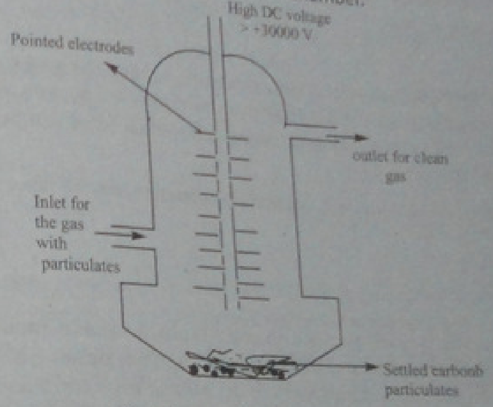


Fig: Electrostatic precipitator (ESP)

Table: Effective methods for gas/solid separation

Equipments	Mechanism of collections	Effective for the particle size range (mm)
Settling chambers	Gravity settlers	>100
Cyclones	Centrifugal settling	>5
Scrubbers	Inertia	>3
Electrostatic precipitators	Electrostatic migration	>0.001

viii. SO_2 pollution can be controlled either by removing the sulphur after combustion or by pre-combustion. SO_2 and acid fumes can be removed by passing the gases through a bed of alkalized ammonia or activated carbon or limestone powder.

$$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3 + H_2O$$
$$2NH_4OH + SO_2 \longrightarrow (NH_4)_2SO_3 + H_2O$$

Calcium sulphite and ammonium sulphite are the solid products and these can be removed frequently.

ix. **Zoning:** Effects of air pollution become more prevalent due to unplanned industrialization. Specifying industrial zone can be more effective to avoid air pollution. There should be a suitable buffer zone between the industrial units and residential units to facilitate the dilution of air pollutants.

x. H_2S and SO_2 emitted from any sources can be reduced by Claus process. It involves following stages.

$$2H_2S\,(g) + 3O_2\,(g) \longrightarrow 2H_2O\,(g) + 2SO_2\,(g)$$

At high temperature,

$$2H_2S\,(g) + SO_2\,(g) \longrightarrow 2H_2O\,(l) + 3S\,(l)$$

xi. Acids and chemical fumes can be removed by passing the gases through a tower filled with coke and against it a counter current of water applied from the top. It is more useful that volatile products having commercial value can be simultaneously recovered by this process.

xii. To be sensitive of health effect, particulate inhalation may be prevented by the use of mask

Water pollution

Normally, natural water is never pure in a chemical sense. It contains impurities of various kinds such as dissolved or suspended. The dissolved impurities include gases and dissolved minerals and suspended matters may be clay, silt, sand or even microbes. Generally, the presence of these in an undesirable concentration affects the human health and this is considered as water pollution. This makes the water unfit for the living organisms. The quality of water is generally expressed in the following terms.

Dissolved oxygen (DO): It refers the amount of free oxygen dissolved into the unit volume of water. Water containing dissolved oxygen is essential for the aquatic life. For e.g., fish cannot survive in the water containing dissolved oxygen below 5ppm.

Biological oxygen demand (BOD): It refers the amount of oxygen required for the complete decomposition of organic substances present in a unit volume of water by micro-organisms (microbial process). More the value of BOD of water, more it is polluted.

Measurement of BOD:

- A known volume of water sample is taken and the concentration of dissolved oxygen is determined.
- Leave it in a closed bottle for five days at temperature 20°C.
- The final concentration of dissolved oxygen is determined. The difference of initial and final concentration of dissolved oxygen gives BOD of the water sample.

Chemical oxygen demand (COD): It refers to the amount of free oxygen required for the oxidization of all the oxidizing impurities present in a unit volume of water sample. Since COD includes BOD as well, COD is always greater than BOD.

Measurement of COD:

- A known volume of water sample is mixed with a known excess of 1N $K_2Cr_2O_7$ and dil. H_2SO_4 in the presence of Ag_2SO_4 (catalyst).
- Leave the mixture for one and half an hours.

- The amount of unreacted $K_2Cr_2O_7$ is determined by titrating against Mohr's salt solution. The oxygen equivalent of $K_2Cr_2O_7$ consumed is the measure of COD.

1ml of 1N $K_2Cr_2O_7$ ⊠ 0.008g oxygen

Introduction:

Any modification in the physical, chemical and biological properties of water due the addition of any foreign substances that would cause harmful effect to the living organisms is called water pollution. Water pollution is categorized into two classes though these are interrelated.

1. Surface water pollution
2. Ground water pollution

Ground water pollution: Pollution of water sources under the ground due to mixing of drainage, wastes from septic tank etc is known as ground water pollution.

Surface water pollution: Pollution of water resources at the surface such as stream, river, sea, ocean etc is known as surface water pollution. Sources of surface water pollution are generally grouped into two categories based on their origin.

Point source pollution

Point source (PS) pollution refers to contaminants that enter into a water source through a discrete way, such as a pipe or ditch. Examples of sources in this category include discharges from a sewage treatment plant of industries, drainage from houses, hospitals etc.

Non-point source pollution

Non-point source (NPS) pollution refers to diffuse contamination that does not originate from a single discrete source. NPS pollution is often accumulative effect of small amounts of contaminants gathered from a large area. For e.g. Water washed off from lands (agricultural run off, surface run off).

In a glance, the chief sources of water pollutants are:

1. **Sewage and other waste:** Sewage is the water borne waste derived from houses, animal or food processing plants. It includes human excreta, soap, detergents etc. Accumulation of sewage and other waste in the water sources results depletion of oxygen level of water and stimulates for algal growth. Undesirable water borne diseases such as cholera, dysentery, typhoid etc are common when people use water from such source.
2. **Industrial effluents:** A wide variety of both organic and inorganic pollutants is present in the effluents from breweries, paper and pulp mills etc. The pollutants include oils, greases, plastics, metallic wastes, suspended solids, phenol, acids, salts, cyanides, DDT etc. a direct discharge of industrial effluent is very alarming for aquatic life.
3. **Petroleum oils:** Oil and chemicals derived from oil are used for fuel, lubrication, plastics manufacturing, and many other purposes. These petroleum products get into water mainly by means of accidental spills from ships, tanker trucks, pipelines,

and leaky underground storage tanks. Many petroleum products are poisonous if ingested by animals, and spilled oil damages the feathers of birds or the fur of animals, often causing death. In addition, spilled oil may be contaminated with other harmful substances, such as polychlorinated biphenyls (PCBs).

4. **Agricultural discharges:** These include the chemicals used in the field such as fertilizers, insecticides and pesticides. Such chemicals are distinguished as hazardous substances or toxicants. These discharges from the agro-land are washed by the rain water and reach in to the water sources. The most harmful are those which either do not degrade or degrade very slowly in nature.
5. **Surface run off:** It refers to the substances on the land surfaces such as solid wastes, pesticides, insecticides, fertilizers etc are run off by the rain water and mixed into the water sources.

Effects:

- ➢ Disposal of sewage into rivers and lakes causes various water borne diseases such as dysentery, cholera, typhoid, worms infections etc.
- ➢ Water resources mixed with agricultural run off are rich in nitrates, phosphates etc. nitrates interfere with oxygen carrying capacity of haemoglobin, thereby causing suffocation and injuring to respiratory and vascular system.
- ➢ Excess nitrates and phosphates in water system cause eutrophication (rapid growth of plants in water due to the rich supply of nutrients) that leads to the depletion of oxygen in water. This leads to endanger the life of aquatic animals.

Control measures of water pollution:

1. **Stabilization of the ecosystem:** This is the most scientific way to control water pollution. The basic principles involved are the reduction in waste input, removal of biomass, aeration and any methods to balance the ecosystem.
2. **Waste water treatment:** The techniques applied in industrial waste-water treatment are classified as primary, secondary and tertiary.

Primary treatment involves the removal of settlement material. It removes the greater proportion of the suspended inorganic and organic solids from the liquid sewage. The continuous flowing sedimentation tanks are employed for this process. Sometimes chemical treatment is used to increase the settling of matters. The chemicals employed are alum, ferrous sulphate etc

Secondary treatment is often called biological treatment. It involves the use of concentrated mass of micro-organisms to break down organic matter into stabilized wastes.. For e.g., **suspended growth method or activated sludge process.** This method involves the aeration and oxidation of suspended organic matters by adding active sludge (a mass of decomposed matter containing micro-organisms). The so added sludge induces the oxidation of suspended organic materials and the settling of oxidized product takes place in the sedimentary tank.

Tertiary treatment involves wide range of physical and chemical methods for appropriate settling or separating. Commonly, the methods employed are filtration, precipitation, adsorption, chemical oxidation, ion exchange etc.

Precipitation involves treatment of effluent from secondary treatment with calcium oxide, which reacts with phosphorous compounds forming insoluble phosphates,

which settles down at the bottom of tank from where it is filtered off.

3. **Reutilization and recycling of waste:** Various kinds of wastes from industrial effluents, thermal pollutants may be recycled to beneficial use such as to generate cheaper fuel gas and electricity (Gobargas plant).
4. In order to ensure the minimum effects of water pollution, **appropriate selection of site for drinking** water has to be done.
5. **Appropriate laws and their execution** have to be effected in all the industrial sectors.

Soil pollution

The addition of chemical substances in indefinite proportion to the soil system where by reducing its fertility is known as soil pollution. Any substances added into the soil that alters its quality are soil pollutants. The sources of soil pollutants are:

1. Domestic refuge such as bottles, plastic containers, polythene etc that are thrown as garbage.
2. The wastes from industries
3. Chemicals like fertilizers, pesticides, insecticides added into the soil
4. Radioactive wastes discharged from industrial and research lab
5. Typical normal to complex wastes from colleges, pathological lab, hospitals etc.

Effects:

- ➢ Soil pollution directly affects the agriculture that it drastically reduces the crops yield.
- ➢ The use of agricultural products grown in radioactive substances enriched soil is very harmful for our health.
- ➢ The piled up garbage at the public places cause obstruction in daily life. There are also more chances of spreading diseases.

Control measures of soil pollution

1. Using sanitary landfills where the untreated wastes from various sources are buried and covered with earth. This should be done by ensuring following factors.
    - ➢ No dispersion of wastes by any means such as atmospheric dilution, mixing into big bodies of water or spreading through large volumes of soil.
    - ➢ Fixation of radionuclides on soil minerals and organic detritus.
    - ➢ Decay of radionuclides, dispersed or fixed, before they are able to affect man.
2. Chemicals which have a relatively high immediate as well as persistent toxicity must not be used normally.
3. Industrial and sewage waste should be properly treated before disposal on land.
4. Composting of organic waste for preparation of manures and biogas.
5. Recycling and reusing of plastic and metallic materials should be highly encouraged.
6. Appropriate laws and their execution has to be done in order for preventing and controlling the effects of soil pollution

Practice Questions

1. Discuss the fact that 'environmental chemistry is the important aspect of engineering science.'
2. Write short note on: a. BOD b. COD c. Global warming d. Acid rain
3. Explain the methods of controlling air pollution regarding engineering efforts.
4. a. What is meant by global warming? Give its causes and consequences.
   b. What is the photochemistry behind ozone layer depletion? **[IOE-'68]**
5. a. What are chlorofluorocarbons? Give their photolytic reactions in the upper atmosphere.
   b. Why oxides of sulphur and nitrogen are assumed as air pollutants? **[IOE-'67]**
6. What are freons? Describe their role in the depletion of ozone layer with the photochemical reactions.
7. List out the four major pollutants of air, their adverse effects on human health and also write their possible remedies. **[IOE-'68]**
8. Describe the causes of water pollution and their control.
9. Describe the causes of soil pollution and their control.
10. What are PAN and PBN? Mention their global effect?
11. Point out four major pollutants of water, their adverse effect on human health and also mention their possible remedies. [2+1+2] **[IOE-'67]**

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Chapter

8

Explosives

Explosives

Introduction

An explosive may be defined as a material, which under the influence of thermal or mechanical shock decomposes rapidly with the evolution of great amount of heat and increased volume of the products causing explosion. At the temperature of explosion, the volume of the evolved gases is perhaps, 15000-20000 times as that of the explosive itself. The first real explosive, called gun powder or black powder was discovered by Roger Bacon. The composition of this explosive is explained behind. This may also be accompanied by the emission of light, sound waves etc.

The explosive reaction is exothermic. Therefore the products get heated to a high temperature and then a high pressure is exerted on the surrounding. If this occurs in a confined space, an extremely high pressure is developed, which shatters the confining walls that it causes explosion.

Characteristics of explosives:

An explosive should have the following characteristics in order to produce the desired effects.

i. The rate of decomposition should be reasonably fast so that tremendous amount of energy within the limited time to cause an effective explosion.
ii. The power to weight (or volume) ratio should be sufficiently high.
iii. It should be cheap and stable at normal condition that it can be stored or transported safely.
iv. It must have at least one chemical bond that can be easily broken. Usually explosive molecules contain N-N, N-O, N-Cl bonds, which have very less electronegative difference.
v. It should have positive oxygen balance.

Oxygen balance:

The oxygen atoms in a molecule that are utilized to oxidize C to CO and H_2O molecule. It is expressed in the percentage of oxygen by weight. E.g.,

$$C_xH_yO_z \rightarrow xCO + \frac{y}{2}H_2O + (z - x - \frac{y}{2})O$$

Then, oxygen balance for the above explosion reaction is given by,

$$\text{Oxygen Balance (OB)} = \frac{\left(z - x - \frac{y}{2}\right)\times 16}{\text{[illegible]}} \times 100\,\%$$

However, the explosives with zero or negative oxygen balance are also known. For example, Lead azide has zero oxygen balance and Trinitrobenzene has -11.3 oxygen balance.

Uses of explosives:

Explosives are used for various purposes accordingly these have proved to be mankind as well as very detrimental to the human kind. Anyway, explosives are the power that may be used for both useful as well as destructive purposes that all depend upon the human brain that uses it.

- The practical application of explosives is to use the power produced to do work. Explosives are widely used for the creation of dams, tunnels, roads in hills, mining of coals, metals, quarrying limestones etc.
- In metal industry, explosives are used for the blasting of the metal ores for extracting pure metals.
- Explosives may have military uses not only for war but also for protective purposes.
- They may also be used for launching projectiles, propelling rockets etc.

Terminology:

Detonation: A dynamic phenomenon in which high pressure shock waves are formed on the surface and passes through the explosive is known as detonation. It is the initial process of the explosion.

Velocity of Detonation (VOD): It is the velocity with which the given explosive detonates.

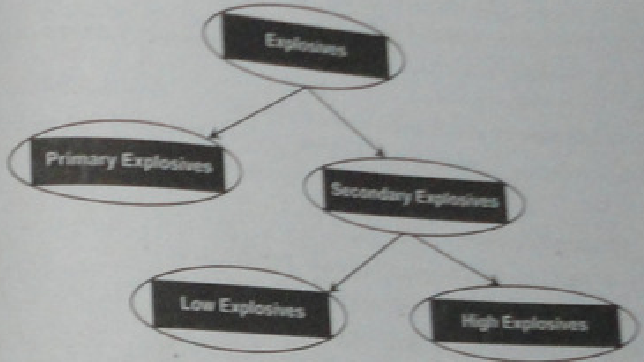
Explosive Strength: It is the quantity of the measure of the energy liberated per unit mass of the explosive. It is calculated by dividing the total amount of energy released during explosion by the total amount of explosive undergoing explosion.

Brisance: It is the measure of the shattering power (i.e. effective power to break the confining wall) of explosive. More the brisance of an explosive more it is destructive.

Sensitivity: It is the sensitivity of explosives to impact, friction, heat etc that how easily an explosive detonates.

Types of Explosives:

Especially on the basis of the sensitivity and explosive strength all the explosives are divided as follows.



