

ELECTROCHEMISTRY

Introduction, Single electrode potential, Origin of single electrode potential theory, Nernst equation to calculate the electrode potential, Numerical problems. Electrochemical cells - galvanic cell and electrolytic cell, representation of galvanic cell, Construction and working of galvanic cell, Liquid junction potential, Functions of salt bridge, EMF of cell, Determination of EMF of cell by Poggendorff's method using Standard cell, Construction, working, application and limitations of calomel electrode, Numerical problems. Construction, working, applications, advantages and limitations of glass electrode, Numerical problems. Classification of Batteries – Introduction, primary and secondary with examples; construction, working and applications of lead acid battery. Construction, working and applications of Ni-Cd and Li-ion batteries, advantages and disadvantages. Fuel Cells – Introduction, construction and working of AFC & PEMFC, advantages and disadvantages. Metal finishing – Electroplating – polarization, over voltage, decomposition potential including determination of decomposition potential. Characteristics of good deposit, Factors influencing the nature of the deposit, Methods of cleaning the metal surface. Electroplating of Cu & Cr & electroless plating of Cu.

1 INTRODUCTION

Electrochemistry deals with the behavior of electrolytes in solution and inter conversion of chemical and electrical energies; that is, the study of chemical changes due to the flow of an electric current and production of electric current due to chemical reaction. Electrolysis, electrometallurgy and electroplating use electrical energy to drive chemical reactions, while chemical energy is transformed into electricity in galvanic cells, batteries and fuel cells. Substances such as metals and alloys conduct electricity under the influence of an applied electric potential through a flow of electrons and hence are known as electronic conductors. The flow of electricity in electronic conductors does not cause any physical or chemical change in the conductor. On the other hand electrolyte solutions and molten salts conduct electricity through the migration of ions and are known as electrolytic conductors or electrolytes. When direct current is passed through an electrolyte solution, decomposition and changes occur in the composition of the electrolyte. The practical importance of

electrochemistry includes electroplating, electroextraction of metals, electrorefining of metals, and electro-production of certain compounds.

1.1 ELECTROCHEMICAL CELLS

An electrochemical cell consists of two electrodes or metallic conductors, in contact with an electrolyte, an ionic conductor. An electrode and its electrolyte comprise an electrode compartment. The two electrodes may share the same compartment. If the electrolytes are different, the two compartments may be joined by a salt bridge, which is a tube containing a concentrated electrolyte solution in agar jelly that completes the electrical circuits and enables the cell to function. So an electrochemical cell can be defined as a single arrangement of two electrodes in one or two electrolytes which converts chemical energy into electrical energy or electrical energy into chemical energy. Electrochemical cells can be classified into two types:

- *Galvanic Cells*
- *Electrolytic Cells*

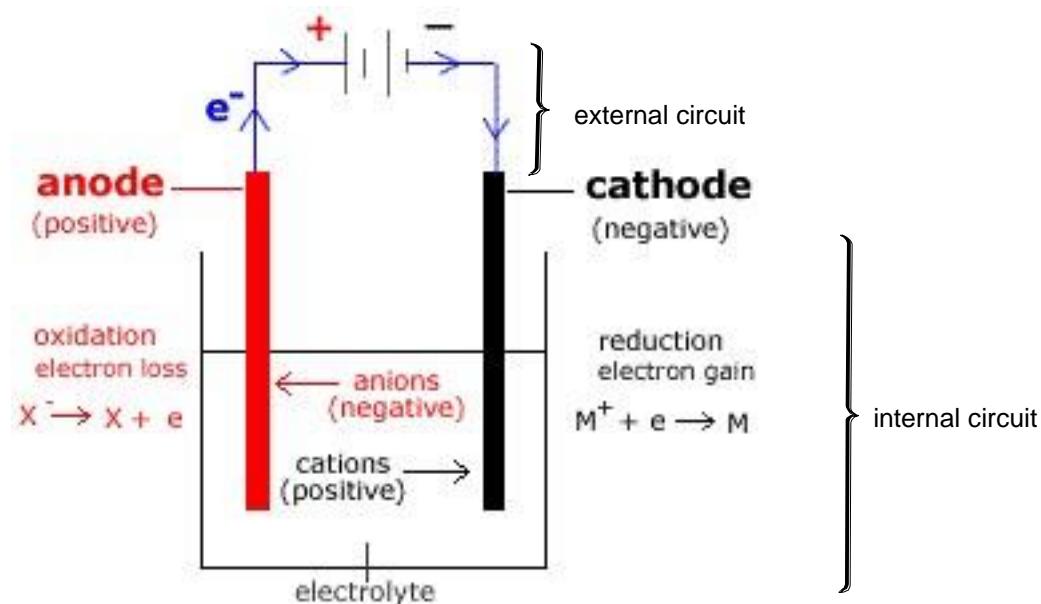


Fig.1.1. A schematic diagram of Electrochemical Cell

1.1.1 Galvanic Cells

A galvanic cell is an electrochemical cell that produces electricity as a result of the spontaneous redox reaction occurring inside it. Galvanic cell generally consists of two electrodes dipped in two electrolyte solutions which are separated by a porous diaphragm or

connected through a salt bridge. It is a single arrangement of two electrodes in one or two electrolytes which converts stored up chemical energy in the form of electroactive materials (anode & cathode active materials) directly into electrical energy. The negatively charged electrons flow from anode to cathode and are attracted to the positive cathode through the external circuit.

Anode vs. Cathode:

Anode :

- the electrode at which oxidation occurs
- is where electrons are produced
- is what anions migrate towards
- has a –ve sign.

Cathode :

- the electrode at which reduction occurs
- is where electrons are consumed
- is what cations migrate towards
- has a –ve sign

A typical galvanic cell can be illustrated by Daniel cell (Fig. 1.1.1)

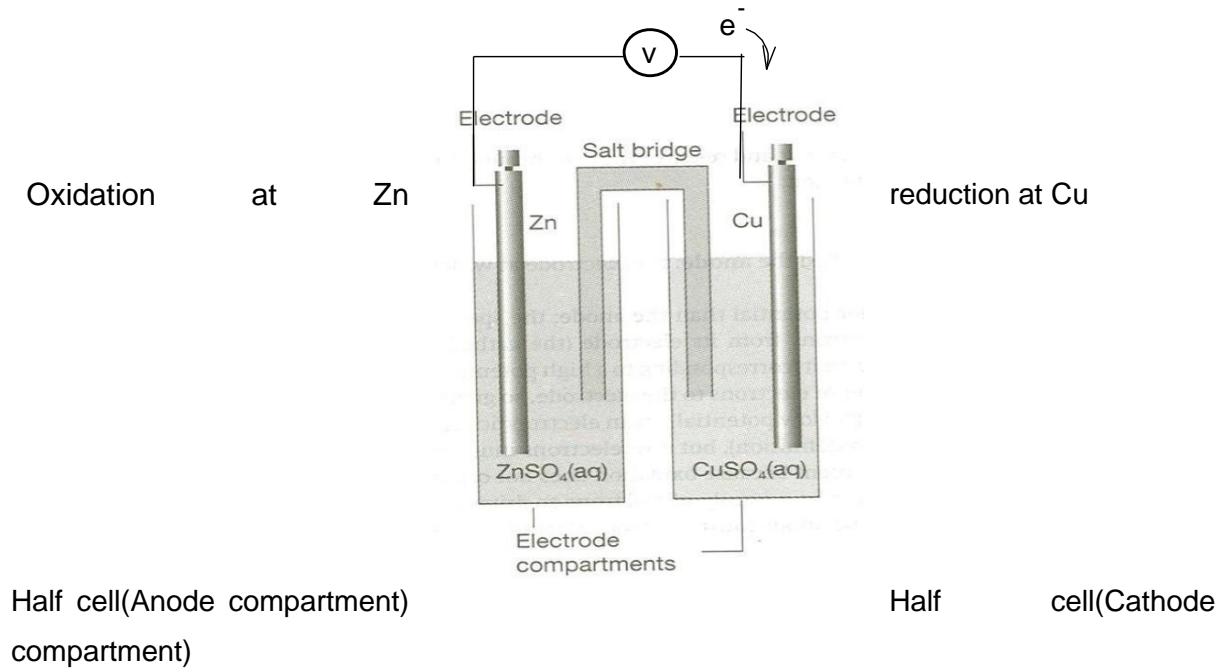
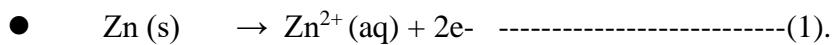
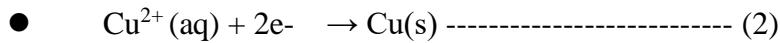


Fig.1.1.1. A schematic diagram of Daniel cell

A Daniel cell consists of two compartments, one of which contains zinc rod dipped in zinc sulphate solution and the other with a copper rod dipped in a copper sulphate solution. The two electrolytes are connected by a salt bridge. When the zinc and copper rod electrodes are connected externally through a voltmeter by using a wire, the following oxidation-reduction reactions taking place at the electrodes. At the zinc electrode, zinc goes into the solution as Zn^{2+} ions, liberating two electrons. In the process zinc undergoes oxidation liberating two electrons. The positive ion flows from the salt bridge to the cathode and the zinc electrode becomes lighter.



At the copper electrode reduction of Cu^{2+} ions takes place with the deposition of metallic copper on the copper rod, by consuming two electrons. The negative ions flow from salt bridge to anode and copper electrode becomes heavier. The ionic conduction in the solution is coupled to the electronic conduction in the electrodes.



Each of these reactions is known as half cell reaction. The reaction (1) in which loss of electrons takes place is called oxidation half reaction; while the reaction 2, in which gain of electrons takes place, is called reduction half reaction. The net reaction is obtained by adding reactions 1 and 2. i.e. $Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$ is called redox or oxidation – reduction reaction. When the circuit is closed, the electrons flow from zinc to copper through the external wire to feed the Cu^{2+} ions in the process of discharging copper and thus electrical energy or current is produced which may be used for the purpose of external work.

As in the case of Daniel cell, by the combination of any two different electrodes materials one can construct a galvanic cell. The electrode with a greater tendency to go into the solution by liberating electrons acts as an anode, & the other one with more tendency to undergo reduction acts as a cathode. In a galvanic cell anode is negative and the cathode is positive. The reason to this nomenclature is that oxidation is accompanied by the liberation of electrons which are given up to that electrode which thereby acquires a negative charge. Reduction on the other hand, is accompanied by absorption of electrons by reactant in solution from the electrode, which thereby acquires a positive charge. Hence the flow of electrons is from the negative electrode to positive electrode and the direction of flow of positive electricity, which is known as conventional current, is from the cathode to anode.

1.1.2 Electrolytic cells

An electrolytic cell is an electro –chemical cell in which a non- spontaneous reaction is driven by an external source of current although the cathode is still the site of reduction, it is now the negative electrode whereas the anode, the site of oxidation is positive.

The electrolytic cell (Fig.1.1.2) find wide applications in the purification of metals & also in electro deposition of a metal on to the surface of another metal, alloy or any conductor in general, by the process of electrolysis.

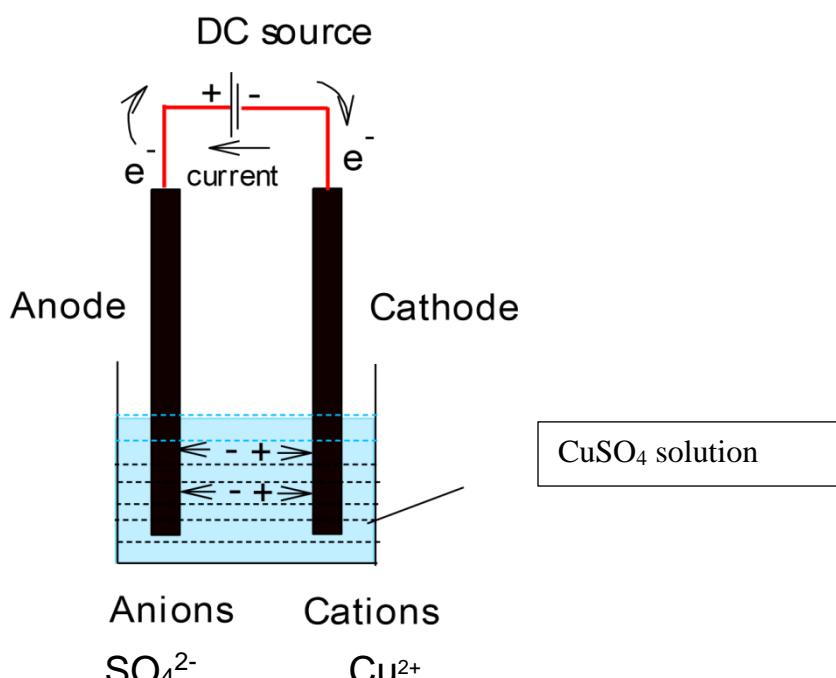


Fig.1.1.2 Schematic diagram of an electrolytic cell

Electrolysis involves the conversion of electrical energy into chemical energy i.e. chemical changes are brought about by the expense of electrical energy. Since electrolysis is a non spontaneous process, the minimum energy required to carry out such a process is equal to the free energy increase accompanying the change, & this is equal but opposite in sign to the free energy decrease accompanying the reverse spontaneous process. This is true when electrolysis is carried out reversibly. However, in irreversible conditions, the potential to be applied for electrolysis is higher than the reversible emf of the cell.

1.1.3 Representation of a galvanic cell

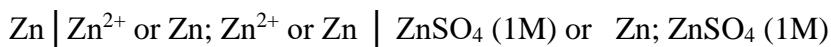
According to the present convention, a galvanic cell is represented by keeping in view the following points:

1. The anode is written on the left hand side and the cathode is written on the right hand side of cell representation.

2. The anode is written by writing the metal (or solid phase) first and then the electrolyte along with the concentration in the bracket. The two are separated by a vertical line or a semicolon. The electrolyte may be represented by the formula of the whole compound or by ionic species.

Anode representation

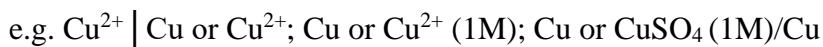
Metal/ Metal ion (concentration) i.e. $M/M^{n+}(c)$



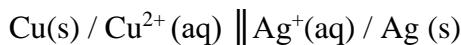
3. The cathode of the cell is represented by metal ion first and then the metal (or solid phase) thereafter. The two are separated by a vertical line or a semicolon.

Cathode representation:

$M^{n+}(c) / M$ i.e. Metal ion (concentration) / Metal



4. A salt bridge is indicated by two vertical lines, separating the two half-cells. Thus the Daniel cell, may be represented as:



Comparisons of Galvanic and Electrolytic cells

Galvanic Cell	Electrolytic Cell
<p>Cell reaction is spontaneous</p> <p>Converts chemical energy to electrical energy</p> <p>Anode is negative and cathode is positive</p> <p>Usually have two electrodes and two electrolytes</p> <p>Used as a portable source of electrical energy in cars, flashlights and calculators</p> <p>Example. Daniel cell</p>	<p>Cell reaction is non-spontaneous</p> <p>Converts electrical energy into chemical energy</p> <p>Anode is positive and cathode is negative</p> <p>Single electrolyte and two electrodes</p> <p>Used for electrolysis apparatus like electroplating and electrorefining</p> <p>Example. Electroplating of nickel</p>

1.1.4 LIQUID JUNCTION POTENTIAL

The potential set up at the junction of the two electrolytes because of the difference in the speeds of the cations in one direction and anions in the other i.e. potential at the junction of the two electrolytes because of unequal migration of ions across the boundary between the two solutions is called the liquid junction potential, E_j . In a Daniel cell, if the concentrations of ZnSO_4 (aq) and CuSO_4 (aq) are equal SO_4^{2-} ions do not diffuse across the junction and the charge cannot flow around the circuit. But Cu^{2+} ions diffuse into ZnSO_4 (aq) and Zn^{2+} ions diffuse into CuSO_4 (aq) because Cu^{2+} ions are slightly more mobile than Zn^{2+} ions. This produces a small excess positive charge on the ZnSO_4 (aq) side of the junction and equal negative charge on the CuSO_4 (aq) side. The liquid junction potential is the difference between the electric potential developed in the two solutions across their interface.

i.e. $E_j = \emptyset^{\text{soln, R}} - \emptyset^{\text{soln, L}}$ where $\emptyset^{\text{soln, R}}$ is the electric potential of the electrolyte solution on the right hand side half-cell in the cell scheme. $\emptyset^{\text{soln, L}}$ is the electric potential of the electrolyte solution on the left hand side half-cell. Generally, LJPs are of the order of a few millivolts.

1.1.5 SALT BRIDGE

The contribution of the liquid junction to the potential can be reduced (to about 1 to 2 mV) by joining the electrolyte compartments through a salt bridge containing salts such as KCl , KNO_3 , and NH_4NO_3 whose ions have the same migration velocities. Then the ions move with equal speed to anode and cathode compartments minimizing the junctions potentials almost zero. A salt bridge is used to connect electrolytically, the two electrolyte solutions of a galvanic cell, as shown in the Fig. 1.1.5.

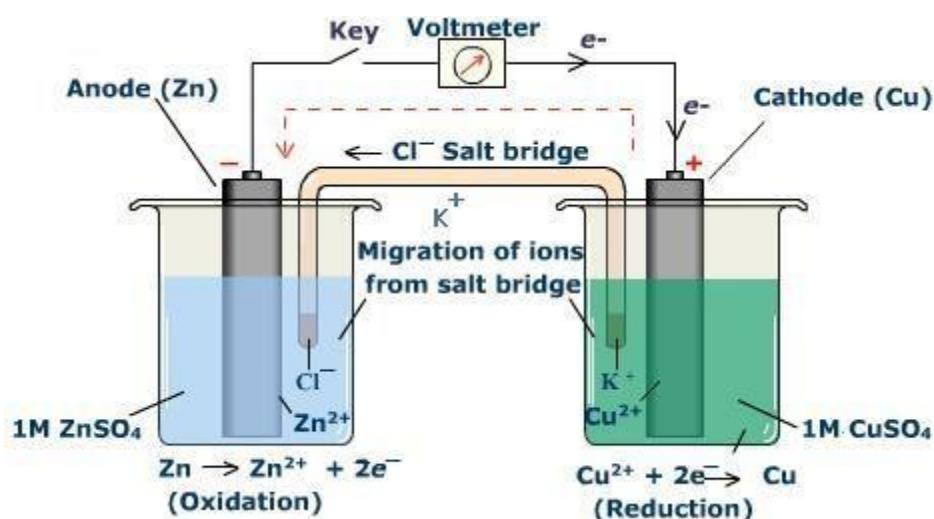


Fig.1.1.5 Daniel Cell indicating the function of a salt bridge

The salt bridge consists of a saturated solution of a salt such as KCl or NH₄NO₃, whose ions have almost same migration velocities. The positive and negative ions of the salt in the salt bridge migrate with equal speed into cathode and anode compartments respectively, thereby minimizing liquid junction potential.

The salt bridge is prepared by dissolving 5g agar in 100 mL aqueous solution of KCl containing 35 g of KCl and filling in a U-tube. On cooling, the agar forms a jell with KCl solution in it. A salt bridge has the following functions:

1. It provides electrical contact between the two electrolyte solutions of a cell i.e., it physically separates the two electrolytes but completes the electrical circuit by altering ions causing charge to move from half-cell to the other.
2. It minimizes liquid junction potential in galvanic cells containing two electrolyte solutions in contact. i.e., it reduces the LJP to a minimum by nearly equal diffusion rates of cations and anions.
3. It maintains the electrical neutrality of the two half cells i.e., it prevents any net charge accumulates in the two electrolytes.

1.1.6 ELECTROMOTIVE FORCE OF THE CELL

Electricity cannot flow from one electrode to another unless there is a potential difference between the two points. The difference of potential, which causes a current to flow from the electrode at higher potential to an electrode at lower potential is called the “electromotive force”(e.m.f.) of the cell “or the “cell potential” and is expressed in volts V.

The emf of a cell is denoted by E_{cell} . Mathematically,

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

The driving force that pushes the negatively charged electrons away from the anode and pulls them towards the cathode is known as emf. The E_{cell} depends on the nature of the electrodes composition, (combination of electrodes, strong tendency to lose or gain electrons produces large cell potential) temperature ($E^{\circ}\text{T}$) and concentration of the electrolyte solutions. To facilitate comparison of different galvanic cells, their standard emf, denoted by E^0_{cell} is used. Standard emf of a cell is defined as the emf of a cell when the reactants & products of the cell reaction are at a unit concentration or unit activity, at 298 K and at 1 atmospheric pressure including pure solids and liquids.

The emf of a cell represents the driving force of a cell reaction. As represented by the thermodynamic relation,

$$\Delta G = -nFE$$

Where ΔG is the free energy change accompanying a cell reaction, n is the number of electron transfer during the cell reaction, and F is the Faraday constant, $F = eN_A$, the magnitude of the charge per mole of electrons. Hence the above equation is the key connection between the electrical measurements on the one hand and thermodynamic properties on the other.

The cell reaction is spontaneous or feasible when ΔG is negative. ΔG can be negative only if the emf of the cell is positive, because, the other two factors, n & F are always positive. Thus emf of a galvanic cell is always positive. The positive emf value indicates the spontaneity of cell reaction in the given direction. When the cell potential is large, a given number of electrons traveling between the electrodes can do a large amount of electrical work. When the cell potential is small, the same number of electrons can do only a small amount of work. A cell in which the overall reaction is at equilibrium can do no work, and then the cell potential is zero.

1.1.7 Measurement of emf of a cell

The emf cannot be measured accurately by connecting directly a voltmeter between the two electrodes, because during such a measurement, a part of the cell current is drawn to deflect the needle as part of the emf is used to overcome the internal resistance of the cell. Consequently, such a measurement would indicate a potential difference less than the actual emf of the cell. For precise emf measurements potentiometers are used, which require extremely small current at the balance point.

The potentiometric measurement of emf of a cell works based on Poggendorff's compensation method. In this method, emf of a test cell is opposed by the impressed emf from an external source of emf, and the measurement is made when there is no net flow of current in the circuit. The basic principle is that the emf of the cell to be measured is exactly balanced by an equal and opposite known emf so that no current flows in the circuit (null point) A schematic diagram of the potentiometer is shown in Fig.1.1.7

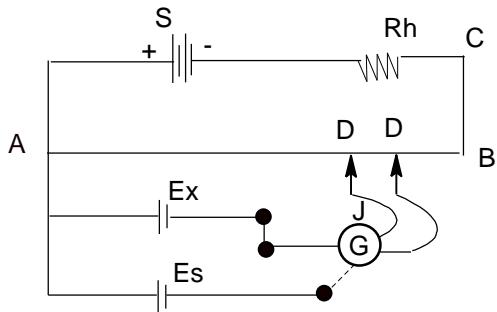


Fig.1.1.7. Potentiometric arrangement for the measurement of EMF of a galvanic cell.1.1.5

AB- Potentiometric wire

S- Storage battery

Es- Standard cell

Ex- unknown cell

G- Galvanometer

J- Sliding contact.

Rh – adjustable resistance

The two terminals of a storage battery(S) which has a constant and higher emf than the test cell, is connected to two ends of a long uniform wire AB of high resistance. The positive terminal of the test cell is connected to the end A, to which the positive terminal of S is connected & the negative terminal is connected to a sliding contact J through a galvanometer (G). The sliding contact is moved along the wire AB until the null point is reached, which is indicated by no current flow in the galvanometer. The position of a null point is noted & the distance AD is measured. The emf of the unknown cell E_x is proportional to the length AD.

- $E_x \propto AD$

Then the test cell Ex is replaced by a standard cell Es, whose emf, is known the position of the sliding contact is readjusted by moving it over AB, as before, till null point D' is reached .The length AD' is measured. The emf of the standard cell E_s is proportional to the length AD' .

- $E_s \propto AD'$
- $E_x = \frac{AD}{AD'}$
- $E_s = AD'$
- $E_x = \frac{AD}{AD'} \times E_s$

Thus the emf of the test cell is calculated by substituting the emf of the standard cell in the above equation.

1.1.8 Standard cell requirements:

1. Its emf should remain constant for a longer period of time.
2. It should be capable of providing highly reproducible emf.
3. The temperature coefficient of emf should be negligibility small i.e $(\delta E / \delta T) = 0$
4. The cell reaction should be reversible.
5. It should not be subjected to permanent damage due to the passage of current.
6. A standard cell is one which has a constant and reproducible known emf with a negligible variation of emf with temperature e.g. Weston standard cell or Weston cadmium cell.

1.2 Energetic of cell reactions:

1.2.1 The relation between E and ΔG :

A cell in which the overall reaction has not reached chemical equilibrium can do electrical work as the reaction drives electrons through an external circuit. The work that a given transfer of electrons can accomplish depends on the cell potential.

The maximum electrical work as per thermodynamics, chemical reaction can do is given by the value ΔG for the reaction.

$$W_e, \text{ max} = \Delta G \quad \dots \dots \dots \quad 1$$

Where, W_e is electrical work. It follows that, to draw thermodynamic conclusions from measurements of the work a cell can do, we must ensure that the cell is operating reversibly. Only then it is producing maximum work and only then we can relate electrical work to ΔG .

Both these conditions are achieved by measuring the cell potential when it is balanced by an exactly opposing source of potential so that the cell reaction occurs reversibly, the composition is constant, and no current flows.

The net electrical energy and the emf of the cell produced in a cell is the product of the quantity of electricity that passes through the cell and the emf of the cell.

$$W_e = QE \text{ Joules.} \quad \dots \dots \dots \quad (2)$$

Q is the quantity of electrical charge in coulombs produced by the reaction and E is the emf of the cell in volts.

Charge on 1 mol (6.02×10^{23}) electrons is F coulombs, where F is Faraday constant. When n electrons take part in the cell reaction, n mols of electrons are involved per mol of a reactant of the reaction. Hence charge on n mol of electrons = nF coulombs. This is the charge, Q in

coulombs produced by the reaction. For 1 mole of electrons transferred in the cell reactions, the quantity of electricity = 1F

If n moles of electrons are transferred in the cell reactions, the quantity of electricity = n F

Therefore electrical energy= nFE, ----- (3)

In a large number of reactions, electrical energy produced is not equal to chemical energy.

Electrical energy produced = decrease in free energy for cell reaction i.e. $-\Delta G = nFE$ or $\Delta G = -nFE$ Joules----- (4)

If we know emf E, ΔG can be calculated. The larger the value of cell potential the further the reaction is equilibrium.

1.2.2 Relation between E and ΔH

Enthalpy Change $\Delta H = nF[T(\delta E/\delta T)_P - E]$ ----- (5)

If we know emf and temperature coefficient of emf, ΔH can be calculated..

1.2.3 Relation between E and ΔS :

$$\Delta S = nF(\delta E/\delta T)_P \text{ ----- (6)}$$

1.2.4 Numerical Problems

- Emf of Weston Cadmium cell is 1.0183 V at 293 K and 1.0181 V at 298 K. Calculate ΔG , ΔH and ΔS of the cell reaction at 298 K.

Solution:- $\Delta G: \Delta G = -nFE$ $n = 2$ for the cell reaction;

$$F = 96,500 \text{ C} \quad E = 1.0181 \text{ V at 298 K}$$

$$\Delta G = -2 \times 96,500 \times 1.0181 \text{ J} = -196.5 \text{ KJ}$$

$$\Delta H: \Delta H = nF [T (\delta E / \delta T)_P - E]$$

$$(\delta E / \delta T)_P = 1.0181 - 1.0183 / 298 - 293 = -0.0002 / 5$$

$$= -0.00004 \text{ VK}^{-1}$$

$$T = 298 \text{ K}$$

$$\Delta H = 2 \times 96,500 \{ [298 \times (-0.00004)] - 1.0181 \}$$

$$= -198.8 \text{ KJ}$$

$$\Delta S: \Delta S = nF(\delta E / \delta T)_P$$

$$= 2 \times 96,500 \times (0.00004) = -7.72 \text{ JK}^{-1}$$

- The emf of the cell $\text{Cd}|\text{CdCl}_2 \cdot 2.5 \text{ H}_2\text{O}$ (saturated) || $\text{AgCl(s)}|\text{Ag}$ is 0.6753V and 0.6915 V at 298 K and 273 K respectively. Calculate ΔG , ΔH and ΔS of the cell reaction at 298 K.

Solution. Here $n = 2$, $E = 0.6753 \text{ V at 298 K and } 0.6915 \text{ V at 273 K}$.

$$\therefore (\delta E / \delta T)_P = (0.6753 - 0.6915) \text{ V} / (298 - 273) \text{ K} = -0.00065 \text{ V/K}$$

$$\text{Now at 298 K, } \Delta H = nF [T (\delta E / \delta T)_P - E]$$

$$= 2 \text{ mol} \times 96,500 \text{ C mol}^{-1} \{ [298 \text{ K} \times (-0.00065 \text{ V/K})] - 0.6753 \text{ V} \}$$

$$= -167.7 \text{ KJ}$$

$$\Delta G \text{ at } 298 \text{ K} ; \Delta G = -nFE = -2 \times 96,500 \times 0.6753 = -130.33 \text{ KJ}$$

$$\Delta S = nF(\delta E / \delta T)_P$$

$$= 2 \times 96,500 \times (0-00065) = -125.45 \text{ J.K}^{-1}$$

1.3 SINGLE ELECTRODE POTENTIAL

The potential of the single electrode is the difference of potential between a metal and the solution of its salt. i.e the tendency of an electrode to lose or gain electrons when in contact with its own ions in the solution. In a cell, the electrode with lower electrode potential has less tendency to undergo reduction and acts as an anode. The electrode with higher electrode potential has a higher tendency to undergo reduction and acts as a cathode.

Example: In case of Zn in ZnSO_4 solution acquires a negative charge (Fig. 1.3a).

$\text{M(s)} \rightarrow \text{M}^{n+} + n\text{e}^- (\text{aq})$ (1) Dissolution reaction and conversely, the metal shows the tendency to go into the solution as metal ion by losing electrons (Fig. 1.3b).

$\text{M}^{n+} (\text{aq}) + n\text{e}^- (\text{aq}) \rightarrow \text{M(s)}$ (2) Deposition reaction

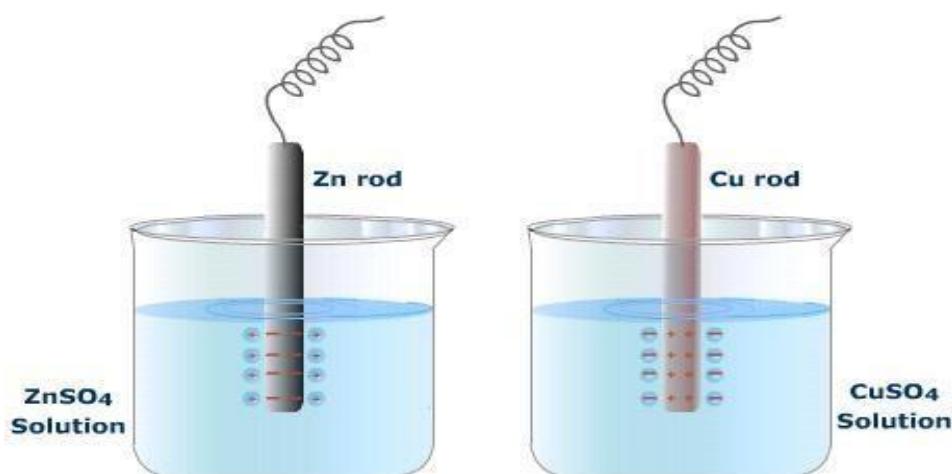


Fig.1.3a. Zinc ions move into solution leaving behind electrons making it electron rich

Fig.1.3b. Copper ions get deposited as copper leaving behind free negatively charged sulfate ions in solution makes the electrode electron poor

The rate of this reaction depends on,

- (i) the nature of the metal
- (ii) the temperature
- (iii) the concentration of metal ions in solution.

When a metal is placed in the solution of its own salt, the chemical reaction (1) or (2), takes place depending on whether the dissolution reactions are faster than deposition or vice versa. A dynamic equilibrium is established, because negative or positive charge developed on the metal attracts the positively or negatively charged free ions in the solution. Due to this attraction, the positive or negative ions remain quite close to the metal. Thus, a short layer of positive ions or negative ions as in the figure is formed at the junction of the electrode and the solution. This layer is called a Helmholtz electrical double layer. A difference of potential is consequently, set up between the metal and the solution. This potential difference will persist as long as the charge is allowed to remain on the metal; and this will prevent any further passing of the positive ions from or to the metal. At equilibrium the potential difference between the metal & solution becomes a constant value. The equilibrium potential difference so established is called the “electrode potential” of the metal. Thus, the electrode potential of a metal is the measure of the tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of unit molar concentration at 298K. Consequently, the tendency of an electrode to lose electrons is a direct measure of its tendency to get oxidized & this tendency, is called oxidation potential. Similarly, the tendency of an electrode to gain electrons is a direct measure of its tendency to get reduced and this tendency is known as reduction potential. By concentration, electrode potential refers to reduction potential.

1.3.1 Measurement of electrode potential

It is impossible to determine the absolute half cell potential We can only measure the difference in potential between two electrodes potentiometrically, by combining them to form a complete cell. All voltage measuring devices determine differences in potential. If one knob of voltmeter is connected to a test electrode, another one will make contact with the solution in the electrode compartment via another conductor. This second contact involves solid/solution interface and acts as a record half cell. The redox reaction must take place if the charge is to flow and potential is to be measured. A potential is associated with this second reaction and absolute half cell potential is not obtained. What we measure ultimately is the

difference between the half cell potential of test electrode and a half cell made up of the second contact and the solution. Therefore, absolute electrode potentials cannot be measured. We can only determine the relative value of electrode potential, if we can fix arbitrarily the potential of any one electrode. For this purpose, the potential of a standard hydrogen electrode (SHE) or normal hydrogen electrode (NHE) (i.e., a platinum electrode in contact with 1 M H^+ ion concentration and hydrogen gas at 1 atmospheric pressure is constantly bubbled through it) has been arbitrarily fixed as zero and the numerical values of electrode potentials of different electrodes are relative values w.r.t SHE. Therefore, single electrode potentials of electrodes are referred to as potentials on the hydrogen scale.

Sign of electrode potential: When an electrode is coupled with a SHE, if reduction occurs then EP is given a +ve sign e.g Copper electrode + SHE

- $Cu^{2+} + 2e^- \rightarrow Cu(s)$ reduction at copper electrode (cathode)
- $H_2(g) \rightarrow 2H^+ + 2e^-$ oxidation at hydrogen electrode (anode) $\rightarrow E^0 = 0.34$ volt

A +ve sign on the EP value indicates that the half cell acts as cathode and accepts electrons from the hydrogen electrode.

Similarly, when an electrode is coupled with SHE, if oxidation occurs then EP is given a -ve sign e.g . Zinc electrode + SHE

- $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$ (oxidation at Zinc electrode)
- $2H^+(aq) + 2e^- \rightarrow H_2(g)$ (reduction at Hydrogen electrode) $\rightarrow E^0 = -0.76$ volt

A -ve sign on the electrode potential value indicates that the half cell acts as an anode by releasing electrons to the hydrogen electrode.

1.3.2 Standard electrode potential:

Standard electrode potential is the electrode potential when the electrode is in contact with a solution of unit concentration at 298 K involving pure solids and liquids. If the electrode involves a gas, then the gas is at 1 atmospheric pressure. It is denoted by E° . When elements are arranged in increasing order (downwards) of their standard electrode potential, a series called electrochemical series is obtained. In a cell, the electrode with lower electrode potential has less tendency to undergo reduction and it acts as anode similarly electrode with higher electrode potential has higher tendency to undergo reduction and acts as cathode.

Reducing agents	Stable ions	Electrode half reaction E° volts
Lithium	Li^+	-3.03
Potassium	K^+	-2.92
Aluminium	Al^{3+}	-1.66

Zinc	Zn^{2+}	-0.76
Iron	Fe^{3+}	-0.44
Lead	Pb^{2+}	-0.13
H_2	2H^+	0
Copper	Cu^{2+}	0.34
Silver	Ag^+	0.80
Gold	Au^{3+}	1.52

Fig. 1.3.2. Selected standard electrode potentials

1.3.3 Nernst equation

Nernst equation is an expression of a quantitative relationship between electrode potential/cell potential and concentration of the electrolyte species in an electro-chemical reaction. i.e. mathematical expression that relates the potential of an electrode to the concentrations of those species in solution that are responsible for the potential. Consider a general redox reaction: $\text{M}^{n+}(\text{aq}) + n\text{e}^- \rightleftharpoons \text{M}(\text{s})$

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

E= Electrode potential at some moment in time

E° = Standard electrode potential

R= Universal gas constant (joules per mol K)

T= Temperature in Kelvin scale F= Faraday constant (96,500 Coulombs)

n = Number of electrons transferred in the half reaction/ cell reactions

$[\text{M}^{n+}]$ = Concentration of metal ion at that moment in time (moles per litre).

At 298 K, when the values of R.T and F are substituted, the equation reduces to,

$$E = E^\circ + \left(\frac{0.0592}{n} \right) \log [\text{M}^{n+}]$$

This expression is known as the Nernst equation for electrode potential at 298 K. From these equations, it is clear that,

- i) If the concentration of the solution (M^{n+}) is increased, the electrode potential increases and vice versa.
- ii) If the temperature is increased, the electrode potential increases and vice versa.

The Nernst equation can also be applied for the calculation of emf of a cell. Consider the cell reaction $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

The Nernst equation for the emf of the cell is

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303RT}{nF} \log [C]^c [D]^d / [A]^a [B]^b$$

At 298 K,

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

Where n is the number of electrons transferred during the cell reaction and E°_{cell} is the standard emf of the cell.

1.3.3.1 Significance of the Nernst equation

1. It can be used to calculate the potential of a cell that operates under non-standard conditions. The Nernst equation tells us that a half-cell potential will change by 59 millivolts per 10-fold change in the concentration of a substance involved in one-electron oxidation or reduction; for two electron processes, the variation will be 28 millivolts per ten fold concentration change. Thus for the dissolution of metallic copper



the potential $E = (-0.337) - .0295 \log [\text{Cu}^{2+}]$ becomes more positive (the reaction has a greater tendency to take place) as the cupric ion concentration decreases.

2. It can be used to measure the equilibrium constant for a reaction. At equilibrium the overall cell potential for the reaction is zero. i.e. $E=0$

Nernst equation,

$$0 = E^{\circ} - \frac{RT}{nF} \ln K_c$$

$$K_c = e^{nFE^{\circ} / RT}$$

1.4 Calomel electrode

The calomel electrode (Fig.1.4.1), a mercury mercurous chloride electrode develops + 0.242 V at 289 K when the KCl solution is saturated. It has been found that the potential of the calomel electrode, on the hydrogen scale varies with the concentration of the potassium chloride solution used. The concentration of KCl solution used is either decinormal, normal or saturated. Correspondingly, the electrode is known as decinormal, normal or saturated calomel electrode respectively.

1.4.1 Construction & Working:

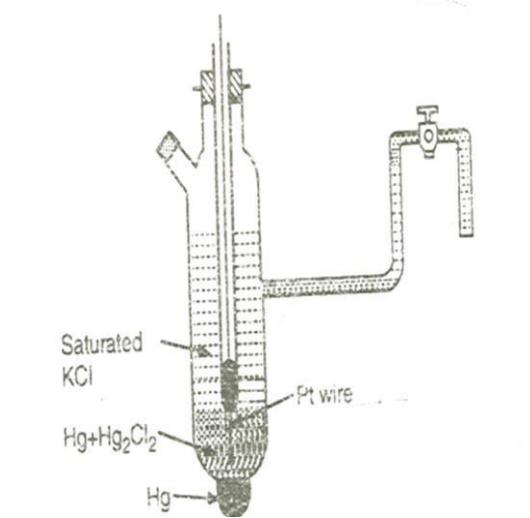


Fig.1.4.1 Schematic diagram of calomel electrode.

It consists of a tube, in the bottom of which is a layer of mercury, over which is placed a paste of mercury and mercury chloride. The remaining portion of the cell is filled with a solution of normal or decinormal or saturated solution of KCl. A platinum wire sealed at its end fixed into the main tube dipping into the mercury layer is used for making electrical contact. The electrode can be represented as $\text{Hg(l)}/\text{Hg}_2\text{Cl}_2(\text{sat'd})/\text{KCl}^-(\text{sat'd/xM})$

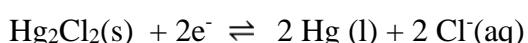
The calomel electrode can act as anode or cathode depending on the nature of other electrode of the cell. When it acts anode, the electrode reaction is

- $2\text{Hg(l)} \rightarrow \text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^-$
 - $\text{Hg}_2^{2+}(\text{aq}) + 2\text{Cl}^-(\text{aq}) \rightarrow \text{Hg}_2\text{Cl}_2(\text{s})$
-
- $2\text{Hg(l)} + 2\text{Cl}^-(\text{aq}) \rightarrow \text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^-$

When it acts as cathode, the electrode reaction is,

- $\text{Hg}_2^{2+}(\text{aq}) + 2\text{e}^- \rightarrow 2\text{Hg(l)}$
 - $\text{Hg}_2\text{Cl}_2(\text{s}) \rightarrow \text{Hg}_2^{2+}(\text{aq}) + 2\text{Cl}^-$
-
- $\text{Hg}_2\text{Cl}_2(\text{s}) + 2\text{e}^- \rightarrow 2\text{Hg(l)} + 2\text{Cl}^-(\text{aq})$

The net reversible electrode reaction is,



Electrode potential is given by

$$E = E^{\circ} - \frac{2.303 RT}{2F} \log [Cl^-]^2$$

$$\frac{2F}{}$$

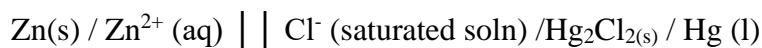
$$= E^{\circ} - 0.0591 \log [Cl^-] \text{ at } 298 \text{ K}$$

1.4.2 Uses:

Since the electrode potential is a constant it can be used as a secondary reference electrode to replace the inconvenient SHE for potential measurements.