1. **Primary Explosives:**

   These explosives are highly sensitive to heat, friction or impact. Therefore they should be handled with the utmost care. But these explosives generally have less energy content and these are mainly used in small quantity just to initiate the explosion of main explosives (Secondary explosives). This is the reason why primary explosives are also called detonators. Some common examples of the detonators are mentioned as below.

   a. **Lead azide:**

   Molecular formula- $Pb(N_3)_2$

   Molecular Structure- $N^-=N^+=N\text{-}Pb\text{-}N=N^+=N^-$

   Physical State: white powder

   Preparation: It is prepared by reacting lead nitrate or lead acetate with sodium azide. The required sodium azide is prepared by reacting sodium with ammonia solution as follows.

$$6NH_3 + 2Na \longrightarrow 2NaNH_2 + 3H_2$$

$$NaNH_2 + N_2O \longrightarrow \underset{\text{sodium azide}}{NaN_3} + H_2O$$

$$\underset{\text{Lead acetate}}{(CH_3COO)_2Pb} + 2NaN_3 \longrightarrow Pb(N_3)_2 + 2CH_3COONa$$

$$Pb(NO_3)_2 + 2NaN_3 \longrightarrow \underset{\text{lead azide}}{Pb(N_3)_2} + 2NaNO_3$$

Uses:

- It is very popular for military uses because of its low cost, excellent initiating action and stability in storage. However it cannot initiate explosion of less sensitive secondary explosives.
- It reacts with brass and hence the caps loaded with it are made up of aluminium.

It decomposes as follows during the explosion.

$$Pb(N_3)_2 \longrightarrow Pb + 3N_2\uparrow + \text{energy}$$

b. **Mercury Fulminate**

The chemical name is mercury cyanate; Hg(CNO)$_2$.

Molecular structure: $^-$O-N$^+$⍰C-Hg-C⍰N$^+$-O$^-$

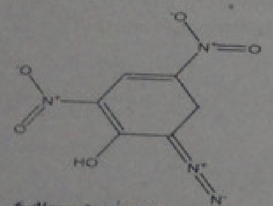
Physical state: Grey crystalline solid

Use: *Mercury fulminate is more sensitive than lead azide and it may be used as detonator of other higher explosives. It has the detonation rate of 5.4Km/sec at 4.2g/cm^3. Since mercury is more toxic, it is used in lesser extent.*

c. ***Diazodinitrophenol (DDNP):***

The chemical name is 6-diazo-2,4-dinitrophenol.

Molecular structure:

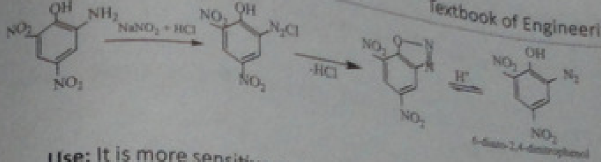


6-diazo-2,4-dinitrophenol

Physical state: Yellowish brown powder

Preparation: It is prepared by reacting 6-amine-2,4-dinitrophenol with nitrous acid (prepared by mixing sodium nitrite in dilute hydrochloric acid) at low temperature.

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$

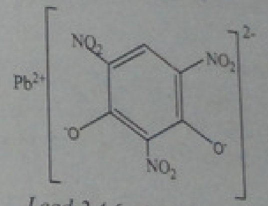


Use: It is more sensitive explosive and it has high brisance that can detonate even the less sensitive high explosives. It is commercially used in blasting caps.

d. **Lead styphnate:**

The chemical name is lead-2,4,6-trinitroresorcinate.

Molecular structure:



Lead-2,4,6-trinitroresorcinate

It is a solid detonator that ignites and initiates the explosion of high explosives. However, it is found less sensitive than mercury fulminate and lead azide.

2. **Secondary explosives:** These explosives are generally less sensitive but have high energy content. These are sensitized for explosion by primary explosives or detonators. Furthermore, depending mainly on the velocity of detonation (VOD) and explosive strength, secondary explosives are categorized into two groups.

i. Low explosives

ii. High explosives

i. **Low explosives:**

These explosives are less sensitive to heat, friction or any impact than primary explosives but are more sensitive than high explosives. These simply burn and do not explode suddenly. The chemical reactions taking place in such explosives are comparatively slower and burning proceeds from the surface to inward layers. Therefore they can be controlled easily at the time of explosion. Some common examples of low explosives are mentioned as below;

a. **Gun powder:** It is a black powder made by mixing 75% KNO$_3$, 15% charcoal and 10% sulphur. It contains sufficient oxygen to oxidize the other elements when it is ignited. The burning proceeds with the following decomposing reaction,

$$10KNO_3 + 3S + 8C \longrightarrow 3K_2SO_4 + 2K_2CO_3 + 6CO_2\uparrow + 5N_2\uparrow$$

The excess of carbon and sulphur take part in slower reduction process, leading to the evolution of more gases.

$$4K_2CO_3 + 7S \longrightarrow K_2SO_4 + 3K_2S_2 + 4CO_2\uparrow$$

$$4K_2SO_4 + 7C \longrightarrow 2K_2CO_3 + 2K_2S_2 + 5CO_2\uparrow$$

Thus, the so produced large volume of gases account for the explosion.

Uses:

- *It is an excellent and cheap explosive for blasting down of coal mine.*
- *It is commonly used as igniters and primer assemblies for propellants, practice bombs etc.*

b. Nitrocellulose (Smokeless powder):

It is called smokeless powder because it burns by producing CO_2, CO, N_2, water vapour and almost no smoke (solid particles spreaded in gas). This is also known as Gun cotton. Cellulose is the insoluble polymer form of glucose and is represented as,

$$\left[C_6H_{10}O_5\right]_n$$

cellulose

Preparation: *It is prepared by treating cellulose with conc. HNO_3 and conc. H_2SO_4.*

$$\underset{\text{a unit of cellulose}}{C_6H_7O_2(OH)_3} \xrightarrow{\text{conc.}HNO_3 + \text{conc.}H_2SO_4} \underset{\text{a unit of cellulose nitrate}}{C_6H_7O_2(NO_2)_3}$$

The product nitrocellulose is dissolved in ether and alcohol. When the solvent is *evaporated, a jelly solid is left behind. Then adding diiphenyl ammine as a stabilizer, it is pressed into cylindrical rods.*

Uses:

- It explodes very rapidly and it is commonly detonated by mercury fulminate.
- It is used as a propellant in rifles.
- It provides mechanical strength and readily available energy to gun and rocket propellants.

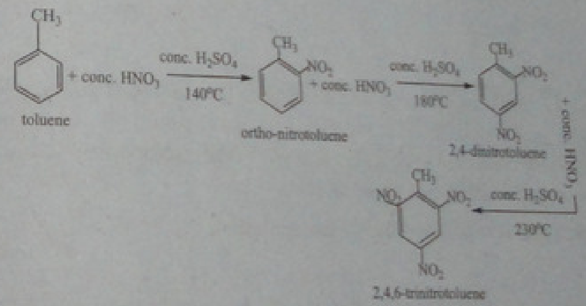
ii. High explosives

These are the most powerful explosives. However, in general, they are quite stable and less sensitive to fire and mechanical shock. Therefore, these are detonated by the most powerful detonators. High explosives are further divided into four groups.

a. *Single compound explosives-* *Examples; Trinitro Toluene (TNT), Nitroglycerine (NG), Pentaerythritol tetranitrate (PETN), Picric acid, cyclonite (Cyclotrimethylene trinitroammine) or RDX etc.*

Trinitrotoluene (TNT)

✓**Preparation:** It is prepared by the nitration of toluene using conc. HNO_3 and conc. H_2SO_4 in 1:1 ratio. The contents are continuously in the reactor and the reaction is carried out in different temperature as follows.



The liquid TNT product is washed with ammoniacal solution of sodium sulphite (Na_2SO_3) and then with cold water. The pure TNT is crystallized out. This is then filtered and further purified by melting. The melt is dried and pour into containers.

It decomposes as follows during the explosion.

$$TNT \rightarrow 3.5CO + 3.5C + 2.5H_2O + 1.5N_2 + 190kcal$$

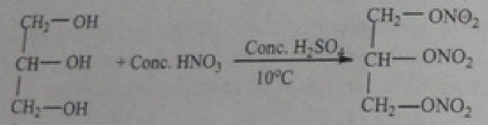
Uses:

- It is widely used in shell-firing and under water explosions.
- It is the major gradient of binary explosives.
- It has military uses as it is safe explosive in manufacture, transportation and storage. It in non-hygroscopic.
- Bombs and projectiles are filled with steam-melted TNT.
- Melted TNT also serves as the liquid carrier for RDX, ammonium nitrate etc. to form castable slurries.

Trinitroglycerine (TNG) or Nitroglycerine (NG) or Glyceroltrinitrate (GTN):

Nitroglycerine is an oily liquid, which is easily detonated by pressure, shock or spontaneously above 50°C. The explosion is so sudden that nitroglycerine would shatter the breech of rifle, before the bullet had time to move.

Preparation: It is prepared by adding glycerol to a cooled mixture of conc. H_2SO_4 (60%) and conc. HNO_3 (40%) at 10°C with constant stirring. The reaction occurs as follows.



$$\begin{array}{l} CH_2-OH \\ | \\ CH-OH \\ | \\ CH_2-OH \end{array} + \text{Conc. } HNO_3 \xrightarrow[10^\circ C]{\text{Conc. } H_2SO_4} \begin{array}{l} CH_2-ONO_2 \\ | \\ CH-ONO_2 \\ | \\ CH_2-ONO_2 \end{array}$$

Glycerol Glyceroltrinitrate

The mixture product is run into a container and allows standing. Nitroglycerine forms upper layer and it is separated out by the method of separating funnel. This is then washed with water and with dilute solution of sodium carbonate (2%) in order to remove traces of acids.

It decomposes as follows during the explosion.

$$\underset{\text{1 volume}}{4C_3H_5(NO_3)_3} \longrightarrow \underset{\text{10,000 volumes at temperature of explosion}}{10H_2O\uparrow + 6N_2\uparrow + 12CO_2\uparrow + O_2\uparrow}$$

Uses:

- It is important gradient of dynamite which is very popular explosive. Dynamite is made by absorbing nitroglycerine into the inert substances such as saw dust, wood pulp etc.
- It has high shattering effect and is used in firing bullet.
- It is also used as plasticizer for nitrocellulose in double and multiple base propellants.
- It pulverizes the rock instead of breaking only.

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b. **Binary explosives-** It consists of a mixture of TNT with other explosives. Examples,

Amatol: (TNT + 50 to 80% NH_4NO_3)
Pentolite: (TNT + PETN, 50% each)
Tetrytol: (70% tetryl + 30% TNT)
Tropex: (40% RDX + 40%TNT + 20% aluminium powder)

Binary explosives are designed to have high explosive strength in possible low cost.

c. **Plastic explosives:** These are the combination of explosives, which are in plastic state that can be moulded and made into various shapes without any serious risk.

Preparation: In general, plastic explosives are prepared by mixing a high explosive with wax or oil, which makes it less sensitive and more plastic.

Uses:

- It has wide engineering applications as they are available in flexible sheets that can be easily moulded into any shape and produce the desired effect of explosion.
- Also, these can be cut into small shapes and special caps are used to start the explosion.

d. **Dynamites:** These are the most powerful high explosives made by absorption of nitroglycerine into the inert absorbent such as saw-dust, wood pulp etc. This was discovered by Alfred Bernhardt Nobel and made the safe use of nitroglycerine in practice.

The amount of absorbent that is added to the dynamite varies with its relative strength.

i. ***Straight dynamites***: These contain 15-60% nitroglycerine absorbed in wood meal with sodium nitrate. Sodium nitrate is used as an oxidizing agent and increases the oxygen balance. These are mainly used for blasting hard rocks, coal mine etc.

ii. ***Blasting gelatin dynamites:*** In these dynamites, NG has been partly gelatinized by nitro-cotton. The usual approximate composition is 91.5% NG, 8% nitro-cotton, 0.5% $CaCO_3$. The chief uses are submarine explosion, deep-water shooting and where there maximum shattering effects are desired.

iii. ***Cordite***: It is made by dissolving gun-cotton (65%), NG (30%) and petroleum jelly (5%) in acetone. The resulting paste is rolled and cut into pieces of different dimensions, according to the rate of explosion desired. The petroleum jelly acts as a stabilizer and gun-cotton slows down the explosive [illegible] reaction of NG. The cordite [illegible] guns.

iv. ***Gelignite:*** It consists of 65% blasting gelatin and 35% of absorbing powder. It is powerful explosive for under water explosion.

Precautions during storage of explosives

1. Different explosives should be stored in separate boxes.
2. Detonators should be stored safely and separate from high explosives.
3. Use torch for lighting purpose in the storage not the flame lantern.
4. Explosive store is known as magazine, it should be constructed at least 500m far away from working kiln and furnaces.
5. Jerks and drops of explosives should not be allowed.
6. Electric wirings in the magazine should be properly insulated and frequently examined.
7. Smoking/fire is strictly prohibited in this area.

Practice Questions

1. Define explosives? Give the preparation, properties and use of trinitrotoluene (TNT). What are plastic explosives?[1+3+1] [IOE-'67]
2. Define the following terms:
    i. Detonation
    ii. Oxygen balance
    iii. Explosive strength
    iv. Brisance
3. Calculate the oxygen balance of the following explosive compounds.
    i. Trinitrotoluene
    ii. TNG
    iii. Lead azide
    iv. Picric acid
    v. Ammonium nitrate
4. List the important characteristics of explosives. Give the preparation of glycerol trinitrate (GTN) and trinitrotoluene (TNT). Point out the industrial applications of explosives. [IOE-'67]
5. Write the preparation and uses of lead azide.
6. What are low explosives? Write their uses. Give the preparation and applications of GTN. [IOE-'68]
7. Describe the preparation and uses of the following explosives.
    i. Trinitrotoluene
    ii. Glyceroltrinitrate
    iii. Nitrocellulose
    iv. Gun powder
8. What are the essential requirements for a substance to be explosives?
9. Write short notes on
    i. Classification of explosives
    ii. Plastic explosives
    iii. Dynamites
10. Explain the term detonation. Give examples of a few detonators and high explosives.
11. Detonators are used in conjunction with high explosives. Give reason.

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Chapter

9

Lubricants

Lubricants

Introduction

In all types of machines, the surfaces of moving parts rub against each other. Due to mutual rubbing of one part against another, a resistance is offered to their movement. This resistance is known as friction. Friction is a force of resistance to the relative motion of two contacting surfaces. Friction causes a lot of wear and tear of surfaces of moving parts and such parts require repeated replacement. Due to friction, large amounts of energy are dissipated in the form of heat, thereby causing loss in the efficiency of the machine. Moreover, the moving parts get heated up damaged and sometimes even result in seizure.

Lubrication may be defined as the reduction of friction and wear between two relatively moving surfaces by the interdeposition of some substance between the surfaces. The substance thus introduced is known as lubricant. A lubricant may be defined as a substance which reduces the friction when introduced between two rubbing surfaces.

Any chemical substance introduced between two moving (rolling/sliding) surfaces in order to reduce the frictional resistance between them is known as lubricant. And the phenomenon of reducing the frictional resistance between two surfaces moving in contact by using lubricants is known as lubrication.

Functions of lubricants:

Reduction of every ill-effects of friction in the machinery parts are the functions of lubricants. With these, some important functions of lubricants are mentioned as below:

1. It reduces wearing, tearing and surface deformation of the two substances moving in contact.
2. It acts as coolant that it reduces loss of energy in the form of heat.
3. It reduces expansion of metal by local frictional heat.
4. It reduces the maintenance and running cost of the machine as a result it enhances the efficiency of the machine.
5. Sometime, it also acts as seal. For example, lubricants used between piston and cylinder wall of the internal combustion engine acts as seal that it prevents the leakage of gases under high pressure from the cylinder.
6. It avoids seizure of the moving surfaces and increases the durability of the substances.

Types of lubricants

In a broad sense, the lubricants are classified on the basis of their physical state however they may be sub-divided according to the chemical compositions. The three broad groups of lubricants are as follows:

1) Liquid lubricants or lubricating oils
2) Semi-solid lubricants or greases
3) Solid lubricants

1. **Lubricating oils:** Lubricating oils reduce the friction by providing the continuous fluid-film in between the surfaces moving in contact. All the liquid substances cannot be used as lubricants but a lubricating oil should have certain characterisitics.

Basic terms regarding the characteristics of lubricating oils

Pour point: The temperature at which oil ceases to flow.

Viscosity index: It is the average decrease in viscosity per degree rise of temperature.

Cloud point: The temperature at which the cloudiness appears in the sample oil because of wax separation is known as cloud point.

Flash point: It is the lowest temperature at which the vapours of the oil ignite for a moment when a small flame is brought near it.

Fire point: It is the lowest temperature at which the vapours of the oil burn continuously for at least 5 seconds when a small flame is brought near to it. Generally the fire point is 5-40°C higher than the flash point.

Aniline point: The aniline point of oil is the temperature at which equal volumes of oil and aniline are just miscible. The aniline point of oil gives an indication of the deterioration of oil when it comes into contact with rubber sealings, packings, etc.

Neutralization number: The neutralization number is an indication of acidic or basic impurities in the lubricating oil. Determination of acidity is more common and is expressed in terms of acid value or acid number.

Saponification number: Saponification is the alkaline hydrolysis of ester to give alcohol and sodium or potassium salt of the acid. The saponification number is defined as the number of milligrams of KOH required to saponify the fatty material present in 1 gram of oil. This is usually determined by refluxing a known quantity of oil with a known excess of KOH solution and titrating the unused alkali against an acid.

A good lubricating oil must possess following characteristics.

- High flash point and fire point
- Minimum pour point and cloud point
- Least neutralization number
- Suitable viscosity and high viscosity index
- High stability to heat at working condition
- Corrosion preventive
- High resistance to oxidation that means they should not be easily oxidized.

Lubricating oils are further classified as-

a. ***Vegetable oils and animal oils:*** In earlier days, the oils of vegetable origin such as castor oil, mustard oil etc and the oils of animal origins (whale oil, mutton oil etc)

were the most commonly used lubricants. They possess good oiliness character which is important for reducing friction. However they are less in use at present because of high cost, easily oxidizing and hydrolyzing tendency in contact with air. But they are used as blending agent with petroleum oil.

b. **Petroleum oils or mineral oils:** These oils are obtained by distillation of petroleum that is extracted from the earth crust. Crude petroleum oils contain lot of impurities such as;

Wax- it raises the pour-point and makes oil unfit for lubricating at low temperatures,

Oxidizable impurities: Constituents which are easily oxidized cause the formation of thick pigments (sludges)

Asphalt-It is dark pigmented oil (tar) which decomposes at high temperatures causing the deposition of carbon and reduces the lubricating efficiency of oil.

Therefore the petroleum oils should be well refined before its use. The commonly adopted methods of purification of petroleum oils are;

Dewaxing- It is a method of removing wax from oil. It is carried out by mixing oil with a suitable solvent such as mixture of benzene and ethylene dichloride followed by cooling. The wax precipitates out and can be removed by filtration or centrifugation.

Acid refining- This is a method of removing asphaltic impurities by treating dewaxed oil with conc. Sulphuric acid and then agitated. The impurities get dissolved in acid and some other impurities form sludges, which are then removed by filtration. Finally, the filtrate is neutralized with required quantity of NaOH solution.

Solvent refining- In this method, the oil is mixed with a suitable solvent mixture e.g., sulphur dioxide and benzene. Impurities and oil are separated into two solvent layers and the pure oil is extracted by using separating funnel.

Petroleum oils are highly used for lubrication because they are cheap, available in abundance and high stability under working conditions. However, they have poor oiliness and it can be enhanced by adding vegetable and/or animal oils.

c. **Blended oils or compounded oils:** The more improved lubricating oils are obtained by mixing specific additives into the petroleum oil. The petroleum oils compounded with such specific additives are known as blended oils. Specific additives into the petroleum oil produce the desired lubricating properties required for a particular working condition. The commonly employed special additives are as follows:

Oiliness carriers: The oiliness of the lubricants can be improved by adding oiliness carriers like vegetable oils and animal oils.

Viscosity index improvers: High molecular weight compounds are generally added to improve the viscosity index of lubricants. For e.g., Hexanol

Oxidation inhibitors or antioxidants: Aromatic or amino compounds are added to control the oxidation of lubricants. They do work it by the preferentia oxidization of themselves.

Corrosion-preventors: Organic phosphorous compounds are added into the lubricants, which prevents the metal surfaces from exposing into the corrosive environments and hence protect from corrosion.

High pressure additives: To make the lubricating oils working at high pressures, certain additives like organic sulphur, organic chlorine and organic phosphorous compounds are added. These additives are adsorbed on the metal surfaces or react there producing the smooth surface and provides the lubricating effects. High pressure lubricants may also contain lead which produces the thin film of lead sulphide for lubrication.

Anti foaming agents: Glycerols are added into the lubricants that it reduces the foam formation. Etc.

2. Semi-solid lubricants:

Greases and Vaseline are commonly employed semi-solid lubricants.

Greases:

Greases are semi-solid lubricants made by dispersion of soaps into liquid lubricating oil. When lubricating oil films cannot exist, the greases may be better option for the lubrications. The conditions of using greases are as follows:

- When lubricating oil film does not exist due to heavier load, low speed or sudden jerks etc.
- When contamination due to lubricant is very sensitive and it has to be avoided. For e.g., in foodstuffs industry and textile industry.
- When bearing needs to be sealed and screening the entry of dirt and moisture.
- In gears that work at high temperatures etc.

Preparation of greases:

Greases are prepared by saponification of fats with strong alkalis and adding hot lubricating oil with continuous agitations. The consistency of greases varies from heavy liquid to rigid solid state and it is determined by the total amount of petroleum oil added. The main function of soap is gelling or thickening the lubricating oil so that greases sticks properly to the metallic surfaces. According to the types of alkali used during saponification, different types of soaps are formed. The nature of soap determines the important properties of greases like temperature resistance, oxidation resistance and consistency.

Types of greases:

Greases are of the following types especially according to the types of soaps used:

a. **Calcium-based greases:** These are prepared by saponification of fatty acids with calcium hydroxide followed by adding hot petroleum oil with agitation. They are most commonly used greases as they are cheaper and good water resistant. They are found working well at the temperature below 80°C.

b. **Soda-based greases:** Greases prepared by saponification of fatty acids with sodium hydroxide and adding hot lubricating oil with agitation are known as soda-based greases. They can be used at slightly higher temperature up to 175°C but they are not water resistant.

c. **Lithium-based greases:** Greases made by adding hot lubricating oil into lithium soap with agitation are called lithium-based greases. They are suitable only at low temperature up to 15°C and are water resistant.

d. **Axle greases:** These are also called resin greases as they are prepared by adding heavy metal hydroxide into resin and fatty oils. They are suitable for the equipments working at heavy loads and low speed. They are also water resistant.

Greases may also be prepared by dispersing solid like graphite into lubricating oils and such greases are called **graphite greases.**

Vaseline:

Vaseline is a petroleum jelly, which is a mixture of mineral oils, paraffin and microcrystalline waxes. When these are blended together, a smooth jelly that has a melting point just above body temperature is formed.

It does not oxidize on exposure to air, and is not readily acted on by chemical reagents.

3. Solid lubricants:

Dry lubricants or solid lubricants are materials which despite being in the solid phase are able to reduce friction between two surfaces sliding against each other without the need for a liquid media. Such lubricants, including materials such as graphite, hexagonal boron nitride, molybdenum disulfide and tungsten disulfide are also able to offer lubrication at temperatures higher than liquid and oil-based lubricants are able to operate. Such materials can operate up to 350°C in oxidizing environments and even higher in reducing / non-oxidizing environments (molybdenum disulfide up to 1100°C). Their lubricating properties are attributed to a layered structure on the molecular level with weak bonding between layers. Such layers are able to slide relative to each other with minimal applied force, thus giving them their low friction properties.

The conditions of using solid lubricants are as follows:

- Solid lubricants are preferred when the lubricating films cannot be secured by oils or greases at the moving surfaces.
- When the operating temperatures or load is too high at which even greases cannot exist.
- When the contamination due to lubricating oils or greases is highly unacceptable for e.g., in textile, foodstuffs industry and commutator brushes of electric

generator (whose conductivity is not to be affected by the lubricating films).

- When the combustible lubricants are to be strictly avoided.

The most commonly employed solid lubricants are graphite and molybdenum disulphide.

Graphite:

The chemical structure of graphite explains its lubricating and conducting effect. Each carbon atom of graphite is sp^2 hybridised and they are connected together so as to form sheets and these graphite sheets are held by only weak bonds. Therefore a sheet of carbon in graphite can slide over another. This is only responsible for the conducting and lubricating characteristics. The structure of graphite is shown as below:

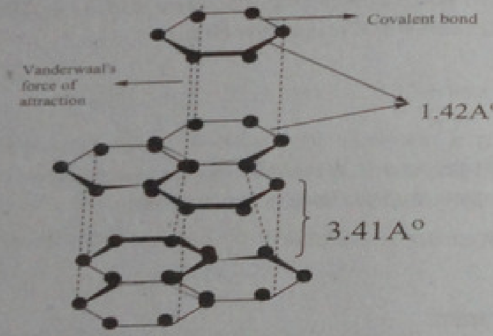


Fig: Layered Structure of Graphite

It acts as lubricant because it is very soapy in touch, non-inflammable and not oxidized in air below 375°C. Again, in the absence of oxygen, it can be used up to higher temperatures. It may be used either in the powder form or suspension.

Suspension of graphite in oil is known as **oildag** and the suspension of graphite in water is known as **aquadag.**

Uses of graphite as lubricant:

- ➢ Oildag is particularly useful in internal combustion engines as it forms a film between piston and cylinder to give tight fitting.
- ➢ It is found commonly employed in foodstuffs industry, air-compressors, chains etc.
- ➢ It is also very common for lubricating locks, since a liquid lubricant allows particles to get stuck in the lock worsening the problem.
- ➢ As it is a good conductor of electricity, it is found best lubricant in commutator brushes of electric generator.
- ➢ Natural graphite is mostly consumed for refractories, steelmaking, expanded graphite, brake linings, and foundry facings-lubricants.

Molybdenum disulphide:

MoS_2 with particle sizes in the range of 1-100 µm is a common dry lubricant. Few alternatives exist that can confer the high lubricity and stability up to 350°C in oxidizing environments. Sliding friction tests of MoS_2 using a pin on disc tester at low loads (0.1-2 N) give friction coefficient values of < 0.1.

Molybdenum disulfide is often a component of blends and composites where low friction is sought. A variety of oils and greases are used, because they retain their lubricity even in cases of almost complete oil loss, thus finding a use in critical applications such as aircraft engines. When added to plastics, MoS_2 forms a composite with improved strength as well as reduced friction. Polymers that have been filled with MoS_2 include nylon (with the trade name Nylatron), Teflon, and Vespel. Self-lubricating composite coatings for high-temperature applications have been developed consisting of molybdenum disulfide and titanium nitride by chemical vapor deposition.

This compound has a sand witch like structure, where a layer of Mo atoms lies between two layers of sulphur atoms. The poor force of attraction between the Molybdenum and sulphur layers is responsible for its lubricating effect.

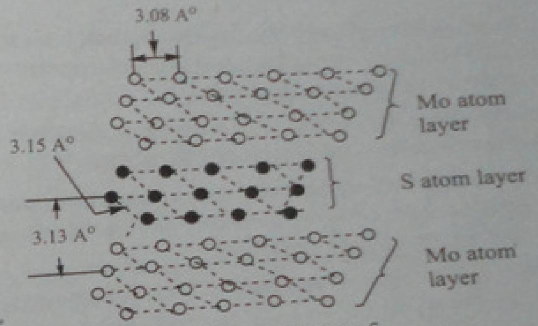


Fig: Sandwitch like structure of molybdenum disulphide

Uses:

- ➢ It is found good for lubrication at higher temperature condition as it is stable in air up to 400°C. So, it is often used in two-stroke engines; e.g., motorcycle engines. It is also used in space vehicles.
- ➢ The fine powder of Molybdenum disulphide is used on the surfaces sliding at high velocities. During the Vietnam War, the molybdenum disulfide product "Dri-Slide" was used to lubricate weapons, although it was supplied from private sources, not the military. MoS_2-coatings allow bullets easier passage through the rifle barrel causing less barrel fouling allowing the barrel to retain ballistic accuracy much longer.
- ➢ It is also used in the suspension form over the metallic surfaces.

4. **Synthetic lubricants:**

Lubricants synthesized for using at abnormal conditions like high temperature, chemically reactive atmosphere etc are called synthetic lubricants. These are made by using specific types of additives.

Modern synthetic lubricants possess the characteristics such as,

i. They are non-inflammable
ii. They have high flash points
iii. High stability to heat
iv. High viscosity index and
v. Chemical stability etc.

Some examples of synthetic lubricants are,

Polymerized hydrocarbons- they are chemically non-reactive and high temperature lubricants.

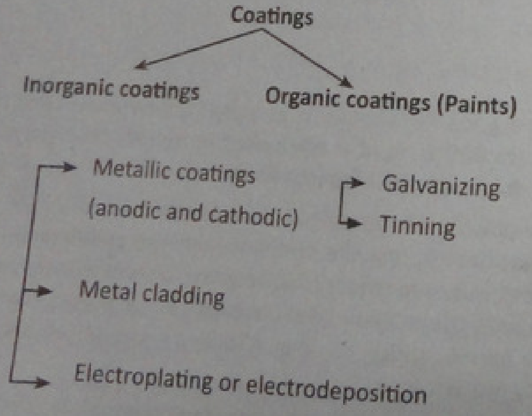
Polyglycols and related compounds- they have high viscosity index and are used in roller bearings of glass manufacturing machine. Since they are decomposed at high temperature, they are not used at high temperature condition.

Organic amines, imines and amides- They have low pour points, high viscosity index and can be used under wide temperature range of -50°C to 250°C.

Silicones are also good synthetic lubricants as they possess high viscosity index and high oxidation resistance. These are generally used in low temperature condition as they are easily oxidized at the temperature above 200°C.

Fluorocarbons are chemically inert and stable to heat. These are used as lubricants at high temperature conditions.

Paints



Terminology:

Pigments: solid substances which provide desired colour to the paint. Some of the commonly used pigments are; White pigments: zinc oxide, titanium oxide etc

Red pigment: red lead, ferric oxide etc.
Blue pigment: Prussian blue
Black pigment: Carbon black, Etc.

Vehicle: A liquid mixture of volatile and non-volatile solvent

Thinner: Solvent used to reduce the viscosity of paints.

Drying oil: Oil containing high percentage of conjugated fatty acid esters and they dry quickly by absorbing oxygen from air (oxidation polymerization) is known as drying oil. This is also known as hardening oil. For e.g., linseed oil, Tung oil, castor oil etc.

Definition:

Paints are organic coatings and it is defined as a dispersion mixture of pigments in a liquid consisting volatile solvent, film forming material and drying oil. Therefore in a simple sense, paint is a mixture of pigments and vehicle.

Constituents of the paints:

Basically paints consist one or more pigments in a liquid consisting volatile oil, film forming material and drying oil. However, in order to produce the desire characteristics into the paints, specific types of additives are used. According to the effects produced by the additives into the paints, they are of various types as follows;

a. **Extenders or fillers:** These are the materials which serve to fill the gaps in the film and hence to form the uniform film of the paints. They also help in the arrangement of pigment particles and increase the durability of the paint film. The commonly employed extenders are; $BaSO_4$, $CaSO_4$, $CaCO_3$ etc

b. **Driers:** These are the substances which accelerate the drying of paint film through oxidation, polymerization and condensation. The most effective driers are resinates, tungstates of Co, Zn etc.

c. **Thinners:** These substances are added to reduce the viscosity of the paint to a suitable consistency, suspend the pigments and help to drying of the paint. Common thinners in practice are turpentine, mineral spirits (from petroleum), benzene, kerosene etc.

d. **Plasticizers**: These are the substances which increase the elasticity of the paint film. eg, vegetable oils, triphenyl phosphate etc.

e. **Stabilizers:** These are the substances which provide chemical inertness to the emulsions of the paints. E.g., proteins like dextrin, casein etc and starch.

f. **Preservatives:** These are added to prevent the decomposition of proteins and eliminate the growth of fungus. E.g., mercuric chloride.

g. **Antifoaming agents:** These are the substances added to check the formation of foams especially during the manufacture and application of paints. E.g., pine oil, kerosene etc.

h. **Antiskinning agents:** These are added to prevent gelling and skinning of the paint film. Important antiskinning agents are polyhydroxy phenols.