- To determine the electrode potential of the unknown electrode

For example: The test electrode, $Zn_{(s)} / Zn^{2+}_{(aq)}$ is coupled with a saturated calomel electrode.



The emf of the so formed cell is determined experimentally by potentiometric method.

Then

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} = 0.2444 - E_{\text{zn}}$$

$$E_{\text{zn}} = 0.2444 - E_{\text{cell}}$$

- To determine the pH of a solution cell: $Hg(l) / Hg_2Cl_2(s) // H^+ / pt, H_2(g)$

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

$$= 0.242 - (-0.0592 \text{ pH})$$

$$pH = E_{\text{cell}} - 0.242/0.0592$$

1.4.3 Advantages

- It is very simple to construct.
- It can be used for a long time without much attention.
- Electrode potential is stable over a long period (reproducibly).
- It has the low temperature coefficient of emf.
- It is less prone to contamination because the mercury/ mercurous chloride interface is protected inside a tube not in direct contact with the electrolyte.

1.4.4 Disadvantages

- Calomel electrodes should not be used above 50°C because the mercurous chloride breaks down, yielding unstable readings. This is important if substantial temperature changes occur during measurement.
- Calomel electrode should be used with proper precaution as mercury compounds are toxic.

1.5 Ion Selective Electrode.

The electrode which is sensitive to a specific ion present in an electrolyte whose potential depends upon the activity of a specific ion in the electrolyte is called an ion selective electrode. The magnitude of the potential of this electrode is an indicator of the activity of the specific ion in the electrolyte. Example for this type of electrode is glass electrode.

1.5.1 Glass electrode: Construction

Glass Membrane

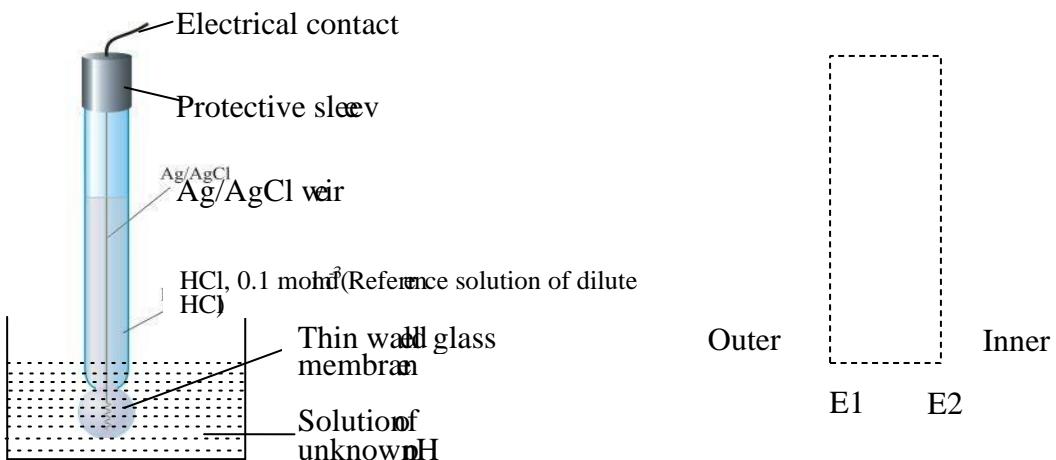


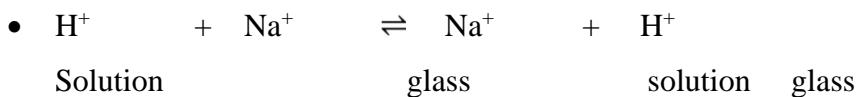
Fig.1.5.1a. Schematic diagram of the Glass electrode

Fig. 1.5.2b. Line sketch of a glass membrane showing outer analyte solution and internal reference solution.

The electrode consists of a thin glass membrane, typically about 0.03 to 0.1 mm thick, sealed onto one end of a heavy-walled glass tube. A special variety of glass (Corning 015 glass with approximate composition 20 % Na₂O, 6 % CaO & 72 % SiO₂) is used which has a low melting point and high electrical resistance. The glass bulb is filled with a solution of constant pH (0.1 M HCl). A small volume of saturated silver chloride is contained in the tube. A silver wire in this solution forms a silver/silver chloride reference electrode which is connected to one of the terminals of a potential measuring device. The internal reference electrode is a part of the glass electrode and it is not the pH sensing element. Only the potential that occurs between the outer surface of the glass bulb and the test solution responds to pH changes.

1.5.2 Working: A silicate glass used for membranes consists of an infinite 3D-network of SiO₄⁴⁻ groups in which each silicon is bonded to four oxygen and each oxygen is shared by two silicones. There are sufficient cations to balance the negative charge of the silicate groups within the interstices of this structure. Singly charged cations such as sodium and lithium are mobile in the lattice and are responsible for electrical conduction within the membrane. The glass is a partially hydrated aluminosilicate containing sodium or calcium ions. The hydration of a pH sensitive glass membrane involves an ion-exchange reaction between singly charged cations in the interstices of the glass lattice and protons from the solution. The process involves univalent cations exclusively because divalent cations are too strongly held

within the silicate structure to exchange with ions in the solution and hence immobile. The ion-exchange reaction can be written as



The Na^+ ions on the glass membrane are exchanged for H^+ ions in the solution. The potential of the electrode is controlled by the difference between the hydrogen ion concentration inside and outside the thin glass membrane. Since the H^+ ion concentration inside the electrode is constant, the electrode's potential varies only with the concentration of H^+ in the solution outside. Thus the potential arises from the difference in positions of ion-exchange equilibrium on each of the two surfaces. The surface exposed to the solution having the higher H^+ concentration becomes positive with respect to the other surface. This charge difference or potential serves as the analytical parameter when the pH of the solution on one side of the membrane is held constant. Evidently the selectivity of glass electrodes is related both to the ability of the various monovalent cations to penetrate into the glass membrane and to the degree of attraction of the cations to the negative sites within the glass.

1.5.3 Electrode Potential of GE

The overall potential of the glass electrode has three components; 1) The boundary potential E_b , which varies with the pH of the analyte solution. It is made up of two potentials, E_1 & E_2 which develop at the two surfaces of the glass membrane i.e. the potential developed at the inner glass surface & the potential developed at the outer glass surface.

$$E_b = E_1 - E_2 \quad \text{_____} \quad (1)$$

Where E_b is the boundary potential

E_1 = potential developed at the interface between the exterior of the glass and the analyte solution

E_2 = Potential developed at the interface between the internal solution and the interior of the glass. The boundary potential is related to the concentration of hydrogen ion in each of the solution by the Nernst-like equation.

$$E_b = E_1 - E_2 = 0.0592 \log C_1 / C_2 \quad \text{_____} \quad (2)$$

Where C_1 = concentration of the analyte solution

C_2 = concentration of the internal solution

For a glass pH electrode the hydrogen ion concentration of the internal solution is held constant.

So eqn. (2) becomes

$$E_b = K + 0.0592 \log C_1 \quad (3) \quad (\text{Recall } \text{pH} = -\log [H^+])$$

$$E_b = K - 0.0592 \log \text{pH} \text{ where } K = -0.0592 \log C_2$$

The boundary potential is then a measure of

- 1) the hydrogen ion concentration of the external solution.
- 2) The potential of the internal Ag/AgCl reference electrode. $E_{\text{Ag/AgCl}}$.
- 3) A small unpredictable contribution called the asymmetry potential, E_{asym} .

The sources of the asymmetry potential include the following.

- i) Differing conditions of strain in the two glass surfaces during manufacture
- ii) Mechanical abrasion on the outer surface during use
- iii) Chemical etching of the outer surface during use.

The asymmetry potential changes slowly with time. The glass electrode potential can be written in the equation form as

$$E_G = E_b + E_{\text{Ag/AgCl}} + E_{\text{asym}} \quad (4)$$

Substitution of eqn – (3) for E_b , gives

$$E_G = K + 0.0592 \log C_1 + E_{\text{Ag/AgCl}} + E_{\text{asym}}$$

$$= K - 0.0592 \log \text{pH} + E_{\text{Ag/AgCl}} + E_{\text{asym}} \quad (5)$$

$$E_G = E_G^{\circ} - 0.0592 \text{ pH} \quad (6)$$

where $E_G^{\circ} = K + E_{\text{Ag/AgCl}} + E_{\text{asym}}$. a combination of three constant terms = constant To measure the hydrogen ion concentration of the test solution, the glass electrode (indicator electrode) must be combined with an external reference electrode, which is required for all kinds of ion-selective electrode determinations.

1.5.4 Applications: Determination of pH:

The glass electrode has an emf that changes with hydrogen ion concentration, i.e the glass electrode is the most important indicator electrode for hydrogen ion. It is used for the

measurement of pH under many conditions and normally calomel electrode is used as reference electrode to complete the cell (Fig.1.4.4)

Cell: SCE / Test solution / GE

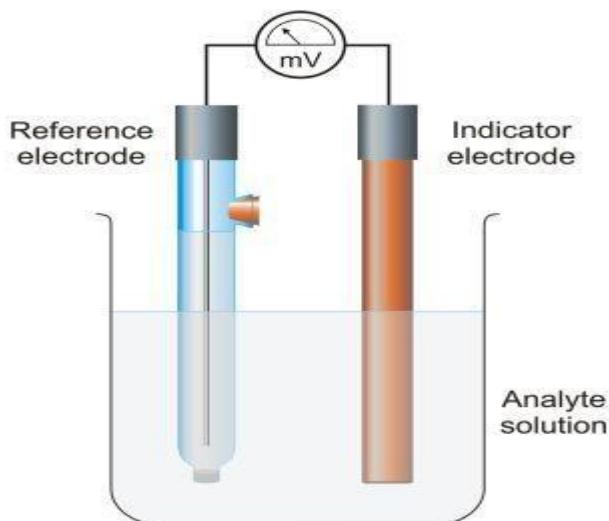


Fig.1.4.4. Set up of indicator electrode and reference electrode for the measurement of pH.

$$E_{\text{cell}} = E_{\text{glass}} - E_{\text{calomel}} \text{ where } E_{\text{glass}} = \text{the E.P. of the glass electrode.}$$

$$E_{\text{calomel}} = \text{the E.P. of the SCE}$$

$$E_{\text{cell}} = E^{\circ}_{\text{G}} - 0.0592 \text{ pH} - 0.2444$$

The E°_{G} value of a glass electrode can be determined by dipping the glass electrode in a solution of known pH. Typical fields are the clinical & food analysis, environmental monitoring (industrial waste acidity of rain) and process control (fermentation, boiler water, galvanization & precipitation)

1.5.5 Advantages:

- It can be used without interference in solutions containing strong oxidants, strong reductants, proteins, viscous fluids and gases as the glass is chemically robust.
- The glass electrode gives accurate results in the pH range 2 – 10. With some special glass (by incorporation of Al_2O_3 or B_2O_3) measurements can be extended to pH values up to 12.
- It is immune to poisoning and is simple, robust and easy to operate.

- The equilibrium is reached quickly & the response is rapid.
- It can be used for very small quantities of the solutions. Small electrodes can be used for pH measurement in one drop of solution in a tooth cavity or in the sweat of the skin (micro determinations using microelectrodes)
- The glass electrode is much more convenient to handle than the inconvenient hydrogen gas electrode.
- Glass electrodes which are selective for Li^+ , Na^+ , Cs^+ , Ag^+ and NH_4^+ ions are commercially available and these special electrodes are useful for measuring the above ions.

1.5.6. Disadvantages:

- The bulb of this electrode is very fragile and has to be used with great care. The sensitive tip is easily scratched and ruined.
- The alkaline error arises when a glass electrode is employed to measure the pH of solutions having pH values in the 10-12 range or greater. In the presence of alkali ions, the glass surface becomes responsive to both hydrogen and alkali ions. Hence the measured pH values are low and thus the glass pH electrode gives erroneous results in highly alkaline solutions.
- The acid error results in highly acidic solutions (pH less than zero) Measured pH values are high.
- Dehydration of the working surface may cause erratic electrode performance. It is crucial that the pH electrode be sufficiently hydrated before being used. When not in use, the electrode should be stored in an aqueous solution because once it is dehydrated; several hours are required to rehydrate it fully.
- As the glass membrane has a very high electrical resistance (50 to 500 $\text{M}\Omega$), the ordinary potentiometer cannot be used for measurement of the potential of the glass electrode. Thus special electronic potentiometers are used which require practically no current for their operation.
- Standardization has to be carried out frequently because asymmetry potential changes gradually with time. It is better to determine E°_G for a glass electrode before use.
- The commercial version is moderately expensive.
- To some extent, the constant E°_G is a function of the area of glass in contact with the acid analyte. For this reason, no two glass electrodes will have the same value of E°_G .

Note that E°_G depends on a particular glass electrode used & it is not a universal constant.

1.6 BATTERY TECHNOLOGY

1.6.1 Introduction

Can you imagine a world without batteries? The clock on your wall requires a battery for it to work. The watch on your wrist goes on a battery. The motor vehicle needs a battery for it to start and take you to your destination. Battery is the backbone of UPS to run your computer without interruption. After a day's work, if you pick-up the remote control of the television, it is again the battery that helps you to change channels of the T.V. Cameras, laptop computers, cellular phones, key chain laser, heart pacemaker and children toys – they all require batteries.

Batteries are used for so many different purposes and different applications require batteries with different properties. The battery required to start a car must be capable of delivering a large electrical current for a short period of time. The battery that powers a cardiac pacemaker must be small, rugged, leak proof, compact and capable of delivering a steady current for an extended period of time. In UPS systems, longer and consistent backup is needed. Batteries for hearing aids must be above all tiny. Batteries for torpedoes and submarines must be stable during storage and give high power for short times & certainly rechargeable. For a lap-top computer, a battery in the form of a flexible sheet distributed around the case is much preferred. Batteries remain an enormous industry with a turnover of billions of pounds worldwide.

1.6.2 Classification of commercial cells

Primary Cells: They are galvanic cells which produce electricity from chemicals that are sealed into it when it is made. This type of cells cannot be recharged as the cell reaction cannot be reversed efficiently by recharging. Once the cell reaction has reached equilibrium the cell must be discarded. No more electricity is generated and we say the battery is ‘dead’. These are also known as ‘throw – away’ batteries or irreversible batteries.

Eg: Dry cell, Lithium copper sulfide cell

Secondary cells: A secondary cell is rechargeable by passing current through it. In the charging process, an external source of electricity reverses the spontaneous cell reaction and restores a non-equilibrium mixture of reactants. After charging, the cell can be used for supplying current when required, as the reaction sinks toward equilibrium again. Thus as the

secondary cell can be used through a large number of cycles of discharging and charging. Such cells are also known as rechargeable cells, storage cells, or accumulators.

Eg. Lead-acid batteries, Nickel-cadmium cell, Lithium- ion battery

1.6.2.1 Requirements of Primary Battery:

- Compact, lightweight and must be fabricated from easily available raw materials.
- Economic and have benign environmental properties
- Should have a high energy density, longer shelf life
- Provide constant voltage and should have a long discharge period

1.6.2.2 Requirements of Secondary Battery

- Long shelf-life in both charged & discharged conditions
- Longer cycle life and design life
- High power to weight ratio
- Short time for a recharge.
- High voltage & high energy density

1.6.2.3 Differences between Primary and Secondary batteries

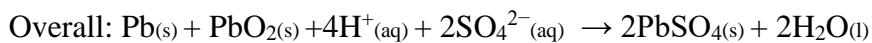
Primary Batteries	Secondary Batteries
1. Cell reaction is irreversible	Cell reaction is reversible
2. They must be discarded after its active elements have been consumed	They may be recharged a number of times from an external d.c. source during its useful life
3. Have a relatively short shelf life	Have a very long shelf life
4. Function only as galvanic cells	Function as galvanic cells during discharge as & as electrolytic cells during the charging process.
5. They cannot be used as energy storage devices	They can be used as energy storage devices (e.g. solar/ thermal energy converted to electrical energy)
6. They cannot be recharged	They can be recharged.
e.g. Dry cell, Li-MnO ₂ battery	e.g. Lead acid battery, Ni-cd battery

1.6.3 Lead Storage Battery (Lead Accumulator or Car Battery or The acid battery)

Construction: The electrodes are lead grids to maximize its surface area. The anode grid is filled with finely divided spongy lead (Pb) and the cathode grid is packed with lead dioxide (PbO₂). Both electrodes are submerged in a sulfuric acid solution (H₂SO₄) having a specific gravity of about 1.25 that acts as the electrolyte. Anode and cathode grids are separated by insulators like strips of wood, rubber or glass fiber. In car batteries, six cells are connected in series (anode to cathode) to produce a 12–volt battery. The battery is encased in a plastic container or hard vulcanized rubber vessel. The cell doesn't need to have a separate anode and cathode compartments because the oxidizing and reducing agents are both solids (PbO₂ & Pb) that are kept from coming in contact by the presence of insulating spacers between the grids. Both anode and cathode are immersed in a common electrolyte (i.e. cell without liquid junction). This is an example of a ‘wet cell’, because the electrolyte is an aqueous solution of sulphuric acid. The lead acid battery is very widely manufactured – 300 million units are made each year.

At the cathode:

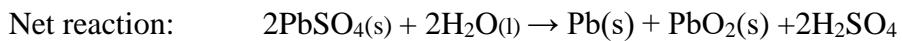
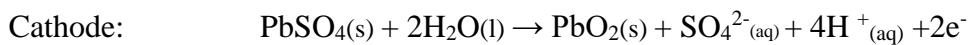
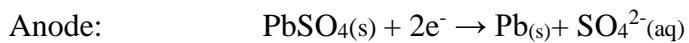
- PbO_{2(s)} + 4H⁺_(aq) + 2e⁻ → Pb²⁺_(aq) + 2H₂O_(l)
 - At anode
 - Pb²⁺_(aq) + SO₄²⁻_(aq) → PbSO_{4(s)}
-
- PbO_{2(s)} + 4H⁺_(aq) + SO₄²⁻_(aq) + 2e⁻ → 2 PbSO_{4(s)} + 2H₂O_(l)
-



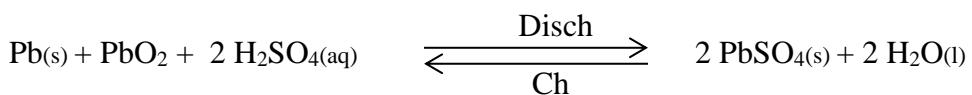
Explanation: At the anode, lead atoms lose two electrons (e⁻) and become positively charged lead ions (Pb²⁺). The lead ions combine with the sulfate ions (SO₄²⁻) in the sulfuric acid solution to produce lead sulfate (PbSO₄). At the cathode, lead dioxide gains electrons, releasing oxygen, which attaches to hydrogen ions (H⁺) to produce water (H₂O (l)) and lead ions. The lead ions react with sulfate ions to produce lead sulfate. As this reaction progresses, the flow of electrons creates an electric current. Lead sulfate adheres on each electrode and water increases. The concentration of sulfuric acid decreases and the amount of lead and lead dioxide decrease. When the reactants are depleted, the battery stops producing electricity. The reaction can be reversed by recharging the battery & the PbSO₄ formed during discharge remains adhered on each electrode and is available at the site during recharging. The nominal

voltage of each cell is about 2.1 V. The lead storage battery is designed to operate reversibly, so that it can be used for the storage of electrical energy. They are called storage batteries because their essential function is to store electrical energy. It is used to store energy in chemical form.

Reactions during Charging:



Recharging is possible because PbSO_4 formed during discharge adheres to the electrodes. By attaching an external power source to a battery (>2 volts), a current runs through the poles in the opposite direction from normal discharge. This changes the lead sulfate and water back into the original reactants, lead dioxide and sulfuric acid, i.e. the electrodes return to their former composition and the sulfuric acid is regenerated. Charging, therefore, produces a gradual increase in the sulfuric acid concentration. Since the level of charge on a storage battery is related to sulfuric acid concentration, **the specific gravity of the H_2SO_4 solution is a measure of the operational condition of a battery.** A charged battery at room temperature with its electrolyte at normal concentration supplies a potential difference of 2.1 to 2.2 V. The complete reaction cycle of a lead acid storage battery is as follows.



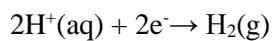
In an automobile, the energy necessary for recharging the battery is provided by the generator driven by the engine. As the external source forces electrons from one electrode to another, the PbSO_4 is converted to Pb at one electrode & to PbO_2 at the other.

Overcharging:

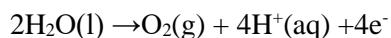
Electrolysis of water: The net reaction can be summarized by the equation.



No gases will be liberated on charging as long as lead ions are present in solution. If the electrolysis is permitted to proceed further, hydrogen gas is formed at the cathode and oxygen gas is evolved at the anode. The hydrogen ions are discharged at the cathode through the reaction



Sulphate ions are resistant to oxidation and are not discharged at the cathode. Water is oxidized at the anode in preference to SO_4^{2-}



Consequences: (i) Excessive charging may reduce the acid level and may damage the exposed electrode grids (ii) In extreme cases, there will be dangerous high-pressure build-up that can lead to a serious risk of explosion. In more normal circumstances, the older version of the battery needs to be ‘topped up’ from time to time.

Recent years have seen the introduction of “maintenance – free batteries” without a gas – release vent. Here the gassing is controlled by careful choice of the composition of the lead alloys used i.e. by using a Pb-Ca (0.1 %) as the anode which inhibits the electrolysis of water. Alternatively, some modern batteries contain a catalyst (e.g. a mixture of 98% ceria (cerium oxide) & 2% platinum) that combines the hydrogen and oxygen produced during discharge back into the water. Thus the battery retains its potency and requires no maintenance. Such batteries are sealed as there is no need to add water and this sealing prevents leakage of cell materials.

Applications: The many battery designs available for a wide variety of uses can be classified into three main categories. (a) Automotive (b) Industrial & (c) Consumer batteries.

The automotive type is used in cars and trucks, to provide a short burst of power for starting the engine. It is incorporated as an essential accessory into the starting circuit of internal combustion engines for starting, lighting & ignition (SLI). Units normally have nominal voltages of 12 V for LMVS and 24 V for HGVS. It is still playing a major role in transportation, powering literally millions of ICES in automobiles. The industrial batteries are used for heavy-duty applications such as motive and standby power. This class of batteries is used to operate electric trucks, submarines and mine locomotives. They also provide power for the air conditioning and lighting systems. It is used in the stationary back-up power applications such as telecommunication systems, to ensure that, for example, the telephone network will continue to operate even in the event of a mains power failure. Such batteries are kept in hospital operating theaters, railway signal centres and other places where a power failure might be disastrous and is used to supply electrical power during emergencies. The consumer batteries are used in emergency lighting systems, security and alarm systems, public address systems, power tools, UPS in computers, and small engine starting including electronic vehicles.

Advantages:

- A lead storage battery is highly efficient. The voltage efficiency of the cell is defined as follows.
- Voltage efficiency = average voltage during discharge

- average voltage during charge
- The voltage efficiency of the lead – acid cell is about 80 %.
- The near reversibility is a consequence of the faster rate of the chemical reactions in the cell i.e. anode oxidizes easily and cathode reduces easily leading to an overall reaction with a high negative free energy change.
- A lead – acid battery provides a good service for several years. The number of recharges possible range from 300 to 1500, depending on the battery's design and conditions. The sealed lead-acid batteries can withstand up to 2000 – recharging. Time required for recharging is relatively low i.e about 2-8 hours.
- The battery has low internal self – discharge.
- A typical car battery provides a voltage of 12 V. This is not a large voltage, but the battery can provide a large current. E.g. over 10 A, without being destroyed.

Disadvantages:

- If left unused in partially charged condition, it can be ruined in a short time by nucleation and the growth of relatively large PbSO_4 crystals, which are not easily reduced or oxidized by the charging current. This disaster is known as ‘sulfation’.
- The lead acid battery has low energy storage to weight ratio i.e. its chief disadvantages is its great weight.(energy density $\sim 35 \text{ wh / kg}$)
- The cell potential decreases with a decrease in concentration of sulfuric acid. During the discharge process sulfuric acid is consumed and water is produced. So the solution of sulfuric acid in the cell becomes less concentrated. The state of charge of the cell can be judged by the concentration of sulfuric acid in the liquid and this is usually done with a simple device to measure the density of the liquid. The density of a healthy, fully charged battery is $\geq 1.25 \text{ g/mL}$.
- The battery is not efficient at a lower temperature. For a battery to function properly, the electrolyte must be fully conducting. There will be an increase in the viscosity of the electrolyte due to a decrease in the temperature. This leads to a decrease in the cell potential.
- Overcharging may damage the exposed electrodes and may also lead to an explosion in extreme cases. Sulfuric acid is highly corrosive liquid. In the event of an explosion, the electrolyte is sprayed on to the individual who is working on the battery. Therefore, safety goggles must be worn when working with these batteries.

- Lead is toxic and hence environmental & health problems arise due to careless disposal by consumers.
- The corrosion of the lead grid at the lead dioxide electrode is one of the primary causes of lead acid battery failure.

1.6.4 Nickel-Cadmium Cell

Construction: NiCad cell consists of a nickel wire gauze electrode grids. The anode grid consists of spongy cadmium metal and the cathode grid contains the nicked (III) compound NiO(OH) . The electrolyte is a concentrated solution of KOH. It is the electrolyte of choice because of its compatibility with the various electrodes, good conductivity and low freezing point temperature (about -30°C). Anode and cathode are separated by a very thin separator. The contents are encased as a sealed unit in a steel case.

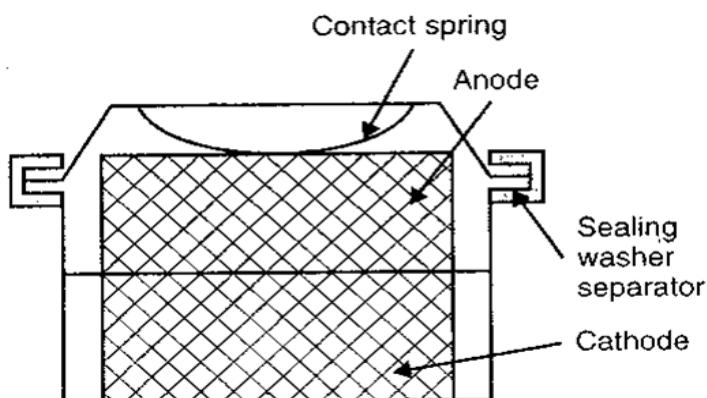
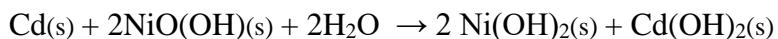
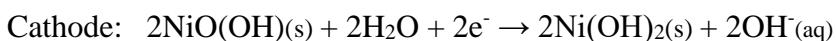
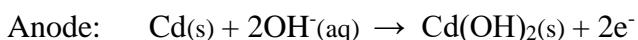


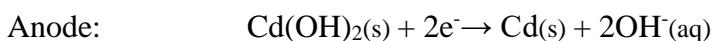
Figure 1.6.4 Schematic representation of NiCad cell

Working:

Discharging reactions

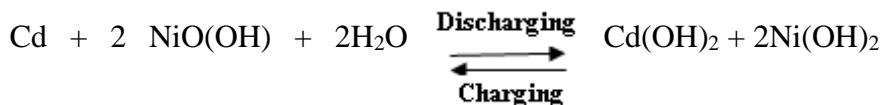


Charging reactions:



Explanation: At anode cadmium metal undergoes oxidation from 0 to +2, leaving behind two electrons for every atom oxidized, as the cell discharges. At cathode nickel is reduced

from the +3 oxidation state (in nickel oxide hydroxide) to +2 (in nickel hydroxide). Note that OH⁻ is not used up as the cell is discharged. Therefore, there is no voltage drop through most of the useful life of the battery as it discharges. The net reaction can take place until the active materials are exhausted, during charging process, the cadmium hydroxide is reconverted into cadmium and the nickelous hydroxide is reconverted to nickeloxide hydroxide. The overall chemical reaction of the Ni-Cd system may be represented as



The cell must be recharged by applying the correct dc charging voltage.

Applications: Nicad cells are available in standard sizes (AA, D, C,F etc.) for use in flash lights, photoflash units and portable electronic equipment such as radios, micro tape recorders, calculators, cordless phones, electronic shavers, drills & garden tools. It is also used in emergency lighting systems, alarm systems, personal audio equipment (walkman type cassette players), kitchen appliances and other battery powered small tools, toys & games.

Advantages:

- Ni-cad batteries can be recharged many times because the solid products of the electrode reactions adhere to the surface of the electrodes. Normally this battery can withstand up to 3000 – recharging (longer cycle life)
- They maintain nearly constant voltage level throughout their discharge. Note that there is no change change in the electrolyte composition during the operation.
- It can be left unused for long periods of time at any state of charge without any appreciable damage (i.e. long shelf life).
- It can be encased as a sealed unit like the dry cell because gassing will not occur during nominal discharging or recharging.
- They possess a longer design life. It can be extended upto 30 years or more if maintained.
- They exhibit good performance ability at low temperatures.
- They can be used to produce large instantaneous currents as high as 1000-8000 A for one second.

Disadvantages:

- It poses an environmental pollution hazard due to careless disposal by consumers and produces health problems (decreases range from asthma to cancer) due to higher toxicity of metallic cadmium than lead.

- Cadmium is a heavy metal and its use increases the weight of batteries, particularly in larger versions. The energy density is approximately 40 Wh/kg.
- Cost of cadmium metal and hence the cost of construction of NiCad batteries is high. The overall capital cost of these batteries is roughly then higher than that of lead storage batteries.
- The KOH electrolyte used is a corrosive hazardous chemical. It is a poison and if ingested attacks the throat and stomach linings. Eye contact can result in serve burns and blindness. Protective clothing and face shields or goggles should be worn while performing maintenance work.

1.6.5 Lithium ion cells

Lithium metal cannot be used safely in secondary batteries. Hence, various lithium compounds have been made, which are used in rechargeable batteries, commonly known as Lithium –Ion Cells. In these type of batteries, a lithiated metal oxide such as LiCoO_2 , LiV_2O_5 , LiMn_2O_4 etc is inserted into the cathode which consists of a layered graphite crystal. The electrolyte is normally LiPF_6 , but LiBF_4 can also be used as LiPF_6 is not corrosion resistant.

Construction:

The anode is a lithium-carbide type intercalate (Li_xC_6). The cathode is a transition metal oxide MO_2 of variable oxidation state (MnO_2 , CoO_2 , NiO_2) which can intercalate lithium usually cobalt dioxide, CoO_2 is used. The electrolyte is usually inert polar dry ether or carbonate (diethyl carbonate or propylene carbonate), in which a conductivity salt such as LiPF_6 or LiBF_4 is dissolved.

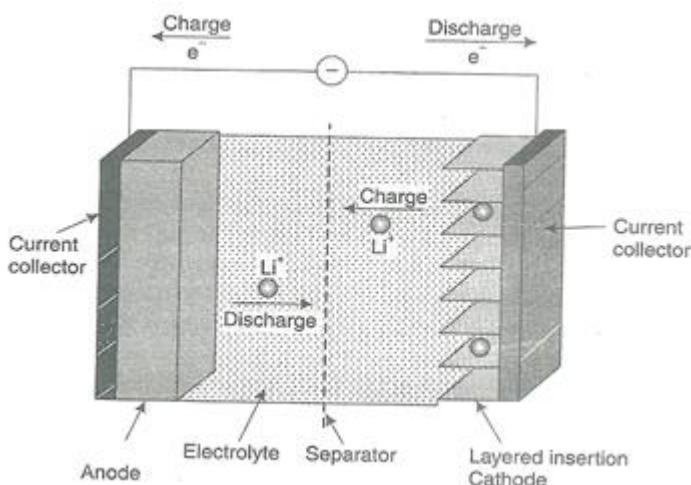


Figure 1.6.5 Schematic diagram of Rechargeable lithium ion battery

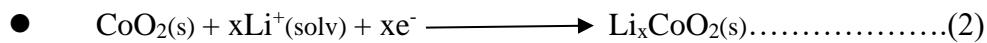
Working: Graphite has a layered structure and its electrochemically reduced in an aprotic organic electrolyte containing lithium salts and lithium ion intercalated (or doped) between the layers of graphite to form Lithium-Graphite intercalated compound (GIC). Li-GIC undergoes oxidation leaving an electron.

At anode:

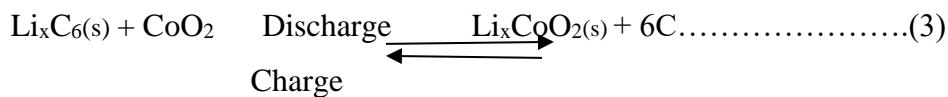


When a negative electrode is discharged, lithium is deintercalated (undoped) from lithiated graphite and lithium ions dissolve into the electrolyte. The lithium content in the LiCoO₂ electrode reversibly changes during charge and discharge as indicated in the following equation:

At cathode:



Net cell reaction:



Explanations: It is called as a lithium ion battery to emphasise that it contains no lithium metal. Both the electrodes are intercalation compounds. The electrode on the left serves as the anode when the cell discharges. It is a special intercalation compound consisting of a graphite host into which lithium ions have been electrochemically inserted between the carbon atom layers. The lithiated graphite is written as Li_xC_6 . During the discharge, the lithium ions are extracted by the half-reaction (1). The electrode that serves as cathode during discharge is normally cobalt dioxide. The reduction half reaction is cathode during discharge is normally cobalt dioxide. The reduction half reaction shown in eq.(2), where cobalt undergoes reduction from IV to III oxidation state. The overall reaction is shown in eq.(3). During discharge the Li^+ ions spontaneously migrate from the lithium graphite anode to the CoO_2 cathode enabling current to flow through the external circuit. When charged, cobalt ions are oxidized and lithium ions migrate into the graphite, when discharging the battery delivers energy to the external load and when charging it receives energy from a d.c. power source. The electrode that acts as an anode, during discharging becomes a cathode when its charging.

Applications:

- Lithium-ion batteries are most commonly used in applications where one or more of the advantages (size, weight or energy) outweigh the additional cost, such as mobile telephones and mobile computing devices.

- Lithium-ion-polymer batteries are used when the battery design matters in a particular application as different designs are possible (Cylindrical, jelly-roll design, flat rectangular).
- It is used in current-generation laptops, cellular phones, video-recorders.
- It is also used in portable CD players, televisions and implantable medical devices.

Advantages:

- Lithium-ion batteries were designed to overcome the safety problems associated with the highly reactive properties of Lithium metal.
- Long cycle life (400-1200 cycles).
- They are smaller, lighter and provide greater energy density than either nickel-cadmium or nickel-metal-hydride batteries
- They can be operated in a wide temperature range and can be recharged before they are fully charged.
- Typically designed to be recharged in the device rather than in an external charger.
- The average voltage of a Li-ion battery is equivalent to three Ni-Cd cells.

Disadvantages:

- Poor charge retention.
- The self discharge rate is about 10% per month.
- Its prices are high compared to other types of cells commonly used.

1.7 Fuel cells

A fuel cell is a galvanic cell of a special type in which chemical energy contained in a fuel – oxidant system is converted directly into electrical energy in a continuous electrochemical process. It is an energy conversion device or electricity producer. The fuel cell has two electrodes and an electrolyte like a primary cell. The reactants (i.e. fuel + oxidant) are constantly supplied from outside and the products are removed at the same rate as they are formed.

Cell: Fuel/ electrode/electrolyte/electrode/oxidant.

Anode: Fuel + oxygen ----->Oxidation products+ ne-

Cathode: Oxidant + ne⁻ ----->Reduction products

A fuel cell consists of fuel, electrodes, electrolyte, & oxidant. Fuel undergoes oxidation at the anode and oxidant gets reduced at the cathode. The cell can produce current as long as the reactants are supplied. Most fuel cells produce low voltages, commonly less than one volt, So a number of them are connected in series in “fuel batteries.”

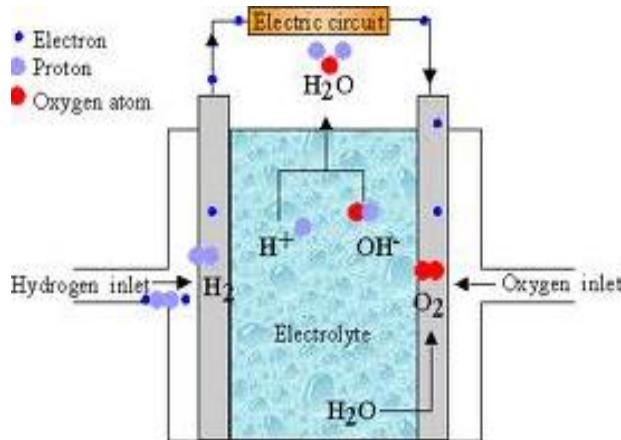


Figure 1.7 Fuel cell

Eg:- H_2-O_2 fuel cell, CH_3OH-O_2 fuel cell, Solid-oxide fuel cell, Molten carbonate fuel cell

1.7.1 Advantages of fuel cells

- High fuel to electricity conversion efficiency of 70-75 % while a thermal power plant converts 35-40% chemical energy of coal into electrical energy.
- Fuel cell products do not cause pollution problems such as noise pollution, chemical pollution and thermal pollution normally associated with conventional power plants.
- Fuel cell power plants can be located near the point of use electricity such as on an urban location,rather than at a remote place. So transmission and distribution loss (~30%) could be avoided.
- A fuel cell will produce a steady electric current as long as fresh reactants are available.

1.7.2 Classification of fuel cells

S. No.	Fuel cell type	Electrolyte used
1	Polymer electrolyte	Polymer membrane
2	Direct methanol	Polymer membrane
3.	Alkaline	Potassium hydroxide
4.	Phosphoric acid	Phosphoric acid
5.	Molten carbonate	Lithium/potassium carbonate
6.	Solid oxide	Yittria stabilized zirconia

1.7.3 Alkaline fuel cell (AFC)

The hydrogen gas is continuously supplied at the anode and pure oxygen gas is continuously supplied at the cathode from an external reservoir. The cell operates at about $80\text{ }^\circ\text{C}$ and the normal voltage is 1.10 V. At the anode, hydrogen is oxidized to the H^+ ions, which are

neutralized by the OH^- ions of the electrolyte, forming water and electrons are released. At the cathode, oxygen and water take electrons to form hydroxide ions. The overall reaction is equivalent to the combustion of hydrogen. The only product discharge by the cell is water vapor that escapes through the exhaust point. Note that the gases H_2 and O_2 diffuse into the electrode pores and so does the electrolyte solution.

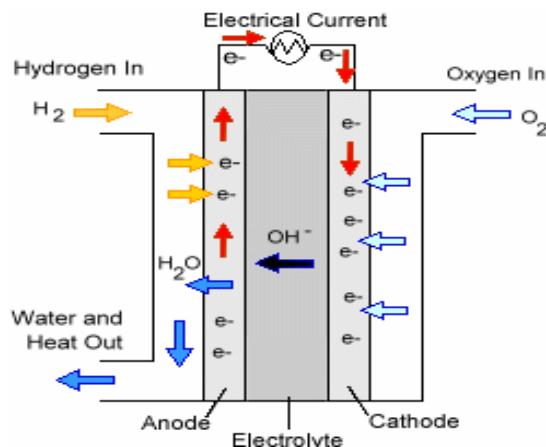
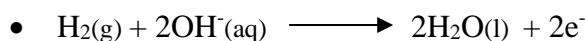


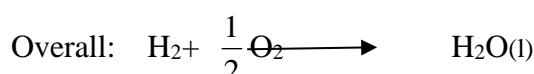
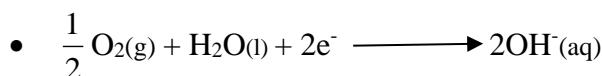
Figure 1.7.3 AFC

Working:

At Anode:



At Cathode:



Advantages: Desirable attributes of the AFC include its excellent performance on hydrogen (H_2) and oxygen (O_2) compared to other candidate fuel cells due to its active O_2 electrode kinetics and its flexibility to use a wide range of electro-catalysts.

Disadvantages:

- The sensitivity of the electrolyte to CO_2 requires the use of highly pure oxidant and fuel.
- As a consequence, the use of a reformer would require a highly effective CO and CO_2 removal system.
- If ambient air is used as the oxidant, the CO_2 in the air must be removed. While this is technically not challenging, it has a significant impact on the size and cost of the system.

Applications: AFC is widely used in US space programs to produce electrical energy and water onboard spacecraft.