Mechanism of drying up of the paints:

When paints are applied on the surface of the base materials, the paints film dry up by the process of evaporation of thinner (volatile oil) followed by oxidation and polymerization of drying oils.

Diagrammatically, it may be shown as below,

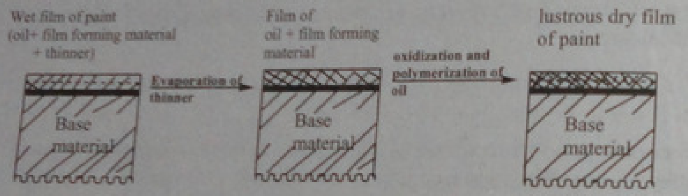


Fig: showing mechanism of drying paint

Requisites of a good paint:

Paints are mainly used for the protective, decorative and functional purposes. In order to cover the purposes of using paints, a good paint should have following requisites;

- It should form a uniform, impermeable and tough film when applied onto the surface.
- It should have good adhesive property.
- It should be fluid enough to spread over the surface and should have high surface area covering property.
- It should be aesthetic appealing type that it should have good texture and glossy and pleasing appearance.
- It should protect the surface from corrosion.
- The film should not get cracked on drying.
- The film should be highly stable at the operating condition.

Types of paints:

Paints are broadly classified into five groups especially according to the chemical composition and their effects on the surface of the base materials.

1. *Varnishes*
2. *Enamels*
3. *Lacquers*

4. Emulsion paints
5. Special paints

1. **Varnishes:**

Varnish is a homogeneous colloidal solution of resin (natural or synthetic) in drying oil or volatile solvent or both. It dries by evaporation, oxidation and polymerization of its constituents and forms a hard, transparent and glossy film.

There are two main types of varnishes:

i. **Oil varnish or oleoresinous varnish:** It is a homogeneous colloidal solution of resins in drying oil and volatile solvent. This type of varnish dries up by the evaporation of volatile solvent followed by oxidation and polymerization of the drying oil. The presence of oil reduces the brittleness of the resin and increases the elasticity of the varnish film.

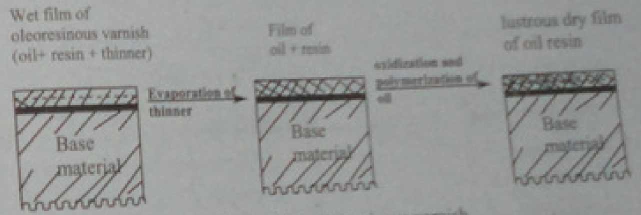


Fig: Drying of an oleoresinous varnish

ii. **Spirit varnish:** It is a homogeneous colloidal solution made by dissolving resin in a volatile solvent. This type of varnish dries up rapidly by the process of evaporation. The film so formed is comparatively brittle and peel off more easily. An example of spirit varnish is a solution of shellac resin in alcohol.

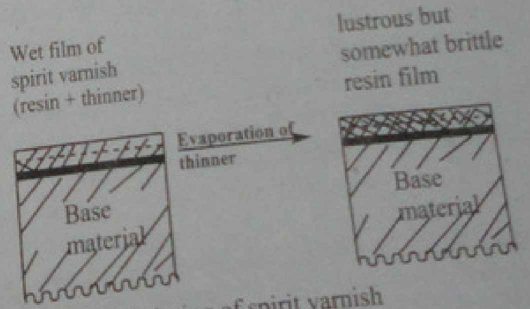


Fig: drying of spirit varnish

Uses of Varnishes:

Varnishes are commonly employed for protective and decorative purposes. Some of the main uses of varnishes are as follows:

- It is used to give brightening coat to a painted surface.
- It is used for improving the appearance of wood surfaces.
- It is found more effective to protect the metal surfaces from corrosion as it forms more uniform coating layer.

Enamels:

In a simple sense, enamel is a pigmented varnish i.e. it is a dispersion mixture of pigments in a varnish. It forms a hard and glossy film on drying. There are two types of enamels:

a. ***Air drying enamel:*** It dries up by oxidation and polymerization at room temperature.

b. ***Baking enamel:*** It dries up at elevated temperatures either in the presence or absence of oxygen.

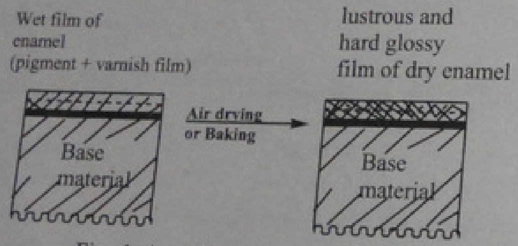


Fig: drying of an enamel film

General composition of enamel is given by,

Enamel = pigments + vehicle + driers + thinner

2. **Lacquers:**

It is a colloidal dispersion solution of resins of cellulose derivate (such as cellulose nitrate or cellulose ester etc) and plasticizer in volatile solvent. It mainly dries up by evaporation and forms hard, transparent and water-proof film.

Uses:

Lacquers are used

- For paintings of furniture.
- giving finishing coats to automobiles and
- Coating cotton fabrics and preparing artificial leathers.

3. **Emulsion paints:**

It is a dispersion mixture of rubber-like resin in water and film forming vehicle. In addition it also contains some specific additives such as extenders, stabilizers, pigments, driers, antifoaming agents and preservatives.

When emulsion paint is applied onto the surface, water evaporates and resinous particle unite to form uniform, homogeneous and clear film.

Uses: Emulsion paints are very useful in coating porous surfaces because of low penetration of water solutions. It is easier to apply as it is less odorous and non-inflammable. Also it can be recoated several times which is not possible in ordinary paints.

4. **Special paints:**

There are several types of special paints according to the special effects obtained in paints by using specific type of additives.

i. **Luminescent paints:** This contains the pigments which fluoresce under the influence of ultra violet light and these pigments are called luminophor pigments. For e.g., zinc sulphide, cadmium sulphide etc, they absorb UV light and emit visible radiation so that they add special brightness to the paints. Colour modifiers also called activators such as Cu, Ag, Mn may also be added.

ii. **Heat resistant paints:** These paints are stable even at high temperatures i.e. red heat. This effect is achieved by using metallic powders such as Al, Zn etc.

A high heat resistant paint developed by NASA is found stable up to 1000°C. It contains titanium oxide, water, alkali metal silicate and aluminium orthophosphate.

iii. **Fire retardant paints:** These paints contain poly vinyl chloride (PVC), chlorinated rubber etc. these compounds break up at high temperature producing non-inflammable gases such as CO_2, NH_3, HCl etc and helps to retard the probable firing by diluting the concentration of inflammable gases.

iv. **Temperature indicating paints:** It contains a special additive that undergoes colour change at specific temperatures. Such additives usually are the double salts or amine salts of Cu, Fe etc. These paints indicate the temperature change of the environment at the range of 45- 1450°C with 10% error.

v. **Cement paint:** The composition of cement paint is; white cement (70%) + Calcium hydroxide + fine sand + pigments + water repellant compounds. It is found in the powder form. It is mixed with a suitable solvent and makes slurry before use. It is widely used to interior and exterior coatings of the brick-walls.

vi. **Aluminium paint:** It is made by mixing fine powder of aluminium in spirit varnish or oil varnish. It dries up by evaporation of thinner followed by oxidation and polymerization of drying oil. It forms a bright and uniform coating on the painted surface.

It is widely used to paint the metal surfaces as it is less corrosive and bright in appearance.

vii. **Cellulose paint:** It is made by dissolving nitro-cellulose in thinner that it dries up by evaporation leaving hard, glossy and durable film.

viii. **Coal-tar paint:** It is made by dissolving coal-tar in spirit or other volatile solvent. It is always applied at hot condition and it is found good for protecting iron under the ground.

ix. **Distempers:** These are the water paints made by mixing chalk powder, glue and pigments in water. These are commonly used for finishing the paintings on the surface of the walls, plastered surfaces of the walls.

x. **Antifouling paints**: These are used in ship coatings which retard the fouling of ships due to marine worm, fungi etc. It contains antifouling agents such as mercuric oxide, cuprous oxide etc.

xi. **Water repellant paints:** These paints are made by hydrolysis and condensation of organoethoxy silanes and organochloro silanes. After the application of this paint, it forms a highly cross linked film that is more water repellant which makes the paints to be more durable.

Applications of paints:

Paints are mainly used for three purposes;

Protective- to protect the surface of base material from corrosion

Decorative- to make the surfaces pleasing in appearance and

Functional- for special functions such as making road-lines for trafficking purposes. Thus, in summary, paints have following applications:

1) Paints are widely used to coat the metallic surfaces in order to protect it from the corrosive environments.
2) Modern synthetic paints are applied to make the furniture attractive in appearance.
3) Cement paints are almost compulsorily used for finishing the buildings as it protects as well as decorates the buildings.
4) Heat resistant paints are used as finishes of ovens, furnaces, aircraft combustion chambers etc.

5) Varnishes are used to give brightness to the paints and make uniform protective coatings over the surface.
6) Antifouling paints are used in marine ship which reduces the foul smelling in ships due to marine worms and fungus attack.
7) Some of the paints also have the special characteristic that they can indicate the temperature change in environment by the change of colour.

Practice Questions

1. What do you mean by the term 'lubrication' and 'lubricants'? Write the chief functions of lubricants.
2. What are lubricating greases? Write their functions. **[IOE-'67]**
3. Describe the different types of greases in practice.
4. What are lubricating oils? Indicate their importance in engineering. **[IOE-'68]**
5. What are the requisites for an oil to be better lubricants?
6. What are blended oils? Write the names and functions of different additives used in blended oil.
7. What is paint? Give the requisites of a good paint. **[IOE-'67]**
8. Describe the different types of paint?
9. Describe the mechanism of drying paint.
10. What are the major constituents of paint? Write with their functions.
11. Write short note on the following.
    a. Luminescent paint
    b. Lacquers
    c. Enamel
    d. Varnish
12. Write short note on synthetic lubricants.

• • •

Chapter

10

Organic reactions and their mechanism

Organic reactions and their mechanism

In general, all the organic reactions are molecular and involve the breaking and formation of covalent bonds. The reaction pathway of how the reaction occurs is known as the mechanism. Some important types of organic reactions and the involved mechanism are discussed below.

Types of organic reactions:

1. Addition reactions
2. Substitution reactions
3. Elimination reactions
4. Rearrangement reactions

Substitution reactions

Introduction

There are various types of the organic chemical reactions. Among which the substitution reaction is one of the common reactions. A substitution reaction may be defined as one in which an atom or group of atom attached to carbon is substituted by another atom or group of atoms. Now, according to the types of the reagents- electrophiles, nucleophiles and radicals, the substitution may be categorized into three classes:

A. Nucleophilic substitution reactions: The reactions in which a weaker nucleophile is substituted by the stronger one. It is denoted by S_N.

$$CH_3—Br \xrightarrow{OH^-} CH_3—OH + Br^-$$

B. Electrophilic substitution reactions: The reactions in which a weaker electrophile is substituted by the stronger one. It is denoted by S_E.

$$C_6H_6 \xrightarrow{\overset{\oplus}{NO_2}} C_6H_5NO_2 + H^+$$

C. Free radical substitution reactions: The reactions in which a radical is displaced by another.

$$CH_4 \xrightarrow{2Cl^\cdot} CH_3Cl + HCl$$

Nucleophilic Substitution reactions

The reactions in which one of the weaker nucleophile is substituted by the stronger one are known as Nucleophilic substitution reactions. It is abbreviated as S_N-reactions. S_N-reactions are the characteristic reactions of the alkyl halides.

The hydrolysis of alkyl halide by aq. NaOH is an example of S_N-reaction.

$$R{-}X + \overset{\ominus}{Nu} \longrightarrow R{-}Nu + X^{\ominus}$$

Substrate Nucleophile
(Alkyl halide)

For e.g.

$$CH_3{-}X + \overset{\ominus}{O}H \xrightarrow{aq.NaOH} CH_3{-}OH + X^{\ominus}$$

Nucleophiles: Nucleus Loving species having a free lone pair of electron or negative charge which can attack to the electron deficient centre are known as nucleophiles. For example,

NO_2^-, N_3^-, $RCOO^-$, CN^-, I^-, Br^-, Cl^-, OH^-, CH_3O^-, H_2O, ROH, NH_3, RNH_2 etc

The reactivity of the nucleophile is known as nucleophilicity and it is characterized by their basicity and polarisability. In a nut shell, it can be said that,

- Nucleophilicity of an atom increases with the increase of negative charge on it. So, OH^- is a stronger nucleophile than H_2O.
- Nucleophilicity increases on going down of a group of the periodic table. So, the nucleophilicity of halides in the protic solvent is in the order,

  $I^- > Br^- > Cl^- > F^-$

- Nucleophilicity decreases on going right side of a period of the periodic table. So the order of nucleophilicity is,

  $C^- > N^- > O^- > F^-$ and similarly $NH_3 > H_2O > HF$.

Leaving group: The nucleophiles which are usually substituted by the stronger are said to be the leaving group. Leaving nucleophiles are usually, I^-, Br^-, Cl^-, H_2O, $-NR_3$, $RCOO^-$, NO_3^- etc. In general, the most polarisable and the least basic groups are better leaving groups.

Types of S_N-reactions

Depending upon the kinetics of the reaction, the nucleophilic substitution reactions are divided into two categories.

1. S_N2-reactions
2. S_N2-reactions

1. **S_N2 Reaction:** - S_N2 stands for the nucleophilic substitution bimolecular reaction. When the rate of nucleophilic substitution reaction depends upon the concentration of both the substrate (e.g. alkyl halide) and nucleophile, then the reaction is of second order kinetics and represented as S_N2.

Kinetics: Rate α [Substrate] [Nu^-]

e.g. the reaction between methyl bromide and aq. NaOH is an example of S_N2 reaction.

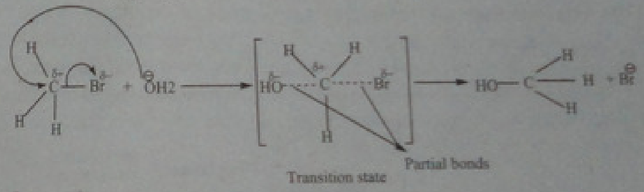
$$CH_3{-}Br + OH^{\ominus} \xrightarrow{aq.NaOH} CH_3{-}OH + Br^{\ominus}$$

Rate α [CH_3Br] [OH^-]

✓ **Mechanism of S_N2 reaction:** - The mechanism of S_N2 reaction consists of a single step and it proceeds through a single transition state (T.S). Thus, the mechanism involves the attack of nucleophile (hydroxide ion) to the electron deficient carbon and breakage of the leaving group takes place at the same time. The nucleophile attacks to the halogen containing carbon just opposite side to that of leaving group (halogen). Hence, S_N2 reaction is an example concerted step mechanism.

Example:

$$CH_3{-}Br + OH^{\ominus} \xrightarrow{aq.NaOH} CH_3{-}OH + Br^{\ominus}$$



In the transition state, the C----Br bond is not completely broken and C----OH bond is not completely formed. Thus in T.S, the C---Br and C---OH bond are represented by partial bonds. Thus the central carbon atom seems to be pentavalent in the T.S. with three complete and two partial bonds. Highly unstable T.S. suddenly gives the final stable substituted product by the complete breakage of the bond between carbon and leaving group.

This may be shown in the energy profile diagram as,

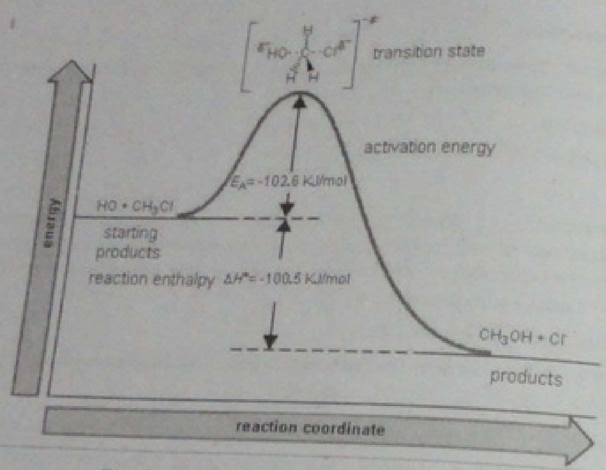
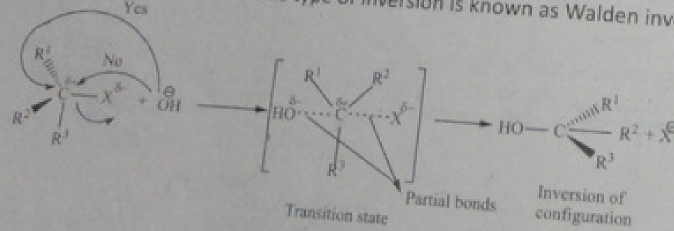


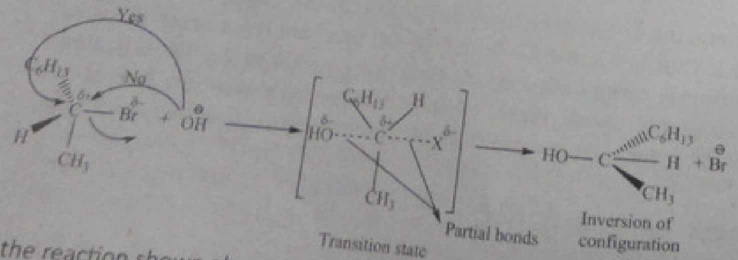
Fig: Energy profile diagram of S_N2-reaction

Stereochemistry of S_N2 reaction:

The S_N2 reactions proceed through the complete inversion of configuration. When alkyl halide reacts with aqueous NaOH, the configuration of central carbon of alkyl halide changed into the alcohol. If the alkyl halide is laevorotatory then the product, alcohol will be dextrorotatory and vice-versa. This type of inversion is known as Walden inversion.



Example:



In the reaction shown above, the hydroxide ion attacks to the halogen containing carbon just opposite side to that of leaving group which gives the product alcohol with opposite

configuration . The hydroxide ion cannot attack to the carbon from the same side of the leaving group (halogen) because the leaving group (Bromide) is negatively polarized and nucleophile (OH^- ion) is also negatively charged and there is repulsion between leaving group and nucleophile. So, the nucleophile (hydroxide ion) has best way to attack the electropositive carbon from opposite side to that of leaving group (bromide ion) hence one can get the SN^2 product with opposite configuration.

Reactivity:

The rate studies of the bimolecular nucleophilic substitution reaction (S_N2-reaction) in varieties of substrates revealed that the relative reactivities of the alkyl halides with nucleophile follow the following order.

CH_3X > 1°alkyl halide > 2°alkyl halide > 3°alkyl halide

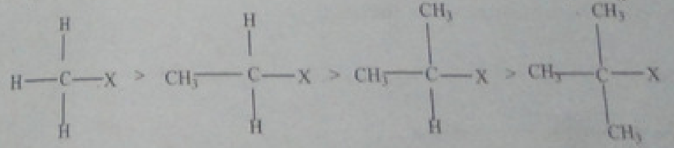
Example:

$CH_3Br > CH_3CH_2Br > (CH_3)_2CHBr > (CH_3)_3CBr$

This order of reactivity of alkyl halide with nucleophile can be explained on the basis of steric effect and inductive effect.

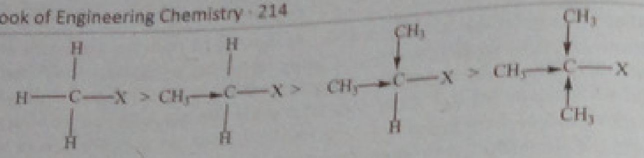
Steric effect:

As the size of substituent at halogen bonded carbon increase the rate of S_N2 reaction falls down because the large substituent causes greater steric effect. Because of the steric hindrance there is difficult to attack the central electron deficient carbon by the incoming nucleophile. In the above series of alkyl halide, the size of substituents increase from 1° to 3° and thus, steric effect also increases which slowed down the reactivity of S_N2 reaction.



$$\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}X > CH_3{-}\overset{H}{\underset{H}{C}}{-}X > CH_3{-}\overset{CH_3}{\underset{H}{C}}{-}X > CH_3{-}\overset{CH_3}{\underset{CH_3}{C}}{-}X}$$

Inductive effect: As we proceed from CH_3X; 1° to 3° alkyl halide, the electron density at the positively polarized carbon (halogen bonded) increases by the increasing +I- effect of alkyl group. This neutralizes the intensity of the positive charge on the central carbon, thus reducing attraction of incoming nucleophile towards it causing slow down of the rate of S_N2 reaction. Therefore the reactivity towards S_N2 mechanism decreases on going from 1° to 3° alkyl halide.



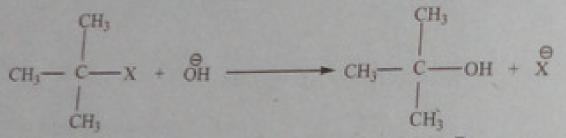
S_N1 Reaction

S_N1 stands for the nucleophilic substitution unimolecular reaction. When the rate of S_N reaction depends only upon the concentration of substrate, then the reaction is of first order and is represented as S_N1.

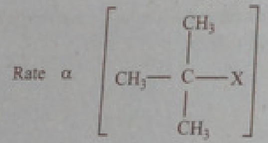
Kinetics of S_N1 reaction:

Rate α [Substrate]

Example:



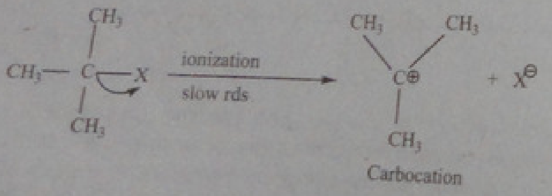
$$CH_3-C(CH_3)_2-X + \overset{\ominus}{O}H \longrightarrow CH_3-C(CH_3)_2-OH + \overset{\ominus}{X}$$



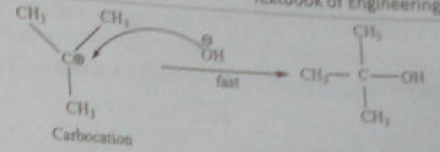
$$\text{Rate } \alpha \left[CH_3-C(CH_3)_2-X \right]$$

Mechanism of S_N1 Reaction: - The mechanism of this S_N1 reaction consists of two steps.

1. *The first step is the ionization of alkyl halide to form carbocation. This step is the slow step and hence rate determining step (rds).*



2. *The second step is the attack of nucleophile to the carbocation to form the product.*



In S_N1 reaction, the first step i.e. carbocation formation step is the slow step and hence is rate determining step (rds). The first step involves only the substrate molecule. So the rate depends only upon the concentration of substrate (alkyl halide). This may be shown in the energy profile diagram as,

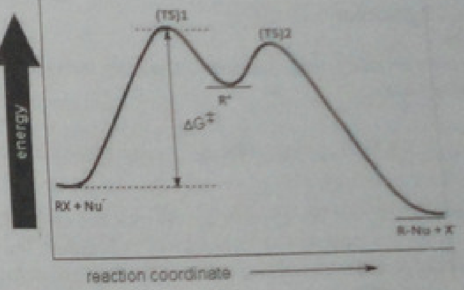
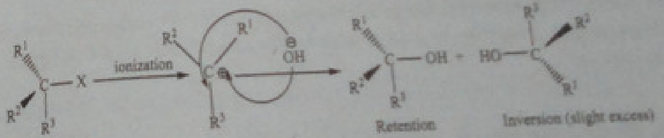


Fig: Energy profile diagram of S_N1-reaction

Stereochemistry of S_N1 reaction:

The stereochemistry of the product of S_N1 reaction has partial racemization with slight excess of inversion of configuration.



Explanation:

The S_N1 reaction proceeds with the formation of carbocation. The carbocation has trigonal planar structure, thus the incoming nucleophile can attack it from either side of the leaving group and forms the product of both retention as well as inversion of configuration. However, the product of inversion of configuration is formed in slight excess comparing to the concentration of the product of retention of configuration. This is because, the leaving group (negatively charged) is not so far just after the ionization and the leaving group side way is slightly blocked for incoming nucleophile (due to the solvent separated ion pair) and so there forms slightly higher proportion of inversion product than retention. Thus we can say that S_N1 reaction proceeds with partial racemization plus net inversion.

Diagrammatically, above explanation can be summarized as shown below,

$$\overset{\oplus}{R}\|\overset{\ominus}{X}$$

Solvent separated ion pair

OR

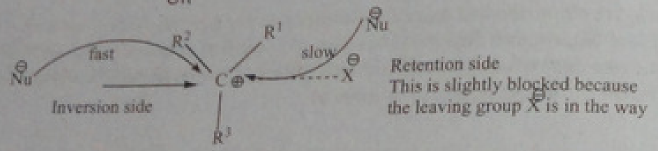


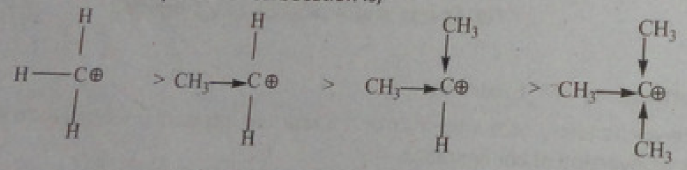
Fig: Ion pair mechanism

Reactivity:

The reactivity of alkyl halides towards S_N1 reaction increases on going from primary to tertiary alkyl halides.

$CH_3X < 1^0 -$ alkyl halide $< 2^0 -$ alkyl halide $< 3^0$ alkyl halide.

The reactivity of alkyl halides towards S_N1 reaction can be explained by the first step of the mechanism. This involves the formation of carbocation. Thus, the reactivity of alkyl halide towards S_N1 reaction can be explained on the basis of formation and stability of carbocation. The stability order of carbocation is,



More stable the carbocation faster it is formed. Thus the 3^0- carbocation is formed faster and the rate of S_N1 reaction is greater with tertiary alkyl halide than that with 2^0-and then 1^0-alkyl halide.

Factors affecting the rate of S_N-reactions

There are four main factors which determine the rate of the S_N-reactions.

1. *Nature of substrate molecule (effect of substrate molecules)*
2. *Nature of nucleophiles*
3. *Nature of solvent*
4. *Nature of leaving group*

1. **Nature of substrate**

As we know the reactivity order of alkyl halide with nudeophile in S_N2 and S_N1 reaction is

S_N**2:** $CH_3X > 1^0 > 2^0 > 3^0$ (RX)

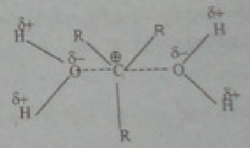
S_N**1:** $3^0 > 2^0 > 1^0 > CH_3X$ (RX)

From the above reactivity order we can say that the alkyl halide CH_3X and primary prefer to undergo S_N2 mechanism as they are less sterically hindered and tertiary halide prefer to undergo S_N1 mechanism as they give stable carbocation. This is explained above in the reactivity of S_N1 and S_N2 reactions separately.

2. **Nature of the solvent:**

For S_N1 reactions: Since its rate determining step involves the ionization of the alkyl halide, a solvent with high dielectric constant and ion-solvating ability enhances the rate of S_N1 reactions. Polar solvents such as water, methanol, formic acid etc have high dielectric constant as well as ion-solvating ability. Therefore, they are the better solvents for the S_N1 reactions and the rate of reaction is high. The solvent effect is supposed to operate through mainly two ways;

- The solvent molecules tend to orient themselves in such a way as to decrease the electrostatic forces between the ion pair. More the polarity of the solvent, more this effect is. Water has dielectric constant 78.5, so it can decrease the electrostatic force of attraction between two opposite ions and separate them.

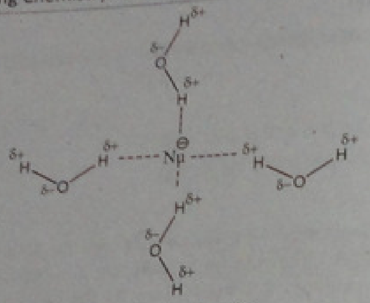


- The solvent molecules stabilize the T.S. and the product through solvation.

For S_N2 reactions:

In general S_N reactions, where both the nucleophile and leaving group are negatively charged, the solvent polarity has no dramatic effect on the reaction rate of S_N2 reactions but it has been found that the rate is slightly decreased with the increasing polarity of the solvent. For e.g., the reaction of acetate ion with the methyl iodide is ten million times faster in DMF (Dimethyl formamide) than in methanol.

It can be explained in terms of the solvolysis effect of the more polar protic solvent to the nucleophile. Due to the greater solvolysis of the nucleophile, they cannot attack the central carbon readily but aprotic solvent cannot solvate the nucleophile.



solvolysis of nucleophile

However, when the nucleophile is neutral and the leaving group leaves as negatively charged species, the rate of reaction increases with the increase of the polarity of the solvent. This is because the transition state (TS) in this case is more polar and it is more stabilized by the polar solvent.

3. **Nature of nucleophile:**

In S_N1 reactions, **Rate α [Substrate]** i.e. the rate is independent of the concentration of the incoming nucleophile neither its nucleophilicity. Therefore, the S_N1 reaction can proceed with weak nucleophiles of low concentration.

In S_N2 reaction, **Rate α [Substrate] [Nu⁻]** i.e. the rate is dependent on the concentration of both the nucleophile and substrate. Therefore, the strong nucleophile with its higher concentration increases the rate of S_N2 reaction while the weak nucleophile and low concentration decreases the rate. Thus the hydrolysis of alkyl halide with water as a nucleophile has a slower rate than those with aqueous alkali. However, the nucleophilicity order is substrate dependent.

$$NH_2^- > OR^- > OH^- > NH_3 > I^- > Br^- > Cl^- > F^- > H_2O$$

4. **Nature of the leaving group**

For S_N1 reactions: As the ionization of the substrate is rate determining step, highly better leaving group increases the rate. This is because better leaving group increases the ionic character of the substrate and this facilitates the ionization. The best leaving groups are those which are least basic i.e. their conjugate acids are strong. For example, the order of leaving tendency of the following species is,

$$H_2O > ROH > CH_3COO^- > OH^-$$

Moreover, the more polarisable a group the more is its leaving tendency. Thus the leaving reactivity of the halides is;

$$I^- > Br^- > Cl^- > F^-$$

For S_N2 reactions: Since the breaking of the leaving group starts at the rate determining step, the nature of the leaving group also affects the rate of the S_N2 reaction. Groups of lower basicity and higher polarisability increase the rate of the reaction. Example,

$$I^- > Br^- > Cl^- > F^-$$

Depending on the basicity, the reactivity order is

$$H_2O > ROH > CH_3COO^- > OH^-$$

Thus, the leaving group has similar effect in both S_N1 and S_N2 reactions while the extent of effect is higher in S_N1 reaction.

Effects of neighboring group's participation (NGP)

The group with lone pair of electrons at the β-carbon assists to remove the leaving group in the substrate itself that can participate as a nucleophile during the reaction is known as neighboring group participation (NGP). This mechanism essentially constitutes two S_N2 reactions. When the neighbourig group is participated to eliminate the leaving group, a cyclised product is formed. Then it undergoes substitution reaction with the incoming nucleophile. In this case, the electron cloud of the NG blocks the incoming nucleophile to attack the central carbon from the back side. Thus the substitution occurs from the side of the leaving group and forms the product with retention of configuration.

Differences between S_N1 and S_N2 reactions

S.N.	S_N1 reactions	S_N2 reactions
1.	It is unimolecular substitution reaction and follows first order kinetics.	It is bimolecular substitution reaction and follows 2nd order kinetics.
2.	It involves two step mechanism.	It involves the single step mechanism.
3.	It proceeds by the formation of carbocation.	It proceeds by the formation of transition state which involves the partial bonding of nucleophile and leaving group.
4.	Rate of reaction depends on the concentration of substrate only.	The rate of reaction depends on the concentration of both substrate and nucleophile.