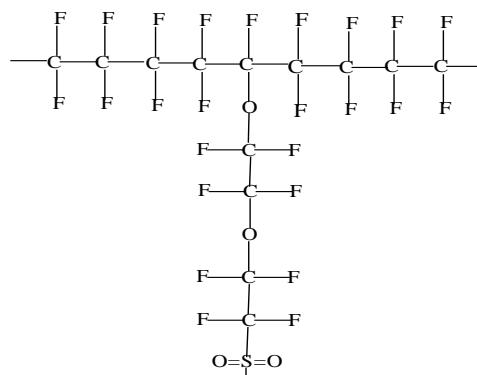
1.7.5 Proton exchange membrane fuel cell (PEMFC)

Polymer electrolyte membrane fuel cells – also called proton exchange membrane fuel cells – deliver high power density and offer the advantages of low weight and volume, compared to other fuel cells. PEM fuel cells use a solid polymer as an electrolyte and porous carbon electrodes containing a platinum catalyst. They need only hydrogen, oxygen from the air, and water to operate and do not require corrosive fluids like some fuel cells. Polymer electrolyte membrane fuel cells operate at relatively low temperatures, around 80 °C (176 °F).

Low temperature operation allows them to start quickly (less warm-up time) and results in less wear on system components, resulting in better durability. However, it requires that a noble-metal catalyst (typically platinum) be used to separate the hydrogen's electrons and protons, adding to system cost. The platinum catalyst is also extremely sensitive to CO poisoning, making it necessary to employ an additional reaction to reduce CO in the fuel gas if the hydrogen is derived from an alcohol or hydrocarbon fuel. This also adds cost. Developers are currently exploring Pt/Ru catalysts that are more resistant to CO.

Role of Proton conducting membranes:

- The membrane function in two ways: It acts as the electrolyte which provides ionic communication between the anode and the cathode and also it serves as the separator for the two-reactant gases.
- Optimized proton and water transport properties of the membrane and proper water management are crucial for efficient fuel cell operation.
- Dehydration of the membrane reduces the proton conductivity and excess of water can lead to the flooding of the electrolyte. Both conditions result in poor performance.
- The absence of solution-phase electrolyte in PEF fuel cells, compared to alkaline and phosphoric acid fuel cells greatly reduces the complexity of the fuel and oxidant flow controls.
- Polymeric electrolyte is carbon dioxide tolerant.
- The most important breakthrough came with the development of perflourinated membrane by DuPont. From 1966, the membrane requirements were best met by nafion family of perfluorinated ionomer membranes. Lifetimes over 60,000 hrs have been achieved at 353 K. Their general formula is



Construction:

Electrolyte:- Ion exchange polymeric membranes. This is an excellent insulator, but an excellent conductor of H^+ ions. The material used, consists of a fluorocarbon polymer backbone, similar to Teflon, to which sulphonic acid groups are fixed to the polymer and cannot leak out, but the protons of these groups are free to migrate through the membrane.

Electrodes:- Typical gas diffusion electrodes, made up of porous C impregnated with Pt catalyst. Noble metal treated carbon fiber paper/cloth which is directly bonded to the polymer membrane at an elevated temperature and pressure (The catalytic electrode/membrane configuration is referred to as membrane electrodes assemble, MEA).

Fuel:- Hydrogen

Oxidant:- Air

Catalyst:- Platinum

Interconnect:- Carbon or metal

Operating temperature:- $40 - 80^\circ\text{C}$.

Charge-carrier:- H^+

Electrode:-

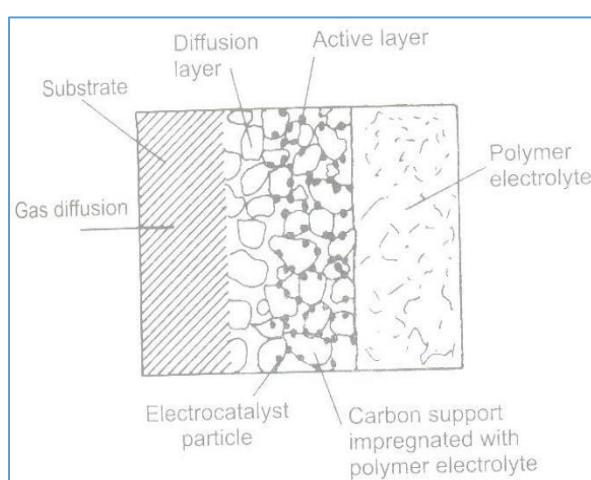


Fig.1.7.5.1 schematic of a typical PEMFC electrode, which displays three layers

- (i) A Teflonized substrate (typically, carbon cloth)
- (ii) A diffusion layer, generally formed by carbon particles of about 0.1 μm size with Teflon.
- (iii) An active layer, where Pt catalyst grains are supported on carbon particles (Pt loading is usually 0.4 mg/cm² or less) with or without Teflon.

Cell reactions and Function of PEMFC:

PEM fuel cells operate at around 80 °C and practical efficiency of 60 %. Power output is in the range of 5-200 KW. They are ideal for transportation and portable power. Additional advantages are their high response, small size and low cost. A polymer electrolyte membrane fuel cell is unusual in that its electrolyte consists of a layer of solid polymer which allows protons to be transmitted from one part to the other. Porous carbon is used as the anode and cathode of the PEMFC, as shown in Fig. It basically requires H₂ and O₂ as its inputs, though the oxidant may also be ambient air, and these gases must be humidified. It operates at a low temperature because of the limitations imposed by the thermal properties of the membrane itself. The operating temperatures are around 90°C and a Pt catalyst is used.

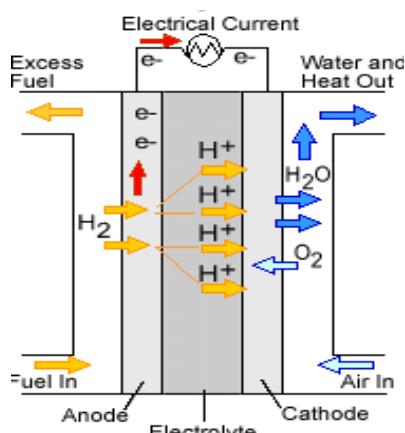
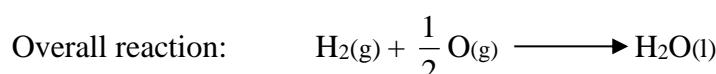
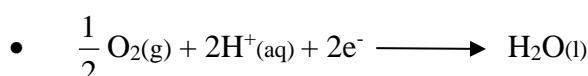


Fig.1.7.5.2 PEMFC

At anode:



At cathode



Applications:

- PEM fuel cells are used primarily for transportation applications and some stationary applications.

- Due to their fast startup time, low sensitivity to orientation, and favorable power-to-weight ratio, PEM fuel cells are particularly suitable for use in passenger vehicles, such as cars and buses.

Advantages:

The PEMFC has a solid electrolyte which provides excellent resistance to gas crossover.

The PEMFCs low operating temperature allows rapid start-up and, with the absence of corrosive cell

constituents, the use of the exotic materials required in other fuel cell types, both in stack construction.

PEMFCs are capable of high current densities of over 2 kW/I and 2 W/cm².

Disadvantages:

- The low and narrow operating temperature range makes thermal management difficult, especially at very high current densities, and makes it difficult to use the rejected heat for cogeneration.
- Optimized proton and water transport properties of the membrane and proper water management are crucial for efficient fuel cell operation. Dehydration of the membrane reduces the proton conductivity and excess water can lead to the flooding of the electrolyte. Both the conditions lead to poor performance.
- Perflourinated membranes have a high cost.
- PEMFCs are quite sensitive to poisoning by trace levels of contaminants including CO, sulfur species and ammonia.

1.7.6 Differences between the fuel cell and galvanic cell:

Fuel Cell	Galvanic Cell
1. They do not store chemical energy	They store chemical energy
2. Reactants are fed from outside the cell continuously	The reactants from an integral part of its construction.
3. Need expensive noble metal catalysts & an optimum to an operative for their efficient functioning.	These special conditions are not required
4. Do not get discharged and no need of charging	Get-discharged when stored – up energy is exhausted.
5. Such cells never become dead as long as	Limited life span in use

fresh reactants are available	
6. Useful for long-term electricity generation.	Useful as portable power services.
7. Reaction products must be continuously removed	No such problem
8. No pollutants are generated (significant environmental benefits)	Pollutants are generated after their useful life
9. Produce power from fuels	They cannot generate electricity from fuels
10. Significantly higher power densities	Lower power density

1.8 Metal finishing

1.8.1 Introduction

Metal objects such as car components, kitchen utensils, juice cans, window frames, railings and so on which we see in everyday life will have undergone a surface modification, referred to as finishing. It covers a wide range of processes carried out to modify the surface properties of a metal. The process involves deposition of a layer of another metal or a polymer, conversion of a surface layer of atoms into oxide film or any other inorganic compound film or any process which can finally improve the surface characteristics. Metal finishing is done by electroplating, electroless plating, grinding wheels and honing, lapping and burnishing tools to obtain a smooth surface of a component with desired characteristics. Metal finishing is a process of electro deposition of an adherent metallic film of uniform thickness on the surface of the substrate for the purpose of modifying its surface properties. The metal finishing techniques were originally introduced in the industry for improving the physical appearance of the metal objects by imbuing a decorative appeal. Since then a wide range of technological developments in the field was taken place for imparting additional desirable surface properties to the material other than their intrinsic properties to enhance the utility of the metal. Some of them are

- Improving resistance to corrosion
- Enhancing resistance to chemical attack, abrasion and wear
- Imparting thermal resistance and resistance to impact
- Improving thermal and electrical properties
- Increasing hardness, thermal and optical reflectivity to the surface
- Making the surface resistant for moisture attack

1.8.2 Electroplating

The techniques of metal finishing include electroplating of metals and alloys and Electroless plating of a modified surface. Electroplating is the process by which coating metal is deposited on the base metal by passing a direct current through an electrolytic solution, containing the soluble salt of the coating metal. It is primarily used for depositing a layer of material to bestow a desired property (e.g., abrasion and wear resistance, corrosion protection and aesthetic qualities) to a surface that otherwise lacks that property and sometimes to build up thickness on undersized parts. The common metals used for coating purpose are Zn, Cu, Ni, Cr, Ag, Au and Pt.

1.8.3 Theory of electroplating

Electroplating is the process of coating a metal on a substrate made up of another metal, alloy or non-metal by the process of electrolysis. The process used in electroplating is called electrodeposition and the principle is electrolysis. The electroplating device is an electrolytic cell in which two electrodes (anode and cathode) are dipped in an electrolytic solution. The part to be plated is the cathode of the circuit. In one technique, the anode is made of the metal to be plated on the part. Both components are immersed in a solution called an electrolyte containing one or more dissolved metal salts as well as other ions that permit the flow of electricity. A rectifier supplies a direct current to the anode, oxidizing the metal atoms that compromise it and allowing them to dissolve in the solution. At the cathode, the dissolved metal ions in the electrolyte solution are reduced at the interface between the solution and the cathode, such that they ‘plate out’ on to the cathode. The rate at which the anode is dissolved is equal to the rate at which the cathode is plated, ie the current flowing through the circuit. In this manner, the ions in the electrolyte bath are continuously replenished by the anode. Other electroplating processes may use an inert anode such as lead or graphite. In these techniques, ions of the metal to be plated must be periodically replenished to maintain proper coating metal ion concentration in the bath. The device used for electroplating is an electrolytic cell in the form of a tank having two electrodes immersed in the electrolyte solution. The schematic representation of various components of the electroplating unit is shown in Fig. 1.8.3.

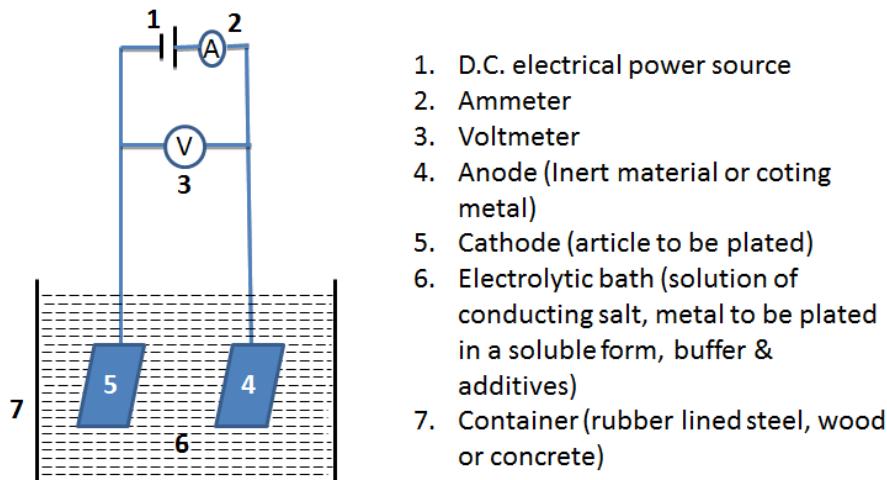


Fig. 1.8.3 Schematic of the electroplating bath

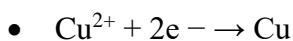
Essential components include:

- An electroplating bath containing a conducting salt and the metal to be plated in a soluble form as well as a buffer and additives.
- The article to be plated - electronically conducting cathode.
- The electronically conducting anode, the coating metal itself, or an inert material of good electrical conductance like graphite.
- An inert vessel to contain the above mentioned materials made up of either rubber lined steel, concrete or wood.

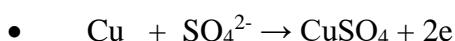
Suppose the anode is made of coating metal itself. During electrolysis, the concentration of the electrolytic bath remains unaltered, since the metal ions deposited from the bath are replenished continuously by the reaction of free anions with the anode metal. As an example, if the CuSO_4 solution is used as an electrolyte, it ionizes as



On passing current, Cu^{2+} ions go to the cathode and get deposited there.



The free SO_4^{2-} ions migrate to the copper anode and dissolve an equivalent amount of copper to form sulfate.



Thus there is a continuous replenishment of electrolytic salt during electrolysis. If however, the anode is made of some inert material like graphite, then electrolytic salt is added continuously in order to maintain proper coating metal ion concentration in the bath. Moreover the process of electroplating goes on nonstop, since the anode is not consumed and its replacement is not required. The process involves the passage of current and electrolysis

of conducting media. Three important factors governing the electroplating process include decomposition potential (E_D), polarization and overvoltage.

1.8.3.1 Decomposition Potential (E_D):

When an electric current is passed through the electrolyte solution the electrolysis starts and the products formed, gather around the electrodes. Concentration in the vicinity of the electrodes changes and a back emf sets in. e.g., in the electrolysis of water, if a small voltage (~ 0.75V) is applied between two platinum electrodes immersed in the 1M sulphuric acid solution, the electrolysis starts, proceeds to some extent and then decreases rapidly finally to stop. The reason for this observation is the initial passage of current causing release of a small amount of hydrogen and oxygen at the cathode and anode respectively. The gases are adsorbed at the surface of electrodes and the inactive platinum electrode is converted into active gas electrodes. This produces a back emf of the polarization current, which resists the emf of the battery or applied voltage. At potential below 1.7V the back emf counterbalances the effect of applied emf and the process of electrolysis is not sustained. If the applied voltage is slowly increased, there is a slight increase in the current until the applied voltage just exceeds the back emf (1.7 V), the current suddenly increases appreciably at that point. Thus, the minimum external potential or voltage, at which the electrolysis current begins to increase appreciably and continuous electrolysis sets in is known as decomposition potential of the electrolyte. It is equal to back emf.

Measurement of decomposition potential (E_D):

The schematic diagram for the determination of decomposition potential is shown in Fig.1.8.4.1a The electrolytic cell consists of two platinum electrodes (E_1 and E_2) dipped in the electrolytic solution. The applied voltage (V) is measured at different resistance and the corresponding current is measured with the help of milliammeter (M).

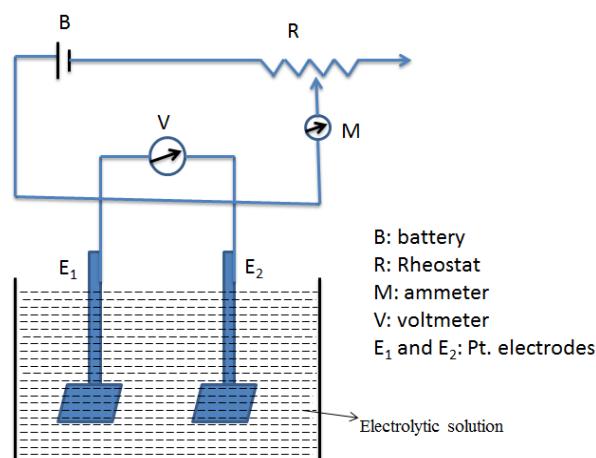


Fig. 1.8.3.1a Setup for measurement of decomposition potential

A series of readings for current passing through the electrolyte cell at corresponding applied voltage is recorded and a graph is plotted to measure the electrode potential. A graph between applied emf and the current density is shown in the following Fig.1.8.3.1b

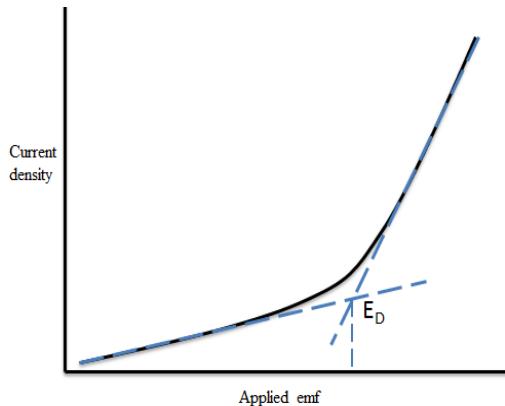


Fig. 1.8.3.1b A graph of external voltage applied vs current density

The linear portions of the graph are extended, until they intersect. Voltage corresponding to the point of intersection is the E_D of the electrolyte.

Factors influencing decomposition potential:

Decomposition potentials of different electrolytes are different. Even the E_D of an electrolyte is not a constant. It depends upon the following factors;

- Strength of the current flowing through the cell
- Chemical nature of the electrodes
- Physical nature of the electrodes
- Activity of the electrolyte
- Absolute temperature.

Use of decomposition potential values:

- Knowledge of E_D value enables the calculation of actual emf which is required for setting in continuous electrolytic processes, electroplating and electrorefining.
- It helps in predicting the sequence of discharge process to occur.
- Used in the separation of a mixture of metal ions from a solution by electrolysis.

1.8.3.2 Overvoltage

The decomposition potential of an electrolyte is approximately equal to the emf of the galvanic cell formed due to the discharge of products at the electrodes. The decomposition of an electrolyte is therefore expected to start as soon as applied potential reaches the value of reversible emf of the cell. This is true with respect to metal ions. But when products discharged at the electrodes are gases, then the actual decomposition potential is invariably

much higher than its theoretical reversible electrode potential. The excess voltage is referred to as overvoltage (η) of the gas. It may occur at both the electrodes.

O vervoltage (η) is the difference between the actual applied emf to bring about continuous electrolysis and the theoretical emf needed for such electrolysis. For instance, the reversible potential of oxygen gas with smooth Pt electrode is 1.23 V. But actual gas evolution takes place at a potential of 1.68 V. The excess 0.45 V is the overvoltage of oxygen on smooth Pt surface. The following factors influence the overvoltage of an electrolyte;

- Nature of the electrode surface (or material)
- Current density and temperature
- Nature of the electrolyte

O vervoltage is believed to be a surface phenomenon at the electrodes. Of the many steps involved in gas evolution at electrodes, at least one is rather a slow process and requires energy. The extra energy is supplied by the applied voltage and this extra energy is related to overvoltage.

e.g., electrolysis of water



The step (ii) being slow, consumes energy and accounts for overvoltage. Hydrogen overvoltage is the measure of the tendency of hydrogen to be liberated at the cathode. Higher the value of overvoltage more difficult is the liberation of hydrogen on that metal.

1.8.3.3 Polarization

Since the electrolysis is a non spontaneous process, the minimum energy required to carry out such a process is equal to the free energy increase accompanying the change. However, in irreversible conditions, the potential to be applied for electrolysis is higher than the reversible emf of the cell. A cell that requires excess voltage over the theoretical is said to be polarized and the phenomenon is referred to as polarization. Electrolytic processes occur at the electrodes of the cell. Polarization sets in the cell when the electrode processes become slow and irreversible. Thus polarization in the cell is due to polarization at the electrodes. Magnitude of overpotential is directly proportional to the extent of polarization. The observed polarizations are of two types.

- (a) Concentration polarization (b) Kinetic polarization

Concentration polarization:

An electrochemical reaction occurs only at the surface of the two electrodes. Reactant concentration decreases in the electrolyte adjacent to the electrode surface. The reactant species are transported to the electrode surface by processes like diffusion, migration and convection from the bulk of the solution. When the rate of transport is insufficient to match the rate of electrode reaction, current flowing through the cell drops. A higher potential than the theoretical value is required to maintain the current at the necessary level. This phenomenon is called concentration polarization. The steps involved in electrolytic processes are

- (i) Diffusion of reactant species towards the electrode and
- (ii) Diffusion of product away from the electrode, cause concentration polarization.

Concentration polarization can be eliminated or at least minimized by increasing the convection, by raising the temperature or mechanical agitation of the solution.

Kinetic or Activation polarization:

Activation polarization is caused when steps

- i) Adsorption of the reactant on the electrode
- ii) Charge transfer across the metal-solution interface and
- iii) Desorption of the product from the electrode become slow and need activation energy.

A higher potential than the theoretical value is to be applied to maintain current at the necessary level. It is not possible to eliminate or minimize kinetic polarization by any means. Activation polarization is normally very low, when metal deposition or metal dissolution is the electrode process. When the electrode process is a gas (H_2 and O_2) evolution, kinetic or activation polarization is usually very high.

Factors influencing polarization:

- Size and nature of the electrode
- Nature of ions accumulated on electrodes
- Electrolytic concentration
- Temperature
- Conductivity of electrolytic solution
- Stirring of electrolytic solution
- Use of depolarizer

Importance of polarization effect:

An impervious or non-porous film, contributes to the increase of polarization at an electrode. Considerable polarization effect can also be seen where loosely adhering and even porous films are formed. Such films either formed naturally (during manufacturing) or artificially (by the application of special coatings or products of corrosion) are important in determining the rate of corrosion of a metal or an alloy and also for the protection from corrosion.

1.8.4 Applications of electroplating

- *Plating for aesthetic appearance:*
- *Plating for protection*
- *For electroforming*
- *Plating on non-metals*

1.8.5 Characteristics of a good deposit

- The deposit should be bright and lustrous
- The deposit should be continuous, uniform, non porous and adhesive
- It should be hard and ductile
- It should be of fine grained nature

1.8.6 Factors influencing the nature of the deposit

There are several factors which affect the nature of an electro deposit.

(a) Current density

Higher the current density, more the deposition rate but will enforce the poor adhesion and loose and brittle plating quality. There is the possibility of a burnt and spongy deposit. Whereas low current density takes extra time to finish the job and is uneconomical. Therefore, optimum moderate current densities should be applied.

(b) Metal ion concentration

As the electroplating involves the discharge of free metal ions, the concentration of free metal ions plays an important role. If the concentration of metal ion is low the crystal size will be smaller and a fine adherent film may be coated. Thus the ideal situation is low free metal ion concentration in a concentrated solution of a metal compound which can be attained by addition of a compound with a common ion or by the formation of complex compound and ions. e.g., when copper is deposited from an electroplating bath containing copper sulphate solution, sulphuric acid is added to increase the concentration of sulphate ion. The concentration of cupric ions is reduced due to common ion effect.

(c) Temperature:

Generally, the solution to be deposited is used at room temperature. However, warm baths are used for increasing solubility of electrolyte and current density. The size of the crystals increases with increasing temperature and renders lower adherence. But on the other hand the solubility and metal dissociation increase at higher temperature leading to the higher conductance of the solution. Also, the mobility of ions increases at a higher temperature and decreases the viscosity of the electrolyte solution so that the cathode film is replenished at a faster rate. This increases the current density for a given voltage and reduces the tendency towards treeing. There are disadvantages also of using high temperatures. Since, the possibility of corrosion of equipment, decomposition of the organic addition agent and evolution of hydrogen gas at cathode would increase at a higher temperature. So the optimum range of temperature needs to be selected.

(d) pH of the electrolyte

The pH of the electrolyte solution should be properly maintained. The range of the pH varies for different types of the plating bath. If pH is more towards the acidic side the nature of the deposit will be affected adversely as the evolution of hydrogen gas is expected at cathode thereby forming a burnt deposit. If pH is more towards the basic side the plating is delayed, so uneven and thick deposit is obtained. Suitable buffers may be used for maintaining the appropriate pH.

(e) Presence of additives:

To obtain electroplate with desire qualities and specifications, additional substances called additives are added in small quantities to the electrolyte bath. These additives have the capacity to modify the structure, appearance and characteristics of the deposit. The different types of additives used are

(i) Complexing agents:

(ii) Brighteners:

(iii) Levellers:

(iv) Wetting agents:

(v) Structure modifiers:

(f) Throwing power of the plating bath

Throwing power is defined as the degree of uniformity of metal distribution or evenness of deposit thickness obtained on a cathode of irregular shape. If the distribution of the deposit is uniform throughout the surface of the article to be coated, the throwing power is considered good.

1.8.7 Methods of cleaning the metal surface

It is essential to clean the surface of base metal before the application of the electroplated coating. The common impurities found on the metal surface are grease, oil, oxide layer and other extraneous matters. The following methods are employed to clean the metal surfaces.

(iii) ***Physical (Solvent) cleaning:-*** Physical cleaning is done with the help of solvents to make the surface free from oil, grease, superficial dirt, and buffing, polishing and fatty substances. The commonly used solvents such as chlorinated hydrocarbons, xylene, toluene, aqueous cleaning agents are used with or without electric current. Solvent cleaning is made more effective by vapour degreasing. An organic volatile solvent like trichloroethene is heated and vapours are passed over the metal surface to be cleaned. The vapours condense on the surface and condensed liquid dissolves and washes away the oil, grease and other organic matter from the surface. The emulsifying agents are also added to the solvent to remove organic impurities from the surface of the metal.

(ii) ***Chemical (Alkali) Cleaning:*** It is used to remove the minute residue of soil and grease and for removal of tarnish and oxide film. The commonly used alkali cleaners consist of a number of alkalies, soap, chelating agents like Na_2O_3 , sodium phosphates, NaOH etc. Alkali cleaning is made more effective by passing current through a hot alkaline solution, with the article to be cleaned constituting the cathode. The evolution of H_2 at the cathode and O_2 at the anode, metal helps to dislodge the greasy substance. It is followed by thorough rinsing with water and then immersing in a very dilute solution of acids to remove traces of alkali after cleaning is completed.

(iii) ***Mechanical Cleaning:*** Involves removal of the oxide layer (tarnish), loose rust and other inorganic deposits from the surface to obtain better appearance, protection and optimum effects. This is done by hand cleaning with bristle brush and some abrasives like sand papers, polishing tools (grinding with grinding stone), scratch rubbing with chisel, knife, scrapers, wire brush or a abrasive stone or paper and detergent.

(iv) ***Pickling:*** The oxides sometimes cannot be removed by simple alkali or mechanical cleaning. The extraneous fragments like heavy scales of oxides, scratches and strains can be removed from the surface by dissolving in the acid solution. The acid pickling involves the removal of such oxides; rust or tarnish by immersing the material (except Al) in acid like dil. HCl or dil. H_2SO_4 or dil. HNO_3 . Pickling of Al is done in alkaline solution, whereas pickling of Cu, Ni or brass articles are accomplished in a solution of dil. HNO_3 or a mixture of dil. HNO_3 and dil. H_2SO_4 . Pickling is usually followed by polishing and buffing.

(v) ***Electro polishing*** :- In this method, the metal to be cleaned is made anode in a suitable solution. During the process, a surface layer of the metal gets dissolved along with the impurities. It also helps to remove minor surface irregularities. The most commonly used baths for electro polishing contain sulphuric acid, phosphoric acid, chromic acid, nitric acid etc. After the process, the metal is thoroughly rinsed with water, dried and used for electroplating.

1.8.8 Electroplating of chromium

Chromium plating is a finishing treatment utilizing the electrodeposition of a thin layer of chromium on a metal object. This layer can be decorative or corrosion protective to the base surface. The process of chromium plating includes degreasing to remove heavy soiling, manual cleaning to remove all residual traces of dirt and surface contamination and various pretreatments depending on the objectives of the coating. Different etching solutions such as hydrochloric, hydrofluoric, sulphuric acid and ferric chloride are used. Further, the treated base material is placed into the chrome plating bath for electroplating of desired thickness.

- Chromium coatings are generally thinner and have micro pores in it. As the thickness of the coating increases, cracks develop in the coatings. Hence, chromium coatings are always plated on nickel/copper undercoats. Ni gives protection and chromium gives a decorative finish.
- Chromium anodes are not used in electroplating of chromium on account of two difficulties. These electrodes become passive in acidic medium and they result in a black deposit.
- Chromium has higher electrode potential and can be easily coated on the iron to protect from rusting/corrosion
- The anode efficiency is nearly 100 % whereas cathode efficiency is at best around 20 %. It may be inferred that metal going into the solution is five times of the metal getting deposited, resulting in building up of excessive chromic acid concentration. This disturbs the ratio of Cr(III) to Cr(VI) and the conductivity of the bath and dull deposits called burnt deposits are obtained. To avoid this, inert material is used as anode and chromium electrolyte in the bath.

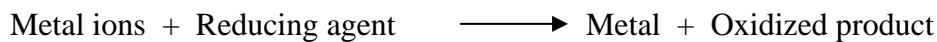
Table 1.8.8 Comparison of decorative and hard coating of chromium

	Decorative coating	Hard coating
Bath	Chromic acid (250 g) +	Chromic acid (250 g) +

composition	H ₂ SO ₄ (2.5 g) + Trivalent chromium (1g)	H ₂ SO ₄ (2.5 g) + Trivalent chromium (1 g)
Operating Temperature	45 – 55 °C	45 – 55 °C
Anode	Insoluble anodes like Pb – Pb : 6% Sb - Pb--7% Sn	Lead – lead : 6% Sb – Pb: 7% Sn
Cathode	Article to be coated	Article to be coated
Current density	145--430 A/ft ²	290--580 A/ft ²
Cathode efficiency	10 – 15	17 – 21
Applications	Decorative applications with corrosion resistance finish on cycles, automobiles, furniture, household fittings, aircraft, surgical and dental instruments.	Coating of industrial components like gauges, dies, cutting tools, piston rings and hydraulic rams.

1.8.9 Electroless plating

Electroless plating is a method of depositing a metal film on a substrate surface (conductor or non-conductor) from metal salt solution using a suitable reducing agent without using electrical energy. The reaction can be depicted as

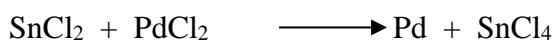


The method involves the deposition of metals such as Cu, Ag, Ni, Au or Pd on the surface of the base material by means of a reducing agent. Electroless plating results in a fine grained metal deposit that has similar finishing as that of traditional electrodeposit finishing. In industries, such process is used for plating on non-conductors like plastic, electroformed dies, hard memory disks, printed circuit boards (PCBs) or to obtain an extremely uniform plate. This technique is also used for the prevention of corrosion.

Process of electroless plating: The process of electroless plating involves the following steps:

(i) **Preparation of active surface:** This is the most important step and the surface is activated by any of the following ways.

- (a) etching – by acid treatment
- (b) electroplating with a thin layer of metal or insulators like plastic surfaces followed by heat treatment
- (c) Alternate treatment with SnCl_2 and PdCl_2 on the plastic surface



Pd is coated on plastic.

(ii) **Preparation of plating bath:**

- (a) Metal to be coated in the form of chloride or sulphate solution
- (b) Reducing agents like formaldehyde and sodium hypophosphate for reduction of metal ion to metal
- (c) Complexing agents like EDTA, tartrates, citrates to form metal complexes to prevent excess deposition
- (d) Stabilizers like thiourea, calcium ions too prevent decomposition of the bath and to impart stability to the solution
- (e) Exaltants (accelerators) like succinates, glycinate and fluorides to increase the rate of plating
- (f) Brighteners like thiosulphate to give a lustrous appearance
- (g) Buffers like boric acid to maintain the pH

(iii) **Reduction step:** Active surface is dipped in the bath and deposition is carried out. The plating is carried out in a series of tanks where the object is immersed to plate the desired metal. The rate of deposition is controlled by the amount of reducing agent present and the type of chelating agent used. The deposition rate is normally $12.5 - 25 \mu\text{m}$, although, it has been done up to $650 \mu\text{m}$ in thickness.

Advantages of electroless plating

The following are main advantages of electroless plating

- More uniform coating on the surface of object whatever shape it may have. Even the objects having irregular shapes, holes, recesses, internal surfaces, valves or threaded parts get uniform deposit since it has better throwing power than electroplating.
- Electrical power and other accessories are not required.

- Coating is harder than regular plating and better wear resistance.
- Deposits have compatible wettability for oils, inherent lubricity and non-galling characteristics, unlike electrolytic nickel.
- Deposits are much superior to electroplated nickel and hard chrome, as they are less porous and provide better corrosion protection to steel substrates.
- Electroless plating of Ni on aluminum substrate enhances the solderability together with providing a non-magnetic under lay in magnetic components. The deposits are less porous and possess unique characteristic chemical, mechanical and magnetic properties.
- Additives or levelers are not required in the process nor the complex filtration method requirement.
- It is a simple process, so requires simple equipment.

Disadvantages of electroless plating

The main disadvantages of the process are the following;

- Due to speedy chemical renewal, cost of waste treatment is high.
- The frequency of dumping electroless bath is high as it is sensitive to contamination
- Costs per unit weight of the deposited metal are more.
- It needs pure chemicals.
- Chemical reductants are more expensive than electricity.
- Metal salts and reductant used in electroless plating solutions are thermodynamically not stable.
- Impurities or dust or colloidal matter (even if present in trace amount) promote the decomposition of bath components.

1.8.9.1 Electroless plating of Copper

It is an auto-catalytic reaction used to deposit a coating of electroless copper on a substrate without the use of electrical energy. It is commonly used to plate plastic for decorative purposes and parts for engineering applications, particularly to render conductivity for electronic and printed circuit boards.

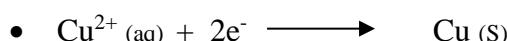
Reducing agents generally react with the plating bath, resulting in slow, deposition rates and poor deposit quality. It can be prevented by rejuvenating the bath at regular intervals. The bath solution undergoes spontaneous decomposition, resulting in an additional waste stream of copper and etching solution as copper built up on the tanks from the bath solution, must be stripped with an etchant such as sulphuric acid and hydrogen peroxide.

Electroless plating bath for copper includes;

- Coating solution : CuSO₄ soln
- Reducing agent : HCHO
- Buffer: NaOH & Rochelle salt
- Complexing agent: EDTA di sodium salt
- Optimum pH: 11
- Optimum temperature: 25 °C

The reactions involved at two electrodes are

At cathode:



At anode:



Overall reaction:



Since Cu²⁺ ions and HCHO are consumed during the redox reaction, these are replenished periodically. The redox reaction involves consumption of hydroxyl ions and pH of the solution decreases as the reaction progresses. Hence addition of buffer is essential. Usual plating rate is 1-5 μm h⁻¹.

Applications of electroless plating:

- Electroless copper plating is widely used for metalizing printed circuit boards (PCBs)
- It is used as a base coating for subsequent conventional electroplating
- It is used for producing through hole connections and for decorative plating on plastics. When double sided PCBs are fabricated then holes are drilled for making electrical connections. These holes are plated by electroless plating.

1.8.10 Comparison of electroplating and electroless plating

Table 1.8.9 Comparison of electroplating and electroless plating

Property	Electroplating	Electroless plating
Driving force	Electric current	Autocatalytic redox reaction
Anode reaction		
Cathode	Article to be plated	Article to be plated with a

		catalytic surface
Anode	Separate anode	Article to be plated
Reducing agent	Electrons bring about	Chemical reagents bring about reduction reaction
Anode reactant	M or H ₂ O	R, the reducing agent in solution
Nature of deposit	Pure metal or alloy	Usually metal contaminated with species derived from the redox reaction
Thickness limit (μm)	1 - 100	1 – 100
Applicability	Applicable to conductors only	Can be used for conductors and non-conductors
Throwing power	Less throwing power; cannot be used for irregular shapes and intricate parts	More throwing power and can be used for irregular and uneven shaped objects

3: CORROSION AND ITS CONTROL

Syllabus: Introduction, Consequences of corrosion, Classification, Electrochemical theory of corrosion, Galvanic series, Description of galvanic, pitting stress and inter-granular corrosion, Factors affecting corrosion- nature of metal, overvoltage, relative areas of the anode and cathode, pH of the medium, temperature and polarization, Corrosion prevention- materials selection and design, Inhibitors, cathodic and anodic protection, Metallic coating-galvanizing and tinning.

Learning Objectives:

1. Understand the terms: Corrosion, Galvanic Series, Inhibition
2. Explain how consequences of corrosion lead to destruction and loss in the domestic and industrial sectors.
3. Be able to describe the mechanism of corrosion by electrochemical theory
4. Describe different forms of corrosion- galvanic, pitting, stress, and inter-granular
5. Demonstrate an understanding of the importance of the factors affecting corrosion
6. Know about the different established and modern techniques to control corrosion such as anodic/cathodic protection methods
7. Distinguish between galvanizing and tinning, electrochemical series and galvanic series
8. Unfold the practical aspects of metal corrosion with real life examples.

1. INTRODUCTION

Residents of industrialized nations live in metal- based societies. Various types of metals are used in residential and commercial structures, in bridges, in automobiles, passenger trains, railroad cars, ships, in pipelines and storage tanks. In addition, metals are also used in various electronic applications such as printed circuit, computer discs, connectors and switches. Metals also find use as coins of daily commerce, in jewelry, in historical landmarks and in objects of arts. Metals are also used in the human body as replacements, as stents, as surgical plates, screws and wires. Whatever be their end use all common metals tend to react with their environments to different extents and at different rates. Thus, Corrosion is a natural phenomenon and is the destructive attack of a metal by its environment so as to cause a deterioration of the properties of the metal.

Corrosion can be defined as spontaneous destruction or deterioration of a metal or alloys by the surrounding environment because of chemical or electrochemical interaction. Free metals, as such are unstable and whenever favorable situation arises they combine with other elements like oxygen and form the compounds of minimum energy and maximum stability. Hence corrosion can be viewed as the reverse process of extractive metallurgy.

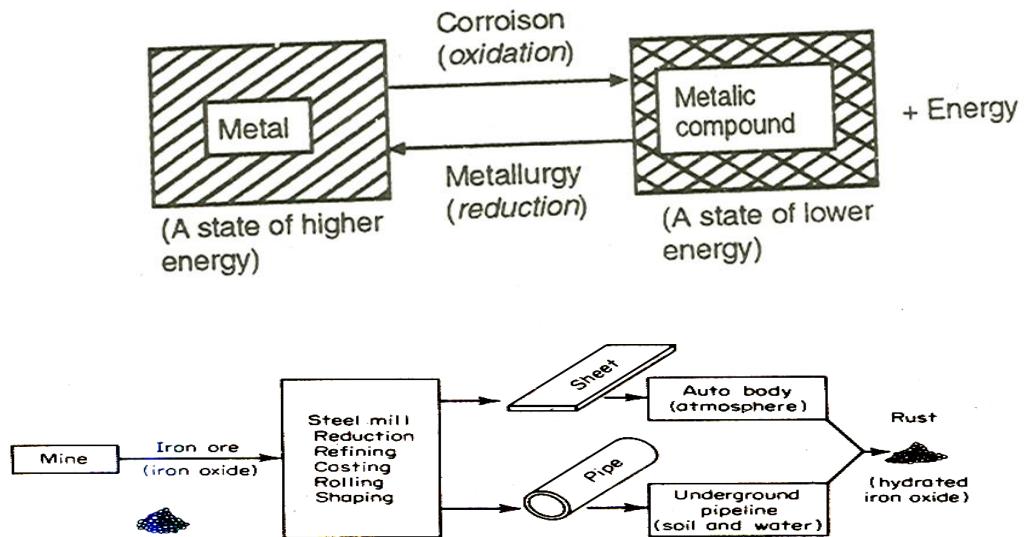
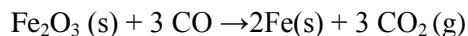
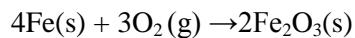
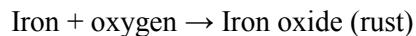
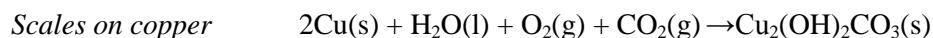
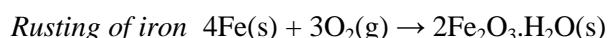


Figure 1. Corrosion as reversal of metallurgy



Three most common examples of corrosion include rusting of iron objects forming reddish brown scale, tarnishing of silver in contact with traces of H₂S or SO₂ in the atmosphere or eggs rich in sulfur compounds and formation of green scales on copper vessels. The process and the products formed in these reactions are described in the following equations.



1.1 Importance of corrosion study

The study of corrosion is an interdisciplinary area embracing chemistry, material science and mechanics. The study of aqueous corrosion process involves the intersection of chemistry and materials science. But the science of mechanics must be added to understand mechanically assisted corrosion process, such as stress corrosion cracking and corrosion fatigue.