5.	Stereochemistry of the product is found with partial racemization plus inversion i.e. both the retention and inversion of configuration are formed but the later is in slight excess.	Stereochemistry of the product is found with complete inversion of configuration, which is also known as Walden inversion.
6.	Tertiary alkyl halides undergo S_N1 reaction and reactivity sequence is 3° > 2° > 1° > CH_3X.	Primary alkyl halides undergo S_N2 reaction and the reactivity sequence is CH_3X > 1° > 2° > 3°.
7.	A weak nucleophile favors the SN^1 reaction.	A strong nucleophile favors the SN^2 reaction.
8.	Rearrangement of methyl groups may take place to form more stable carbocation.	No rearrangement of methyl groups is possible during the reaction.
9.	Reaction is favored by polar solvents.	Reaction is favored by non-polar solvents.

Elimination reactions

The reaction which involves the elimination of a hydrogen halide molecule from an alkyl halide is known as elimination reaction. It is also known as dehydrohalogenation as it involves the removal of hydrogen halide.

The alkyl halides on heating with conc. Alcoholic solution of KOH produce alkenes. For examples,

$$\underset{\text{Ethyl bromide}}{CH_3CH_2Br} + KOH\,(alc.) \xrightarrow{\Delta} \underset{\text{Ethylene}}{CH_2{=}CH_2} + KBr + H_2O$$

It clearly shows that the reaction involves the loss of two substituents from two adjacent carbon atoms resulting the formation of a double bond. The function of a base is to abstract the hydrogen as a proton.

Kinetics: duality of mechanism

Hughes and Ingold proposed that elimination, like nucleophilic substitution can proceed by two different mechanistic pathways and these are named as E_2 *and* E_1 *mechanism.*

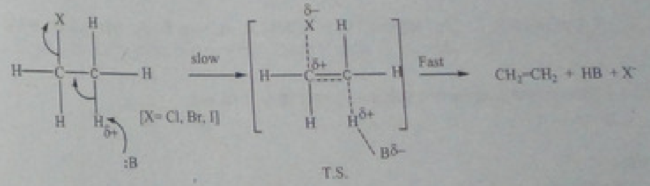
E_2 reaction:

E_2 stands for bimolecular elimination reaction. The rate of this reaction depends on the concentration of both the substrate and base and is of second order kinetics.

Rate α [RX][Base]

Mechanism:

The mechanism of E_2 reaction involves a single step. The base abstracts a proton away and at the same time a halide ion leaves from adjacent carbon atom forming the double bond. Thus the reaction proceeds with the formation of transition state. In transition state, partial bonds exist between the base and the β-hydrogen and between α-carbon and the halogen [carbon attached to halogen is called α-carbon and the carbon adjacent to it is called β-carbon]. Finally, by the removal of hydrogen halide a carbon- carbon double bond is fully formed. This all is represented as below,



This may be shown in the energy profile diagram as,

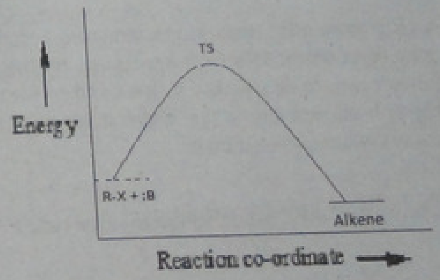
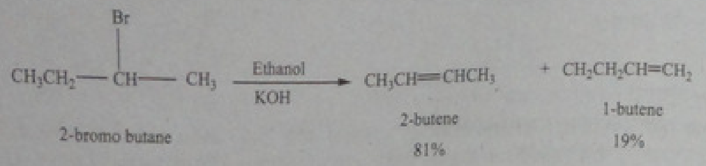


Fig: Energy profile diagram of E_2*-mechanism*

Orientation and reactivity:

The elimination reactions of unsymmetrical alkyl halides usually yield a mixture of alkenes. For example,



$$CH_3CH_2-\overset{Br}{CH}-CH_3 \xrightarrow[KOH]{Ethanol} CH_3CH{=}CHCH_3 + CH_3CH_2CH{=}CH_2$$

The orientation in E_2 reaction is governed by an empirical rule called Saytzeff's rule. It states that, 'in the elimination reactions of unsymmetrical alkyl halides, the alkene having the greater number of alkyl groups attached to the doubly bonded carbon atoms is the preferred product'. Thus the ease of the formation of alkenes is in the following order:

$R_2C{=}CR_2 > R_2C{=}CHR > R_2C{=}CH_2$, $RCH{=}CHR > RCH{=}CH_2$ where R represents an alkyl group.

This shows that more stable the alkene faster it is formed.

Reactivity:

The reactivity of alkyl halides towards E_2 reaction depends on the rate of the formation of the transition state and the transition state resembles the alkene in characteristics. Thus in E_2 reaction, the stability of alkene not only determines orientation of the double bond in the alkene but also is an important factor in determining the reactivity of alkyl halides towards E_2 mechanism.

Going from primary to tertiary alkyl halides, the structure becomes more branched at the carbon carrying halogen atom. This high branching, on the one hand, provides a greater number of β-hydrogens to be attacked by base and on the other hand elimination is favored to form highly branched alkene (i.e. more stable alkene). Hence the order of reactivity of alkyl halides towards E_2 reaction is:

Tertiary alkyl halide > Secondary alkyl halide > Primary alkyl halide

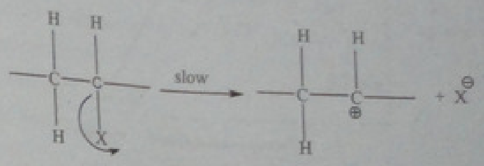
E_1-mechanism

It is a two-step unimolecular elimination reaction. Since the rate of reaction depends only on the concentration of substrate i.e. alkyl halide, the reaction is of first order kinetics.

Rate α [substrate]

The reaction involves the following steps;

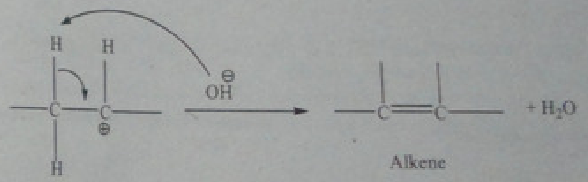
Step 1: Heterolytic fission of alkyl halide to form carbocation.



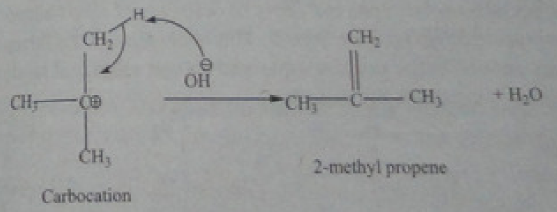
Carbocation

It is a slow step and hence the rate determining step (rds). The rate of reaction depends only on the concentration of alkyl halide, so the reaction is of first order kinetics.

Step 2: Base abstracts a proton from the β-carbon to produce alkene.



Since the tertiary carbocation is highly stable, generally tertiary alkyl halide follows E_1 mechanism. For example, the reaction mechanism of tertiary butyl chloride on heating with alcoholic KOH may be explained as follows.



Mixture of products is formed when the reaction is accompanied by rearrangement. The rearrangement occurs to form a more stable carbocation.

This may be shown in the energy profile diagram as,

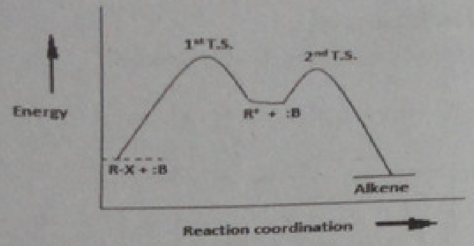
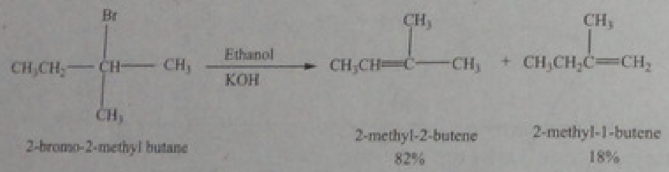


Fig: Energy profile diagram of E_1-reaction

Orientation and reactivity:

The orientation of the products in E_1 reaction follows the Saytzeff rule. This states that, '*when there is a possibility of formation of more than one alkene, then more highly branched alkene is the preferred product.*' For example,



$$CH_3CH_2-\underset{CH_3}{\overset{Br}{CH}}-CH_3 \xrightarrow[KOH]{Ethanol} CH_3CH=\overset{CH_3}{C}-CH_3 + CH_3CH_2\overset{CH_3}{C}=CH_2$$

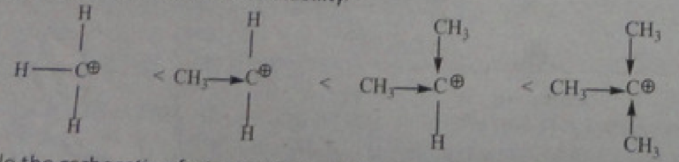
2-bromo-2-methyl butane

2-methyl-2-butene 82%

2-methyl-1-butene 18%

The orientation and reactivity of E_1 reaction are determined by the relative rates of reaction in different steps. The reactivity is determined by step I and orientation is by step II of the E_1 mechanism. Therefore, it can be predicted that the orientation in this reaction is independent of the nature of halogen that departs already in step I.

Since the reactivity of E_1 reactions depends on step I of the mechanism, the stability of then forming carbocation determines the order of reactivity of alkyl halides. The stability of carbocation increases on going from 1° to 3°. This is because of the increasing +I-effect of the alkyl groups bonded to the positively charged carbon atom that tends to neutralize the positive charge and increases the stability.



$$H-\underset{H}{\overset{H}{C}}^{\oplus} < CH_3\rightarrow\underset{H}{\overset{H}{C}}^{\oplus} < CH_3\rightarrow\underset{H}{\overset{CH_3}{C}}^{\oplus} < CH_3\rightarrow\underset{CH_3}{\overset{CH_3}{C}}^{\oplus}$$

More stable the carbocation faster it is formed. That means tertiary carbocation is formed in the rapid rate than the secondary or primary carbocation. Therefore, the reactivity order of alkyl halides towards E_1 reaction is,

Tertiary alkyl halide > secondary alkyl halide > primary alkyl halide

Factors governing the E_1 and E_2 mechanism

There are four main factors which determine the mechanism of the SN reaction.

1. Nature of substrate molecule (effect of substrate molecules)
2. Nature of nucleophiles
3. Nature of solvent
4. Nature of leaving group

1. Nature of substrate

Since the E_2 mechanism involves a single step, the stability of alkene not only determines the orientation but also reactivity of alkyl halides. More stable the alkene, faster it is formed. And highly branched alkenes are more stable, so the alkyl halides follow the following reactivity order towards E_2 reaction.

$$3^0 > 2^0 > 1^0 > CH_3X \ (RX)$$

Whereas E_1 mechanism involves double step and formation of carbocation is a rate determining step. Therefore, stability of carbocations formed determines the reactivity of alkyl halides. Tertiary carbocations are more stable than primary carbocation, so the order of reactivity of alkyl halides towards E_1 reaction is:

$$3^0 > 2^0 > 1^0 > CH_3X \ (RX)$$

2. **Concentration of base:-** The kinetics of the E_2 and E_1 reaction is:-

E_2: Rate α [Alkyl halide] [Base]
E_1: Rate α [Alkyl halide]

From above equation, it is clear that in the E1 mechanism, an external base is not required but the solvent acts as the base. Therefore, the strength and concentration of base have nothing to do with the rate of E1 reactions. But, the nature and concentration of base has strong to the rate of E2 reaction and it is found that the stronger base at high concentration increases the rate of E_2 reaction. The order of basicity among sodium hydroxide, sodium ethoxide and sodium amide is:

$$NH_2^- > {}^-OC_2H_5 > OH^-$$

3. **Nature of solvent:**

For any reaction that involves ionic intermediates, the rate is enhanced by the more polar environment. Therefore, the polar solvent favours the E_1 mechanism and non-polar solvent favours E_2 mechanism.

Since, the E_1 reaction proceeds with ionization of alkyl halide to form carbocation and polar solvent help to ionize the substrate molecule, the polar solvent favors E_1 reaction. On the other hand, E_2 mechanism has a single step proceeds by the formation of transition state and non-polar solvent favors the E_2 reaction.

4. **Nature of leaving group:**

Both of the mechanism needs good leaving group. From the mechanism it can be said that better leaving groups favor the E_1 mechanism since they make ionization easier and faster. Better leaving groups are those which are least basic and more polarisable. In alkyl halide series, the order of good leaving groups is

$$I^- > Br^- > Cl^-$$

Thus when β-phenyl halides are treated with sodium ethoxide in ethyl alcohol, the rate of the E_2 reaction increases in the order as,

Substrate:	$PhCH_2CH_2F$	$PhCH_2CH_2F$	$PhCH_2CH_2F$	$PhCH_2CH_2F$
Rate:	1	7	4.2×10^3	27×10^3

According to the basicity, the order of leaving tendency of the following species is;

$$H_2O > ROH > CH_3COO^- > OH^-$$

Differences between E_1 and E_2 reactions

E_1- reaction	E_2-reaction
It is a unimolecular elimination reaction.	It is a bimolecular elimination reaction.
It involves the double step mechanism.	It involves the single step mechanism.
It is of first order kinetics.	It is of second order kinetics.
It proceeds by the formation of carbocation.	It proceeds by the formation of transition state.
Polar solvent favors the E_1- reaction.	Polar solvent does not favor the E_2-reaction.
Better leaving groups favor the E_1-reaction since they make ionization easier and faster.	Leaving groups do not have significant influence in E_2-reaction.

Practice Questions

1. *What do you mean by* nucleophilic substitution reaction? Write the chemical reaction when primary alkyl halide is treated with aqueous KOH.

2. What do you mean by dehydrohalogenation reaction? What happens when isopropyl chloride is treated with alcoholic KOH?
3. Explain the S_N2 reaction mechanism with reference to hydrolysis of alkyl halide. What type of solvent favors this type of path? How can you say that carbocation is not formed during S_N2 reaction? **[IOE-'67]**
4. Write the mechanism of unimolecular elimination reaction. How does it differ from bimolecular elimination reaction? **[IOE-'67]**
5. Discuss the unimolecular Nucleophilic substitution reaction mechanism in alkyl halide showing the stereochemistry. What type of solvent favors this type of mechanism? **[IOE-'68]**
6. Write the mechanism of S_N2 reaction with suitable examples.
7. What is meant by elimination reaction? Discuss E_1 and E_2 reaction mechanisms. **[IOE-'68]**
8. Discuss the factors affecting E_2 and E_1 reactions.
9. Discuss the factors affecting S_N2 and S_N1 reactions.
10. Write the mechanism of S_N reactions when primary, secondary and tertiary alkyl halide reacts with aq. NaOH.
11. Write the mechanism when primary and tertiary alkyl halide reacts with alcoholic alkali.
12. Discuss the kinetics and orientation of S_N1 and S_N2 products.
13. Write the mechanism of S_N reaction where complete inversion of configuration and partial racemization plus inversion takes place.

◆◆◆

Chapter

11

Stereochemistry

Stereochemistry

Introduction:

Chemistry, like everyday life, takes place overwhelmingly in three dimensions. Stereochemistry is a sub discipline of chemistry that deals with the study of the relative spatial arrangement of atoms within the molecules. Stereochemistry is also known as 3D chemistry because the prefix 'stereo' means 'three dimensionality.'

Before beginning the stereochemistry, one cannot remain silent about isomerism. Isomers are molecules that have the same molecular formula, but have a different arrangement of the atoms in space and the phenomenon is known as isomerism. That excludes any different arrangements which are simply due to the molecule rotating as a whole, or rotating about particular bonds. Isomerism is broadly divided into two groups.

i. Structural isomerism and
ii. Stereoisomerism

Structural Isomerism: Isomerism due to the differences in the arrangement of atoms within the molecule is known as structural isomerism. There are various sub groups of structural isomerism.

a. Chain isomerism
b. Position isomerism
c. Ring chain isomerism
d. Functional group isomerism
e. Metamerism
f. Tautomerism

Stereoisomerism: Isomerism due to the different spatial arrangement of atoms or group of atoms in the space is known as stereoisomerism. Stereoisomers have identical molecular structures but differ in their configuration (the spatial arrangement of atoms or group of atoms in space).