There are four reasons to study corrosion as science and engineering subjects. They are:

- **Human life and safety:** Loss of life results due to combined effects of stress and corrosion when structures collapse. Safety issue can be due to the buildup of certain toxic product due to corrosion, sudden failure of equipment may cause fire or explosion.

- **Cost of corrosion:** The annual losses due to corrosion are approximately 3-4% of GDP in many advanced countries and it is even more in developing countries.
- **Conservation of materials:** Corrosion destroys metals by converting them into corrosion products. Thus corrosion affects the supply of the earth's material resources.
- **Academic interest:** The study of corrosion is in itself a challenging and interesting as corrosion science is an interdisciplinary area involving chemistry, materials science and mechanics. A blend of these must be included to understand the various forms of corrosion.

1.2 Economic considerations of corrosion

Corrosion consumes 3-5% of the Gross National Product of that particular nation. Corrosion costs could be divided into direct and indirect costs. The direct losses include inability to use otherwise desirable materials, overdesign to allow for corrosion, the cost of repair or replacement of corroded component, cost of anticorrosive painting or other protection methods. Indirect losses may be either economic or social. These may include shutdown of power plants and manufacturing plants, loss of product due to leakage, contamination of product, loss of production and safety issues. In fact our economy would be drastically changed if there were no corrosion. For example, automobiles, ships, underground pipelines, and household appliances would not require coatings. The stainless steel industry would essentially disappear and copper would be used only for electrical purposes. Aside from its direct costs in dollars, corrosion is serious problem because it definitely contributes to the depletion of our natural resources. The rapid industrialization of many countries indicates that the competition for and the price of metal resources will increase.

1.3 Corrosion science versus corrosion engineering

Corrosion science is directed towards gaining basic scientific knowledge to understand corrosion mechanisms. Corrosion engineering involves the use of accumulated scientific knowledge to corrosion protection and prevention. Corrosion science and corrosion engineering complement and reinforce each other. Understanding of corrosion mechanisms can lead to possible new corrosion-resistant alloys, better surface treatments, and improved corrosion control measures. Understanding of corrosion engineering aspects will trigger the interest in doing research in finding out actual mechanisms involved in the process.

1.4 Negative Consequences of Corrosion

- Maintenance and operating costs: One fourth of the iron produced is used to replace bridges, buildings and other structures that have been destroyed by corrosion. The corrosion causes damage to chemical process plants and other equipment.
- Plant shutdowns, loss of production while the plant is inoperable during repairs/replacement work.

- Contamination and loss of valuable products- Leaking containers, tanks, pipelines results in significant losses in product, which have a high cost. Soluble corrosion products can spoil and contaminate chemical preparations.
- Effects on safety- The contaminated products when dumped cause environmental pollution problems.
- Loss in aesthetic value- Reduced value of goods due to degraded appearance
- Loss of technically important surface properties such as friction, surface reflectivity, heat transfer and electrical conductivity.
- Loss of efficiency- the corrosion products decreases the heat transfer rate in heat exchangers.

2. CORROSION CLASSIFICATION

The process of corrosion of metals depends on the environment to which the metals are exposed. The corrosion of the metals can be classified into two major types. They are

* *Dry or Chemical Corrosion*

* *Wet or Electrochemical Corrosion*

2.1 Dry or Chemical Corrosion



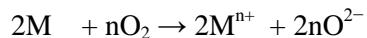
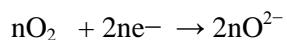
Dry corrosion of steel equipment

This type of corrosion occurs by direct chemical reactions between the environment and the metals and alloys. Presence of an electrolyte/conducting medium is not at all essential for this type of corrosion to occur. Therefore this kind of corrosion is also known as dry corrosion. Dry corrosion may be further classified into three types. They are

- Oxidation corrosion
- Corrosion by gases
- Liquid metal corrosion

Oxidation corrosion occurs when metals are attacked by dry oxygen (absence of moisture) at extreme

conditions like low or high temperature leading to oxidation type of corrosion. The direct oxidation of metals takes place according to the following reaction scheme:



In general: Metal + Oxygen → Metal oxide (corrosion product)

When the oxidation starts, a thin layer of oxide formed on the metal surface, and the nature of this film decides the further action. If a stable film is formed, it behaves as protective coating in nature, thereby shielding the metal surface. Consequently, further oxidation of metal is prevented. e.g: Al, Sn, Pb, Cu and Pt. Unstable metal film decomposes back into the metal and oxygen. Hence oxidation corrosion is not possible in such cases: e.g. Ag, Au, and Pt. In some cases, volatile film layer volatilizes as soon as it is formed, thereby accelerating the corrosion. e.g: MoO₃.

Corrosion by other gases like SO₂, Cl₂, CO₂, and H₂S, depends mainly on the chemical affinity between the metal and the gas involved. For example, dry Cl₂ attacks silver metal and forms AgCl as a thin protective and non-porous layer on the metal. As a result of this protective layer on the metal surface, the intensity of corrosion decreases.

Liquid metal corrosion occurs when a molten liquid is continuously passed on a solid metal surface or on alloy. This behavior may be either due to the dissolution of the molten liquid or due to penetration of the molten liquid into the metal phase.

2.2 Wet or Electrochemical Corrosion

Wet corrosion occurs due to the existence of separate anodic and cathodic areas, between which current flows through the conducting solution. It involves flow of electron current between the anodic and cathodic areas through electronic conductor. This type of corrosion can be observed when

- (a) A metal is in contact with an acid solution and
- (b) Dissimilar metals are dipped partially in a corrosive environment.

2.2.1 Electrochemical theory of corrosion

Corrosion usually occurs not by direct chemical reaction of a metal with its environment but rather through the operation of coupled electrochemical half-cell reaction. According to electrochemical theory of corrosion, when a metal is exposed to corrosive environment, the process of corrosion sets in by the formation of a large number of ‘anodic’ and the ‘cathodic’ areas on the metal surface (micro-galvanic cells). A driving force is necessary for electrons to flow between the anodes and the cathodes. This driving force is the difference in potential between anodic and cathodic areas. This difference exists because oxidation and reduction reaction has associated with it a potential determined by the tendency of specific elements for the reaction to take place spontaneously. This electrode potential is a measure of the

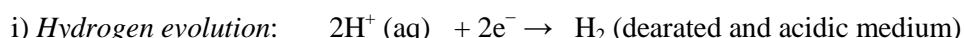
tendency of a metal to undergo oxidation or reduction reactions. Corrosion always occurs at the ‘anodic area’ of the metal due to oxidation process and thus electrons are liberated.

Anodic reaction:

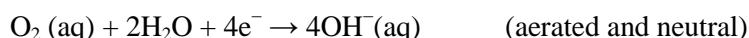
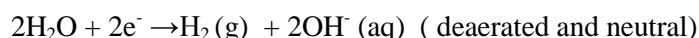


Cathodic reactions:

The electrons set free at the anodic area flow through and are consumed at the cathodic area by following processes:



H_2 liberation along with OH^- ions formation



In addition to the above mentioned cathodic reactions, following reactions may also occur at cathodic region.



Oxygen reduction is the most common cathode reaction, since any aqueous solution in contact with air contains dissolved oxygen. Hydrogen evolution occurs in acidic media. Metal ion reduction and metal deposition are rare. Schematic representation of electrochemical theory of corrosion is shown in Figure 2.

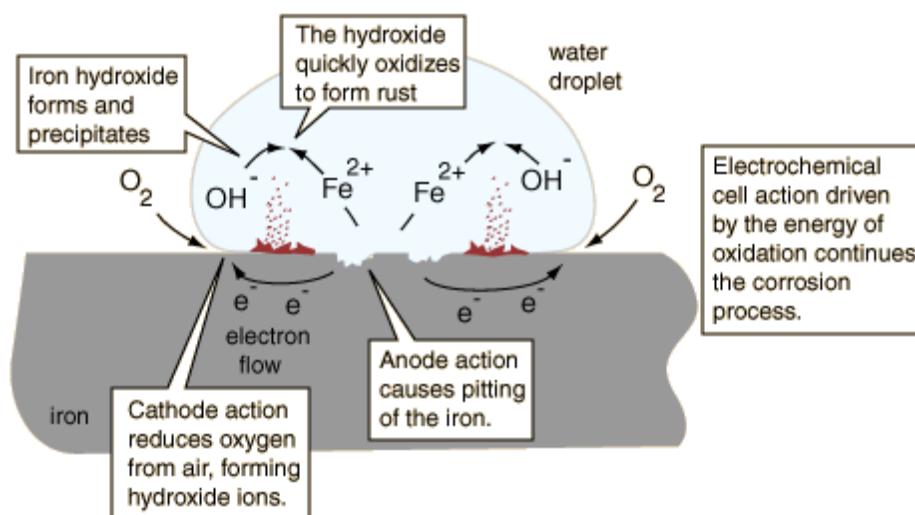


Figure 2. Schematic representation of electrochemical corrosion showing the formation of small local electrochemical cells on the surface

Figure 2 illustrates the four conditions which are necessary for electrochemical corrosion to occur. These are i) An anodic reaction, ii) A cathodic reaction, iii) A metallic path of contact between anodic and cathodic sites., iv) The presence of an electrolyte (i.e. a solution which contains dissolved ions capable of conducting a current)

From, electrochemical theory, it must be clear that no corrosion take place at the cathodic area, since cathodic reaction does not involve metal dissolution. Corrosion and hence metal dissolution takes place only at anodic area. Cathodic area stimulates corrosion of the anodic part by utilizing the electrons produced at anodic area.

2.2.2 Mechanism of rusting: Rusting is the name more commonly referred for the corrosion of iron. When iron is exposed to atmosphere, in the presence of moisture, it undergoes corrosion. Depending upon the concentration of oxygen present in the environment different types of corrosion products are produced. Figure 3 illustrates the rusting process of iron.

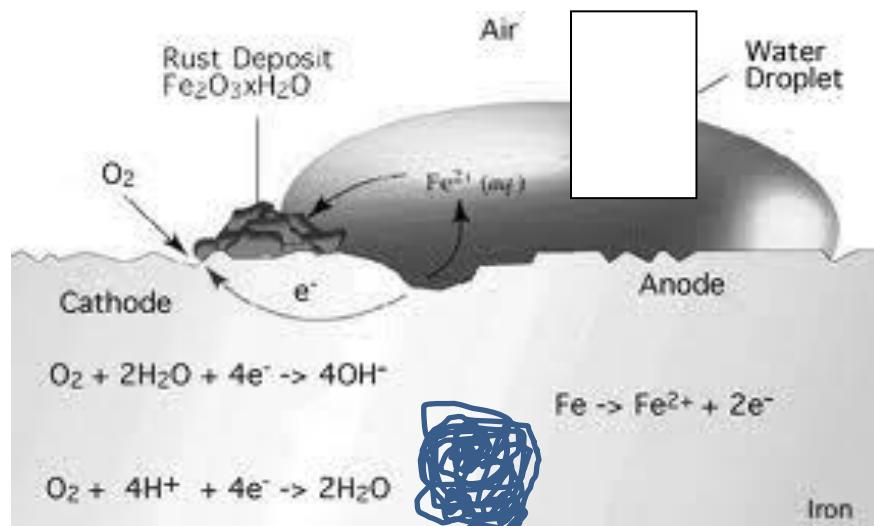
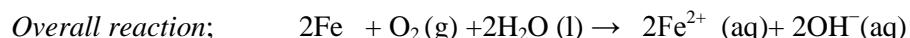
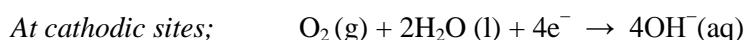
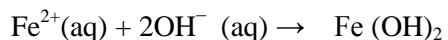


Figure 3. Schematic representation of rusting of iron

The electrons liberated at the anode migrate to the cathode causing corrosion current. The Fe^{2+} ions formed at the anode combine with OH^- liberated at the cathode to form the corrosion product (ferrous hydroxide) somewhere between the anode and cathode, after diffusing towards each other through the conducting medium.



Reactions to the formation of hydrated ferric oxide (rust)



In presence of enough oxygen, ferrous hydroxide reacts with moisture and oxygen to give yellow rust.



If the supply of oxygen is limited, the corrosion product may be black anhydrous magnetite.



Rust is a brittle substance that easily flakes off the surface to expose more iron atoms and the process starts over again. It is too porous to shield the underlying metal from further oxidation.

2.2.3 Differences between dry corrosion and wet corrosion

Dry Corrosion	Wet Corrosion
Involves direct attack of atmospheric gases	Occurs due to existence of separate anodic and cathodic areas between which current flows through the medium
No need of a corroding medium	Need of a corrosive medium
Types include oxidation corrosion, liquid metal corrosion and corrosion by gases	Types include galvanic, pitting, stress and intergranular
Less prevailing	More common

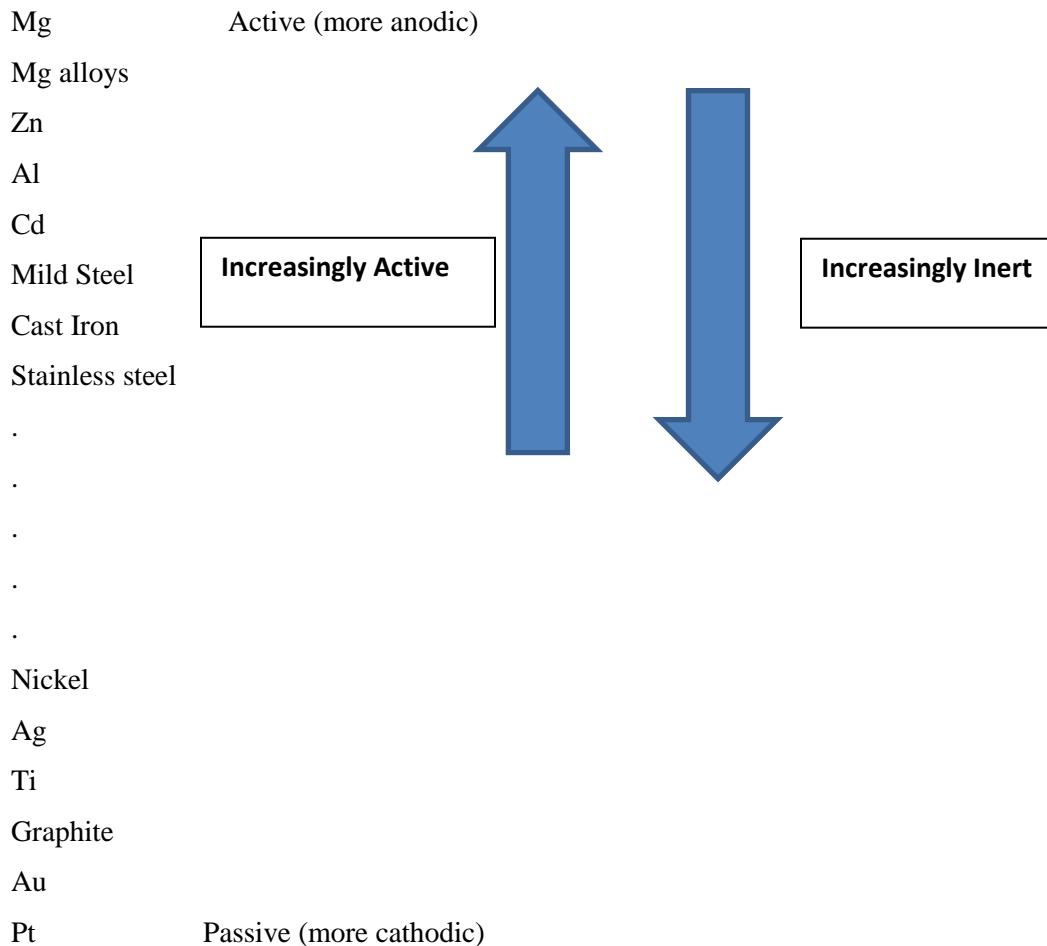
3 GALVANIC SERIES

The galvanic series is an ordered listing of experimentally measured corrosion potentials of metals and alloys in natural sea water. They are arranged in the order of their corrosion tendencies/corrosion resistance.

3.1 Need for galvanic series

1. In the electrochemical series a metal high in the series is more anodic and undergoes corrosion faster than the metal below it. For example, Li corrodes faster than Mg, Zn corrodes faster than Fe and so on. However, some exceptions to this generalization are known. In Zn-Al couple, Zn (below Al in the electrochemical series) is corroded; while aluminum acts as cathodic is protected. These observations, exactly opposite to that predicted by the e.m.f series are due to the fact that metals like Al and Ti develop strongly adhering oxide layers on their surfaces. The electrochemical series does not take passivity into account.
2. The electrochemical series does not account for corrosion behavior of alloys. The electrochemical series lists E° values of pure metals. But engineering applications involve many alloys under various circumstances. Consequently, a more practical series called galvanic series has been prepared by studying corrosion of metals and alloys in a given environment like sea water.

3.2 Galvanic Series



3.3 Characteristics of galvanic series.

- Galvanic series include both metals and alloys.
- Electrode potentials in the galvanic series are measured relative to a saturated calomel electrode.
- Metals and alloys are arranged in the increasing order of their corrosion resistance in sea water.
- Metals and alloys having almost same corrosion characteristics are grouped together within a square bracket.
- Same metal can occupy two positions in the galvanic series For example, aluminum occurs both active and noble region depending upon its active and passive states.

3.4 Comparison between electrochemical and galvanic series

- In electrochemical series electrode potentials are measured by dipping pure metals in their salt solution of 1M concentration without any oxide film on it. The galvanic series was developed by studying corrosion of metals and alloys in unpolluted sea water, without their oxide films.
- In electrochemical series electrode potentials are measured with respect to standard hydrogen

electrode. Electrode potentials in the galvanic series are measured relative to a saturated calomel electrode.

- The position of a given metal in electrochemical series is fixed based on the electrode potential value. The position of a given metal may shift in galvanic series as it takes active and passive states, irrespective of its electrode potential.
- Electrochemical series gives no information regarding the position of alloys. Alloys are included in galvanic series based on their corrosion behavior
- In electrochemical series, metals and non-metals are included. In galvanic series only metals and alloys are included.

Similarities: In both, base metals are placed higher and noble metals lower in the series.

4. TYPES OF CORROSION

4.1 Galvanic corrosion

Galvanic corrosion occurs when two dissimilar metals are in physical contact in an aqueous electrolyte. The less resistant metal acts as anode (metal with lower electrode potential) and the more resistant metal (metal with higher electrode potential) acts as cathode. Figure 4 depicts galvanic corrosion showing the anodic and cathodic regions and direction of electron flow.

Some real world examples of galvanic corrosion include:

- *copper piping connected to steel tanks.
- * Zinc coated screws in a sheet of copper,
- *A stainless steel screw in contact with cadmium plated steel washer.
- * Steel propeller shaft in bronze bearing

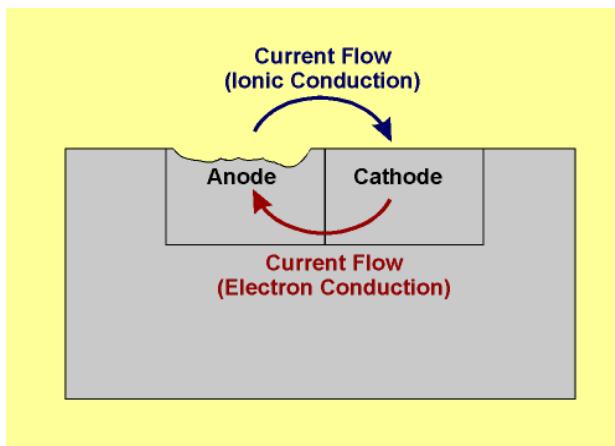


Figure 4. Galvanic corrosion



Image 5(a)



Image 5(b)

Figure 5. Illustration of galvanic corrosion

Images in 5a and 5b show the picture of metal along with corrosion product. Galvanic corrosion also occurs in the atmosphere. The severity depends largely on the type and the amount of the moisture present. Corrosion is greater in the seashore than in a dry rural atmosphere. Condensate near a seashore contains salt and therefore is more conductive (and corrosive) and a better electrolyte than condensate in an inland location. Accelerated corrosion due to galvanic effects is usually greatest near the junction with attack decreasing with increasing distance from that point. In the galvanic couple like Zn/Fe, Fe/Sn, Fe/Cu, Zn/Sn, Zn/Cu; the first metal is anodic with respect to the second metal and hence undergoes corrosion. It is to be noted that nuts, bolts, and hinges are made up of one single metal or alloy in order to prevent the galvanic corrosion.

4.2 Pitting Corrosion

Pitting corrosion is a localized attack that results in extreme cases holes in the metal. Pits are sometimes isolated or close together that they look like a rough surface. Generally a pit may be described as a cavity or hole with the surface diameter about the same length as or less than the depth. Pitting is localized and intense form of corrosion and failure often occurs with extreme suddenness without prior indication. The important reasons for the pitting corrosion include

- * Surface roughness or non- uniform finish.
- * Scratches or cut edges.
- * Local straining of metal due to non- uniform stress.

*Deposition of extraneous matter such as sand, scale, water drop and dust

Whenever dust particles are deposited, owing to the different amount of oxygen in contact, with metal, the small part becomes the anodic areas and the surrounding large parts become the cathodic areas. Intense corrosion starts just underneath the impurity.

Examples: peeling of tin coat on iron, deposition of dust, sand on the steel surface
 Pitting form of corrosion can be represented as shown in Figures 6(a) and 6(b)

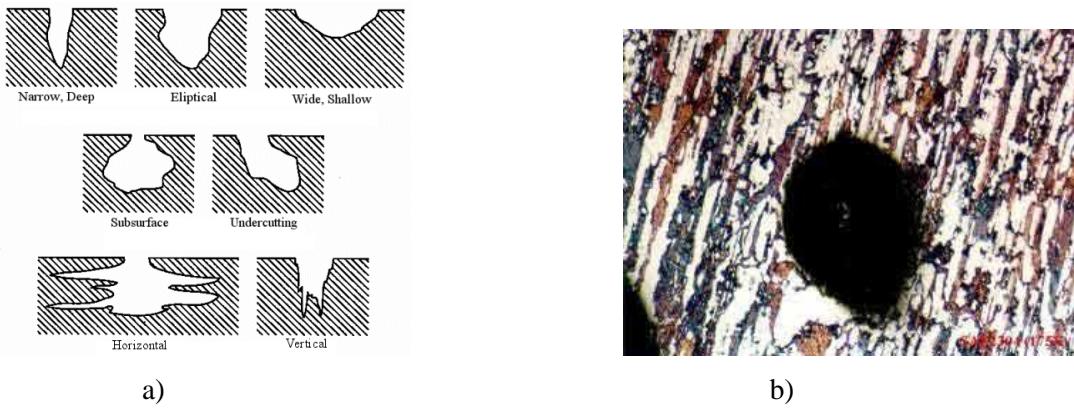


Figure 6. Illustrations for pitting corrosion

4.2.1 Autocatalytic Nature of Pitting

A corrosion pit is a unique type of anodic reaction. It is an autocatalytic process. That is, the corrosion within a pit produce conditions which are both stimulating and necessary within a pit produce conditions for the continuing activity of the pit. It is illustrated in the Figure 7.

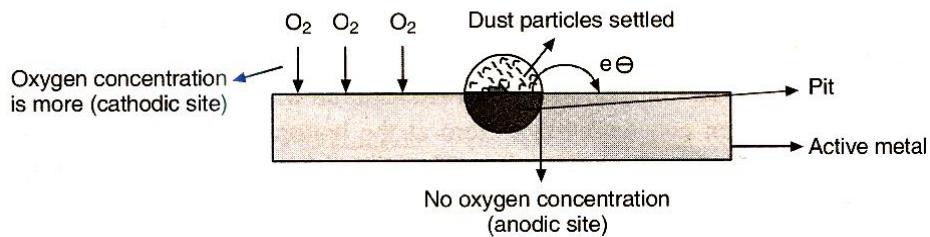
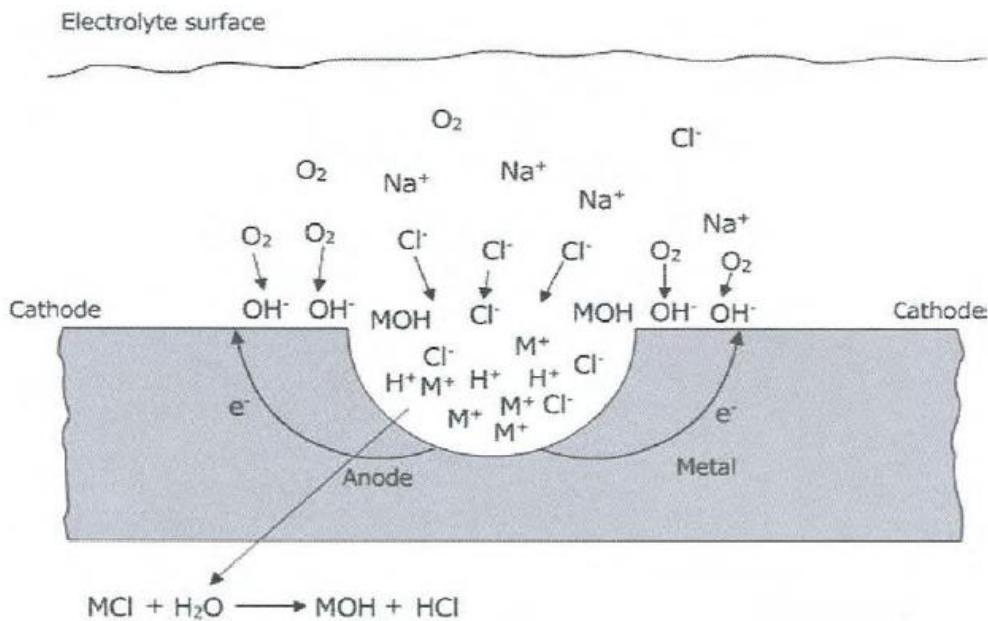


Figure 7. Autocatalytic nature of pits

This process is self-stimulating and self-propagating. The gravity effect is a direct result of the autocatalytic nature of pitting. Since the dense, concentrated solution within a pit is necessary for continuing its activity pits are more stable when growing in the direction of gravity.



Pitting corrosion of stainless steel

Pitting corrosion rate increases largely due to chloride ions present in the solution. This is probably due to acid forming tendency of chloride salts and higher strength of HCl. Oxidizing metal ions with chlorides are aggressive pitters. Pitting is usually associated with stagnant conditions such as a liquid in a tank or liquid trapped in a low part of an inactive pipe system. Velocity or increasing velocity often decreases pitting attack. Pitting corrosion is characterized by small anodic area and large cathodic area, resulting in accelerated corrosion at the anodic area. It causes equipment to fail because of perforation with only a small percent weight loss of the entire structure. It is often difficult to detect pits because of their small size and because the pits are often covered with corrosion products.

4.3 Inter-granular Corrosion

Grain boundaries are slightly more reactive than the bulk matrix. Under certain conditions grain interfaces are very reactive and inter-granular corrosion results. Localized attack at and adjacent to grain boundaries with relatively little corrosion of grains is inter-granular corrosion. The alloy disintegrates and or loses its strength. Inter-granular corrosion can be caused by impurities at the grain boundaries, enrichment of one of the alloying elements or depletion of one of these elements in the grain boundary areas. For eg: small amounts of iron in aluminum where the solubility of iron is low, have been shown to segregate in the grain boundaries and cause inter-granular corrosion. It has been shown that based on surface tension consideration the zinc content of brass is higher at the grain boundaries. Depletion of chromium in the grain boundary regions results in inter-granular corrosion of stainless steels. Numerous failures of stainless steels have occurred because of inter granular corrosion. When these steels are heated in approximately the temperature range $265\text{--}419^{\circ}\text{C}$ they become susceptible to inter-granular

corrosion. The chromium carbide in the grain boundary is not attacked. The chromium-depleted zone near the grain boundary is corroded because it does not contain sufficient corrosion resistance to resist attack in many corrosive environments. The common 18-8 stainless steel contains from .06 to .08 % carbon, so excess carbon is available for combining with the chromium to precipitate the carbide. This situation is shown schematically in Figure 8.

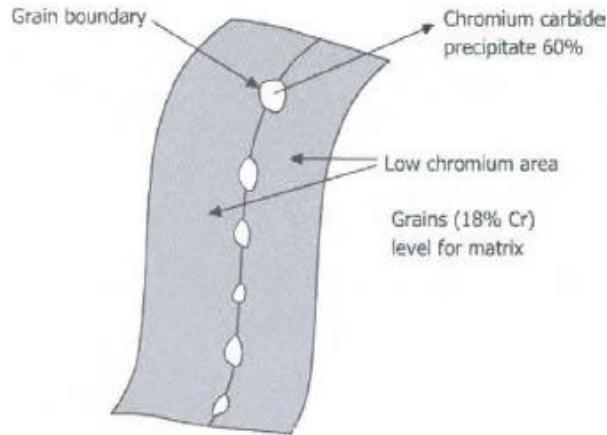


Figure 8. Schematic representation of a grain boundary in stainless steel

Carbon diffuses towards the grain boundary quite readily at sensitizing temperatures, but chromium is much less mobile. The surface already available at the grain boundary facilitates the formation of a new surface, namely that of the chromium carbide. Chromium carbide precipitates have been described for as particles because they are too small. This type of corrosion occurs along grain boundaries and only where the material, especially sensitive to the corrosive attack exists and corrosive liquid possesses a selective character of attacking only at the grain boundaries, but leaving the grain interiors untouched or only slightly attacked. This type of corrosion is due to the fact that the grain boundaries contain material, which shows electrode potential, more anodic than that of the grain center in the particular corroding medium. This may be due to precipitation of certain compounds at the grain boundaries, thereby leaving the solid material solution (just adjacent to the grain boundary) impoverished (or depleted) in one constituent. The impoverished solid solution is anodic with respect to the grain centers as well as to the precipitated compound, so that it will be attacked preferentially by the corrosive environment.

Eg. During the welding of stainless steel chromium carbide is precipitated at the grain boundaries, thereby just adjacent to grain boundaries becomes depleted in chromium composition and is more anodic with respect to the solid solution within the grain (which is richer in chromium). For the same reason it is also anodic to the particles of the chromium carbide so-precipitated. Illustrations for inter granular corrosion is given in Figure 9.



Figure 9. Illustration for inter-granular corrosion

4.4 Stress Corrosion: Stress corrosion or cracking refers to cracking caused by the combined effect of a tensile stress (residual, applied or thermal) and a specific corrosive environment. During stress corrosion/cracking, the metal or alloy is virtually un-attacked over most of its surface, while fine cracks progress through it. The two classic cases of stress corrosion cracking are “season cracking” of brass cartridges and caustic embrittlement of steel boilers.

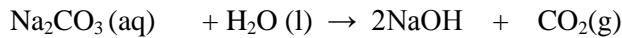


Stress cracking of brass

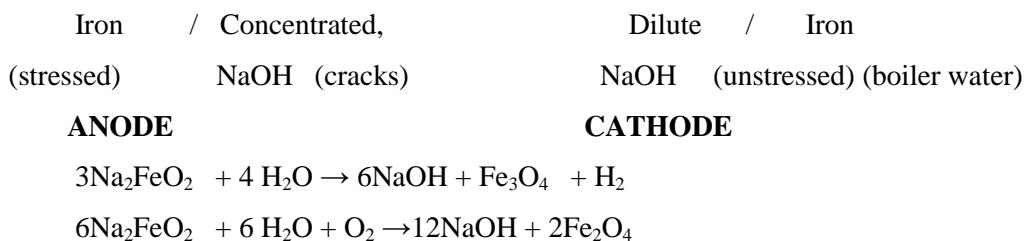
The metal atoms under stress are at higher energy levels compared to those free from stress. The stressed part of the metal becomes more reactive than the stress free part. Corrosion cell are formed with stressed part acting as anode and stress-free part acting as cathode. The stressed part undergoes corrosion under specific corrosive environment, initiating the crack. It grows and propagates through the metal until the metal failure occurs or it may stop after propagating a finite distance when either the tensile stress or the corrosive environment is eliminated. Thus the stress corrosion is characterized by three distinct steps of crack initiation, crack propagation and final failure. In the first step a small crack forms at some point of high stress corrosion. Then crack propagation takes place as this crack advances incrementally with each stress cycle. The final failure occurs very rapidly once the advancing crack has reached a critical size.

The caustic embitterment is a typical example of stress corrosion. This is a dangerous form of

stress corrosion observed in boiler. Water fed into boilers may contain free alkali. Water softened by lime soda process contains sodium carbonate. Under high temperature and pressure prevailing within boilers sodium carbonate hydrolyses to sodium hydroxide and carbon dioxide.



Thus water inside the boiler becomes very dilute NaOH solution. Local stresses exist in metal sheets of boiler under rivets. Minute cracks develop on the metal sheets when the stress is relieved. Dilute NaOH solution flows into these minute hairline cracks. Water evaporates by the heat of the metal, depositing sodium hydroxide within the cracks. Fresh water flows into them and evaporates again depositing more NaOH. Concentration of NaOH increases in these cracks due to the repetition of this process. NaOH concentration cell forms between the stressed and unstressed part of the metal. The sodium hydroxide attacks the metal forms sodium ferroate (Na_2FeO_2) which further undergoes hydrolysis according to the following equation regenerating NaOH enquire



When iron changes to these oxides metallic properties like malleability and ductility are lost. It becomes brittle. The brittleness is caused by caustic alkali. Hence it is called caustic embrittlement. The minute hairline cracks are caused by local stresses under the rivet heads. The continuation of caustic embrittlement of boiler parts often results in boiler failure and in extreme cases may lead to boiler explosion. The caustic embrittlement can be minimized by the following methods;

- (i) Na_2SO_4 , tannin or lignin is added to water. These substances deposit within the cracks and prevent the infiltration and accumulation of NaOH.
- (ii) Boiler can be constructed by welding the sheets to avoid local stresses.
- (iii) Caustic embrittlement is minimized by using demineralized water that does not contain NaOH and Na_2CO_3 .

5 FACTORS AFFECTING CORROSION

The rate of corrosion of a material in a given environment is influenced to a varying degree by several factors. These factors can be classified into two types given below:

- A) *Primary factors* – the factors associated mainly with the metal
- B) *Secondary factors* – the factors which vary mainly with the environment

5.1 Primary factors

Factors related to the corroding metals are known as primary factors.

(a) *Nature of metal and relative electrode potentials of metals*

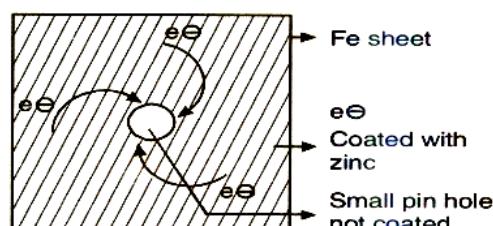
In general the metals with lower electrode potential values are more reactive than the metals with higher electrode potential values. However, there are few exceptions for this general trend, as some metals show the property of passivity. Magnitude of corrosion cell potential is one of the major factors which decide the corrosion rate. The larger the potential difference between the anodic region and cathodic region of the corrosion cell, higher is the corrosion rate. When two different metals with large difference in their electrode potential are in contact with each other, the more reactive metals undergo corrosion. When potential difference is more, higher corrosion current is produced and the free energy decrease accompanying the process is higher and corrosion rate is also higher. Example; Corrosion of zinc is faster than iron when in contact with copper in a medium. This is because the electrode potential difference between Zn and Cu is greater than that of Fe and Cu.

(b) *Relative Cathodic and Anodic area*

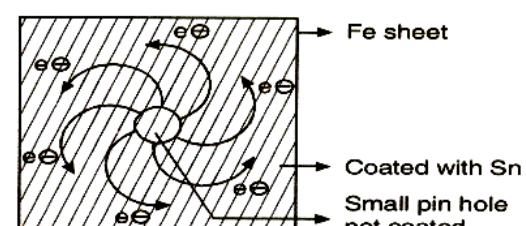
The rate of corrosion is greatly influenced by the relative areas of anode and cathode. If a metal has a small anodic area and large cathodic area, then the corrosion is more intense and faster is the corrosion rate at the anodic region. This is shown schematically in Figure 10.(a)

At anode oxidation takes place and electrons are liberated. At the cathode these electrons are consumed. When the anode is smaller and cathode region is large all the electrons liberated at the anode are rapidly consumed at the cathode region. The demand for electrons by the large cathodic areas can be met by the smaller anodic areas by undergoing corrosion at a faster rate. This makes the anodic reactions to take place at its maximum rate thus increasing the corrosion rate. Example; Small steel pipe fitted in a large copper tank, iron bolt and nuts in copper boilers.

If the cathode is smaller, the consumption of electrons will be slower and the corrosion reaction as a whole will be slower as shown schematically in figure 10(b).



(a) Large anodic area and small cathodic area



(b) Large cathodic area and small anodic area

Figure 10. Schematic representation to explain the ratio of anodic and cathodic area

(c) *Hydrogen Overvoltage*

The difference between the observed potential at which reduction of H^+ ions to H_2 gas occurs at a cathode

and the theoretical potential at which it should have occurred is known as hydrogen overvoltage. The magnitude of hydrogen overvoltage depends upon the nature of the metal used as cathode. Increased hydrogen overvoltage at a cathode reduces corrosion rate, when the reduction of H^+ ions is the cathodic process. When the hydrogen evolution reaction on the metal surface is low, H_2 gas is liberated easily and then the cathodic reaction rate is faster. This makes the anodic reaction also faster, thereby promoting overall corrosion reaction.

(d) *Nature of corrosion product*

The corrosion product is usually an oxide of the metal which may or may not form a protective layer on the metallic surface. If the corrosion product deposits and is insoluble, stable, uniform adherent and non-porous, it acts as a protective film preventing the further corrosion of metal.

If the corrosion product is not deposited and is soluble, unstable, non-uniform, non-adherent and porous, the corrosion continues unabated since in such cases fresh metal surface is continuously exposed to the corrosion environment and corrosion of the metal surface takes place continuously.

In strong oxidizing environments, metals like aluminum, chromium, and titanium are highly passive as their oxides form protective films on the metal surface preventing further corrosion. Metals such as iron, and zinc, do not form any protective film and are highly susceptible for continuous corrosion when exposed to oxidizing environments.

If the corrosion product is soluble in the corrosion medium, then corrosion proceeds at a faster rate as fresh metal surface is exposed continuously to the corrosive environment and the destruction of the surface occurs continuously. If the corrosion product interacts with the medium to form another insoluble product, then protective film formed on the metal prevents further corrosion.e.g. $PbSO_4$ formed in the case of Pb in H_2SO_4 .

5.2 Secondary factors

Factors related to the environment are known as secondary factors

(a) *Concentration and nature of electrolytes*

Conductance of an electrolyte medium depends upon its ionic concentration. Corrosion current, $I = V/R$ becomes large at small R. Resistance is low and conductance is high at high ionic concentrations. Hence rapid corrosion rate is observed at high ionic concentration. Conductivity of deionized water is 1-10 millimhos per meter. Conductivities of tap water and sea water are 10-20 milli-mhos per meter and 5.3 mhos per meter respectively. Therefore, corrosion rate in sea water is nearly 500 times as fast as that in tap water and 5000 times as fast as that in demineralized water, based on their conductivity. In the marine atmosphere, the presence of sodium and other chlorides leads to increased conductivity of the liquid layer in contact with the metal surface. So the corrosion rate is increased and the salt air of coastal cities is very damaging to exposed metal when compared to that at interior places. In the vicinity of industrial areas,

atmosphere contains corrosive gases like CO_2 , SO_2 , H_2S and fumes of HCl , H_2SO_4 . So the acidity of the liquid adjacent to the metal surfaces increases and its electrical conductivity also increases. This increases the corrosion current in the electrochemical cells on the metal surface.

Nature of electrolyte is another factor. Some electrolyte cause polarization and bring down the corrosion rate. The phosphate ions form an insoluble, protective phosphate film of metal ions on the surface of a metal and reduce its corrosion rate. The chloride ions penetrate the protective oxide film of a metal increasing the ionic conductance of the film. Protective action of this film decreases as a result of this and corrosion rate gets enhanced.

(b) pH of the medium

In general, lower the pH of the corrosion medium, higher is the corrosion rate. The acidic media provides more conducive environment than the alkaline or neutral media. The corrosion rate increases slowly and gradually with decreasing pH and becomes rapid at pH less than 4. At $\text{pH} > 10$, corrosion of iron practically ceases due to the formation of a protective coating of hydrated oxides of iron. However, some metals like Al, Zn and Pb, undergo fast corrosion in highly alkaline solution.

(c) Temperature

The rate of a chemical reaction in general, increases with rise in temperature. Curve A of Figure 11 indicates the corrosion of Nickel in HCl . Increase in temperature increases the conductance of the corrosion medium, which also contributes to the increase in corrosion rate. In the case of corrosion resistant passive metals the rise in temperature decreases the passive range and thereby increases the corrosion rate. However in some cases, initial negligible temperature effect will be followed by a very rapid increase in the corrosion rate at a very high temperature. This trend is reflected in Curve B of Figure 11. Example is the corrosion of stainless steel in HNO_3 . This is due to the fact that increasing the temperature of nitric acid gently increases its oxidizing power. At low or moderate temperature, stainless steels exposed to the nitric acid are in the passive state very close to the trans-passive region. Hence at elevated temperature, there will be increase in the oxidizing power of the medium which results in the increase in the rate of corrosion. However, if the corrosion medium contains dissolved gases the solubility of the gases decreases with temperature. In such a situation corrosion rate also decreases. Presence of too much humidity also decreases the rate of corrosion.

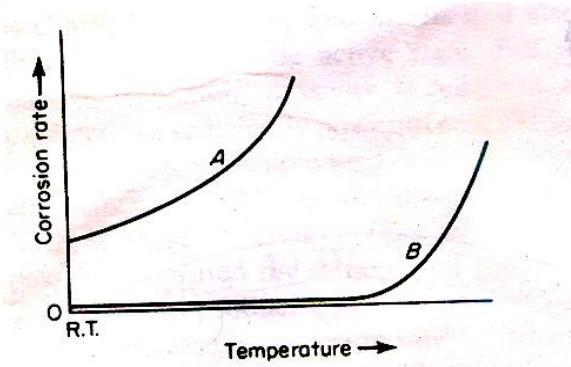


Figure 11. Effect of temperature on corrosion rate of Ni in HCl and stainless steel in HNO₃

(d) Polarization at anodic and cathodic region

During electrochemical corrosion both anode and cathode can no longer be at their reversible equilibrium potentials. The deviation from reversible equilibrium potential of an electrode when brought in contact with another electrode is called polarization. There is a variation of electrode potential due to inadequate supply of species from the bulk of the solution to the electrode. In the process of corrosion the polarization of an anode or cathode decreases the corrosion rate substantially as anode and cathode polarization retards anode and cathode reactions respectively. Because of anodic polarization (i.e. shifting of potential to more positive values and the current to lower value), the tendency of anodic metal surface to undergo oxidation decreases. It slows down the anodic reaction and thus decreases the overall corrosion rate. Cathodic polarization retards the cathodic reaction. This can be due to chemical polarization of the cathode reactant with electron. The retarded movement of the cathodic reactant to the cathode surface or retarded removal of the cathodic reaction product from the surface of the cathode also makes the cathodic reaction slower. For the corrosion to continue both anodic and cathodic reaction should take place simultaneously. The slow rate of any one of the reactions makes the corrosion reaction slower.

6. PROTECTION AGAINST CORROSION

Corrosion of metals occurs when they come in electrical contact with a corrosive environment. Therefore metallic corrosion can be prevented by either changing the metal or altering the environment or by separating the metal from the environment. In addition, corrosion can also be prevented by changing electrode potential of the metal. The most effective and economic method; however is to deal with the corrosion problem at the design stage itself.

Various methods available for corrosion control are listed below;

*Selection of material & design improvement

*Change of metal

*Change of environment

*Use of coatings for separating metal from environment

6.1 Selection of materials and proper design

Selection of materials:- Planning of corrosion prevention starts with selection of proper metals and alloys.

Therefore one has to take into account the following material selection principles.

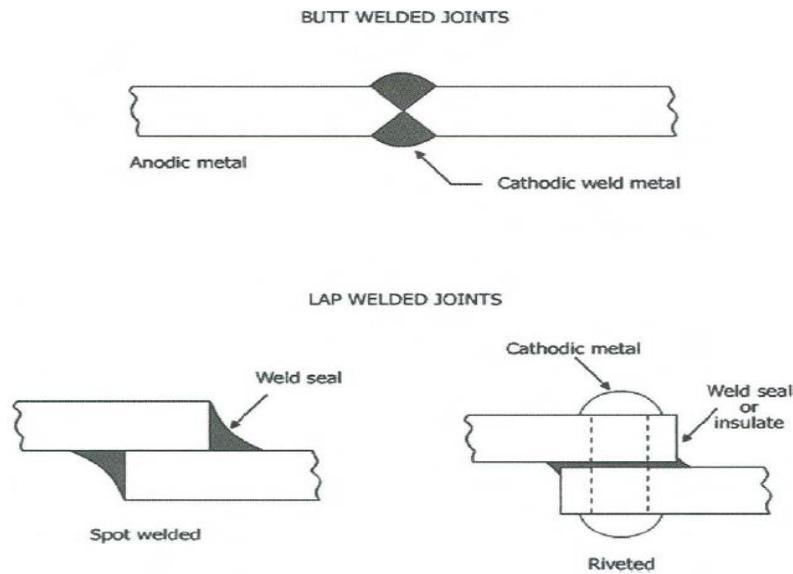
- a) Noble metals such as Pt, Au and Pd do not undergo corrosion. But one cannot use noble metals because of its prohibitive price. Pure metals show greater resistance to corrosion than impure one.
- b) Rate of corrosion can be controlled by using an anodic material of larger area and cathodic material of smaller area.
- c) Suitable alloying of metals in some cases improves its corrosion resistivity.
- d) Avoid residual stress in fabricated articles by proper heat treatment (annealing)

e) The use of two dissimilar metals having large difference in their electrode potentials should be avoided. Under unavoidable circumstances, the metals chosen should be very close in the galvanic series. Proper insulator fitting may be used in between to avoid direct contact of metals.

Proper design:- A good design minimizes corrosion in metallic structures or equipment. A large number of corrosion failures are due to improper design and failure to use available knowledge.

Corrosion possibilities can be controlled by proper designing of the equipment. Some of the more important general rules for design which should be observed are described below:

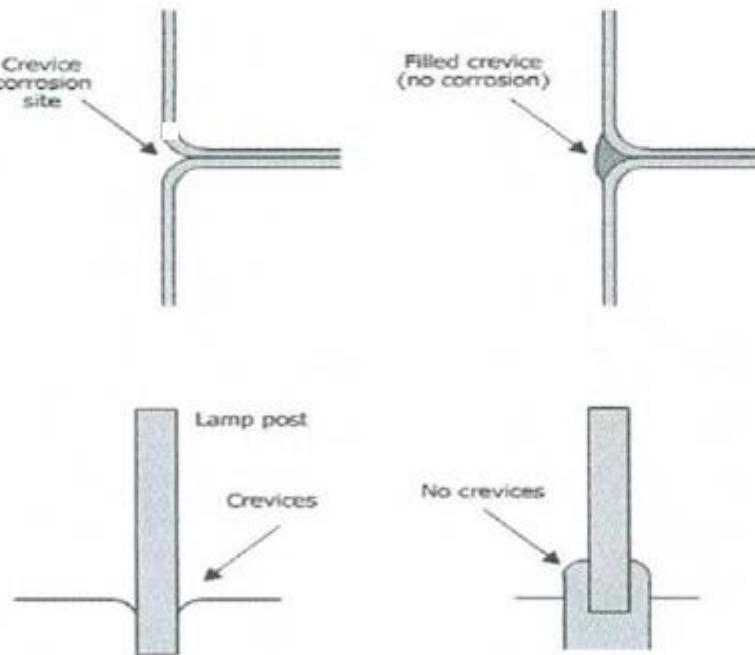
- a) **Simplify forms**: structures having simpler forms can be protected easily and efficiently. A complicated shape having more angles, corners, edges and internal surfaces will have a larger surface area exposed to the corrosive environment and will be difficult to protect by painting or other surface treatment



Improvement of design by welding the joints

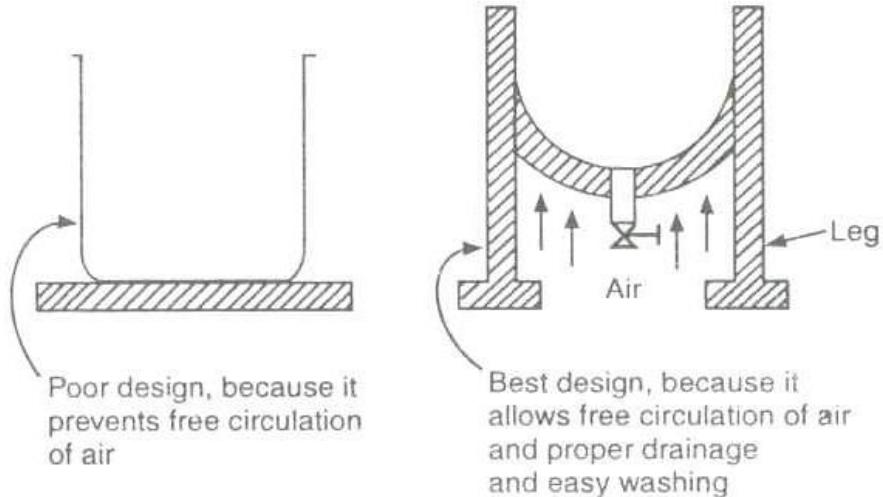
Electrical boxes exposed to atmosphere should be so designed that water does not collect at the top or in the crevices. Profile should be so designed that water is drained completely and moisture retention should be as low as possible.

b) Avoid crevices: Crevices allow moisture and dirt to be trapped which result in increased corrosion. If crevices are either present in a structural or cannot be avoided they should be filled by welding or by using filler.



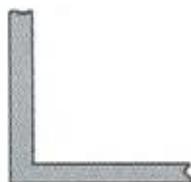
Improved designs to minimize crevice corrosion

c) Avoid residual moisture: The design should be such as to protect the structure from retained or residual moisture. In order to avoid residual moisture, ventilation is usually as important as drainage. Condensation should be reduced by free circulation of air.

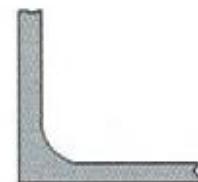


Improved design to minimize differential aeration corrosion

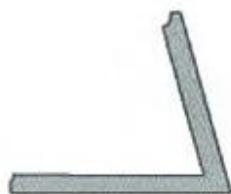
- d) **Avoid sharp corners and bends:** These are the potential corrosion sites and these must be replaced by round corners. Sharp corners result in thin coating at corners and are not protected effectively rounding the corners resulting in an even coating. Sharp bends and other areas where the fluid direction is changed rapidly can promote corrosion and should therefore be avoided.



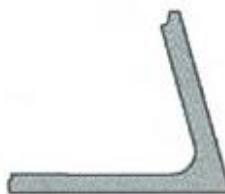
BAD: Dirt not easily removed



GOOD: Dirt easily removed



BAD: Dirt not easily removed



GOOD: Dirt easily removed

6.2 Cathodic protection

Corrosion of a structure can be controlled if the entire article can be changed into the cathodic part of a corrosion cell. This is called cathodic protection. Ship's steel hulls, offshore drilling platforms, oil and gas under sea pipelines, containers used to store water and other liquids are protected by this method.

Cathodic protection is done by two different methods.

a) Sacrificial anode method

A more reactive metal is kept in contact with the metal structure to be protected by this method. The reactive metal becomes anodic part and the structure becomes cathodic part of the corrosion cell. The anode is sacrificed to protect the structure. Hence this method is called sacrificial anode method.

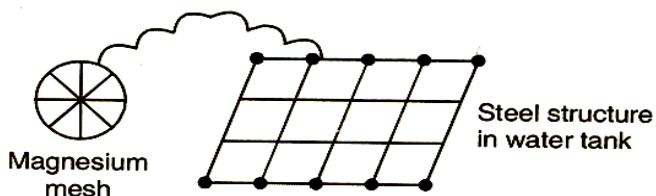
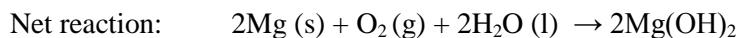
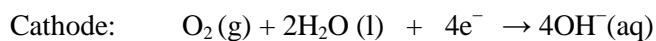
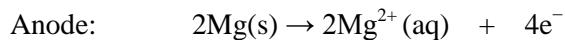


Figure 13. Mg being used as sacrificial anode for protecting iron article

Mg is more reactive metals than iron and hence it is usually used as anode. It becomes anodic part in contact with iron. Following reaction take place when Mg is made to couple with Iron.



Advantages: * No external power supply is necessary.

* Can be used in remote and difficult to reach areas.

* Low installation cost.

* Minimum maintenance

* Replacement is much cheaper.

Current Method

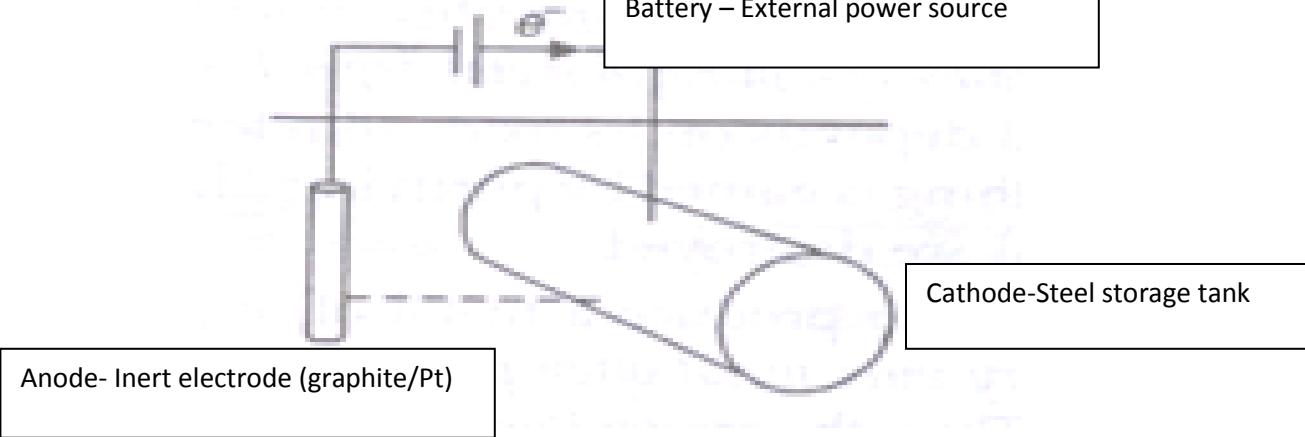


Figure 14. Schematic diagram of impressed current method

In this method the metallic structure is made cathode with the use of impressed current by connecting the negative terminal of the external DC power source to the metallic structure to be protected and positive to an inert anode. The anode may be made up of steel, graphite and platinum group metals. The anode may be consumed very slowly or may not be consumed at all depending on the anode material. The anode is surrounded by back film consisting of coke breeze, gypsum to improve electrical contact between the anode and the environment if it is a poor ionic conductor. Schematic representation of impressed method to control corrosion is shown in the Figure 14.

Advantages:

- * Applicable to large structures and long term operations.
- * Uncoated parts can be protected.

Disadvantages:

- * Larger installation cost.
- * Higher maintenance cost.
- * High energy consumption
- * Localized corrosion may occur if the impressed current is not uniform on the entire surface.

6.3 Anodic protection method

Anodic protection is based on the fact that under certain ranges of potentials a metal or alloy becomes passive, resulting in the lowering or prevention of corrosion. Anodic protection may be understood by means of potential current density diagram as shown in Figure 15.

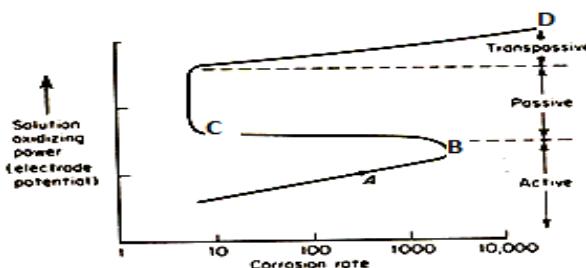


Figure 15: Plot of Potential Vs Corrosion rate.

Certain metals and alloys lose chemical reactivity under certain environmental conditions .This is a phenomena of complex nature and it occurs under specific conditions. This phenomenon is called passivity of metals. Eg; Al, Ti, Cr, Ni, Mo and alloys containing major amount of these metals. The curve

is obtained by applying a known potential to a metal specimen and measuring the current changes. As the potential is increased, initially current also increases (AB) indicating the dissolution of the metal. This trend continues until the current reaches a critical value (I_{crit}) and passivation due to the development of an oxide layer sets in. This potential is called passivating potential (E_p).

Above E_p the current flow decreases and reaches a minimum value called the passivating current, $I_{passive}$. The decrease in current is due to the formation of a passive film on the metal. If the potential is further increased the metal remains unattacked up to a particular potential is reached (CD). In this range corrosion rate of the metal is very small.

The potential range in which the anodic protection can be achieved is called passive region. The optimum potential for anodic protection is midway in the passive region since it permits slight variations in the controlled potential without affecting corrosion rate. Beyond the point D any further increase in potential tends to increase the current due to the dissolution of metal. It is called trans-passive region.

The mechanism of protection thus lies in the act of applying certain potential range in which no corrosion takes place. This potential range depends primarily on the relationship between the metal and reactants resulting in passivity. Iron, Nickel, Chromium, Titanium and their alloys are protected by this technique.

The anodic protection to a structure is applied by using a device called potentiostat. It is an electronic device that maintains a constant potential with respect to a reference. The anodic protection of steel tank containing sulphuric acid is shown in the Figure 16.

Potentiostat has three terminals. One connected to the storage tank, other to an auxiliary cathode (Pt) and third to a reference electrode (Calomel). In operation the potentiostat maintains a constant potential between the tank and the reference electrode, corresponding to the passive range.

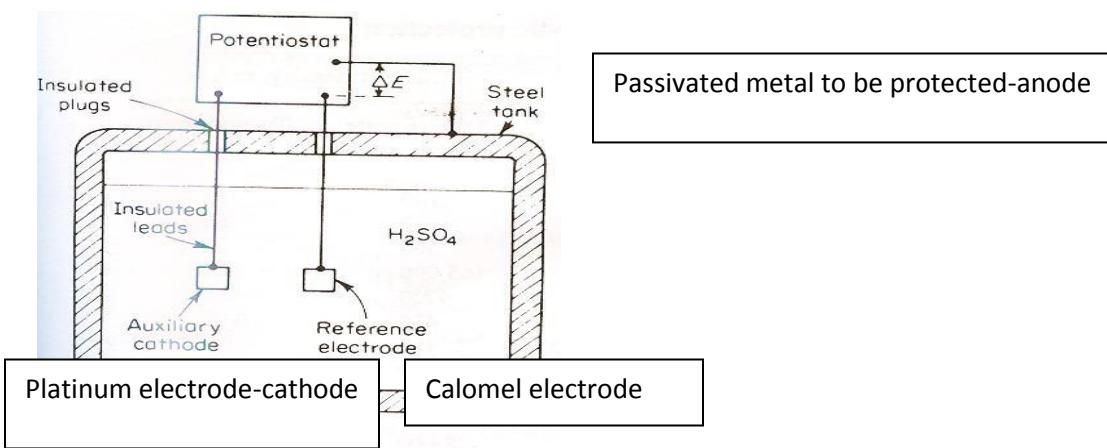


Figure 16. Potentiostat used in anodic protection

The potential is initially increased to E_p for the corrosion to occur, then increased to E_f (fade potential) when the current decreases to a small value. Now the potential is kept at constant E_p and the current is

maintained at I_p . Example: Stainless steel containers used for transporting corrosive chemicals are protected from corrosion by maintaining them at proper E_f and I_p .

Advantages:

- Reduced equipment cost-i.e. it is possible to protect two or more vessels with one controller
- Cost of anodic protection is generally independent of tank capacity.
- Applicable in extremely corrosive environments
- Low current demand

Disadvantages:

- Cannot be applied in case of corrosive medium containing aggressive anions such as chloride.
- Needs continuous supply of electric current
- Applicable only to those metals that show active passive behavior
- Initial installation cost is high
- It cannot reduce the corrosion rate to zero.

6.4 Use of corrosion inhibitors

The use of corrosion inhibitors is a possible means of corrosion control by altering the environment. A corrosion inhibitor is any chemical substance which when added to a solution (usually in small amounts) increases the corrosion resistance. Corrosion inhibitors are used in various industrial applications, including cooling water systems, automobile engine coolants, acid pickling solutions, in surface treatment of metals, in paints and organic coatings. The mechanisms of corrosion inhibition are different for acidic and neutral solutions. In acid solutions, natural oxide films initially present on the metal surface are dissolved away so that inhibitors then interact directly with the metal surface. In neutral solutions, the system is more complex because the metal surface is oxide covered and also because dissolved oxygen may participate in the electrode reaction. Many inhibitors provide protection against corrosion either by retarding anodic dissolution process or cathodic reduction process or both the processes. On the basis of this property, inhibitors can also be classified either as anodic or cathodic inhibitors.

a) **Anodic Inhibitors:** Substances used to stop anodic reaction are called anodic inhibitors. They form insoluble compounds with the metal ions formed at the anodic part due to its initial corrosion. These insoluble compounds form a protective film on the anode surface. This film isolates the anode from the electrolyte medium and stops its corrosion. The anions such as chromate, tungstate, molybdate and phosphate are used to arrest anodic processes. Anodic inhibitors are found to be effective provided they are added above their critical concentrations. If the added inhibitor is insufficient, it cannot plug all the anodic sites. This leads to severe pitting corrosion.

b) Cathodic Inhibitors: Substances used to stop cathodic reaction are called cathodic inhibitors. They form a protective film on cathodic surface and isolate it from the electrolyte medium. Cathodic reaction stops as a result of this.

There are two major reactions taking place on cathodic surface depending on the nature of corrosive environment. They are: 1) Hydrogen evolution type 2) Oxygen absorption type

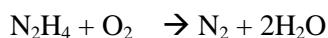
1) Hydrogen evolution type inhibitors:- $2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$ (acid medium)

The evolution of hydrogen gas over the cathode can be prevented either by retarding the diffusion of H^+ ions to the cathode or by increasing the hydrogen overvoltage. The diffusion of H^+ to the cathode is retarded by the addition of certain organic compounds which contain N or S. Urea, thiourea, mercaptans and heterocyclic nitrogen compounds are widely used as cathodic inhibitors. Such substances are adsorbed on the cathodic sites forming a protective film that suppresses cathodic reaction. Even the use of insufficient concentration of these substances does not have any adverse effect.

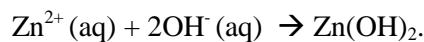
The evolution of H_2 at the cathode can also be prevented by increasing overvoltage of hydrogen. This is achieved by the addition of oxides of Arsenic, Antimony or salts like sodium meta-arsenite. They deposit as adherent metallic film on the cathode areas thereby prevents the evolution of H_2 , since hydrogen overvoltage for those metals is quite high.

2) Oxygen absorption type inhibitors:- $\text{O}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 4\text{OH}^-(\text{aq})$ (in neutral or slightly alkaline medium)

This cathodic reaction can be easily controlled either by removing the oxygen from the corrosive media or by decreasing the diffusion rate of oxygen to cathode. Reducing agents such as N_2H_4 and Na_2SO_3 remove oxygen from the corroding environment by combining with it.



Decreasing the diffusion rate of oxygen is achieved by adding salts such as ZnSO_4 , MgSO_4 , NiSO_4 to the aqueous environment. They undergo hydrolysis and form a deposit of their insoluble hydroxide on the cathodic sites.



The protective film being impermeable to oxygen prevents its further diffusion to cathodic sites.

6.5 Surface Coating

A protective coating on the metals and alloys isolates them from electrolyte medium and hence corrosion cells do not work. This prevents corrosion.

Metallic Coating: Coating of a metal on a substrate metal requiring protection against corrosion is metallic coating. There are two types of metallic coating. They are

* *Anodic metal coating* – coating the substrate metal with a more anodic metal eg. galvanizing

* *Cathodic metal coating* - coating the substrate metal with a more cathodic metal eg. tinning

Galvanization: Giving a Zn metal coating on iron and mild steel is known as galvanization.

When the coating covers the entire surface of the substrate metal, the coating isolates it from the environment and protects it against corrosion. When the coating breaks or cracks zinc act as anode and the substrate iron and mild steel acts as cathode. Thus zinc becomes sacrificial anode and provides protection to iron and mild steel sheets, pipes, wires are usually galvanized.

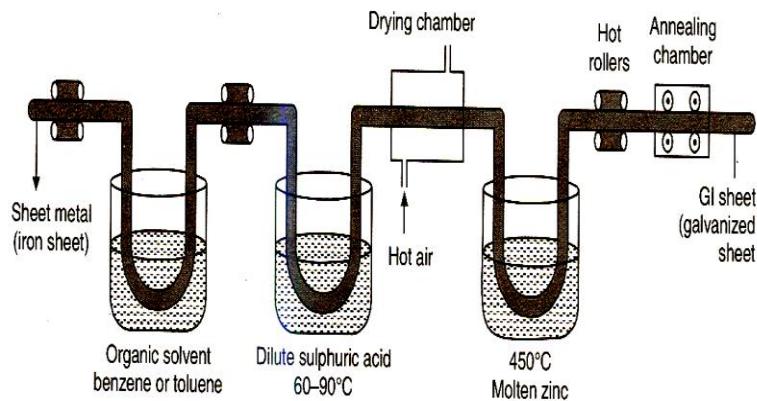


Figure 17. Galvanization process

Pretreatment: The metal surface is cleaned to remove organic matter like grease/oil by washing with organic solvents. The rust and other deposits are removed by washing with dilute sulfuric acid and the surface is finally washed with water and air dried.

Process: Galvanization is done by hot dipping processes. Melting point of Zn is 419°C. Zn is melted and kept at 425–430°C. Ammonium chloride flux is spread over it to prevent its oxidation by air. Iron and mild steel objects are degreased, pickled and cleaned. They are then dipped in molten Zn bath. Pair of hot rollers wipes out excess of zinc coating to produce a thin uniform coating on the objects which are then cooled. It is shown schematically in the Figure 17. Galvanized sheets cannot be used to prepare tins or cans for storing food materials, because zinc salts are toxic.

Applications: Used in the manufacture of fencing wire, roofing sheets, buckets, bolts, nuts, nails and screws.

Tinning: A process involving a coating of tin on iron and mild steel is called tinning. Tinning protects the article until the coating covers the surface completely, by isolating it from the environment. When the coating cracks or breaks intense or pitting corrosion of the articles at the exposed region occurs, because tin is cathodic with iron and small anodic regions are in contact with large cathodic area.

Pretreatment: Steel sheet is washed with organic solvents to remove grease/oil deposits. It is then treated with dilute sulfuric acid to remove rust deposits and finally washed with water and air dried.

Process: Tinning is done by hot dipping. Melting point of Sn is 232°C . Tin is melted and kept at 250°C . It is covered with ZnCl_2 and NH_4Cl flux to protect liquid tin from oxidation by air. It is dipped in molten tin and the passed through rollers kept in palm oil to squeeze out excess tin from it. Sheet is cooled, rolled and stored. It is shown in Figure 18.

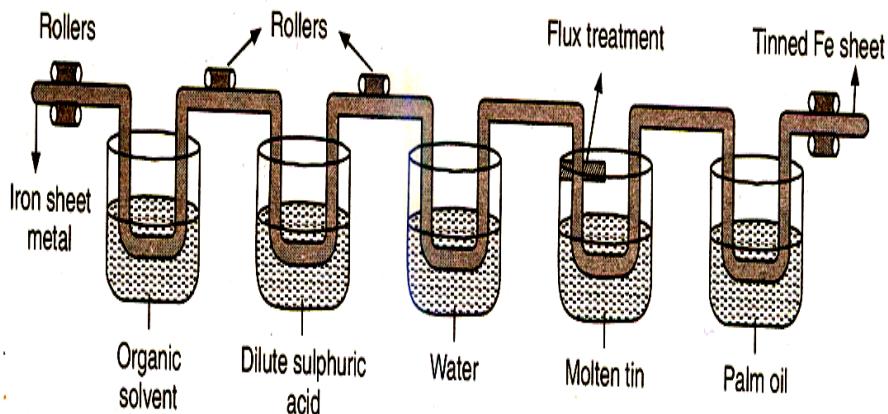


Figure 18. Tinning process

Applications:

- Used for coating steel, copper and brass
- Used in the manufacture of containers for storing food stuffs
- For making cooking utensils and refrigeration equipment.

Comparison of Galvanizing and tinning

Galvanizing	Tinning
A process of coating Zn over iron/ steel to prevent it from rusting (anode metal coating)	A process of coating Sn over iron to prevent it from corrosion (cathode metal coating)
Hot rollers used to wipe excess coat are not immersed in oil	Hot rollers are immersed in oil
Galvanized containers cannot be used to store acidic foodstuffs because zinc reacts with food acids forming highly toxic zinc compounds.	Tin coated containers can be used to store foodstuffs because tin is nontoxic and does not react to cause any food poisoning
Zinc protects the underlying iron by sacrificial action	Tin protects the base metal iron due to its noble nature.
Zinc continues to protect iron by sacrificial action in the event of puncture/break in coating	Tin protects the iron till the coating is perfect and any break causes rapid corrosion of iron

7. SUMMARY

Metallic corrosion is one of the problems often encountered in our industrialized society, and hence it has to be studied. Enormous breadths of engineering systems depend upon corrosion protection for their reliability, performance and safety. These corrosion problems are typically complex phenomena, affected by many variables and not necessarily restricted to one form of corrosion. The different types of corrosion include galvanic, pitting, inter-granular and stress corrosion. Certain factors can tend to accelerate the action of a corrosion cell and these include nature of the metal and their relative environment, cathode and anode areas, nature of corrosion products, hydrogen overvoltage pH of the medium, temperature and polarization. Various measures are taken in almost all industries to control the corrosion rate. In this regard it becomes essential to understand the different forms of corrosion and factors affecting it. Corrosion control techniques include selection of materials and proper design, cathodic and anodic protection methods, surface coating and the use of corrosion inhibitors.

8. Review questions

- 1.** Explain the meaning, importance and consequences of corrosion in industry and in our day-to-day lives.
- 2.** Describe the processes occurring at the molecular level during the rusting of iron.
- 3.** Comment on the following statements, which can be either true or false.
 - (i) Al_2O_3 is corrosion resistant but Fe_2O_3 promotes corrosion
 - (ii) A scratch formed on iron sheets coated with tin results in severe corrosion but the case is the reverse when it is coated with zinc.
- 4.** Explain the following terms as they apply to the corrosion;
 - (a) Cathodic protection (b) anodic protection.
- 5.** Distinguish between dry and wet corrosion.
- 6.** Explain briefly the electrochemical theory of corrosion.
- 7.** What are corrosion inhibitors? Explain the types of inhibitors used to control corrosion with examples.
- 8.** Distinguish between the following; i) Electrochemical series and galvanic series ii) Galvanizing and tinning.
- 9.** Discuss the different factors affecting the corrosion process.
- 10.** List the various methods used to control corrosion.

MODERN METHODS OF CHEMICAL ANALYSIS

Introduction, general methods of quantitative analysis, advantages and disadvantages of the methods, principles of classical methods and instrumental methods, spectroscopic methods of analysis – properties of EMR, EM spectrum, interaction of EMR with matter and its phenomenon, various types of spectra, laws of spectrophotometry – Beer Lambert's law, its derivation, deviations of Beer Lambert's law, Applications of Beer Lambert's law in qualitative and quantitative analysis, numerical problems. (4)

Introduction:

A qualitative method gives information about the identity of atomic or molecular or ionic species or the functional groups present in the sample. A quantitative method provides numerical information of the constituents i.e., the relative amounts of one or more of the constituents of the sample. The quantitative methods are often classified as either classical or instrumental/modern. The classical methods are also called as wet-chemical methods.

Classical and modern/instrumental methods of analysis:

In the early years of chemistry, most analyses (which were being analyzed) were carried out by separating the components of interest by precipitation, extraction or distillation. For qualitative analysis, the separated components were then treated with reagents that yielded products that could be identified by their colors, boiling or melting points, solubilities in a series of solvents, odors, optical activities or their refractive indices. These are the classical quantitative methods, which are the volumetry and gravimetry.

The phenomena other than those used for classical methods were exploited for solving the analytical problems in early twentieth century. The measurement of physical properties of analyte such as conductivity, electrode potential, light absorption or emission, mass-to-charge ratio, fluorescence etc. were used for quantitative analysis. The techniques like distillation, extraction and precipitation etc. were replaced by high efficient chromatography and electrophoretic techniques for separation of components of complex mixtures. These newer methods for separation and determination of chemical species are collectively known as instrumental methods of analysis.

Volumetry:

In volumetric analyses, the volume or mass of a standard reagent required to react completely with the analyte will be determined by carrying out the titrations. The titration is a process used to determine the volume of a standard reagent (known concentration) required to react completely with the analyte. The analyte is also called as titrand and the standard reagent used in the process is called as titrant. Equivalence point is the point at which the volume of the standard reagent added is chemically equivalent to the analyte with which it reacts. In volumetric analyses, the volume of the standard reagent reacted stoichiometrically with the analyte is a measuring parameter. The stoichiometric point or equivalence point may be detected by use of a visual indicator, which exhibit different colours or forms the precipitate in different media. There are four types of volumetric methods of analyses, based on the type of reaction between the standard reagent and the analyte. They are

- (i) Acid-Base titrations
- (ii) Complexometric titrations
- (iii) Precipitation titrations
- (iv) Redox titrations

Based on the relative nature of the acid and bases, the acid-base titrations are further classified as strong acid vs strong base, strong acid vs weak base, weak acid vs strong base and weak acid vs weak base titrations. For a particular volumetric analysis method, an appropriate (specific/selective) indicator is to be used. Some examples of indicators used in various types of volumetric analyses methods are given in the following table-1 along with the phenomena (between the standard reagent and analyte) occurred during the titration.

Table-1: Types of volumetric methods and suitable indicators

Sl. No.	Type of volumetric method	Phenomena	Suitable Indicators	Examples
1	Acid – Base titrations: strong acid vs strong base weak acid vs strong base strong acid vs weak base weak acid vs weak base	Neutralization	Phenolphthalein	HCl vs. NaOH
			Phenolphthalein	CH ₃ COOH vs NaOH
		Complex formation	Methyl orange	HCl vs. NH ₄ OH
			No suitable indicator	CH ₃ COOH vs NH ₄ OH
2	Complexometric titrations	E BT	Zn (or Ca) vs. EDTA	disodium salt

3	Precipitation titrations	Precipitation	Potassium chromate	Cl^- vs. AgNO_3
4	Redox titrations	Reduction and oxidation reactions	Diphenylamine	Fe^{2+} vs. Cr^{6+}

The essential conditions for any volumetric method of analysis are:

- (i) The reaction must proceed to completion rapidly
- (ii) The reaction should not be complicated by additional or side reactions
- (iii) There should be a detectable change (such as a sharp change in colour or formation of a precipitate) in the solution undergoing titration at the stoichiometric end point
- (iv) A suitable indicator must be available for detecting the end point.

Gravimetry:

In gravimetric analyses, the mass of the analyte or some compound produced from the analyte after treating it with appropriate reagent was determined. Gravimetric methods are based on the measurement of mass of the analyte or the substance derived from the analyte using an analytical balance. Gravimetric methods are broadly classified as volatilization methods and precipitation methods. Volatilization methods involve the drying or heating of a sample to determine by weight of the content of volatile and or non-volatile components. Precipitation methods involve the formation of a precipitate through an appropriate reaction and weighing the precipitate. The precipitation methods generally proceed through four steps.

- (i) Precipitation: conversion of analyte into a precipitate by an appropriate chemical using a selective reagent
- (ii) Digestion: allow the precipitate to be in contact with its mother liquor and heat it on a steam bath during which recrystallization occurs and pure crystals/product is formed.
- (iii) Filtration: the digested precipitate will be filtered using an appropriate Whatman filter papers or sintered glass crucibles, which are to be selected based on the type of precipitate and the residue forming.
- (iv) Washing, drying and weighing: the filtered precipitate is to be washed with very dilute solution of its mother liquor then dried or ignited followed by weighing and drying till it gives a constant weight.

Instrumental methods of analysis:

The instrumental methods of analysis are based on the measurement of various physical and or chemical properties of the analytes. These methods require the sensing probes or electronic gadgets to measure and quantify the physical/chemical property. The following table-2 shows some of the methods and the corresponding measuring characteristic properties.

Table-2: List of modern methods of analysis

<i>Sl. No.</i>	<i>Instrumental method</i>	<i>Characteristic property</i>
1	Kinetic methods	Rate of reaction
2	Conductometry	Electrical resistance
3	Potentiometry	Electrical potential
4	Polarimetry	Rotation of radiation
5	Refractometry	Refraction of radiation
6	Spectrophotometry and photometry (X-ray, UV, Visible, IR)	Absorption of radiation
7	Emission spectroscopy	Emission of radiation
8	Raman spectroscopy	Scattering of radiation

There is a group of instrumental procedures that are used for separation and resolution of closely related compounds. Most of these procedures are based on chromatography, solvent extraction or electrophoresis. One of the characteristics listed in the above table is usually used to complete the analysis following the chromatographic separations.

Some instrumental techniques are more sensitive than classical techniques. With certain combinations of elements or compounds, an instrumental method may be more selective, but with others, a gravimetric or volumetric approach may have less interference. The instrumental procedures employ is more sophisticated or costlier apparatus.

Spectroscopic methods of analysis:

Spectrometric methods are a large group of analytical methods that are based on atomic and molecular spectroscopy. Spectroscopy is a general term for the science that deals with the interactions of various types of radiation with matter. The interactions of interest were between electromagnetic radiation and matter. But now, spectroscopy has been broadened to include interactions between matter and other forms of energy such as acoustic waves, beams of particles like ions, electrons etc. Spectrometry and spectrometric methods refer to the measurement of the intensity of radiation with a photoelectric transducer or with any other type of electronic device.

If the intensity of absorption of radiation is measured, then it is called Absorption spectroscopy. If the intensity of emission of radiation is measured, it is called Emission spectroscopy.

The most widely used spectrometric methods are based on electromagnetic radiation (the energy is mainly in the form of light and radiant heat). The other forms of energy viz., gamma rays, X-rays, U.V., microwave and radio frequency are less in usage.

General properties of electromagnetic radiation (EMR):

Many of the properties of electromagnetic radiation can be described by a classical sinusoidal wave model, which describes the parameters like wave length, frequency, velocity and amplitude. Unlike the other wave phenomena such as sound, electromagnetic radiation requires no supporting medium for its transmission. So it readily passes through a vacuum.

The wave model fails to account for phenomena associated with the absorption and emission of radiant energy. To understand these processes, it is necessary to consider the particle model of electromagnetic radiation in which the EM radiation is viewed as a stream of discrete packets or wave packets of energy called photons. The energy associated with the photons is proportional to the frequency of the radiation.

Electromagnetic radiation can be represented as electric and magnetic fields that undergo in-phase, sinusoidal oscillations at right angles to each other and to the direction of propagation as shown in the following figure-1.

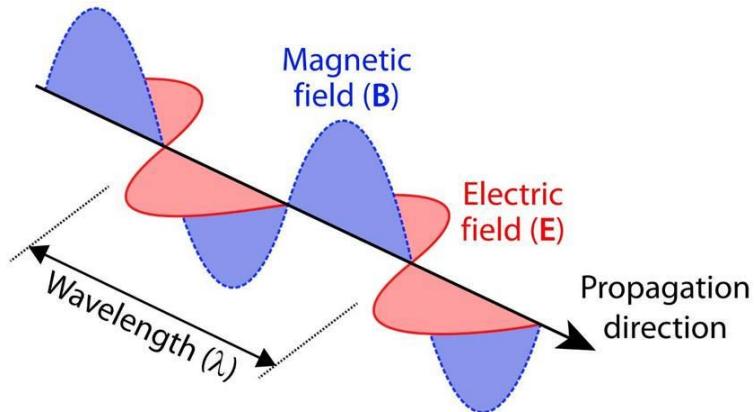


Figure-1: Various components of electromagnetic radiation

The above figure represents a single ray of plane-polarized electromagnetic radiation. The electric field strength is a vector; whose length is proportional to its magnitude. As electric field

is responsible for most of the phenomena, such as transmission, reflection, refraction and absorption, only the electric component of radiation will be considered. However, the magnetic component of electromagnetic radiation is responsible for absorption of radio-frequency waves in nuclear magnetic resonance.

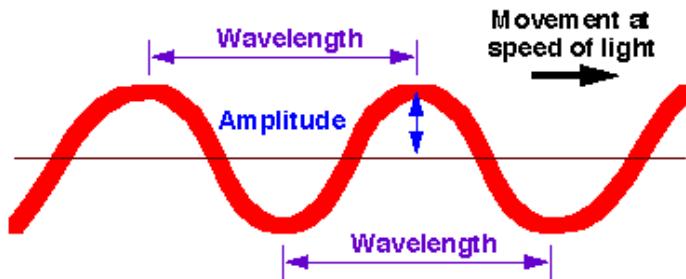


Figure-2: Representation of wavelength and amplitude

The maximum length of the electric vector is known as *amplitude* as shown in figure-2. The time required for the passage of successive maxima or minima through a fixed point in space is called a *period* (p) of the radiation. The *frequency* (v) is the number of oscillations (p) of the field per second and is equal to $1/p$.

$$v = 1/p$$

Wave length (λ) is the linear distance between any two equivalent points on successive waves. Multiplication of the frequency (in cycles per second) by the wave length (in meters per cycles) gives the *velocity of propagation*.

$$V = v \lambda$$

The frequency of a beam of radiation is determined by the source and *remains constant*. But the velocity of the radiation depends upon the composition of the medium through which it passes. Therefore, the above equation implies that the wave length of radiation is also dependent upon the medium.

In vacuum, the velocity of radiation is independent of wavelength and is at its maximum. This velocity is given by ' c ' and is equal to 2.99×10^8 m/sec.

$$c = v \lambda$$

$$v = c / \lambda$$

In any medium containing matter, propagation of radiation is slowed by the interaction between the electromagnetic field of the radiation and the bound electrons in the matter. Since the radiant frequency is invariant and fixed by the source, the wavelength must decrease as radiation passes from a vacuum to another medium.