The two types of stereoisomerism are

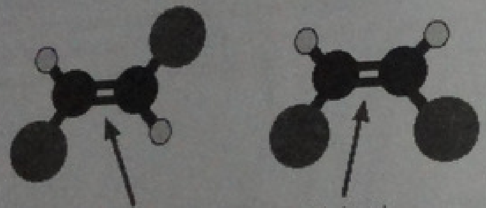
a. Geometrical isomerism and
b. Optical isomerism

a. Geometrical isomerism

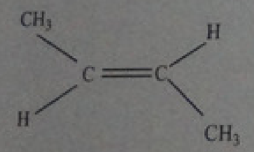
Isomerism arised by the different geometrical arrangement of two different groups about the carbon-carbon double bond is called geometrical isomerism.

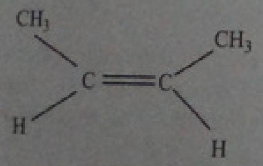
Origin of geometrical isomerism

As two wheels connected by a single bar can freely rotate about the bar but not when the wheels are connected by two bars. Two carbon atoms joined by a single bond can be freely rotated around it and the carbons joined by a double bond cannot be rotated. Consequently, the atoms or groups attached to carbon atoms of the double bond remain fixed in space. If the two different groups are attached into the double bonded carbon atom and same groups are attached to the next double bonded carbon atom, two different arrangements are possible as shown below. And such compounds having the same molecular formula but different geometrical arrangements are known as geometrical isomers.

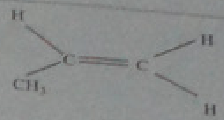


For example, two geometrical isomers of 2-butene are as follows;

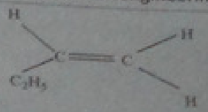




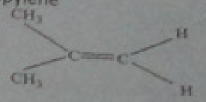
Hence the restriction of rotation about the carbon-carbon double bond is responsible for geometric isomerism of alkenes. Furthermore, a hindered rotation about the carbon-carbon double bond gives geometrical isomerism only if there is a certain relationship among the groups attached to the doubly bonded carbons. For example, propylene, 1-butene, isobutylene have no geometrical isomerism.



Propylene

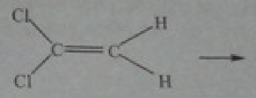


1-butene



Isobutylene

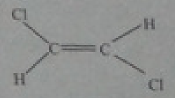
Similarly, 1,1-dichloroethene do not show geometrical isomerism where as 1,2-dichloroethene does.



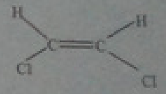
No two different geometrical arrangements are possilble and hence no geometrical isomerism

1,

1-dichloroethene



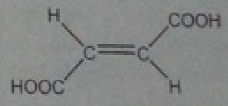
and



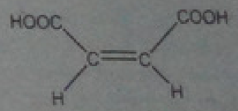
are two different geometrical arrangements of 1,2-dichloroethene and it shows geometrical isomerism1,

2-dichloroethene

Fumeric acid and maleic acid are the commonly known geometrical isomers of butan-1, 2-dioic acid;



Maleic acid



Fumeric acid

Types of Geometric isomers

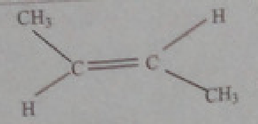
The two types of geometrical isomers are

i. Cis- isomers and

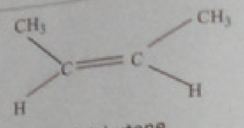
ii. Trans- isomers

The geometrical isomers in which similar groups are attached to the same side of the double bond are called cis-isomers. Whereas the trans-isomers are those in which similar groups are attached on the opposite sides of the double bond. Therefore, the geometrical isomerism is also known as cis-trans isomerism.

Consider the case of 2-butene. It exists in two different arrangements as,



trans-2-butene

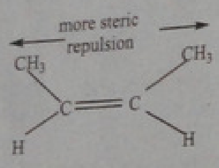


cis-2-butene

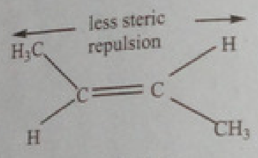
Since the geometrical isomers have different physical and chemical properties they can be separated by various methods such as fractional distillation, gas chromatography etc.

Cis-isomers are less stable than the corresponding trans-isomers.

This is due to steric effect of repulsion. That is, in cis isomers, the bulky groups are on the same side of the double bond and it causes steric repulsion of the groups making the cis isomer less stable than the trans isomer, in which the bulky groups are far apart as they are on the opposite side of the double bond.



cis-2-butene



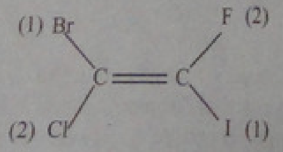
trans-2-butene

E, Z-nomenclature of geometrical isomers

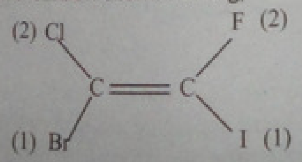
The method of cis-trans isomerism does not work when there are no identical groups on both the double bonded carbons, for e.g., 1-bromo-1-chloro-2-fluoro-2-iodoethane. The configuration of such geometrical isomers can be specified by using the notations E and Z as per IUPAC system of nomenclature.

In this system, the group of highest priority on each carbon atom is first determined. If the two high priority groups are together on the same side, the configuration is Z (zussamen = together) and if they are on the opposite sides, the configuration is E (entegen = opposite).

In general, order of priority for E and Z system of geometrical isomerism is by atomic number of the element attached to the double bonded carbon atom. For e.g,

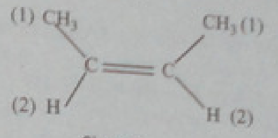


E

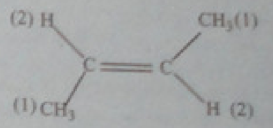


Z

The order of priority in the above group is Br > Cl and I > F. Of course, the same is applied in cis and Trans isomers.

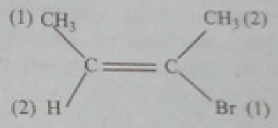


Cis or Z

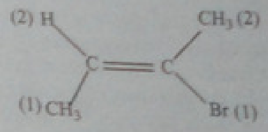


Trans or E

Similarly, in 2-bromo-2-butene,



Trans or E



cis or Z

Optical isomerism

This is defined in terms of the optical activity of the compounds.

Optical activity

An ordinary light consists of rays having different wavelengths vibrating in all directions perpendicular to the direction of propagation. When the light ray is allowed to pass through a suitable mean such as a nicol prism, the vibrations are adjusted in a single plane only. Light having the vibrations in only one plane is called plane polarized light (ppl). Substances that can rotate the ppl are called optical active substances and such property of the substances is known as optical activity.

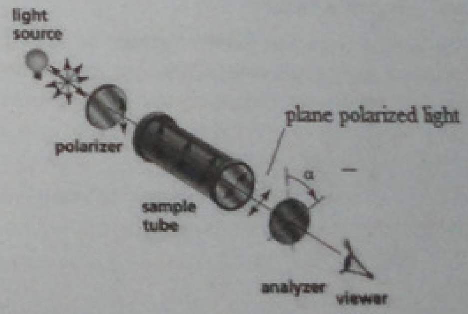


Fig: plane polarization of light

An optically active compound can exist in two isomeric forms which can rotate the plane polarized light in opposite directions. These are called optical isomers and the phenomenon is known as optical isomerism.

The isomer which rotates the plane of polarized light to the right or clockwise direction is known as dextrorotatory isomer or (+) or *d*-isomer. The isomer which rotates the plane of polarized light to the left or anticlockwise direction is known as the laevorotatory isomer or (-) or *l*-isomer. The extent of rotation caused by the two isomers is equal in magnitude but opposite in sign.

Optical isomers have the same physical properties such as melting point, boiling point, density etc but they differ in optical activity that they have same specific rotation but with opposite signs.

Louis Pasteur could rightly be described as the first stereochemist, having observed in 1849 that salts of tartaric acid collected from wine production vessels could rotate plane polarized light, but that salts from other sources did not. This property, the only physical property in which the two types of tartarate salts differed, is due to optical isomerism. In 1874, Jacobus Henricus Van't Hoff and Joseph Le Bel explained optical activity in terms of the tetrahedral arrangement of the atoms bound to carbon.

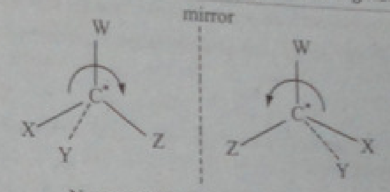
Chiral carbon and optical activity:

An optically active compound is found to have at least one carbon centre bonded with four different groups. A carbon atom in the organic compound bonded with four different groups is known as chiral or asymmetric carbon. As it is already said, if there is only one chiral carbon, the molecule is always optically active. The compound with only one chiral carbon can exist in two isomeric forms and such isomers are called enantiomers. However, the compounds which have more than one chiral carbon atoms may or may not be optically active. Such compounds which are optically inactive may possess a kind of symmetry whether 'plane of symmetry' or 'axis of symmetry'. The molecules without any kind of above symmetry are known as asymmetric molecules.

Enantiomerism and Tetrahedral carbon

If a carbon atom is bonded with four different groups or atoms, such carbon atom is known as chiral carbon or asymmetric carbon. It is denoted by writing asterisk above the carbon. Thus if one such tetrahedral carbon can rotate the plane polarized light in one direction, its mirror image has to rotate the plane polarized light in opposite direction. Consequently, the two optical isomers are arised.

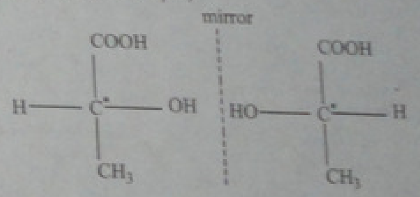
Let us take a model that a carbon atom is attached to 4-different groups say w, x, y and z. Then draw tetrahedral geometry and sketch its mirror image,



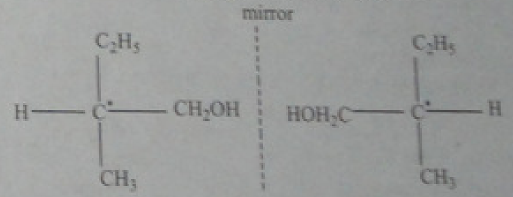
Non superimposable structures

These two models are not superimposable, i.e. they will not coincide in all their parts. Thus these two models represent two isomers of C_{wxyz} and these isomers are called enantiomers or enantiomorphs or optical antipodes. Thus one of the important criteria for a molecule to have enantiomers is chirality.

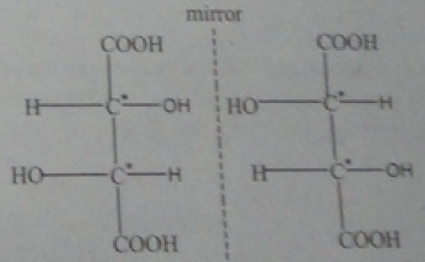
Thus, the stereoisomers that are optically active and non-superimposable mirror images of each other called enantiomers. For example,



Two enantiomers of lactic acid



Two enantiomers of 2-methyl-1-butanol



Two enantiomers of tartaric acid

The two isomers of lactic acid, 2-methyl-1-butanol and tartaric acid are optically active and are also mirror image to each other and hence these are called enantiomers.

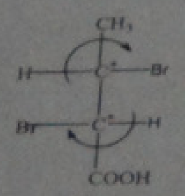
Thus, in short, **mirror image optical isomers are called enantiomers**.

Properties

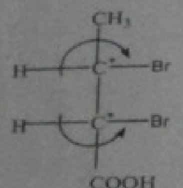
- Enantiomers have identical physical properties except for the direction of the rotation of the plane polarized light.
- Enantiomers have identical chemical properties except toward optically active reagents. For example, (+) glucose is metabolized by animals and fermented easily but (-) glucose is neither metabolized by animals nor fermented by yeasts.

Diastereomers

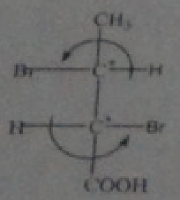
Stereoisomers that are neither *mirror* image of each other nor super imposable to each other are called diastereomers. For example, the isomers of 2,3-dibromobutaric acid are shown as below,



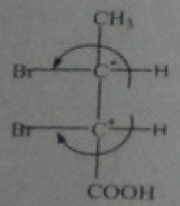
(i)



(ii)



(iii)



(iv)

In the above isomeric structures of 2, 3-dibromobutaric acid, the structures (I) and (ii) are optically active but not enantiomers and similar is the case between the structures (iii) and (iv). Hence, the structures (i) and (ii) and (iii) and (iv) are not enantiomers but these are diastereomers.

Properties

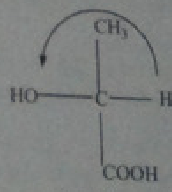
The important properties of diastereomers to distinguish them from enantiomers are:

- Unlike enantiomers, diastereomers have similar but not identical chemical properties.
- They have different physical properties such as melting point, boiling points, solubility, refractive indices, densities etc. These are in contrary to the enantiomers.
- They may or may not be optically active.
- Diastereomers can be separated from one another due to differences in their physical properties.

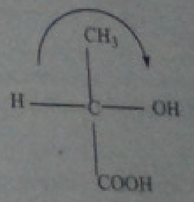
Racemic mixture

A mixture of equal parts of enantiomers is called a racemic modification or racemic mixture. It is always optically inactive because when enantiomers are mixed together, the rotation caused by a molecule of one isomer is exactly canceled by an equal and opposite rotation caused by a molecule of its enantiomer.

Racemic mixture is usually denoted by the prefix (±) before the name of the compound. For example, (±) lactic acid, a racemic mixture made by mixing equal parts of (+) i.e. dextrorotatory and (-) i.e. laevorotatory lactic acid,

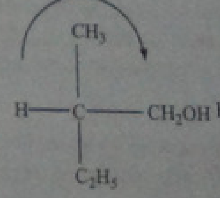


(+)-lactic acid

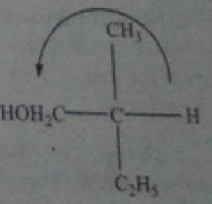


(−)-lactic acid

Similarly (±)-2-methyl-1-butanol,



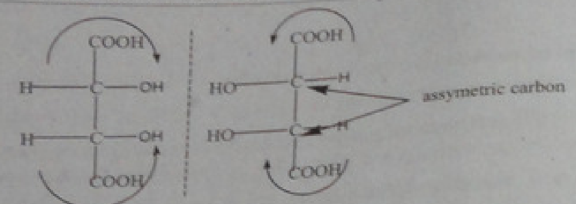
(+)-2-methyl-1-butanol



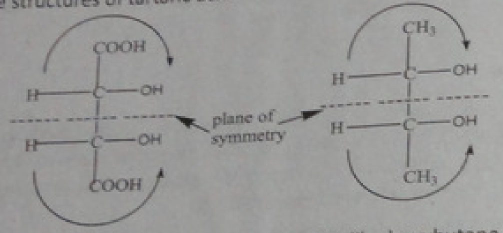
(−)-2-methyl-1-butanol

Meso structure

A molecule containing asymmetric carbon atoms and one half of the molecule is mirror image to its another half is known as meso compound. In other word, the molecule has a plane of symmetry. In such compounds, the rotation caused by any one half of the molecule is canceled by the equal and opposite rotation caused by the other half of the molecule that is the mirror image of the first half. For example, meso-tartaric acid.



Superimposable structures of tartaric acid



meso tartaric acid

meso-2,3-dihydroxybutane

Optical inactivity in a racemic modification is caused by compensation between two molecules rather than between two halves of the same molecule, that is by external compensation.

An optically inactive racemic mixture can be separated into optically active enantiomeric components whereas optically inactive meso compound cannot be separated into optically active components.