The wave number ($\tilde{\nu}$) is defined as the reciprocal of the wavelength in cm. and is another way of describing electromagnetic radiation. The unit for it is cm^{-1} . This is widely used in IR spectroscopy. The wave number is frequently used, because it is directly proportional to the frequency and thus energy of the radiation.

$$\tilde{\nu} = 1/\lambda = v/c$$

The *Power* of radiation is the energy of the beam that reaches a given area per second. The *Intensity* of the radiation is the power per unit solid angle. These two quantities related to square of the amplitude and which are often used in spectroscopy.

The phenomena of refraction, reflection, constructive and destructive interference are examples of wave properties. But the wave nature of EMR fails to explain some phenomena like photoelectric effect etc., In order to explain such phenomena, it is assumed that the EMR consists of a stream of discrete packets (particles) of pure energy, called photons or quanta. These have definite energy and travel in the direction of propagation of the radiation beam with the velocity equal to that of the light. The energy of the photon is proportional to the frequency of radiation and is given by the following relationship.

$$E = h v$$

Where E is the energy of the photon in J s, v is the frequency of the EMR in cycles per sec., and h is called Planck's constant (6.624×10^{-34} J-sec.). The intensity of a beam of radiation is proportional to the number of photons per second that are propagated in the beam. But the intensity is independent of the energy of each photon.

The connection between the wave and particle characteristics of radiation was suggested by Planck. According to him, if a transition occurs between the energy states of a system such that a photon of energy E is emitted or absorbed, the frequency of the emitted or absorbed radiation is given by

$$\begin{aligned} E &= h v = hc \tilde{\nu} \\ &= hc/\lambda \end{aligned}$$

With the help of this equation, a particular wavelength or wave number of frequency can be converted into desired units.

Electromagnetic spectrum:

Electromagnetic spectrum (figure-3) encompasses an enormous range of wavelengths and frequencies (and thus energies). In fact, the range is so great that a logarithmic scale is required. The major characteristics of various regions of spectrum are outlined as follows.

(a) γ -ray region:

$$\nu = 3 \text{ EH}z \text{ to } 300 \text{ EH}z \quad (1 \text{ exa Hz} = 10^{18} \text{ Hz})$$

$$\lambda = 100 \text{ pm to } 1 \text{ pm}$$

This region corresponds to the energy range of 1 to 100 GJ/mole. The γ -rays have sufficient energy to bring about nuclear transformations. The γ -ray resonance spectroscopy is known as Mossbauer Spectroscopy.

(b) X-ray region:

$$\nu = 30 \text{ PH}z \text{ to } 3 \text{ EH}z \quad (1 \text{ Pet Hz} = 10^{15} \text{ Hz})$$

$$\lambda = 10 \text{ nm to } 100 \text{ pm}$$

This region corresponds to the energy range of 10MJ/mole to 1 GJ/mole. The energy of X-rays is sufficient to cause the transitions of core electrons of atoms and molecules. X-ray spectroscopy and X-ray photoelectron spectroscopy (XPS) are associated with the X-ray region.

(c) Visible and Ultraviolet region: These are further made up of the following regions.

$$\text{Vacuum ultraviolet} : 1 - 800 \text{ nm}$$

$$\text{Ultraviolet} : 180 - 400 \text{ nm}$$

$$\text{Visible} : 400 - 750 \text{ nm}$$

(d) Infrared region: This region has been further divided into the following sub-regions.

$$\text{Infrared (near)} : 0.7 - 2.5 \mu$$

$$\text{Infrared} : 2.5 - 15 \mu$$

$$\text{Far infrared} : 15 - 200 \mu$$

(e) Microwave region: (0.1 mm to 1 cm wave length) This region corresponds to changes in the rotation of molecules. Separations between the rotational levels of molecules are of the order of hundreds of joules per mole.

(f) Radio frequency region: (10 m – 1 cm wave length) The energy change involved in this region arises due to the reversal of a spin of nucleus or electron. This is of the order 0.001 – 10 J/mole.

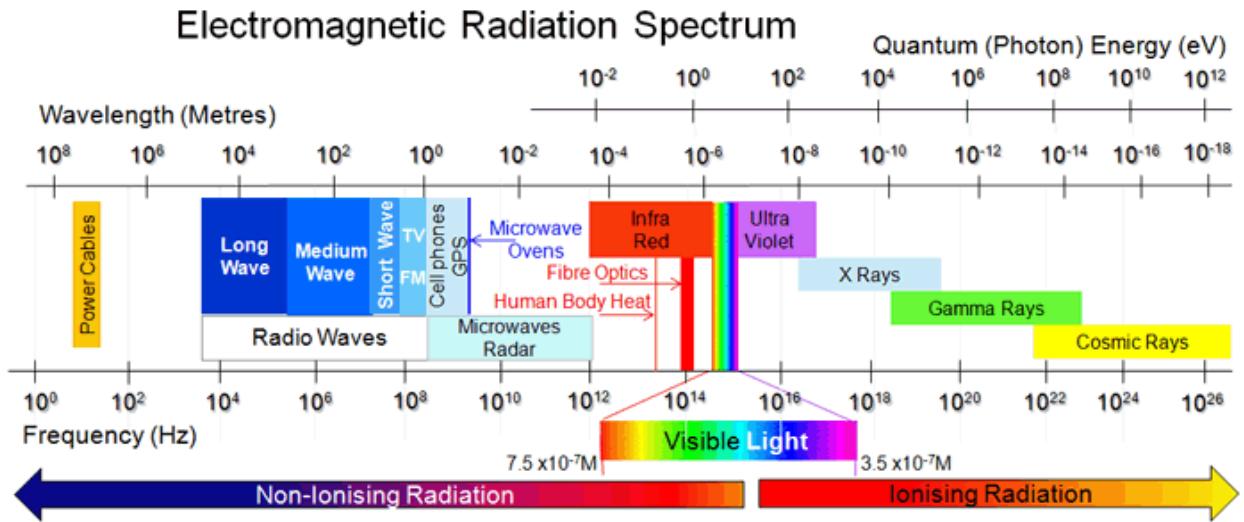


Figure-3: Electromagnetic spectrum

Interaction of EMR with matter:

When EMR passes through matter, a variety of phenomena may occur. Some of these are as follows.

If the photons of radiation possess the appropriate energies, they may be absorbed by the matter and result in electronic transitions, vibrational changes or rotational changes or combination of these. After absorption, atoms or molecules become excited. They give out energy quickly either by losing energy in the form of heat or by re-emitting EMR.

It is not necessarily that the radiation passing through the matter may be absorbed completely. The portion of EMR which passes into matter, instead of being absorbed, may undergo scattering or reflection or may be re-emitted at the same wavelength or a different wavelength.

When EMR is neither absorbed nor scattered, it may undergo changes in orientation or polarization.

In some cases, the molecules after absorbing radiation become excited but they do not lose energy very quickly but with some delay. In such cases the energy is re-emitted as radiation usually of longer wavelength than was originally absorbed. This phenomenon is called as fluorescence. If there is a detectable time delay (in some cases) in re-emission, the phenomena are termed as phosphorescence.

Molecular spectroscopy:

In molecular spectroscopy, the spectra arise from three types of transitions viz., rotational, vibrational and electronic transitions. Broadly speaking, the total energy of a molecule is given by the following equation according to Born-Oppenheimer approximation,

$$E_{\text{total}} = E_{\text{translational}} + E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{electronic}}$$

The molecular energy is the sum of translational energy, rotational energy, vibrational energy and electronic energy. The translational energy is not quantized and furthermore,

$$E_{\text{electronic}} \gg E_{\text{vibrational}} \gg E_{\text{rotational}} \gg E_{\text{translational}}$$

Since the translational energy is negligibly small, we can write the Born-Oppenheimer approximation as

$$E_{\text{total}} = E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{electronic}}$$

Let us illustrate these energies with reference to a diatomic molecule. Rotational energy arises when the molecule rotates about an axis perpendicular to the internuclear axis and passing through the centre of gravity of the molecule. Vibrational energy is associated with the to and fro motion of the nuclei of the molecule such that the centre of gravity does not change. Electronic energy is associated with the transition of an electron from the ground energy level to an excited state energy level of the molecule due to the absorption of a photon of suitable frequency.

Each electronic energy level (designated with E) is associated with a series of vibrational energy levels (designated with the vibrational quantum number, v) and each vibrational energy level is associated with a series of rotational energy levels (designated with R) as shown in the following figure-4.

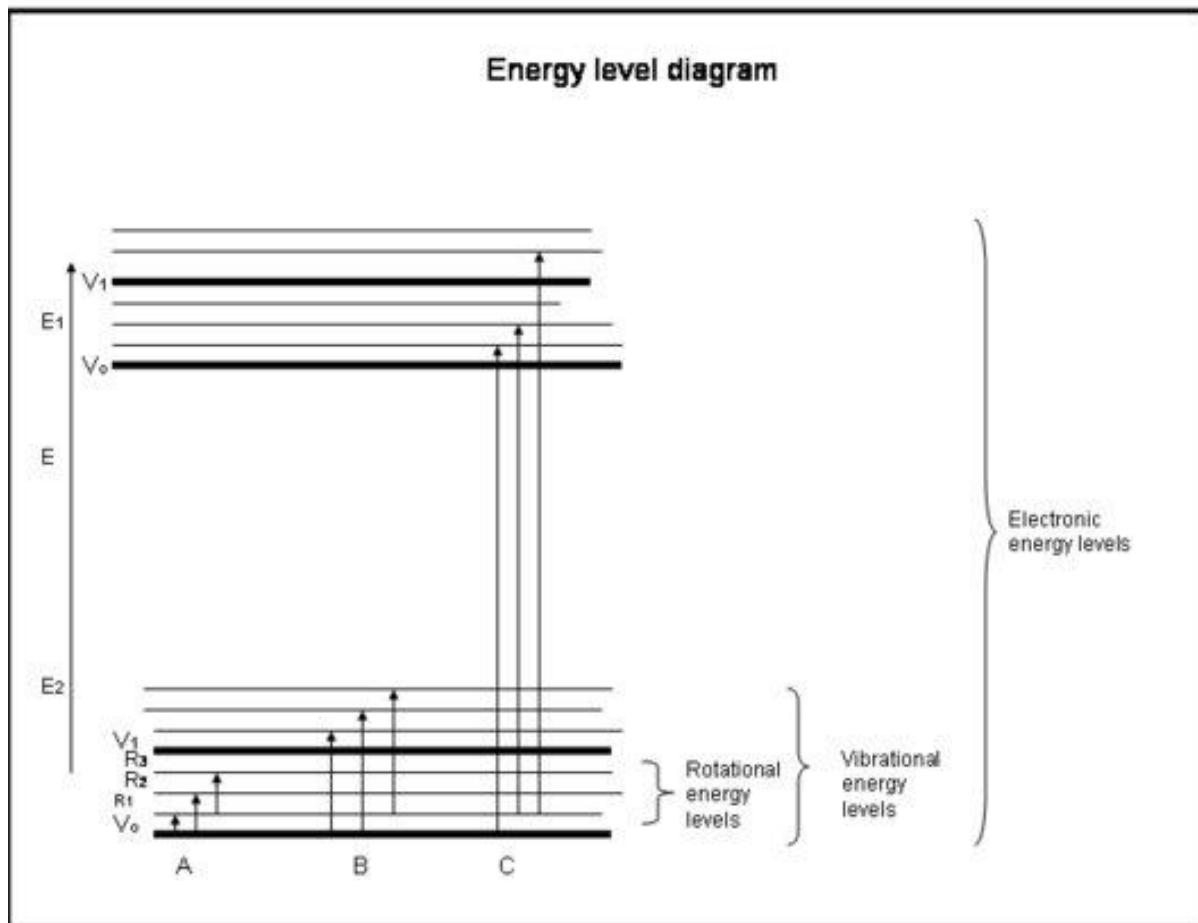


Figure-4: Different energy levels of a molecule with possible transitions

The rotational spectra of a molecule are observed in the microwave region, the vibrational spectra in the infrared (IR) region and the electronic spectra in the ultraviolet (UV) and or visible regions of the electromagnetic spectrum.

The various types of spectra given by a molecule, the regions in which these spectra lie and the energy that take place in the molecule on absorption of radiation are listed below.

Rotational (Microwave) spectra: These spectra result from transitions between the rotational energy levels of a gaseous molecule on the absorption of radiations falling in the microwave region. These spectra are shown by the molecules which possess a permanent dipole moment, e.g., HCl, CO, H₂O vapour, NO etc. Homo nuclear diatomic molecules like H₂, Cl₂, etc., and linear polyatomic molecules such as CO₂ which do not possess a dipole moment, do not show microwave spectra. Microwave spectra occur in the spectral range of 1 – 100 cm⁻¹. From the microwave spectrum of a molecule, the equilibrium internuclear distance between two atoms,

rotational constant, moment of inertia, the shape of the molecule etc. can be determined. A typical microwave spectrum of CO molecule (considering it as a rigid rotator) is shown in the following figure-5.

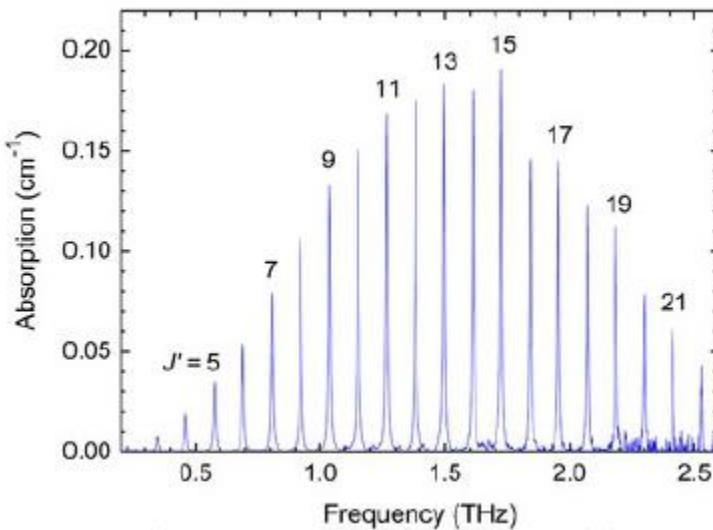


Figure-5: Typical microwave spectrum of rigid rotating CO

Vibrational and vibration-rotation (Infrared) spectra: These spectra originate from transitions induced between the vibrational energy levels of a molecule on the absorption of radiations belonging to the infrared region. IR spectra are shown by molecules when vibrational motion is accompanied by a change in the dipole moment of the molecule. These spectra occur in the spectral range of $400 - 4000 \text{ cm}^{-1}$. The presence or absence of functional groups, the extent of hydrogen bond (HB) interactions (intra and inter) in/between molecules, force constants of various types of bonds etc. can be determined from the IR spectrum of a molecule. A typical IR spectrum (vibration-rotation) of a butyraldehyde is given in the following figure-6.

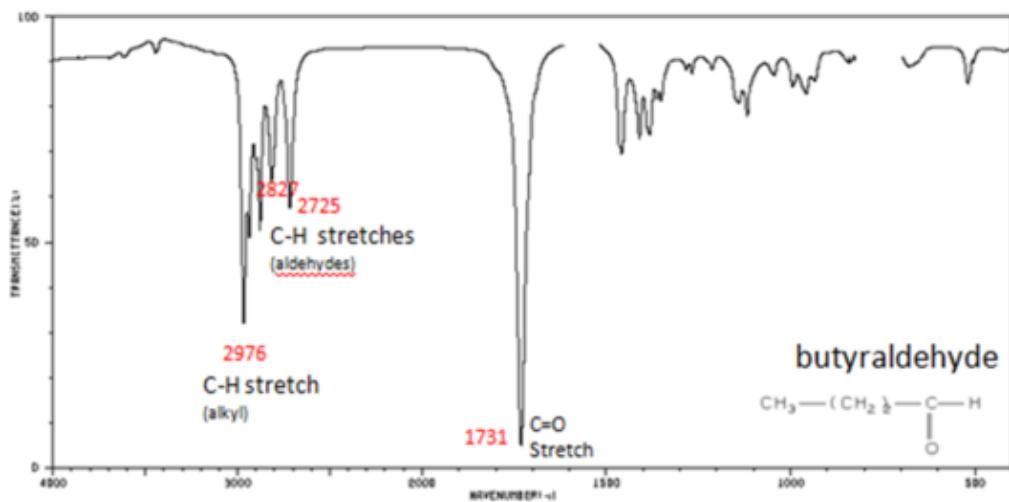


Figure-6: Typical IR spectrum of butyraldehyde

Electronic spectra: Electronic spectra arise from electronic transition in a molecule by absorption of radiations falling in the visible and ultraviolet regions. While electronic spectra in the visible region span 12,500 – 25000 cm⁻¹, those in the ultraviolet region span 25000 – 70000 cm⁻¹. Since electronic transitions in a molecule are invariably accompanied by vibrational and rotational transitions, the electronic spectra of molecules are highly complex. A typical electronic spectrum of a green food coloring agent is given the following figure-7.

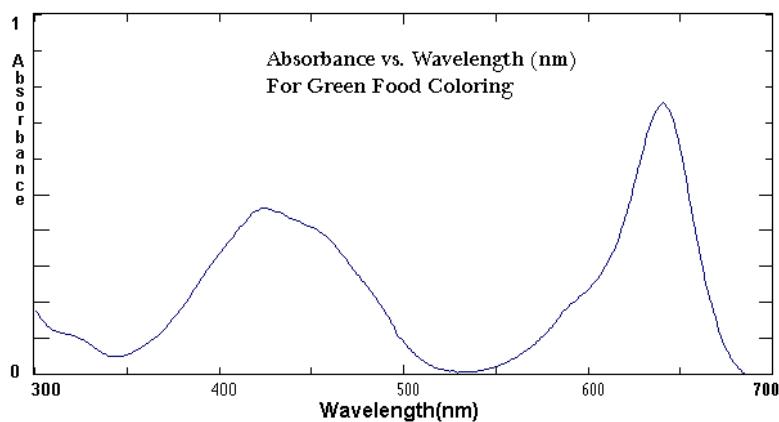


Figure-7: Typical electronic spectrum of a green food color

Spectrophotometry:

Beer and Lambert's law and its derivation:

Lambert's Law:

When a monochromatic light passes through a transparent medium, the rate of decrease in intensity with the thickness of the medium is proportional to the intensity of the light. This is equivalent to stating that the intensity of the emitted light decreases exponentially as the thickness of the absorbing medium increases arithmetically.

We can write it as

$$-\frac{dI}{dt} = kI \quad (1)$$

Where I = intensity of the incident light of wave length, λ

t = thickness of the medium

k = proportionality constant

Integrating eq. 1, and putting $I = I_0$ when $t = 0$

$$\begin{aligned} -\int \frac{dI}{dt} &= \int kI \\ -\int \frac{dI}{I} &= k \int dt \\ \ln \frac{I_0}{I_t} &= kt \\ I_t &= I_0 e^{-kt} \end{aligned} \quad (2)$$

Where I_0 = intensity of the incident light falling upon the absorbing medium of thickness, t

I_t = intensity of the transmitted light

k = constant for the wavelength and the absorbing medium

we can write the eq. 2 as

$$\begin{aligned} \frac{I_t}{I_0} &= e^{-kt} \\ &= 10^{\frac{-k}{2.3036}t} \\ &= 10^{-0.4343kt} \\ I_t &= I_0 10^{-Kt} \end{aligned} \quad (3)$$

Where 'K' is called as absorption coefficient.

The absorption coefficient (K) is generally defined as the reciprocal of the thickness (t , cm) required to reduce the light to $1/10^{\text{th}}$ of its intensity.

$$\text{i.e., in eq. 3, } \frac{I_t}{I_0} = 0.1$$

$$= 10^{-Kt}$$

$$\text{or } Kt = 1 \text{ and } K = 1/t$$

The ratio, $\frac{I_t}{I_0}$ is the fraction of the incident light transmitted by a thickness ‘t’ of the medium and is termed as the transmittance (T). The reciprocal of transmittance i.e., $\frac{I_0}{I_t}$ is opacity. The absorbance (A) of the medium is given by

$$A = \log\left(\frac{I_0}{I_t}\right) \quad (4)$$

Beer's Law:

“The intensity of a beam of monochromatic light decreases exponentially as the concentration of the absorbing substance increases arithmetically”

This can be written as

$$\begin{aligned} I_t &= I_0 e^{-k' C} \\ &= I_0 10^{-0.4343 k' C} \\ &= I_0 10^{-K' C} \end{aligned} \quad (5)$$

Where ‘C’ is the concentration, k' and K' are constants.

Combining eq. (3) and eq. (5),

$$\begin{aligned} \frac{I_t}{I_0} &= 10^{-act} \\ \log\left(\frac{I_t}{I_0}\right) &= aCt \end{aligned} \quad (6)$$

This (eq. 6) is the mathematical expression for Beer-Lambert's law.

The value ‘a’ depend upon the method of expression of the concentration of the solution. If ‘C’ is expressed in mol/l and ‘t’ in cm; then ‘a’ is given the symbol, ϵ and is called the molar absorption coefficient or molar absorptivity.

It is clear that, there is a relationship between the absorbance (A), the transmittance (T) and the molar absorption coefficient.

$$A = \log\left(\frac{I_0}{I_t}\right) = \log(1/T) = -\log T \quad (7)$$

$$\therefore A = -\log(T)$$

$$A = \epsilon Ct$$

The scales of spectrophotometers are often calibrated to read directly in absorbance and frequently in % transmittance also.

$$A = \epsilon Ct$$

$$\epsilon = A/Ct$$

If $C = 1 \text{ mol/dm}^3$, $t = 1 \text{ cm}$; then $\epsilon = A$

i.e., the molar absorption coefficient is the specific absorption coefficient. Specific absorption coefficient is defined as the absorption per unit thickness and unit concentration.

Limitations of Beer-Lambert law

The linearity of the Beer-Lambert law is limited by chemical and instrumental factors. The probable causes of nonlinearity are:

1. Deviations in absorptivity coefficients at *high concentrations* ($>0.01M$) due to electrostatic interactions between molecules in close proximity
2. Scattering of light due to particulates in the sample
3. Fluorescence or phosphorescence of the sample
4. Changes in refractive index at high analyte concentration
5. Shifts in chemical equilibria as a function of concentration
6. Non-monochromatic radiation, deviations can be minimized by using a relatively flat part of the absorption spectrum such as the maximum of an absorption band
7. Stray light

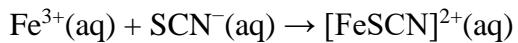
Applications of Beer Lambert's law in qualitative and quantitative analysis:

Estimation of Iron:

Iron is one of the many minerals required by the human body. It is biologically relevant as oxygen-carrying proteins, haemoglobin and myoglobin. A deficiency of iron in the body can leave a person feeling tired and can lead to a disorder called anemia. Many of the foods we eat contain small quantities of iron. The trace quantity of iron also may be present in water sources. Other application of iron is in industrial metallurgy. So, a simple method to estimate iron at very low concentrations is desired using colorimetric analysis.

Method:

In this analysis the iron present in the samples (like an iron tablet or a sample of food) is extracted to form a solution containing Fe^{3+} (ferric) ions. To make the presence of these ions in solution visible, thiocyanate ions (SCN^-) are added. These react with the Fe^{3+} ions to form a blood-red colored complex as given below.



By comparing the intensity of the colour of this solution with the colours of a series of standard solutions, with known Fe^{3+} concentrations, the concentration of iron in the tablet, food or any other sample may be determined. A plot of absorbance vs solution of known concentration and the by comparison of the absorbance of the unknown solution, one can quantitatively estimate the amount of iron present.

Numerical:

The molar extinction coefficient of phenanthroline complex of iron (II) is $1200 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and the minimum detectable absorbance is 0.01. Calculate the minimum concentration of the complex that can be detected in the experiment if the path length is 1.00 cm.

$$A = \epsilon bc$$

$$c = A/\epsilon b = 0.01 / 1.00 * 1200$$

$$= 8.33 \times 10^{-6} \text{ M}$$

4. CHEMICAL FUELS

Introduction, Classification, Gross Calorific value and Net Calorific value. Solid fuel (coal) – proximate & ultimate analysis. Liquid fuels: Petroleum-Refining, Cracking and reforming. Synthetic Petrol: Methods of production. Gaseous fuels: bio-gas production and uses.

Learning objectives

- Define calorific value and describe the classification of fuels
- Understand the terms NCV and GCV
- To know about the petroleum refining, cracking and reforming techniques
- Understand about Synthetic fuels, production process
- To know about the production of bio-gas and their uses

4.1 Introduction

Chemical fuel is a carbonaceous material which on proper combustion in air releases a large amount of heat which can be used for both domestic and industrial purposes economically. Eg. Wood, charcoal, coal, kerosene, petrol, diesel, producer gas, water gas, natural gas, etc. The main elements invariably present in chemical fuels are C, and H. During combustion, C and H of the chemical fuel combine with the oxygen from the air to form CO₂ and H₂O respectively. Chemical fuels release heat during combustion as the heat content of combustion products (CO₂ & H₂O) are lower than that of the reactants (C, H of the fuel). The combustion process can be explained in terms of the three components - temperature, time and turbulence. *Temperature* – To have good combustion, the temperature must be high enough to ignite the fuel constituents and all the gases that are released during the process.

Time – The time (reaction period) must be sufficient to complete the combustion process.

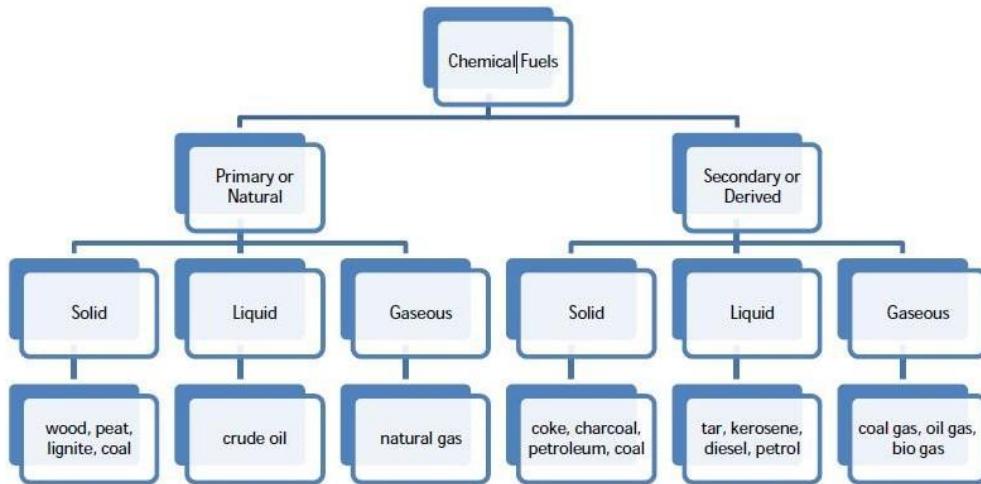
Turbulence – There should be sufficient turbulence to allow complete mixing of combustible elements, fuel, and oxygen. The sustainability of fire depends upon a favorable fuel-oxidant ratio and the maintenance of temperature above ignition temperature. The three components of fire involved in a fuel such as wood, kerosene or gas, energy sufficient to support combustion and an oxidizing agent like air.

4.2 Classification of fuels

Fuels may generally be classified in two ways as follows;

a) Based on occurrence – Primary (natural) and secondary (derived/man-made/synthetic) fuels.

b) Based on the physical state – Solid, liquid and gaseous fuels.



4.3 Calorific value

The calorific value is the amount of heat or energy produced when the substance is allowed to undergo combustion. It is an important property of fuel and is defined as “the amount of heat liberated when unit mass (or unit volume in gaseous fuel) of fuel is completely burnt with pure oxygen”. In the case of solid or liquid fuels, the weight sufficiently defines the quantity of the fuel present. However, in the case of gaseous fuels, it is necessary to specify both temperature and pressure to define this quantity. The calorific value is generally expressed in calorie per gram (cal/g), kilocalorie per kilogram (kcal/kg) or joule per kilogram (J/kg) in case of solid and liquid fuels. In case of gaseous fuels, the units used are kilocalorie per cubic meter (kcal/m³) or joules per cubic meter (J/m³). It is measured either as gross or net calorific value; the difference is given by the latent heat of condensation of the water vapor produced during the combustion process.

Gross or Higher calorific value (GCV /HCV)

The Gross or Higher calorific value is defined as “the amount of heat liberated when unit mass/volume of the fuel is burnt completely in oxygen, and the products of combustion are cooled to room temperature”. When a fuel containing carbon and hydrogen is burnt, C and H are converted into CO₂ and water vapor. Latent heat of steam is released, and water vapor condenses to form water when the combustion products are cooled to room temperature. GCV is higher than NCV as it includes latent heat of condensation of steam.

Net or Lower calorific value (NCV / LCV)

Net or Lower calorific value is defined as “the amount of heat produced when unit mass/volume of fuel is completely burnt in air, and the products of combustion are allowed to escape into the atmosphere”. In actual practice, the combustion products (steam) are not cooled to room temperature but simply let off into the atmosphere. Hence, a lesser amount of heat is available. Since this calorific value does not include the latent heat of condensation of steam, the net calorific value is always lower than gross calorific value.

$$\text{NCV} = \text{GCV} - \text{Latent heat of condensation of steam}$$

$$= \text{GCV} - \text{Mass of hydrogen} \times 9 \times \text{latent heat of steam}$$

$$= \frac{\text{GCV} - 9 \times \text{Percentage of hydrogen} \times \text{latent heat of steam}}{100}$$

$$\text{NCV} = \text{GCV} - 0.09 \times \% \text{ H} \times 587$$

[Note: Because 1g hydrogen gives 9g of water]

If H = Percentage of hydrogen in fuel, then,

$$\text{Water formed by combustion of 1g of fuel} = \frac{18}{2} \times \frac{H}{100} = 0.09H \text{ g}$$

[Latent heat of steam is 587cal/g]

The calorific value of a chemical fuel is determined experimentally using Bomb and Boy's calorimeter. The bomb calorimeter is used for the determination of the calorific value of solid and liquid fuels whereas Boy's calorimeter is used for gaseous fuels.

4.4. Solid fuels

Solid fuels are primarily classified into two;

Natural fuels- wood & coal

Manufactured fuels- charcoal & coke.

Advantages

- (a) Easily transportable.
- (b) Conveniently stored without risk of any spontaneous explosion.
- (c) Low production cost.
- (d) Possess moderate ignition temperature.

Disadvantages

- (a) High ash content.
- (b) Wastage of large proportion of heat.
- (c) Clinker formation when they burn.

(d) Combustion process cannot be easily controlled.

(e) High handling cost.

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

Applications:

Used for many years to create fire.

Coal - a fuel source that aided the industrial revolution

Wood - used to run steam locomotives. Peat and coal – Currently used in the generation of electricity

Charcoal is prepared by the dry distillation of wood. It is the best fuel since it has no sulfur content.

But it is costly Coke is obtained by destructive distillation of soft coals in closed retorts. Briquetted coal is obtained by briquetting the dried coal by applying pressure alone. Pulverised coal is obtained by pulverized the low-grade fuels.

Analysis of coal and its significance

The proximate analysis involves the determination of moisture, volatile matter, ash, and fixed carbon. This gives quick and valuable information about classification and suitability. The ultimate analysis involves the determination of carbon, hydrogen, sulfur, nitrogen, oxygen, and ash.

The ultimate analysis is essential for calculating heat balances.

Proximate analysis of coal

(i) Moisture: About 1 g of air-dried finely powdered sample of coal is weighed into a dry silica crucible and heated for about one hour at 110°C in an electric hot air-oven. The crucible is cooled first in the air, then in a desiccator and weighedW. The loss in weight is noted.

$$\% \text{ of moisture} = \frac{\text{Loss in weight}}{\text{Wt. of coal sample}} \times 100$$

During the burning of coal, moisture in it evaporates by taking some liberated heat in the form of latent heat of evaporation, thereby lowering the effective calorific value of coal. Hence, lesser the moisture content better is the quality of coal as a fuel. But, the presence of up to 10% moisture creates more uniform fuel-bed and less of “fly-ash”.

(ii) Volatile matter: The dried coal sample left in the crucible in step (i) is then covered with a lid and placed in a muffle furnace, maintained at $950 \pm 200^{\circ}\text{C}$. The crucible is taken out after 7 minutes of heating. It is cooled first in air further in a desiccator and finally weighed.

$$\% \text{ of volatile matter} = \frac{\text{Reduction in weight due to loss of volatile matter}}{\text{Wt. of coal sample}} \times 100$$

Higher % of the volatile matter in coal is undesirable as a high proportion of fuel will distill over as vapor and a large portion of which escapes unburnt. Coal sample with high % volatile matter

burns with a long flame, high smoke and has low calorific value. Coal is ranked good if the volatile matter is less.

(iii) Ash: The residual coal left in the crucible in step (ii) is heated without the lid in a muffle furnace at 700-750 °C, until a constant weight of residue is obtained.

$$\text{Percentage of ash} = \frac{\text{Wt. of ash left}}{\text{Wt. of coal sample}} \times 100$$

The mineral matter originally present in the vegetable material from which the coal was formed, consists of oxides of K, Mg and Ca and is called intrinsic ash. Non-essential mineral matters such as clay, gypsum or other inorganic matters, give rise to extrinsic ash. The intrinsic ash content rarely exceeds 1 to 2% whereas extrinsic ash content is relatively higher.

Ash-forming constituents in coal are undesirable for the following reasons:

- (i) The calorific value of the coal is decreased
 - (ii) Removal and disposal of ash poses problems
 - (iii) The ash deposited in the fire bars interferes with the circulation of air
 - (iv) If the ash fuses to form a clinker on the fire bars, it hinders air circulation and also promotes corrosion of the fire bars. However, some ash is desirable since it serves to protect the grates from direct contact with incandescent coal, which might lead to oxidation of the grate bars.
- (iv) Fixed carbon:** It is reported as the difference between 100 and the sum of the percentages of moisture, volatile matter and ash content of a coal sample.

Calorific value and quality of a coal sample increase with the percentage of fixed carbon. Greater the percentage of fixed carbon, smaller is the percentage of volatile matter. It is the fixed carbon which burns in the solid state. Hence information regarding the percentage of fixed carbon helps in the designing of the furnace and the fire-box.

Significance: Grading of a coal or coke sample to determine moisture, volatile matter, fixed carbon, and ash are done by proximate analysis which is important to both the suppliers and users to have a speedy, precise and consistent procedure. It also helps to;

- i) Rank coal
- ii) Show the quantity of combustible and non-combustible constituents
- iii) Provide the basis for buying/selling,
- iv) Identify appropriate coal for different purposes.

Ultimate analysis of coal

(i) Carbon and hydrogen: An accurately weighed coal sample (1-2 g) is burnt in a current of oxygen in a combustion apparatus. As a result, carbon and hydrogen of the coal are converted into CO₂ and H₂O respectively. These are absorbed respectively in weighed KOH and CaCl₂ tubes. The rise in the weights of KOH and CaCl₂ tubes corresponds to the amount of CO₂ and H₂O formed respectively.

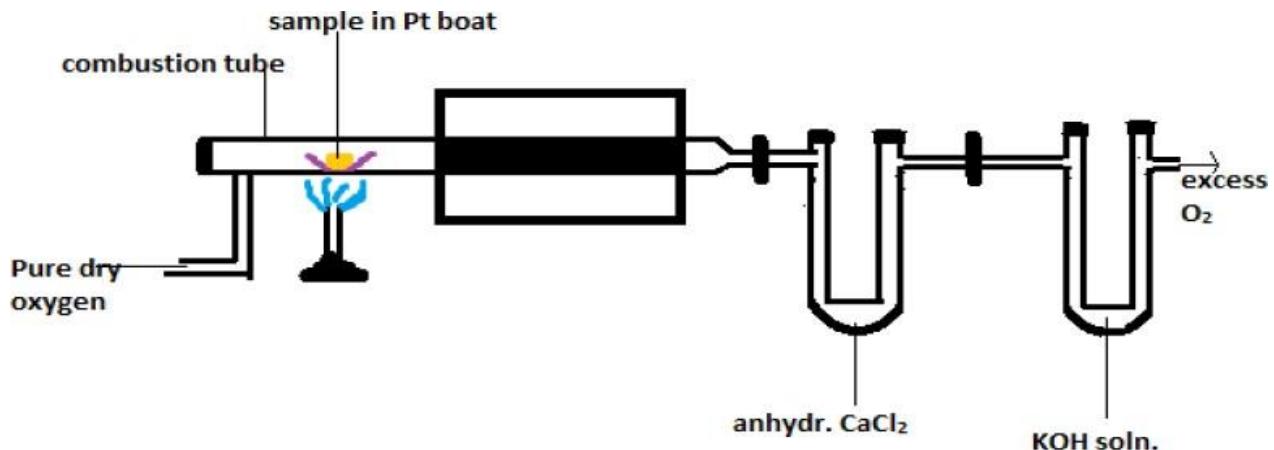
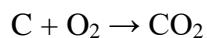


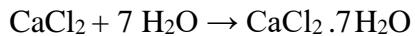
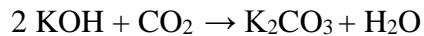
Fig. Schematic diagram of % C & % H analysis



12 44



2 18



$$\% \text{ of carbon} = \frac{\text{Increase in weight of KOH tube} \times 12 \times 100}{\text{Wt. of coal taken} \times 44}$$

$$\% \text{ of hydrogen} = \frac{\text{Increase in weight of CaCl}_2 \text{ tube} \times 2 \times 100}{\text{Wt. of coal taken} \times 18}$$

Carbon and hydrogen in coal directly contribute towards the calorific value of the coal. Greater the percentage of C and H, better is the coal quality and higher is its calorific value.

ii) Nitrogen: The percentage of nitrogen is determined by digesting a known quantity (1 g) of powdered air-dried coal sample with Conc. H₂SO₄ and HgSO₄ in a Kjeldahl's flask using K₂SO₄ as a catalyst. After the solution becomes clear, excess NaOH is added and the ammonia liberated is distilled into a known volume of acid solution of known strength. The volume of unused acid is determined by back titration using standard NaOH solution. The percentage of nitrogen is calculated from the volume of acid neutralized by ammonia liberated, The Kjeldahl's apparatus is shown in Fig.

Nitrogen in the coal does not contribute any useful value to the coal, and since it is generally present in small quantities (~ 1%), its presence is not of much significance. However, the nitrogen content is less in good quality coal.

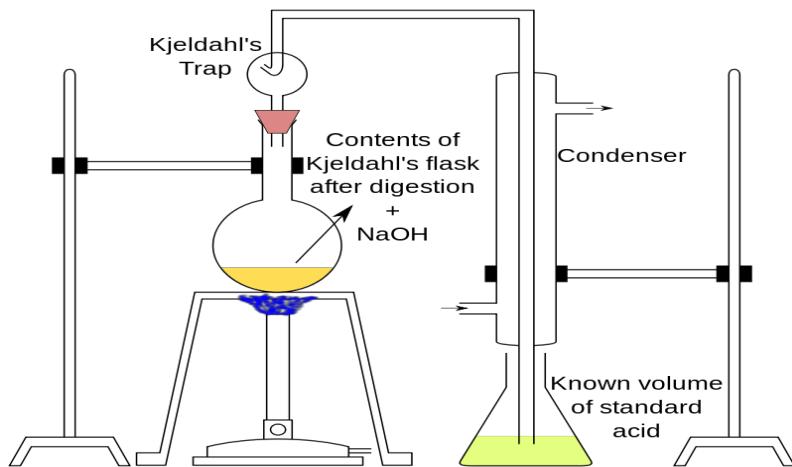


Fig. Schematic diagram of Kjeldahl apparatus

$$\% \text{ of nitrogen} = \frac{\text{Weight of nitrogen}}{\text{Wt. of coal taken}} \times 100$$

$$\text{Where, Weight of nitrogen} = \frac{\text{Volume of acid used} \times \text{Normality of acid} \times 14}{1000}$$

$$\text{Thus, \% of nitrogen} = \frac{\text{V}_{\text{acid}} \times \text{N}_{\text{acid}} \times 1.4}{\text{Wt. of coal taken}}$$

(iii) **Sulfur:** Weighed coal sample is allowed to undergo complete combustion in a bomb calorimeter by which sulfur present in coal is oxidized to sulfates. The ash left after combustion from the bomb calorimeter is extracted with dil. HCl. Barium chloride solution is added to the acid extract barium sulfate, which is then filtered, washed, ignited and weighed. From the weight of barium sulfate obtained the sulfur present in the coal is calculated.

$$\% \text{ of sulfur} = \frac{\text{Wt. of BaSO}_4 \text{ obtained} \times 32 \times 100}{\text{Wt. of coal taken} \times 233}$$

Sulfur present in coal adds to the calorific value of the coal, but its combustion products (SO_2 and SO_3) have corrosive effects on equipment, particularly in the presence of moisture. Further, the oxides of sulfur are undesirable from the atmospheric point of view. Sulfur-containing coal is not suitable for the preparation of metallurgical coke as it adversely affects the properties of the metal.

(iv) **Ash:** The ash content of the coal sample is determined as described under proximate analysis.