Resolution

The process of the separation of enantiomeric components from their racemic mixture is called resolution. In other word, the separation of a racemic mixture into its two optically active components (+ and – isomers) is known as resolution. It has a great practical importance in the study of the naturally occurring optically active compounds. There are various methods of the resolution,

1. **Mechanical resolution-** It is a method of resolution based on the different in physical properties of the enantiomers. Mainly, there are two types of mechanical resolution

   i. *Hand-picking method:* This method is appropriate when the enantiomers form the visually distinct crystals. For example, the sodium ammonium tartarate crystals are produced at the temperature below 27°C, from the racemic tartaric acid. The slow crystallization produces the well shaped crystals. Now with the help of forceps and microscopic visualization, the two kinds of crystals can be separated out.

   Demerits of this method are:

   - Not applicable to racemic compounds and solid solutions
   - It is a tedious process that the crystals are hardly distinct to pick up.

   ii. *By inoculation:* It is also known as the seeding process first developed by Gernez (1866). This method is based on the way of the crystal growth induced by the addition of suitable optically active or sometimes also optically inactive compounds into the racemic solution. For example, *dl* α-amino acid can be resolved by adding (+) or (–) isomer of the corresponding amino acid. Sometimes, other optically active compounds can also be added. Example, (–) asparagines ($H_2NCOCH_2NH_2COOH$) can be used to separate (+) sodium ammonium tartarate from its racemic mixture. It has also been found that optically inactive compound such as glycine can be used to separate dl asparagines.

2. **Biochemical resolution:** It is the method of resolution by using micro-organisms. Louis Pasteur (1851) discovered that some micro-organism like bacteria, yeast, fungi etc can oxidize one of the isomer more rapidly than the other when they are added to the racemic mixture. That is, when the living organisms are kept or developed in a racemic mixture, they eat up one enantiomer preferentially leaving the next behind. This is due to the stereospecificity of the enzymes. For example, pencilium glaucum eats up the (+)-isomer of ammonium tartarate and leaves its (–)-isomer unaffected in the mixture.

   The major demerit of this method is that one of the enantiomer needs to be sacrificed to recover the next. Furthermore, it is also difficult to find the best micro-organism and yield is few because the dilute solution has to be used as the concentrated solution can affect the organism.

3. **Chemical resolution: by diastereomers formation:** In chemical resolution, the racemic mixture is made to combine with another optically active compound to form diastereomers. Thus, the principle of this method is that the diastereomers have different physical properties such as boiling point, solubility, adsorption coefficient etc and they can be easily resolved by fractional crystallization, solvent extraction etc. For example, the racemic lactic acid is allowed to combine with the optically active base (–)-strychnine. The salt formed will be;

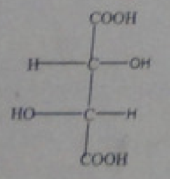
   (–)-strychnine(+)-lactate and

   (–)-strychnine(–)-lactate.

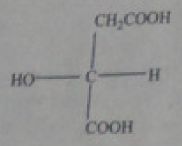
   These salts are not true enantiomers and they differ considerably in properties such as solubility. Thus by fractional crystallization using a suitable solvent, they can be separated. Then treatment with dilute mineral acid removes the optically active base and leaves the two separate samples of (+)- and (–)- lactic acid.

   However, this method may not be appropriate if the separated diastereomers cannot be brought back into original isomers using suitable reagent. Hence the following conditions are said to be essential for the effective chemical resolution.

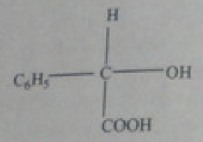
- The so produced diastereomers should be easily separated.
- There should be an easy method to convert the so separated diastereomers into original isomers using suitable reagent.
- The reagent should be cheap and must be recovered easily.
- The reagents should have suitable functional group to produce the diastereomers that may be easily separated. The commonly used acid to resolve the racemic base are;



(+)-tartaric acid

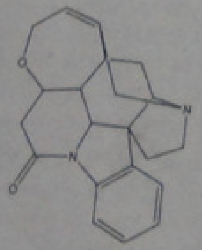


(+)-malic acid

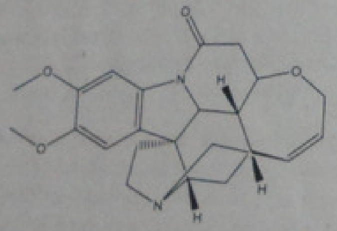


mandelic acid

Similarly the commonly used bases for the resolution of racemic acid are,

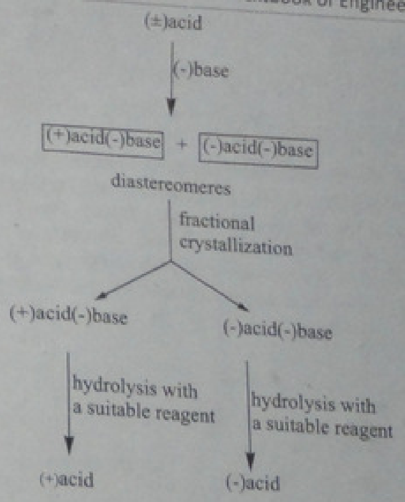


strychnine

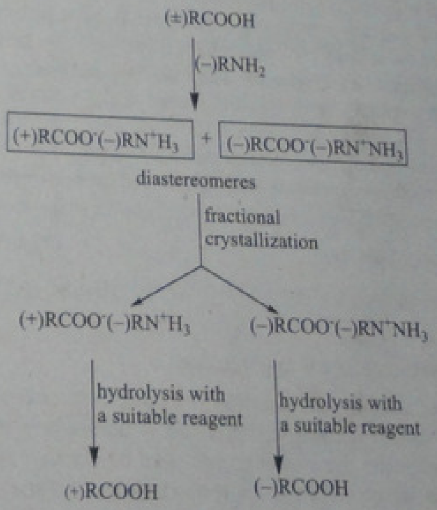


brucine

A general outline of the process of chemical resolution by diastereomers' formation is shown as below,



For example,

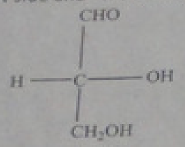


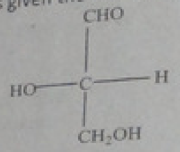
Configuration:

The arrangement of atoms or group of atoms around the carbon atom is known as the configuration. It must be very clear to the reader that there is no significant relation between configuration and sign of optical rotation of an enantiomer because a compound and its derivatives have the same configuration may have different sign of rotations. E.g. lactic acid and its esters although having same configuration, possess opposite sign of rotation. Two systems have been developed for studying the configuration of organic compounds.

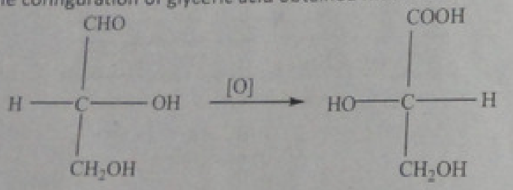
i) Relative configuration (D, L – configuration)

Before 1951, there was no method for determining the absolute configuration (actual arrangement of atoms in space) of a compound and hence the configuration of all compounds were studied with respect to glyceraldehyde (relative configuration), the configuration of which was taken as an arbitrary standard. (+) – Glyceraldehyde having the –OH group on the right and –H atom on the left, the –CHO and –CH_2OH groups being at the top and bottom, respectively was arbitrarily given the configurational symbol D. The mirror image compound, (–)-Glyceraldehyde, in which the –OH group is on the left side and –H atom on the right was given the configuration L.


D (+)-glyceraldehyde


L (–)-glyceraldehyde

Any compound that can be prepared from or converted into D(+)-glyceraldehyde will belong to the D-series and similarly any compound that can be prepared from or converted into L(–)-glyceraldehyde will belong to L-series (relative configuration). For example, D-glyceraldehyde can be converted into glyceric acid by simple oxidation and thus the configuration of glyceric acid obtained must be D.


D (+)-glyceraldehyde

D (–)-glyceric acid

ii) Absolute configuration (R and S configuration)

The D, L system of relative configuration has basic defects and it is very difficult to apply for the compound having complicated structure and more than one chiral centres. These difficulties are however, removed by another system given by Cahn, Ingold and Prelogs which is based on the actual three dimensional formulas. The important features of the system are;

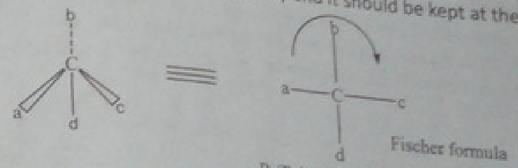
a. *The four different groups attached to the asymmetric carbon atom are arranged in a priority sequence in accordance with a set of rule known as Sequence rule.*

After assigning the priorities of the four groups or atoms attached to the chiral carbon, the molecule is imagined to be in a position where the atom or group of the lowest priority is directed away from us. Now the arrangement of the remaining three groups is viewed in

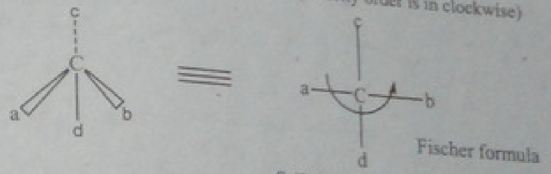
decreasing order of their priorities. In looking so, if the eye travels in a clockwise direction, the configuration is specified as R (*for rectus i.e. right in latin*) while if the eye travels in anti-clockwise direction, the configuration is specified as S (*for sinister i.e. left in latin*).

b. When the molecule contains more than one asymmetric centre, the same procedure is applied to each chiral carbon.

Illustration: Suppose a, b, c and d are attached to a carbon and their priority order is a > b > c > d. d has the lowest priority and it should be kept at the bottom.



R (Priority order is in clockwise)



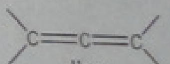
S (Priority order is in anti-clockwise)

Optical isomerism in compounds containing no chiral carbon atom:

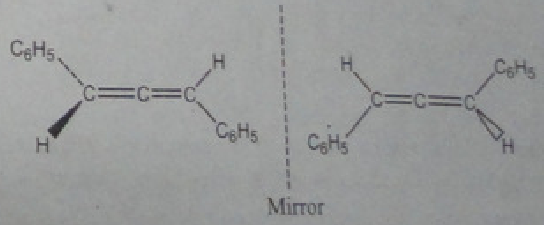
As already described, the basic requirement for a compound to be optically active is its non-superimposability to its mirror image. Although the largest number of known optically active compounds are due to the presence of chiral carbon. But some compounds are also known which do not possess any chiral carbon atom, but on the whole their molecules are chiral (such molecules were earlier called dissymmetric); hence they are optically active. Various types of compounds belonging to this group are described below.

Allenes:

Allenes are the organic compounds of the following general formula,


allene

E.g.,

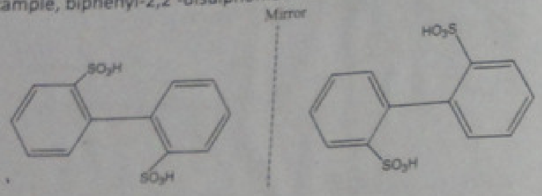


1,3-diphenylpropadiene

In allene, the central carbon is sp-hybridised and the terminal carbons are sp^2 hybridized. The central carbon forms two sp-sp^2 σ-bonds. The central carbon has two p-orbitals which are mutually perpendicular. These form π-bonds with the p-orbitals and the other carbon atoms. As a result, the substituents at one end of the molecules are in a plane which is perpendicular to that of substituents at the other end, so that the compounds exist in two forms which are non superimposable mirror images and are optically active.

Biphenyl derivatives:

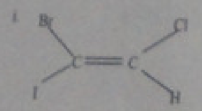
Substituted biphenyls show optical isomerism when substituents in the two positions of phenyl ring are large enough to prevent rotation about the bond joining the two benzene rings. For example, biphenyl-2,2'-disulphonic acid exist in two forms.

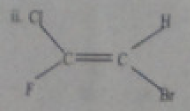


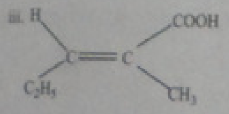
biphenyl-2,2'-disulphonic acid

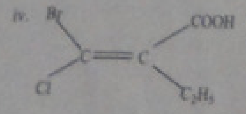
Practice Questions

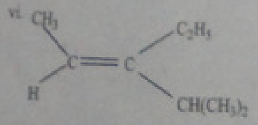
1. *What do you mean by stereoisomerism? Explain with suitable examples.*
2. *What are geometrical isomers? Give an example specifying Z and E configuration.* **[IOE-'68]**
3. *State the required conditions for geometrical isomerism.*
4. *Assign the* **E** *and* **Z** *to following compounds.*











5. *What do you mean by optical activity of a compound? What are the necessary conditions for a compound to show optical isomerism? Illustrate your answer with examples.*
6. *Show your familiarity with enantiomerism and diastereomerism.* **[IOE-'68]**

7. Write notes on:
    - a. chiral carbon
    - b. Assymetric carbon
    - c. Optical isomerism
    - d. Plane of symmetry
8. Write the Optical isomers of
    - a. lactic acid
    - b. Tartaric acid
    - c. 3- bromo –2- butanal
9. What type of isomerism is shown by fumeric and maleic acid?
10. Define with suitable examples:
    - a. Enantiomer
    - b. Meso compound
    - c. Racemic mixture
    - d. Diastereomers
    - e. Resolution

◆◆◆

Model Question

F.M.: 80
P.M.:32

16 × 5 = 80

Attempt all questions:

1. How does single electrode potential originate? A strip of zinc metal is immersed into its electrolytic solution of centimolar concentration at 25°C and it is coupled with standard hydrogen electrode externally via voltmeter and internally via salt bridge. How much would be the reading shown by the voltmeter? Given that the standard oxidation potential of zinc is 0.76V. [2+3]
2. Define buffer solution. What would be the pH of buffer solution resulted by mixing 10 ml of 0.2 M HCl into the 190 ml of 0.3 M ammonia solution where the ionization constant of ammonia solution is 1.8×10^{-5}? [1+4]
3. a. How does a catalytic promoter work? Describe with a suitable example.[3]
   b. Mention the important criteria of choosing the perfect catalyst for its industrial applications.[2]
4. What are freons? Describe the photochemistry of ozone layer depletion with its effects into the human world.[1+4]
5. What are point and non-point source pollutants? Explain the active sludge process to control water pollution.[2+3]
6. Describe the preparation and uses of Polyphosphazines and polymeric sulphur (PS) .[5]
7. What are bio-degradable and non-biodegradable polymers? Mention the uses of epoxy resin and fibre reinforced polymer.[2+3]

8. Differentiate between double and complex salts. Write the correct formulae of the following coordination compounds.[2+3]
   a) Potassium hexacyanocobaltate (II)
   b) Sodium trioxalato aluminate (III)
   c) Dichlorotetraaquachromilum (III) bromide
   d) Tris (ethylenediamine) cobalt (III) chloride
   e) Bis (benzene) chromius (0)
   f) Dicyanoargentate (I) ion
9. a. What is EAN rule? What information does the EAN of a metal ion in a complex convey?[2]
   b. Explain the formation of $[Fe(CN)_6]^{4-}$ complex on the basis of VBT. Also predict its geometry and magnetic behavior.[3]
10. a. What are transition elements? Which element of the 3d-series is called non-typical transition element and why?[1+2]
    b. Show your acquaintance with the applications of transition elements.[2]

11. explain the characteristics of 3d-elements with reference to,
    i) colour formation and
    ii) magnetic behavior
12. What do you mean by detonation? Describe the preparation and uses of nitro-cotton. [1+2+2]
13. State the conditions for geometrical isomerism with suitable examples. Write the structures of following compounds and assign E and Z naming.[2+3]
    i) 3-methyl pent-2-en-1-ol
    ii) 2-bromo-3-methyl-2-pentene
    iii) Hex-2-ene
14. a. Write all possible stereoisomers of a compound that contain two asymmetric carbon atoms but cannot exist in meso forms and assign the name of isomers. [3]
    b. describe the method of chemical resolution.[2]
15. a. Write the mechanism of bimolecular elimination reaction.[2]
    b. Mention the effect of nucleophile, substrate and solvent on the mechanism of elimination reactions.[3]
16. Describe the mechanism and reactivity of different alkyl halides towards S_N reaction taking suitable examples.

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