(v) **Oxygen:** The oxygen content is calculated by difference as follows:

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

The oxygen content of coal is generally associated with moisture. The lower the oxygen content, the more is the maturity of coal, and greater is its calorific value. As the oxygen content increases, the capacity of the coal to hold moisture increases and the coking power decreases.

Significance

- To evaluate the chemical composition of coal in terms of various elements present (C, H, O, N, S) and ash
- To predict the suitability of coal for the purpose of heating
- For combustion calculations
- To determine the composition of flue gases

Numerical problems

1. About 0.6 g of a coal sample was allowed to undergo combustion in a bomb calorimeter. The calorific value of the sample was found to be 8600 cal/g. The ash formed was extracted with acid, and this was heated with BaCl₂ solution. The weight of dried barium sulfate obtained was found to be 0.05 g. Calculate the % of S in the coal sample.

$$\begin{aligned}\% \text{ of S} &= \frac{\text{Wt. of BaSO}_4 \text{ obtained} \times 32 \times 100}{\text{Wt. of coal} \times 233} \\ &= \frac{0.05 \times 32 \times 100}{0.6 \times 233} \\ &= 1.14 \%\end{aligned}$$

2. About 1.6 g of coal sample was kjeldahlised and NH₃ gas thus evolved was absorbed in 50 mL of 0.1 N sulphuric acid. After absorption, the excess of acid required 6.5 mL of 0.1 N NaOH for neutralization. Calculate the % of nitrogen in the sample.

$$\begin{aligned}\% \text{ Nitrogen} &= \frac{\text{Vol. of acid used} \times \text{N}_{\text{acid}} \times 1.4}{\text{Wt. of coal taken}} \\ \% \text{ Nitrogen} &= \frac{43.5 \times 0.1 \times 1.4}{1.6} \\ &= 3.8 \%\end{aligned}$$

4.5. Liquid fuels

Liquid fuels are combustible molecules that can be harnessed to create mechanical energy. They are predominantly used in industries. Most liquid fuels used currently are made from crude petroleum. Gasoline is the most widely used liquid fuel. Liquid fuels have the advantage of higher calorific value per unit mass compared to solid fuels, burn without dust, ash & clinkers and are

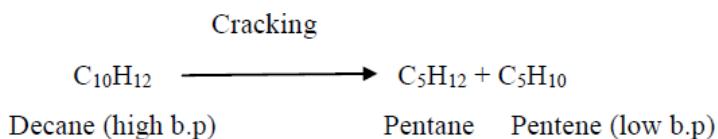
easy to transport through pipes. But liquid fuels are costlier than solid fuels and possess greater fire hazard risks (especially highly inflammable & volatile liquid fuels).

Petroleum

Petroleum was formed in nature by anaerobic decay of marine plant and animal life under high temperature and pressure millions of years ago. It is a complex mixture of organic crude oil and natural gas which consists of hydrocarbons like paraffins, cycloparaffins, olefins, and aromatics with small quantities of nitrogen, oxygen, and sulfur-containing organic compounds and traces of inorganic compounds. The process of separation of crude oil into different useful fractions on the basis of their boiling points using an efficient bubble cap type fractionating column is called petroleum refining.

Cracking

An average grade crude oil on fractionation yields about 20-30 % gasoline, 30-45 % intermediate oils and 25-50 % residual fuel oils. Cracking of the surplus heavier fractions gives greater yields of improved gasoline and better engine performance than that obtained from fractional distillation of crude oil. Cracking is defined as the process of decomposition of hydrocarbons with higher molecular weight into that of lower molecular weight by breaking C-C and C-H bonds producing low boiling alkanes and alkenes.



Types of Cracking:

- 1) Thermal Cracking 2) Catalytic Cracking

Thermal Cracking: In thermal cracking high temperatures and pressures are used to break the large hydrocarbons into smaller ones. Thermal cracking gives mixtures of products containing high proportions of hydrocarbons with double bonds- alkenes. •Thermal cracking doesn't go via ionic intermediates like catalytic cracking. Instead, carbon-carbon bonds are broken so that each carbon atom ends up with a single electron. In other words, free radicals are formed

Catalytic Cracking:

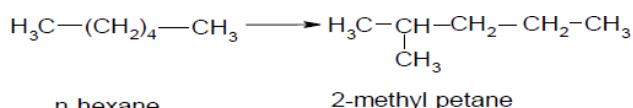
- Modern cracking uses Zeolites as the catalyst. These are complex aluminosilicates and are large lattices of aluminum, silicon and oxygen atoms carrying a negative charge. They are, of course, associated with positive ions such as sodium ions. You may have come across a zeolite if you know about ion exchange resins used in water softeners.
 - The alkane is brought into contact with the catalyst at a temperature of about 500 °C and moderately low pressures.
 - The zeolites used in catalytic cracking are chosen to give high percentages of hydrocarbons with between 5 and 10 carbon atoms- particularly useful for petrol. It also produces high proportions of branched alkanes and aromatic hydrocarbons like benzene.
 - The zeolite catalyst has sites which can remove hydrogen from an alkane together with the two electrons which bound it to the carbon. That leaves the carbon atom with a positive charge. Ions like this are called carbonium ions. The reorganization of these leads to various products of the reaction.

The main advantages of catalytic cracking are as follows

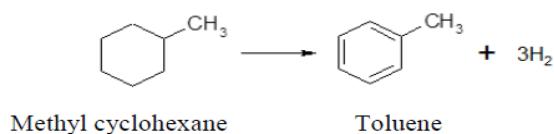
- The octane number and yield of gasoline produced is high.
 - The process can be better controlled.
 - There is a saving in production costs as high temperatures, and high pressures are not required.
 - External fuel is not required. The necessary heat is obtained by burning off the coke deposited on the catalyst itself, during the regeneration process.
 - Catalysts are selective in their action, and therefore, they permit cracking of only high boiling hydrocarbons.

Catalytic Reforming: Process of upgrading gasoline by increasing its octane number in the presence of a catalyst. The main reactions taking place during catalytic reforming process are:

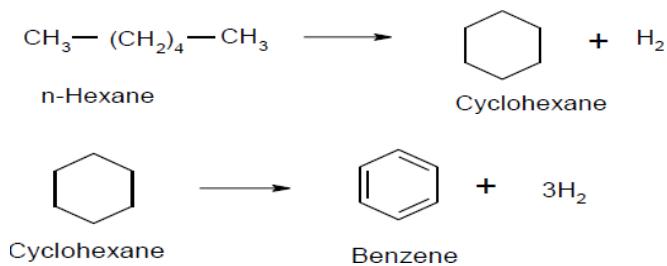
i) **Isomerisation:** Conversion of straight chain hydrocarbons into branched chain hydrocarbons.



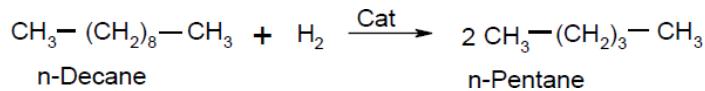
ii) ***Dehydrogenation:*** Dehydrogenation of cycloalkanes to produce aromatic compounds.



iii) **Cyclisation and dehydrogenation:** Straight chain hydrocarbons undergo cyclisation followed by dehydrogenation to produce aromatic hydrocarbons



iv) **Hydrocracking:** n-Paraffins undergo cracking in the presence of hydrogen and catalyst to produce light gases that are removed from gasoline fraction.



Synthetic Petrol

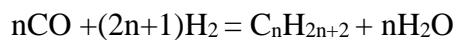
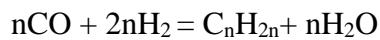
Synthetic fuel or Synfuel is a liquid fuel obtained from coal, natural gas, oil shale, or biomass. It may also refer to fuels derived from other solids such as plastic or rubber waste. It may also refer to gaseous fuels produced similarly. A common use of the term synthetic fuel is to describe fuels manufactured via Fischer Tropsch conversion, methanol to gasoline conversion or direct coal liquefaction.

Method of producing Synthetic Petrol:

1. Polymerisation
2. Fischer-Tropsch method
3. Bergius process

Fischer- Tropsch Process: The Fischer-Tropsch process is a collection of chemical reactions that convert a mixture of carbon monoxide and hydrogen into liquid hydrocarbons. The process, a key component of gas to liquids technology, produces a synthetic lubrication oil and synthetic fuel, typically from coal, natural gas or biomass. The F-T process has received intermittent attention as a source of low sulfur diesel fuel and to address the supply or cost of petroleum-derived hydrocarbon. The water gas is varied with hydrogen, and the combination is purified by transitory

from side to side Fe_2O_3 and then into a mixture of $\text{Fe}_2\text{O}_3 + \text{Na}_2\text{CO}_3$. The cleanse gas is dense to 5 to 25 atm and then led from side to side a converter, which is preserved at a temperature of 200-300 °C. The converter is provided with a catalyst bed consisting of a mixture of 1000 parts cobalt, 5 parts thoria, 8 parts magnesia and 200 parts keiselghur earth.



The outcoming gaseous mixture is led to a condenser, where the liquid crude oil is obtained, The crude oil is fractionated to yield gasoline and heavy oil. The heavy oil is used for cracking to get more gasoline.

Fischer-Tropsch Process

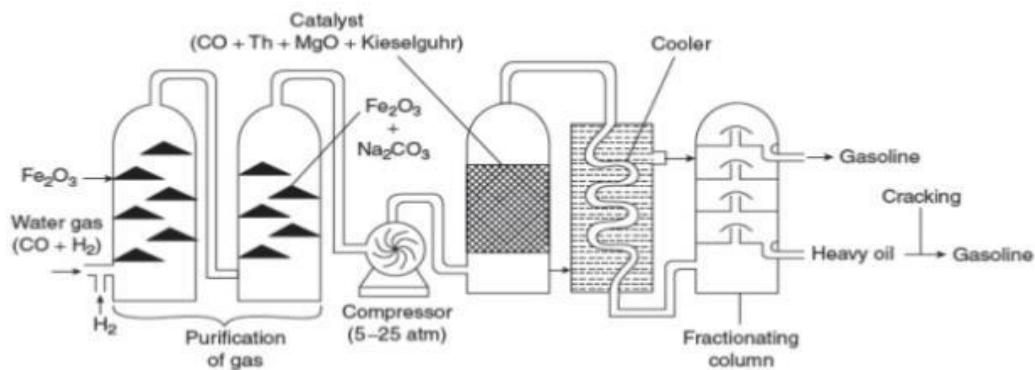


Fig. Schematic diagram of Fischer- Tropsch Process

SYNTHETIC DIESEL vs. CRUDE OIL DIESEL

	Synthetic Diesel	Crude Oil Diesel
Cetane Number	73	51
Aromatic Hydrocarbons, %	< 0,1	< 11
Sulfur Content, ppm	10 -15	< 350

4.6 Gaseous fuels

Biogas

Biogas is a type of biofuel that is naturally produced by the decomposition of organic waste. When organic matter, such as food scraps and animal waste, break down in an anaerobic environment (an environment absent of oxygen) they release a blend of gases, primarily methane and carbon dioxide. Because this decomposition happens in an anaerobic environment, the process of producing biogas is also known as anaerobic digestion

Biogas digesters receive organic matter, which decomposes in a digestion chamber. The digestion chamber is fully submerged in water, making it an anaerobic (oxygen-free) environment. The anaerobic environment allows for microorganisms to break down the organic material, and convert it into biogas. Biogas is a renewable energy source.

Bio gas composition

Compound	Formula	%
Methane	CH ₄	50–75
Carbon dioxide	CO ₂	25–50
Nitrogen	N ₂	0–10
Hydrogen	H ₂	0–1
Hydrogen sulfide	H ₂ S	0.1 –0.5
Oxygen	O ₂	0–0.5

Applications

Biogas can be used for electricity production, cooking, space heating, water heating and process heating. If compressed, it can replace compressed natural gas for use in vehicles, where it can fuel an internal combustion engine or fuel cells.

4.7 Summary

In this chapter, the types of fuels based on their origin and physical state and their characteristics are discussed. Chemical fuel is a material that stores chemical energy in forms that can be practically released and used as thermal energy. The calorific value of a substance is the amount of heat released when its specific amount undergoes combustion. Crude petroleum is processed and refined into more useful fractions such as gasoline, diesel fuel, kerosene and liquefied petroleum gas. Quality of gasoline is upgraded through reforming and cracking processes. Synthetic petrol and their production methods are studied. Production of bio-gases and their applications are discussed.

Questions:

1. What is reforming? Explain the vinous reforming processes with relevant reactions.
2. How is percentage of sulphur estimated in a coal sample?

Materials Science and Engineering

Introduction and basic principles

Everything around us is made up of materials, and they are basic substances that have mass and occupy space. The air we breathe, the water we drink and the food we eat and so on. They can be natural or human-made. Natural materials are materials that come from animals, plants and rocks and manufactured materials are those obtained from natural materials through chemical processes. A wide range of materials in nature form an essential part of the ecosystem in multiple ways. The materials that are used not only in the field of engineering, but on a day to day basis because of their properties are called engineering materials. Material engineers develop and test new materials for different specific applications. A wide range of new products like computer chips, recreational equipment (golf clubs, bicycles), and building materials for houses, bridges, cars, and aircraft will be created. Advanced materials refer to all new materials and modifications to existing materials to obtain superior performance in one or more functional features that are critical for the application under consideration. The functional materials perform specific functions within a system. Some recent advances include shape memory alloys and nanomaterials. Supermaterials of the future include aerogel, carbon nanotube, transparent alumina, e-textiles, metamaterials, nano-diamond and amorphous metal. Graphene is the thinnest material ever invented-only one atom thick yet stronger than steel. Every material has a set of physical and chemical properties that define it. The physical properties include melting point, boiling point, color, hardness, density and so forth. The chemical properties include reactivity with water, oxygen, acids, bases, and others. Traditionally, materials were developed keeping in mind a particular set of properties and were mainly used for making components and structures. With the advancement of materials science, they are expected to perform the role of an ‘intelligent’ structure. An excellent example of this would be applications of shape memory alloys, and they can be used to make deployable antennas. These materials enable people to explore the design and use of new products to improve the quality of life. Modern materials are employed in the primary production or manufacturing of a good, and there are about 3,00,000 different known materials. These include specialty and bulk chemicals, beverages and food products, metal products and alloys, wood and paper products, rubber and plastic products, textile and consumer goods, and those used in mining and metallurgy, and printing and publishing industries.

The kind of questions that a student in materials science would like answers to include the following; What is the densest crystal packing that can be achieved? How do intermolecular attractions arise? Why is glass transparent and brittle while copper opaque and ductile? Why is a diamond an efficient thermal conductor, but electrical insulator? Why is it easier to bend the Al rod as compared to the steel rod? Why is a wire of copper conducting, while a piece of dry wood non-conducting? How can we change properties like hardness, flexibility, biocompatibility in a material? Why does the electrical conductivity of Ag decrease on heating, while that of Si increases? Why does naphthalene (para-dichlorobenzene) solid evaporate? How can we explain the fact that good thermal conductors are also good electrical conductors? How can one understand the observations that when we release the load on a rubber band/spring, it comes back to its original shape while a bent aluminum rod would not come back? Why is it essential for some objects being transparent? Why is glass transparent to visible light, but opaque to UV light? Why can aluminum oxide exist as a transparent, translucent or opaque a material? What are the reasons for the viscosity of honey, mercury and paraffin oil? Why are composites used instead of metals, ceramics, or polymers? What is the mechanism behind functional smart materials? What does material science offer to society? Who can deny the role of materials in human existence? The answers to such questions could lead the learner to take the subject to higher levels of understanding, an understanding of the complex structure-property relationships, molecular mechanisms of material transformations, the development of an active system, to arrive at practical science-based solutions, and finally better materials management solutions.

Materials technology includes a range of materials used for manufacturing products, machines, and structures. For example, plastics are used in solid form as synthetic fibers for textiles, a film for packaging and in composites like fiberglass. Metals like iron or aluminum continue to be essential for building machines and structures. Concrete is the prime material for building civil structures such as bridges. Some building materials like steel, concrete, and bricks are structural while others, such as ceramics and glass are mainly decorative. Appropriate technology serves local needs using local resources such as stone and wood. Rubber is used for the soles of shoes and motor tires because of its resilience and elasticity. It is also used in rubber gloves and rainwear due to its flexibility and waterproof property. Plaster of Paris (POP) has the distinct feature of setting into a hard mass on wetting with water. It is used to make castings for statues, toys and decorative materials, for setting broken or fractured bones in the right position and as a fireproofing material. Thin-film materials are used

extensively in sensor applications. Thin film solar cells like amorphous silicon, cadmium telluride, copper indium gallium selenide and dye-sensitized solar cells are other examples of important novel materials. The nano-scale effects on sterical and biological properties include increased selectivity for specific drug transportation and controlled release, increased permeability through membranes, and improved biocompatibility. The role of materials science research, technology and innovations extend to almost all fields of human activity, and this particular domain has a transformational effect on the development in many areas which include healthcare, food processing, housing, energy, metals and minerals, and aerospace. The future of materials engineering is to obtain optimal performance by combining material design innovation with advances in technology involving several smart features.

Some materials are hard; others are soft. Some are strong; others are weak. Different materials have various properties because they contain different elements (atomic structure) and various combinations of ingredients, contain different types of chemical bonds (bonding between atoms and molecules, have different sizes of units (crystalline structures). The solid-state structure (microstructure + macrostructure) may include different types of assemblies, e.g., molecular packing arrangement may be different, or the geometry of linkage in an extended 3D structure may vary. Physical properties include mechanical and thermal properties (hardness, tensile strength, influence of coating, velocity of sound, thermal data and thermodynamic properties, thermal conductivity), electrical and magnetic properties (electron paramagnetic resonance, nuclear magnetic resonance, electrical conductivity, switching effect, thermoelectric power, magnetic susceptibility, magnetoresistance, optical and spectroscopic properties (index of refraction, dielectric constant, infrared spectra, Raman spectra, absorption in UV and visible range (EMR), photoconductivity, color dichroism, photoluminescence, The chemical properties include reactions of atoms, adsorption of gases, reactions with hydrogen/halogens, and reactions with main group/transition metals. The following factors put together determines the properties of the material; composition, phases present and their distribution, defect structure (in the phases and between the phases) and residual stress. The properties of materials also depend on the properties of individual components, the relative amount of particles, their size, shape, distribution, orientation and the degree of bonding. The goal of materials science and engineering is to design materials with a predetermined set of properties using suitable processing techniques, which gives them a particular microstructure and desired performance. The role of engineers has become very important for meeting the complex and specific challenges of making materials with desired functional characteristics

and solve technical issues with a specialized skill set and knowledge. The specific objective of this chapter is to provide students the vast subject in a structured and useful manner to equip them with a basic familiarity with materials science and engineering. It is a learning journey through the fundamental principles underlying the materials science and engineering and provides the essential vocabulary of these engineering sciences through inspirations, experiences, practices, and evolutions.

Classification of Materials

All materials used for engineering application can be put into six broad categories; pure substances (Cu, Ni, Fe), alloys (brass, NiAl), polymers (polyethene, polyvinyl chloride, polypropylene) ceramics (alumina, glass, zirconia), composites (wood, golf club shaft, bricks), and miscellaneous materials (lime, gypsum, tiles). The common types of engineering materials can be classified into different categories based on various parameters. Based on phase (state of matter) a given material can be divided into gases, liquids or solids. The solid state is a rigid state, the particles of liquids can move with greater freedom and gas particles have total freedom of motion. What distinguishes the crystalline state from the liquid and gaseous states is the nearly perfect positional order of the particles in crystals. Based on the structure of particles (arrangement of atoms/molecules/ions) materials can be classified into crystalline (quartz), quasicrystalline (Al-Pd-Mn alloy) or amorphous (glass). Liquid crystals and solid electrolytes have the properties in between liquids and crystals. Supercritical fluids have properties in between liquids and gases. Homogeneous materials include pure substances and solutions that have fixed, specific features. Heterogeneous materials can be separated into their components by purely mechanical means such as filtration, decantation, extraction, centrifuging and so on. Based on the size of the particles in question we can find nanocrystals, nano-quasicrystals, and bulk materials. Materials can be divided into paramagnetic, diamagnetic, ferromagnetic, ferrimagnetic, and antiferromagnetic materials based on the magnetic states of matter. Based on electrical conduction, we can categorize the materials into conductors (Cu, Al, Ag), semiconductors (Ge, Si, GaAs) and insulators (Al_2O_3 , -($\text{CH}_2\text{-CH}_2$)_n). Based on ductility, we can have two categories- ductile (metals, alloys) and brittle (ceramics, glasses). Materials can be acoustic conductors (bronze) or acoustic insulators (cotton fiber) based on the capacity to transmit sounds. Materials can be classified based on the behavior when light strikes as transparent (clear glass windows, clear plastic food wrap), translucent (frosted glass, wax paper) and opaque materials (aluminum foil, wood). Based on the bonding,

solids can be classified into ionic (table salt, calcium chloride) molecular (ice, solid carbon dioxide) covalent network (diamond, quartz), and metallic solids (iron, silver). There are other categories of materials such as raw materials, in-process materials, finished products, bulk materials, value-added products, and packaging materials. Further classification of chemicals includes bulk chemicals (sulfuric acid), fine chemicals (ibuprofen) and specialty chemicals (adhesives).

Metals can be further classified into ferrous (steel, stainless steel, cast iron) and non-ferrous (aluminum, copper, tungsten) metals. Plastics can be further subdivided into thermoplastics (polyethene, polyvinyl chloride, teflon), thermosets (bakelite, melamine, vulcanized rubber) and elastomers (natural rubber, silicones, styrene-butadiene rubber) based on the response to heat. They can be classified into linear, branched, cross-linked (based on molecular structure), natural, semisynthetic, synthetic (based on origin), addition and condensation (based on the method of formation), plastics, elastomers, fibers and resins (based on applications). Ceramic materials can be categorized into glasses, clay products, refractories (acid, neutral, basic) abrasive materials, cement and advanced ceramics by an application. Composites are classified according to the matrix material into ceramic, metal, and polymer matrix materials, and based on reinforcement geometry into particulate-reinforced, fiber-reinforced and structural composites. Liquid crystalline materials can be subcategorized into calamitic, discotic, polycatenar, and bent-core types based on the shapes, and thermotropic and lyotropic liquid crystals based on the response to temperature or concentration. The classification of smart materials includes piezoelectric, electrostrictive, magnetostrictive, thermoelectric, shape memory alloys, photochromic and thermochromic materials. The classification of biomaterials based on the materials used include polymeric, metallic, ceramic and composite categories. Nanomaterials could be of natural or synthetic based on origin and zero, one, two and three-dimensional based on dimension. Electronic materials are classified into conductors, superconductors, semiconductors, and dielectrics. Based on their behavior in an applied field, superconductors are classified into two types; Type-I – soft and Type-II -hard. There are nine classes of hazardous materials; explosives, flammable gases, combustible liquids, flammable solids, oxidizers, toxic, radioactive, corrosive and miscellaneous materials.

The research and development of various kinds of materials have been exponential, and in the future, these types of materials will be used more extensively to meet the needs of the society. Material design is of vital importance in the development of different functional engineering systems, and it depends on multiple factors, including certain microscopic

structural features, texture, sizes, shapes, and density. Understanding how structural patterns are controlled and how that affects the properties gives engineers greater insight into the preparation of materials with predetermined properties. The materials have conveniently been grouped into various classes, and a combination of these materials will give a variety of other new materials. Apart from the standard categories of materials, future materials include smart materials, nanomaterials and advanced materials for specialized applications. There is a need for well-planned effort to synthesize and explore materials with unique property and use. This overview of the topic should make us think about the identity, composition, structure of materials in question and study the structure-property relationships, mechanism of change and its control, and finally the question about benefits, costs, and risks involved. We also have to take into consideration the ecological properties related to the impact they have on the environment and the function of biological systems can be exploited to find meaningful solutions to engineering problems. The qualities of successful material design include material quality, desired characteristics, ease of use, precision, attractiveness, cost of manufacture, development cost, development time, and enhanced development capacity. A multi-step investigation by researchers, exploration of eco-friendly approaches, preparation of semi-synthetic materials, and preference to use of local materials would go a long way in promoting sustainable and responsible discovery of novel materials and the development of new technological methods. We can achieve success in offering world-class materials through our expertise and experience by doing exceptional and result-oriented, hard work involving systematic and target-based planning with predictable outcomes. The quality of materials and their performance in processes and systems is probably the surest guide to the quality of research in materials science and engineering. These multiple perspectives might help the right-thinking people ask the right questions on the topic and to create future ideas, innovations and stable, sustainable, smart and high-quality materials that power the world through the scientific transformation and paves the way for severe developmental changes.

Effect of Bonding on Properties

The two important contributing factors to the properties of materials are the atomic structure and the nature of bonding. The properties of solids depend both on the arrangements of particles and on the attractive forces between them. A chemical bond is defined as a force that acts between two or more atoms to hold them together in a stable arrangement. Bonding in materials could involve strong interactions such as ionic, covalent and metallic bonds and weak interactions like van der Waals forces and hydrogen bond. Solids can be classified

according to the nature of the bonding between their atomic or molecular components into ionic solids, covalent network solids, molecular solids and metallic solids. Typical examples of these classes have distinctive electron distributions and binding energies, and thermodynamic, electronic, and mechanical properties. We have to note that this is not a rigid classification scheme and bonding in solids can be of mixed or intermediate kinds.

Ionic bond: A net electrostatic attraction between the positive (cation) and negative (anion) ions formed by transfer of electrons from metal to a non-metal atom constitutes an ionic bond (electrovalent bond). There are no rigid, directional bonds in an ionic material and the strong ionic bonding continues throughout the solid crystal resulting in giant structure. Some examples of ionic compounds include $MgCl_2$, CaO , ZnS , Al_2O_3 . The characteristic properties of ionic compounds are the following; They are solids at room temperature. The crystals of ionic solids are hard and brittle. They possess high melting and boiling points. They do not conduct electricity in the solid state but are good conductors of electricity in the molten state or aqueous solution. They are soluble in polar solvents, but insoluble in nonpolar solvents. They do not exhibit isomerism. More common structures are the Rock salt structure which has a face-centered cubic (f.c.c.) unit cell and the Cesium chloride structure, which has a body-centered cubic (b.c.c.) unit cell. Less common structures include the Zincblende structure, Wurtzite, Fluorite, and Rutile structures. An ionic solid consist of cation and anions arranged in such a way that each ion is surrounded by as many nearest neighbours of opposite charge as possible and there is local neutralization of charge. There could be partial ionic character in predominantly ionic bonds in compounds with large anions, small cations, high charge on one of either ion, and non-noble gas electron configuration of the cation.

Covalent bond: Covalent bonds are formed by an overlap of atomic orbitals and mutual sharing of electrons. A covalent bond is typically formed by two non-metals having similar electronegativities and each bonded atom may contribute one electron to the shared electron pair or one atom may contribute both electrons. Covalently bonded compounds usually form molecular structures. Molecular solids are collections of distinct molecules held together by intermolecular forces such as dispersion forces, dipole-dipole forces, and hydrogen bonds. Typical examples of covalent molecular crystals include the noble gases, oxygen, nitrogen, the halogens, CO_2 , H_2O , $C_{12}H_{22}O_{11}$, I_2 , and the vast majority of organic compounds. Depending on the number of shared electrons covalent bonds can be single (F_2), double (O_2) or triple bond (N_2) types. The common spatial arrangements of atoms in covalent molecular solids include linear, angular, trigonal plane, trigonal pyramid, tetrahedron, square plane and octahedral

structures. A covalent network solid has atoms at the crystal lattice sites that are linked together by covalent bonds into a three-dimensional array, e.g. C (diamond), SiO₂ (quartz). These solids are hard and high melting. Silica is the most abundant covalent solid in nature and carborundum (SiC) is the most common synthetic solids. The characteristic properties of covalent molecular compounds are the following; they are gases, liquids or solids at room temperature. Covalent solids are soft and easily deformed. They have low melting and boiling points. They are soluble in organic solvents. They are rigid and directional and can cause stereoisomerism. They do not conduct electricity in any state.

Metallic bond: The bonding which holds the metal atoms firmly together by force of attraction between metal ions and the mobile electrons is called metallic bond. Typical examples of metals include Na, Fe, Cu, Mg and Al. A metallic solid has metal atoms that occupy the crystal lattice sites in hexagonal close-packed (h.c.p.), cubic-close-packed (c.c.p.) or body-centered cubic (b.c.c.) structures. If many metal atoms are brought together, the outer electrons of each can merge together and overlap. These valence electrons are shared by nuclei of all the atoms that make up the solid (giant structure). These electrons have become delocalized and hence more stable. A block of metal can be thought of as an array of positive ions immersed in a sea of delocalized electrons. The great cohesive forces resulting from the delocalization is responsible for the great strength noted in metals. The type of bonding found in metals involves the manifold of closely spaced sublevels that can be regarded as a band. Using the band theory of metals, we can explain the properties of metals. The characteristic properties of metals include the following; they have bright metallic lustre. Metals are malleable and ductile. They have high electrical and thermal conductivity. The melting points vary according to the efficiency of metallic bonding and highest melting elemental metal, tungsten melts at 3410 °C. Those elements with intermediate electronegativity, exist as solids on the border between metallic and covalent, called metalloids. Silicon and germanium are semiconductors, with electrical conductivities significantly lower than those of metals, but far higher than those of true insulators like a diamond.

Intermolecular forces: To explain the properties of different materials, it is necessary to consider several types of intermolecular forces. These bonds are weaker than the intramolecular covalent bonds (for example, it takes only 1.2 kJ to overcome a mole of Ar-Ar interatomic attractions but it takes 239 kJ to break a mole of Cl-Cl covalent bonds). Intermolecular forces are much less directional than covalent bonds and they operate at longer range than covalent bonds. It is useful to distinguish types of forces based on their strength, directionality, and range. It exists in the inert gases, and between molecules in covalent molecular solids that arise

from atomic or molecular dipoles. All inert gas materials are gaseous at high temperatures as the high kinetic energy of the molecules disrupts all possible attractions. At lower temperatures, where materials are in the liquid state, molecules are close together and details of the intermolecular potential energy determine the properties of materials. The physical properties of molecular solids and liquids are because of intermolecular forces. The boiling and melting points of different substances reflect the strengths of the intermolecular forces. The stronger the intermolecular attractive forces, the higher is the boiling point of the liquid and the melting points of solids increase as the strengths of the intermolecular forces increase. The types of intermolecular forces include hydrogen-bonding forces, London dispersion forces, dipole-dipole interactions, and ion-dipole forces. The first three types are also known as van der Waals forces and all are electrostatic in nature.

Hydrogen bond: The electrostatic attraction between an H-atom covalently bonded to a highly electronegative atom X such as nitrogen, oxygen or fluorine and a lone pair of electrons on X in another molecule is called hydrogen bonding. The compounds like H_2O , NH_3 , and HF have abnormally high boiling points because of hydrogen bonding. Water has a high melting point, a high specific heat and a high heat of vaporization because of the abnormally strong intermolecular forces between water molecules. The hydrogen-bond attraction can occur between molecules (*intermolecular*) or within different parts of a single molecule (*intramolecular*). The examples of intermolecular hydrogen bonding include $(\text{HF})_n$, $(\text{H}_2\text{O})_n$, $(\text{NH}_3)_n$ and $(\text{CH}_3\text{COOH})_2$. The examples of intramolecular hydrogen bonding include o-nitrophenol, 2-nitrobenzoic acid and o-fluorophenol. Though the H-bonds are weak forces, they are strong enough to influence physical properties such as boiling points, solubility, viscosity, and crystal structure. The energy associated with hydrogen bonding lies in between 15 to 40 kJ/mole, and they are much weaker than ordinary chemical bonds. These bonds help stabilize the structure of proteins and DNA in biological systems. Ice floats on the top of the water when a lake freezes in winter because of its lower density compared to liquid water, thereby insulating the water below and protecting most of the aquatic life. Hydrogen bonds tend to be the strongest type of intermolecular force.

Ion-dipole forces: This type of force exists between an ion and the partial charge on the end of a polar molecule, e.g. KBr/NaCl in water. The negative ions are attracted to the positive end of a dipole, and positive ions are attracted to the negative end. These are important for solutions of ionic substances in polar solvents.

Dipole-dipole bonds: The strongest secondary bonding type exists between adjacent polar molecules. The associated binding energies are significantly higher than for bonds involving

induced dipoles and they are weaker than ion-dipole forces. HCl, H₂S, and CH₃Cl are some examples of polar molecules. For molecules of approximately equal mass and size, the strengths of intermolecular attractions increase with increasing polarity. The positive end of one dipole attracts the negative end of the other. There is the overall effect of net attraction between the polar molecules because two molecules that are drawing each other spend more time near each other than do those that are repelling each other. Generally, such attractions are about 1 % as strong as a covalent bond. The boiling point increases as the dipole moment increases. They are sufficiently strong to influence melting points, and molecular orientations in solids.

Dipole-induced dipole bonds: Permanent dipole moments exist in some molecules by an asymmetrical arrangement of positively and negatively charged regions. The polar molecules will induce a dipole in adjacent nonpolar molecules, and a bond will form as a result of attractive forces between the dipole and induced dipole. The magnitude of this interaction depends on the magnitude of the dipole moment of the polar molecule and the polarizability of the non-polar molecule. Eg. Solution of polar solutes in nonpolar solvents.

London forces: A dipole may be created or induced in an atom or molecule that is normally electrically symmetric; that is, the overall spatial distribution of the electrons is symmetric with respect to the positively charged nucleus. All atoms are experiencing constant vibrational motion that can cause instantaneous and short-lived distortions of this electrical symmetry for some of the atoms or molecules and the creation of small electric dipoles. One of these dipoles can, in turn, produce a displacement of the electron distribution of an adjacent molecule or atom, which induces the second one also to become a dipole that is then weakly attracted or bonded to the first. The momentary attraction between the molecules of a liquid caused by the instant dipole and induced dipole are called London Forces. These attractive forces may exist between large numbers of atoms or molecules, which forces are temporary and fluctuate with time. Liquefaction [e.g. Ar(l)] and, in some cases, the solidification of the inert gases and other electrically neutral and symmetric molecules such as H₂, I₂(s) and Cl₂ are realized because of this types of bonding. Melting and boiling temperatures are extremely low in materials for which induced dipole bonding predominates; of all possible intermolecular bonds, these are the weakest. Dispersion forces operate between all polar and non-polar molecules. Polar molecules experience dipole-dipole interactions in addition to dispersion forces. The dispersion forces are approximately equal when the molecules have comparable molecular weights and shapes. The strength increases with increasing molecular weight, though molecular shape is also an important factor.

The Road Ahead

It is essential to study the effect of several environmental conditions such as heat, radiation, carbon dioxide, oxygen, water and various pollutants in finer detail to obtain the full picture. The study may reveal the number of critical molecules that can be exploited for both creating new materials and functional purposes. Finally, better technology using the finest ingredients and expert techniques to create innovative materials with practical utility and responsible sourcing becomes critical in this age of specialized domain expertise. Long-term stability and safety standards for new materials matters in some applications. The microscopic details make all the difference in the material world that turn ideas, dreams and the future into reality. Innovating in finding new ways of adding value to unique products makes the complex systems more efficient and make a positive transformation of society. Advanced material characterization remains a challenge because of several factors, including structure related (molecular geometry, 2D structure, perovskite structure), bonding pertaining (bond length, angle, strength, order), and condition/treatment-related (pressure, temperature, radiation) factors. Regular follow up of processes is essential from three perspectives. First, to understand if the method is working and what is the progress of material formation. Second, it helps to modify the method or alter treatment conditions based on the improvement. Lastly, if there are undesired events, necessary actions can be taken to prevent those. The sophisticated techniques such as wide angle X-ray diffraction, field emission scanning electron microscopy (FE-SEM), tensile strength tester, simultaneous TG-DTA/DSC apparatus, and acoustic material testing with impedance tube are used for characterization of final stable material. It remains to be seen that a multipronged approach to preparing modern materials soon could lead to better systems to enable sustainable development and the material progress of human beings.

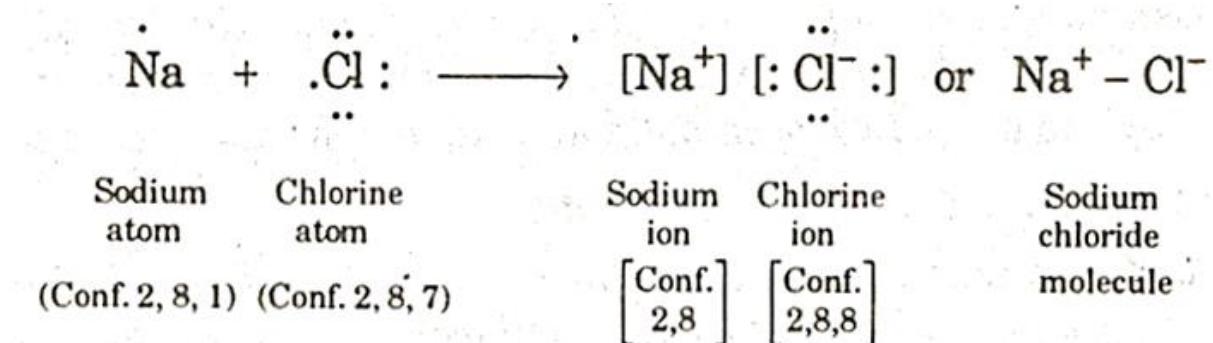
Extra notes in bonding

Example of Ionic bond formation:-

Formation of Sodium chloride

[Na atom (At.No. 11):- $1s^2 2s^2 2p^6 3s^1$] (2,8,1)

[Cl atom (At. No. 17):- $1s^2 2s^2 2p^6 3s^2 3p^5$] (2,8,7)



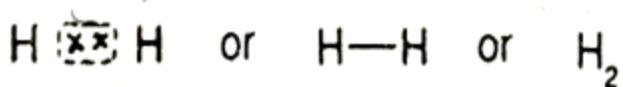
These ions held together by the force of electrostatic attraction between.

The number of electrons lost or gained by an atom, to acquire stable inert gas configuration, is called the electrovalency of the atom. Thus electrovalency of sodium is +1; while that of chlorine is -1.

Covalent bond

Covalent bond:-

It is the type of bond in which the combining atoms share their electrons mutually. If one electron of each of the two combining atoms is shared mutually then a singly covalent bond is formed. For example, formation of H_2 molecule (one electron each is shared by two hydrogen atom).



Similarly, one electron each is shared by hydrogen and chlorine so that HCl is formed, and one electron each is shared by two chlorine atoms so that Cl₂ is formed.

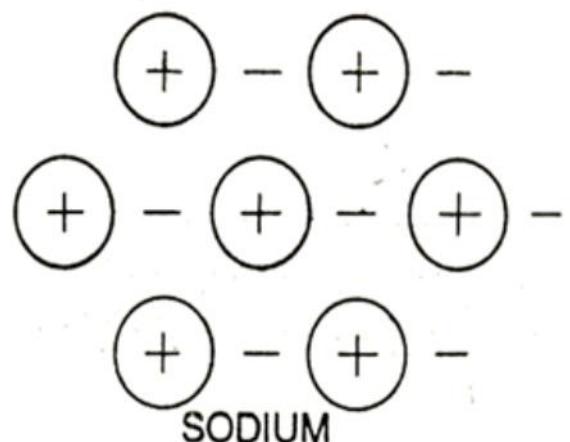


METALLIC BOND:-

- A close packing of atoms in metallic crystal indicates a strong bonding between them. Ionic bonding between atoms of a metal can never take place because all atoms are similar and have equal electronegativity.
- All atoms of a metal have a tendency to lose the electrons, none has a tendency to gain electrons.
- Bonding between metallic atoms does not seem to be covalent either because covalent compounds are gaseous, liquids or soft solids and non-conductors of electricity, whereas metals are generally hard solids and always good conductors of electricity.
- It means that entirely a different type of bonding, which may be called as metallic bonding, takes place in metals.
- The bonding which holds the metal atoms firmly together by force of attraction between metal ions and the mobile electrons

Metallic Sea of Electrons

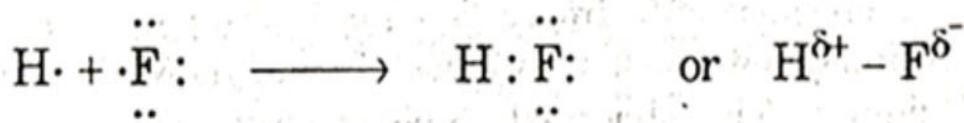
Electrons are not bonded to any particular atom and are free to move about in the solid.



Hydrogen bonds:-

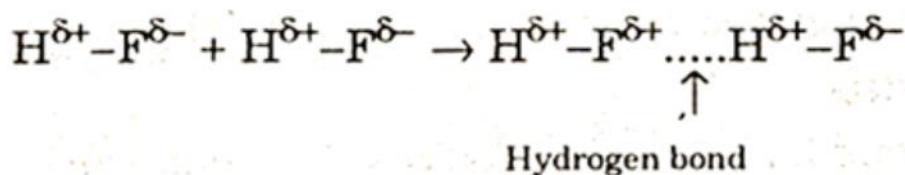
When hydrogen atom is covalently bonded to a strongly electronegative and small-sized atom (N_2 , O_2 & F), results in the development of partial ionic character in the covalent bond, with a fractional + ve charge in the hydrogen atom, and a fractional – ve charge on the fluorine atom.

For Eq:- HF



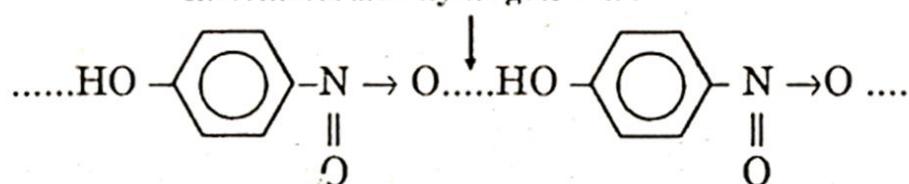
Shared electron pairs lies much nearer the electro-negative F atom

Hydrogen and fluorine atoms acquire respectively a fractional positive and negative charge. Thus, HF is a polar molecule.



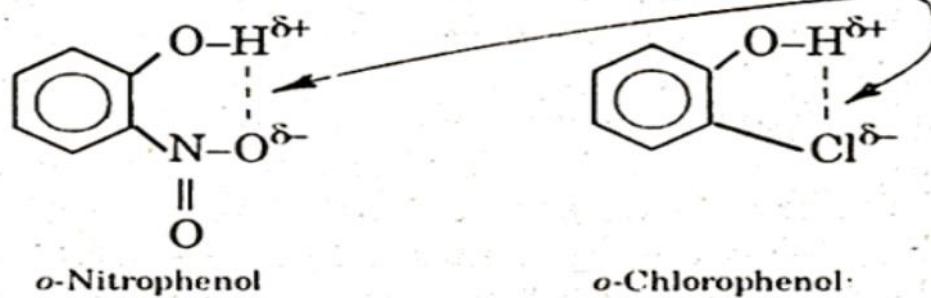
INTERMOLECULAR HYDROGEN BOND

Intermolecular hydrogen bond



p- Nitrophenol

Intramolecular hydrogen bond



Dipole-Dipole bonds:-

HCl is an example of polar molecule. The positive end of one dipole attracts the negative end of the other. There is a net attraction between the polar molecules.

Dipole-Induced dipole bonds:-

Polar molecules will induce a dipole in adjacent non-polar molecules, and a bond will form as a result of attractive forces between the dipole and induced dipole.

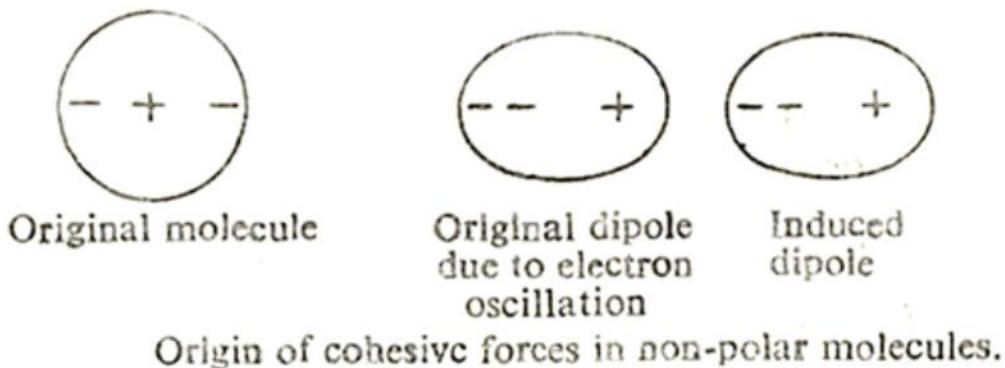
Example:- Ionic solid is dissolved in solvent.

Induced Dipole- Induced Dipole Interaction:- (London Forces or Dispersive Forces)

- As we know, vander Waals forces exist even in non-polar molecules such as O₂ and N₂ and also in non-polar monoatomic molecules such as He, Ne, Ar, etc. This attraction is evident from the condensation of these gases into liquids at sufficiently high pressures and low temperatures.

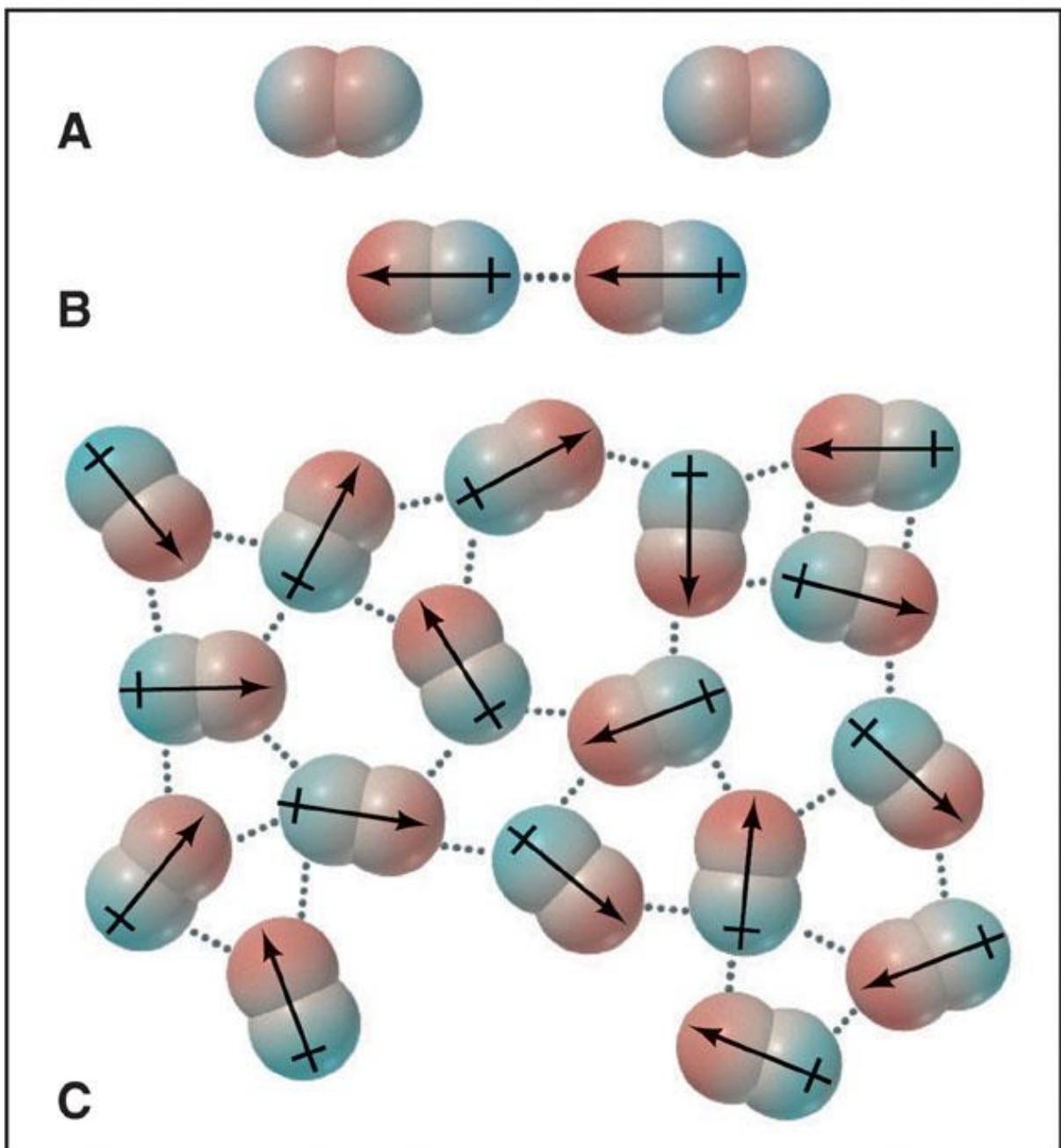
“This concept is explained by London”

- According to this view, electrons of a neutral molecule keep on oscillating with respect to the nuclei of the atoms. As a result of this, at a given instant, positive charge may be concentrated in one region and negative charge in another region of the same molecule.
- This polarized molecule induced the dipole moment in a neighbouring molecule with antiparallel orientation.
- The electrostatic forces of attraction between induced dipoles and the original dipoles (due to electron oscillation) are known as London forces.
- These forces are also called dispersive forces because dispersion of light is also connected with these dipoles.



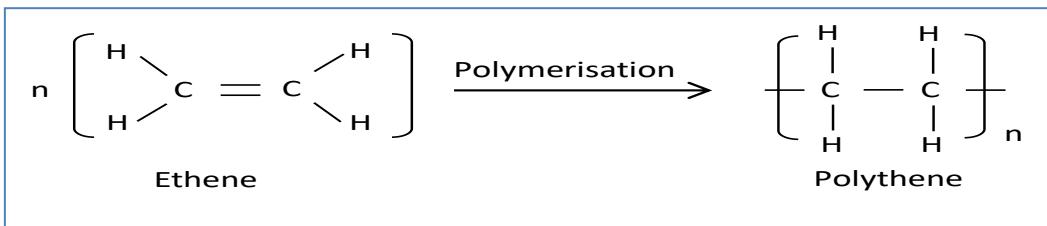
DISPERSION (London) FORCES among non polar molecules

- It is caused by momentary oscillations of electron charge in atoms



Polymers

The word *polymer* is derived from two Greek words, poly and meros, where *poly* means many and *meros* means parts. Polymers are giant molecules formed by the combination of several simple molecules having two or more binding sites linked through covalent bonding.



The simple molecules which are repeating units of the polymer, are called monomers.

Eg: Polythene is formed by the combination of several ethene (ethylene) molecules.

Degree of polymerization (DP): Degree of polymerization is the number which expresses the total number of repeating units (n) in the polymer chain. Polymers with large number of repeating units are called high polymers and those with lower number of repeating units are called oligomers.

DP is used to determine the molecular weight of the polymer by multiplying the number of repeating units (n) with the molecular weight of repeated unit.

Functionality: The total number of functional groups, bonding sites or reactive sites present in the monomer is called the functionality of the monomer. The reactive functional groups can be $-\text{OH}$, $-\text{COOH}$, $-\text{NH}_2$, $-\text{SH}$, $-\text{NCO}$ etc.

Eg: In $\text{CH}_3\text{CH}_2\text{OH}$ one reactive $- \text{OH}$ group is present, hence functionality is one (monofunctional)

$\text{HO}-\text{CH}_2-\text{CH}_2-\text{OH}$ has two $- \text{OH}$ groups hence bifunctional

$\text{HOOC CH}_2 \text{CH (COOH) CH}_2 \text{COOH}$ has three $- \text{COOH}$ groups, hence trifunctional

The presence of double or triple bonds in the molecule imparts polyfunctionality to the molecules.

Eg: Ethylene - due to the presence of a double bond, it can take on two atoms of hydrogen or halogens. Depending upon the functionality of the monomers used linear, branched or three dimensional cross-linked polymers are formed.

Classification of polymers

Polymers can be classified in several ways, based on their

- origin
- structure
- methods of formation
- response to heat and crystallinity
- properties (or applications)

Based on their ***origin***, polymers are broadly classified as

(a) Natural polymers (b) synthetic polymers.

Natural polymers are those which are obtained naturally. Eg: Cellulose, Silk, Starch

Synthetic polymers are those which are man-made. Eg: polythene, PVC, polyester, etc.

Semi-synthetic polymers are chemically modified natural polymers. Eg: cellulose acetate, cellulose nitrate, halogenated rubbers etc.

Based on their ***molecular structure***, the polymers can be classified as

(a) Linear (b) Branched (c) Cross-linked

If all the monomeric units are identical and combine linearly with each other to form a polymer, it is called a *linear homopolymer*.

Eg. - M – M – M – M – M – M -

If the monomeric units are not identical, it is called a *linear co-polymer*.

Eg: -M – M₁ – M – M₁ – M – M₁ – M -

If the linear co-polymers in which the units of each type form fairly long continuous sequences (blocks) are called *block co-polymers*.

Eg.,- M – M – M – M - M₁ – M₁ - M₁ - M₁ - M – M – M – M –

If the linear polymer branches out, then it is called a *branch polymer*.

The polymers can be classified as follows, on the basis of their ***method of formation***

(a) Addition polymers (b) condensation polymers

Addition polymers are formed by a process of self-addition of monomers without the elimination of any byproducts. Eg: Polyethylene & synthetic rubbers.

Condensation polymers are formed by condensation reaction i.e., reaction between two or more monomer molecules with the elimination of simple molecules like water, ammonia, HCl etc.,

Eg: Urea-formaldehyde resins, phenol-formaldehyde resins & polyesters.

The polymers can be classified on the basis of their ***response to heat*** as follows.

(a) Thermo softening (b) Thermosetting

The polymers, which soften on heating and can be converted into any shape, which they can retain on cooling, are called as thermo softening or thermoplastic polymers. The process of heating, reshaping and retaining the same on cooling can be repeated several times. Eg: polyethylene, nylons , sealing wax.

The polymers which undergo some chemical change on heating and convert themselves into an infusible mass are called as thermosetting polymers. Eg: bakelite, egg yolk.

Based on their ***application and properties*** polymers are classified as follows.

(a) Plastics (b) Elastomers (c) Fibers (d) Resins

Plastics are the polymers, which are soft enough at some temperature to be moulded into a desired shape and hardened on cooling so that they can retain that shape. Eg: polystyrene, polyvinyl chloride , poly methyl methacrylate.

Elastomers are polymers in which the structural units are either zig zag or helical chains. They undergo elastic changes when subjected to an external force, but readily regain their original shape when the force is withdrawn. Eg: natural rubber, silicone rubbers.

Fibres are characterized by their molecular chains arranged parallel to each other in a spiral or helical pattern which do not undergo stretching or deformation and the molecular length is at least 100 times its diameter. Eg: nylons, terylene.

Resins are much lower molecular weight polymers either in liquid or solid form used as adhesives or moulding powders. It has a glossy appearance. Resins constitute the major essential part of the plastics. Eg: Polysulphide sealants,epoxy adhesives.

Polymerization

Polymerization is defined as the process by which the monomer molecules are linked to form a big polymer molecule .

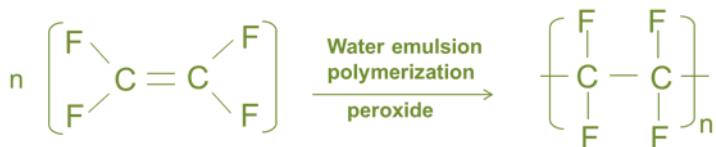
Types of Polymerization:

Polymerization occurs basically in two different modes.

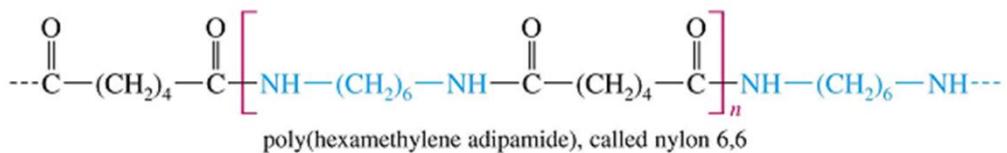
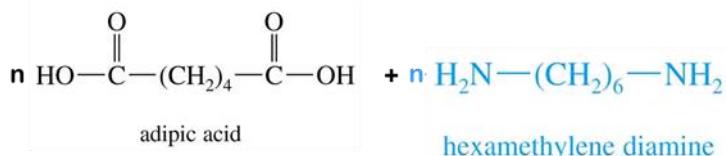
1. Addition (chain growth) polymerization
2. Condensation (step growth) polymerization

Addition polymerization: The reaction in which self-addition of several olefinic monomers to each other takes place without elimination of by products is known as addition polymerization.

The addition polymerization must be initiated by using heat or light or pressure or catalyst for the breakage of the double bonds of monomers.



Condensation Polymerization: The reaction in which monomers containing two or more reactive functional groups (hydroxyl, carboxyl, amino) condensing with each other.



Distinguishing features of addition and condensation polymerisation

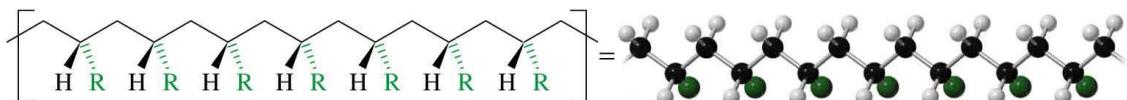
- | Addition polymerisation | Condensation polymerisation |
|--|---|
| ➤ Monomers undergo self addition to each other without loss of by products | ➤ Monomers undergo intermolecular condensation with continuous elimination of by products such as H_2O , NH_3 , HCl , etc., |
| ➤ It follows free radical mechanism (Chain mechanism) | ➤ It follows step mechanism |
| | ➤ Monomers containing the functional |

- Unsaturated vinyl compounds undergo addition polymerization
- Monomers are linked together through C – C covalent linkages
- High polymers are formed fast
- Linear polymers are produced with or without branching
- Examples: polystyrene, plexiglass, PVC, etc.
- Functional groups(-OH,-COOH,-NH₂) undergo this polymerization
- Covalent linkages are through their functional groups
- The reaction is slow and the polymer molecular weight increases steadily throughout the reaction
- Linear or cross linked polymers are produced
- Examples: nylons, terylene, PF resins, etc.

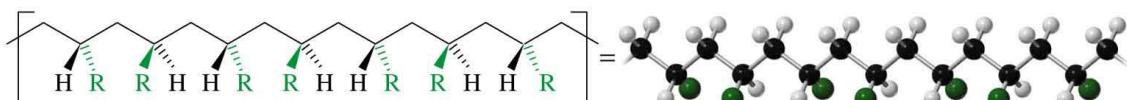
Stereo regular polymers (Tacticity in polymers)

This classification is based on the position of the substituent groups in the polymer chain. Depending on the position and regularity of the repeating substituent groups, three different arrangements can be visualized- isotactic, syndiotactic and atactic.

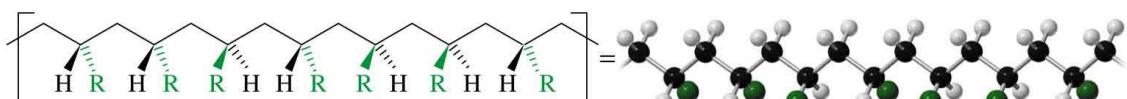
An isotactic polymer (side groups on the same side of the backbone)

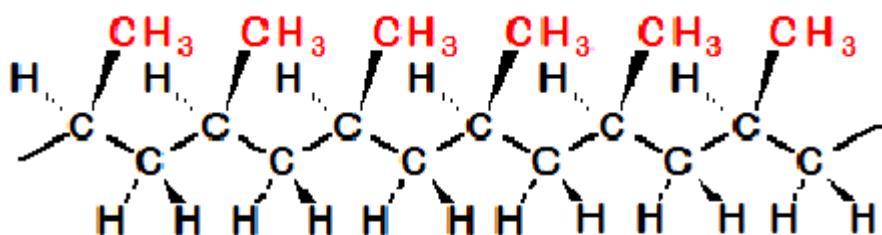


A syndiotactic polymer (side groups on alternating sides of the backbone)

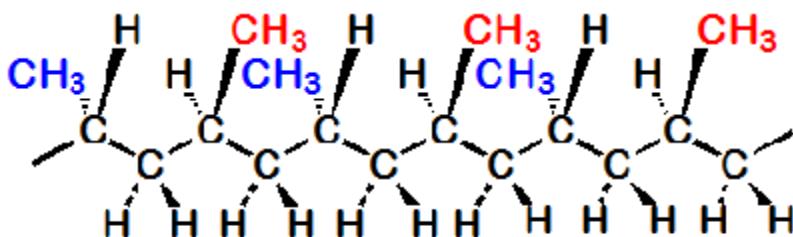


An atactic polymer (side groups on random sides of the backbone)

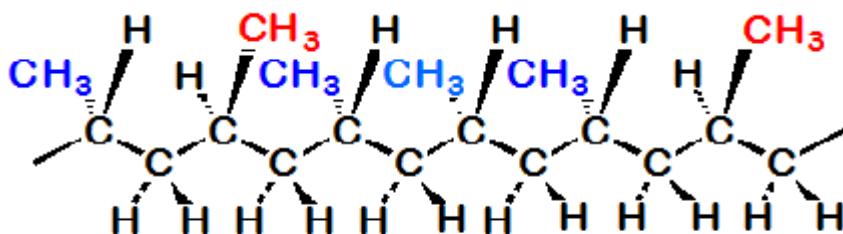




ISOTACTIC all methyl groups on the same side



SYNDIOTACTIC methyl groups alternate sides



ATACTIC methyl groups randomly oriented

Structure and properties of polymers

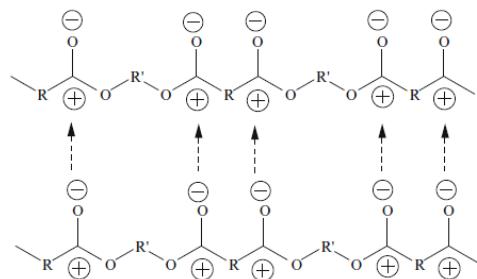
The structure of a polymer has profound influence on some of the properties of polymers .The properties such as crystallinity, tensile strength, elasticity, resistance to chemicals and plasticity depend mostly on the polymer structure and are discussed below.

Strength: This property is discussed based on forces of attraction and slipping power.

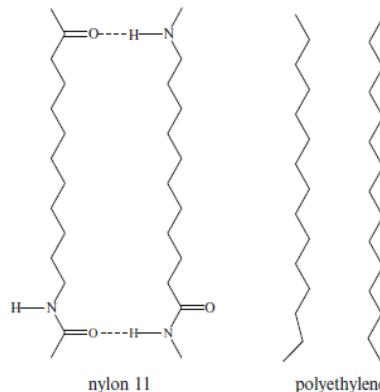
Based on forces of attraction: Strength of the polymer is mainly determined by the magnitude and distribution of attraction forces between the polymer chains. These attractive forces are of two different types viz., primary or covalent bond and secondary or intermolecular forces.

In case of straight chain and branched chain polymers, the individual chains are held together by weak intermolecular force of attraction. But in these polymers, strength increases with increase in chain length (increase in molecular weight) i.e., attains mechanical strength if the chain length is greater than 150 – 200 carbon atoms in the chain. Less than these numbers, the polymers will

be soft and gummy, but brittle at low temperature. Intermolecular forces can be increased by introducing polar groups like carbonyl & hydroxyl.



In cross-linked polymers, monomeric units are held together only by means of covalent forces. Hence possess greater strength than straight and branched chain.



Based on slipping power: Slipping power is defined as movement of molecules one over the other. Eg: polyethylene molecule is simple and uniform, hence movement of molecule one over other is possible, i.e., slipping power is high. Hence it has lesser strength. But in case of polyvinyl chloride (PVC), bulky chlorine atoms are present along the chain length hence, movement is restricted, i.e., slipping power is less. Hence it has higher strength compared to polyethylene. But in case of cross-linked polymer, movement is totally restricted because of the presence of covalent bond. Hence these products are strong, rigid and tough.

Plastic deformation: When a polymer is subjected to some stress in the form of heat or pressure or both, permanent deformation in shape takes place, which is known as plastic deformation. This property actually helps in moulding of plastics. Slippage is more in case of linear molecules than branched and cross-linked, because of the presence of weak intermolecular forces and hence they show greatest degree of plastic deformation. At high pressure and temperature the vander

Waal's forces acting between molecules become more and more weak. No slippage occurs in case of cross-linked polymers, because only strong covalent bonds are present throughout the entire structure. However, when considerable external force or temperature exceeding the stability of material is applied, it will result in total destruction.

Crystallinity: Based on the relative arrangement of polymer chains with respect to each other, polymer can exhibit amorphous and crystalline nature. An amorphous state is characterized by completely random arrangement of molecules and crystalline form by regular arrangement of molecules. The crystallization tendency of a polymer depends on the ease with which the chains can be aligned in an orderly arrangement. Crystalline regions of a polymer are formed when the individual chains are linear (without branching), contain no bulky substituents and are closely arranged parallel to each other. The chains of polymer may be held together by vander Waal's forces, hydrogen bonding or polar interactions. A polymer with high degree of crystallinity will have high tensile strength, impact and wear resistance, high density and high fusion temperature. Polymers with a long repeating unit or with low degree of symmetry do not crystallize easily, hence forms amorphous structure e.g., polystyrene. Crystallization imparts denser packing of molecules due to increase of intermolecular forces of attraction. Such type of polymers will have sharp softening point, greater strength and rigidity. e.g PVC, Polypropylene. Polymers are in general, amorphous with some degree of crystallinity.

Chemical Resistance: Chemical resistance of polymer depends upon the chemical nature of monomers and their molecular arrangement. A polymer is more soluble in structurally similar solvent. For example, polymers containing polar groups like – OH, - COOH, usually dissolve in polar solvents like water, alcohol etc but are chemically resistant to non-polar solvents. Similarly non-polar compounds like hydrocarbons dissolve only in non-polar solvents like benzene & toluene.

As a general rule, the tendency of solubility in a particular solvent decreases with increase in molecular weight of the polymer- (i) high molecular weight polymer on dissolving yield solutions of high viscosities (ii) crystalline polymers exhibit higher resistance than less crystalline polymers of similar chemical character (iii) greater the degree of crystallinity, lesser is its solubility.

Today several drugs and essential oils are stored in plastic bottles for long shelf life. If they disintegrate or change in their chemical composition they may render the drug ineffective or

may cause it to react adversely when used, leading to specific disorder. Therefore, chemical resistance of plastic bottles is important to prevent drug polymer interactions.

Elasticity: Elastic nature in polymers results due to the uncoiling and recoiling of the molecular chains on the application of force. In an upstretched elastomer we can observe a peculiar configuration of irregularly coiled and entangled snarls in a random fashion, indicating the amorphous state. In a stretched state snarls disentangle and straighten out in a proper chain orientation, indicating the crystalline state. The crystallinity in a stretched rubber band can be observed from its opaqueness and warmth it produces when touched by lips. The main criteria for a polymer to show elastic nature is that , the individual chains should not break even after prolonged stretching. This can be done by introducing suitable crosslinking in the chains, by allowing nonpolar groups or side groups in the repeating unit.

Glass transition temperature T_g

Amorphous polymers do not have sharp melting points. They possess softening point. At low temperature, polymers exist as glassy substances. Since the molecular chains cannot move at all easily in this state, the solid tends to shatter, if it is hit. If the solid polymer is heated, eventually it softens and becomes flexible. This softness and flexibility is obtained at the glass transition temperature. After this temperature, crystalline and amorphous thermoplastic polymers behave differently. Heating has little effect on thermosetting polymers and at a high temperature, they are destroyed.

So the ***glass transition temperature*** can be defined as the temperature below which an amorphous polymer is brittle, hard and glassy and above the temperature it becomes flexible, soft and rubbery.



In the glassy state of the polymer, there is neither molecular motion nor segmental motion. When all chain motions are not possible, the rigid solid results. On heating beyond T_g segmental motion becomes possible but molecular mobility is disallowed. Hence flexible,

Factors affecting glass transition Temperature

Glass transition temperature of a polymer depends on parameters such as chain geometry, chain flexibility, molecular aggregates, hydrogen bond between polymer chains, presence of plasticizers and presence of substrates in the polymer chains.

A polymer having regular chain geometry show high glass transition temperature, the bulky groups on chain increases the T_g of the polymer. E.g., polyethylene has T_g -110 °C. The T_g is quite low because there are no strong intermolecular forces and no bulky side groups are present, the side chain is only hydrogen atom. But nylon 6 has T_g 50 °C because of the presence of large number of polar groups in the molecule leading to strong intermolecular hydrogen bonding.

The T_g of a polymer is influenced by its molecular weight. However, it is not significantly affected if molecular weight is around 20000. With increase in molecular mass, the temperature (T_g) will be higher.

In crystalline polymers the polymer chains are arranged in a regular parallel fashion. Each chain is bound to the other by strong forces like H-bonding. Hence crystalline polymers have higher T_g than amorphous polymers.

The added plasticizers reduce the T_g of the polymer by reducing the cohesive forces of attraction between the polymers. e.g., dibutyl phthalate, diacetyl phthalate etc.,

The glass transition temperature is an important parameter of polymeric material. This helps in choosing the right processing temperature. It is a measure of flexibility of a polymer and also gives the idea of the thermal expansion, heat capacity, electrical and mechanical properties of the polymer.

Molecular weight of polymers

A polymer comprises of molecules of different molecular weights and hence, its molecular weight is expressed in terms of an ‘average’ value. Eg. In ethylene gas each of its molecules has the same chemical structure and hence, a fixed molecular weight of 28. But upon polymerization, it forms polyethylene and we encounter an indefinite chemical structure of --(-CH₂ – CH₂ -)_n—where ‘n’ can change its value from one polyethylene molecule to another present in the same polymer sample.

When ethylene is polymerized to form polyethylene, a number of polymer chains start growing at any instant, but all of them do not get terminated after growing to the same size. The chain termination is a random process and hence, each polymer molecule formed can have a different number of monomer units and thus different molecular weights. So a sample polymer can be

thought of as a mixture of molecules of the same chemical type, but of different molecular weights.

In this situation, the molecular weight of the polymer can only be viewed statistically and expressed as some average of the molecular weights contributed by the individual molecules that make the sample.

So the molecular weight of a polymer can be expressed by two most and experimentally verifiable methods of averaging - (i) Number – average and (ii) weight – average.

Number – average molecular weight: Number average molecular mass of a polymer can be defined as the total mass of all the molecules in a polymer sample divided by the total number of molecules present.

Weight – average molecular weight: The sum of the fractional masses that each molecule contributes to the average according to the ratio of its mass to that of the whole sample.

White foam cups, clear plastic cups and ultrathin fishing line are made of polystyrene with different average molar masses while styrofoam cups are made from beads of polystyrene with an average mass of approximately 15000 g/mol. Clear plastic cups are made by melting polystyrene with average mass of approximately 250000 g/ mol. Ultrathin fishing lines are composed of polystyrene with an average mass of 1000000 g/ mol.

Application of Average molecular mass (AMM)

It is used to characterize a polymer. Samples of the polymer prepared under different conditions may have different AMM. It affects the mechanical, solution & melt properties of the polymer. Chain length is related to the ease of processing of the polymer. The longer the chain, the more difficult the melt is to process. The polymer chain becomes more entangled as the molecules get larger and offer more resistance to flow at the molecular level. In most applications, the polymer must be able to flow so that it can be flattened into sheets, moulded into bottles and so on.

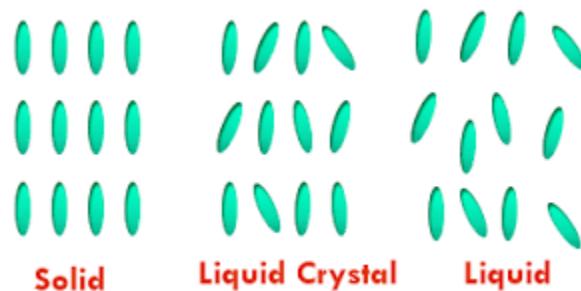
Numerical Problems

- 1) Calculate the number average & weight average molecular weight of a polymer sample in which 40 % molecules have molecular mass of 25000, 20 % have molecular mass of 30000 & rest have molecular mass of 55000.
- 2) A polymer sample contains 1, 2, 3 & 4 molecules having molecular weight 10^5 , 2×10^5 , 3×10^5 and 4×10^5 respectively. Calculate the number average & weight average molecular weight of the polymer.

6.3 Liquid crystals

Liquid Crystals (LC) possess properties of both the conventional liquids and solid crystals. They find application in the areas of science and engineering, particularly in display systems of modern electronic gadgets. Devices using liquid crystal displays have the advantage of low power consumption and hence are widely used in display devices of mobile communication appliances, aircraft cockpit, laptops and other electronic equipments.

In a crystalline state, the molecules (or atoms) are having a definite position and orientation in space in a regular repeated manner in a rigid arrangement and are immobile. They tend to orient in a preferred direction i.e., the molecules in solids have a positional and orientational order. In the liquid state, the molecules neither occupy specific positions nor remain oriented in a particular manner. The molecules are somewhat free to move at random and collide with one another, abruptly change their positions. The liquids have neither positional order nor orientational order. A liquid crystal (LC) is a state of matter exists between solids and liquids with both the properties. Normally when a low molar mass solid melts, it forms an ordinary liquid and is isotropic. Organic substances which are geometrically anisotropic i.e., long and relatively narrow molecular shape exhibits this intermediate state of order between solid crystals and isotropic liquids. They undergo more than a single transition in passing from solid to liquid through different intermediate states on heating. These intermediate states with different molecular ordering are also known as mesophases, derived from a Greek word, *mesos* meaning middle. In mesophase state either the individual molecules align with respect to each other or exhibit some regular position with respect to each other. The molecular arrangement in solids, liquid crystals and liquids can be represented as below.



In a liquid crystal, the molecules possess orientational order, i.e., the molecules tend to remain oriented in a particular direction. The direction of preferred orientation in a liquid crystal is called the **director** (\bar{n}) and may be imagined to be directed towards the top or bottom of the page. Since

the molecules are in constant motion, in liquid crystal phase they spend more time pointing along the director than along any other direction. The extent of orientational order can be described by taking an average. An average of 0° indicates perfect orientation and can be expected in solids. An average of greater than 45° indicates no orientational order and found in liquids. However, in liquid crystals, a smaller average angle with the director is observed which indicates orientational order.

The quality of any device using LCs depends mainly upon the *physical properties* of the LC molecules. To achieve a high performance of the LC device, it is essential to select the most appropriate LC material according to the specific requirements of the desired device. In general, the LCs must satisfy the following characteristic properties

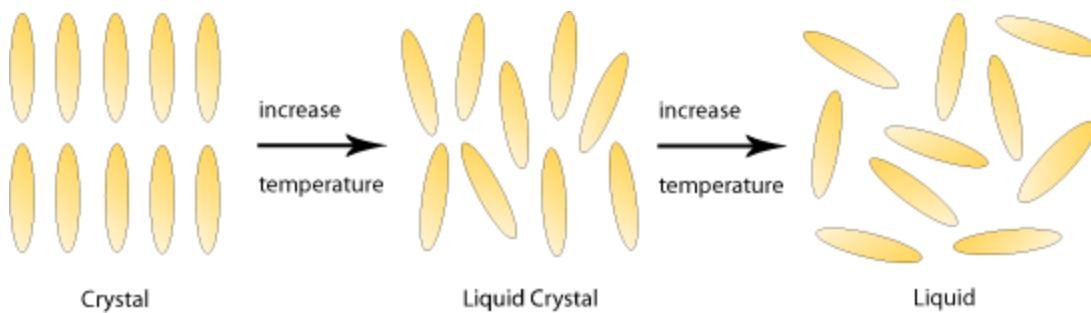
- a. Liquid crystalline nature should be at room temperature and the entire temperature range of the device operation
- b. Chemically, electrochemically, photochemically and thermally stable
- c. Permanent electric dipole
- d. Should possess easily polarizable substituents

6.3.1 Classification of Liquid Crystals

Based on the response to temperature or concentration, Liquid Crystals are broadly classified as

- ❖ Thermotropic LCs
- ❖ Lyotropic LCs

The liquid crystalline substances which undergo transitions by variation in temperature are called thermotropic LCs. Eg. p-azoxyanisole. The liquid crystalline substances which undergo transitions by the influence of solvents are called lyotropic LCs. Eg. sodium stearate. Both these systems can be characterized by anisotropic viscous, electrical, optical and mechanical properties. Organic molecules, which are able to form thermotropic as well as lyotropic mesophases, are termed as amphotropic LCs.



Thermotropic Liquid Crystals: Based on the mesophase, the TLCs are further classified as

- a. nematics
- b. smectics
- c. columnar
- d. cubic

Nematic: The properties of this phase are very close to liquid or they possess most liquid-like structure. The molecular axes are oriented parallel to one another, resulting in a long range of an orientational order. They do not possess positional order.

Smectic: The properties of this phase are very close to solid. They possess layered structures with many possibilities of the state of order inside the layers. They show long-range orientational as well as partial positional order.

Columnar: Structures with columns consisting of parallel arranged disc-like molecules.

Cubic: Structures with micellar lattice units or complicated interwoven networks.

Based on the shape of the constituting molecules, the thermotropic LCs can be further classified as

- (i) *Calamitic LCs*
- (ii) *Discotic LCs*
- (iii) *Polycatenar LCs*
- (iv) *Bent (Banana) LCs*

Calamitic Liquid Crystals: The LC compounds possessing rod-like molecular shape belong to this category. The general molecular structure of a calamitic LC is as given below.

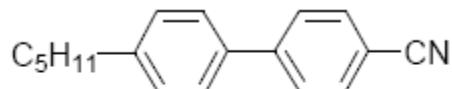


Where A, B, C, and D are called the rigid cores (containing a phenyl, biphenyl, naphthyl, cyclohexyl or five/six-membered heterocycles) of the molecule. In a Liquid crystal, there should be at least one rigid core.

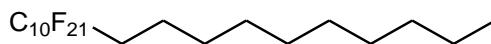
'L' is the linking group (an imine, azo, azoxy, ester, thioester, C=C, and C≡C)

R' or R" is the end group/chain (a halo group, cyano, nitro, alkyl or alkoxy groups)

Some examples of the calamitic LCs are given below.

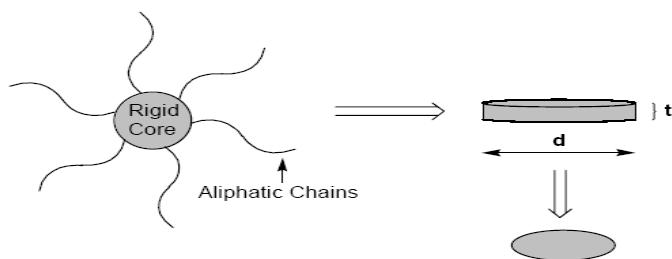


Molecular structure of 4-pentyl-4'-cyanobiphenyl

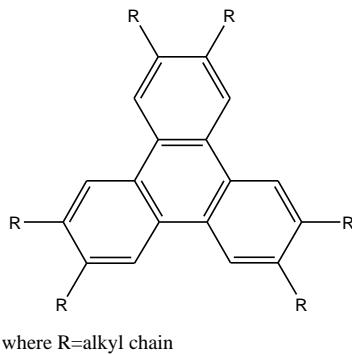


(perfluorodecyl)-decane

Discotic Liquid Crystals: Discotic compounds consist of flat and disc-like rigid cores which are surrounded by flexible chains such as alkyl, alkyloxy or alkanoyloxy. These discotic molecules can be stacked one over another in many ways so as to obtain different columnar structures like hexagonal, rectangular or oblique symmetry. Within the columns, the molecules can have a certain order or disorder. The general structure of discotic LCs can be represented with the following cartoon picture.



In discotic liquid crystals, the molecular diameter (d) is much greater than the disc thickness (t) to form anisotropy. A typical molecular structure of a discotic molecule is shown below.



Polycatenar Liquid crystals: Polycatenar mesogens are considered as a hybrid class of thermotropic LCs, as its molecular features lie intermediate between classical rod-like and disc-like mesogens. Schematically the central core of polycatenar LCs comprises a calamitic region, with half-discs on the extremities. This hybrid molecular structure allows them to exhibit both calamitic (nematics/smectic) and discotic (columnar) phases, depending on the specific molecular structure of the components. E.g., the tetracatenar mesogens (shown below), at shorter chain lengths exhibit nematic and/or smectic-C phases, while at longer chain lengths exhibit columnar phases. The numbers of the flexible end chains of the core can be indicated by using the term, m,n -polycatenary mesogen. The different polycatenar LCs can be represented with the following schematic diagrams.



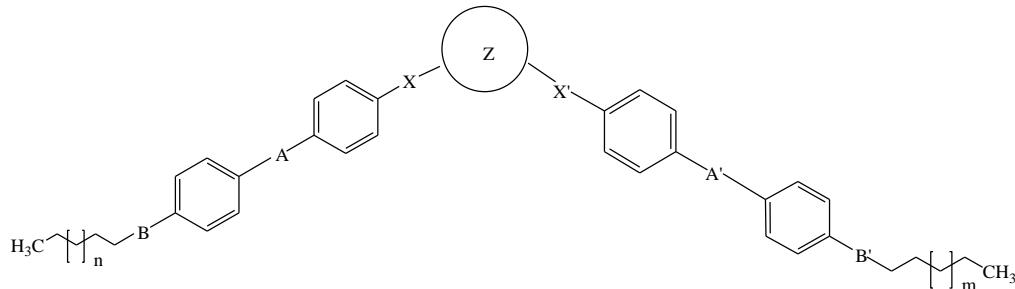
2,2-polycatenary mesogen



3,1-polycatenarymesogen

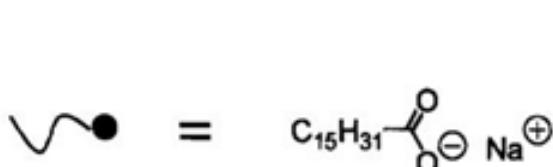
Bent (Banana) Liquid Crystals: Bent (Banana) shaped liquid crystals are constituted of two mesogenic groups linked through a rigid core in such a way that the molecule is not a linear (as shown in the following figure). The central rigid core (Z) may be a phenyl or biphenyl or naphthyl group. The mesogenic groups attached to the central core are mostly the calamitic molecules consisting of two (or more) aromatic rings with different linking groups (A, B, X, A', B', X') and a terminal chain/a substituent in para position to the linking group of the aromatic rings. The angle between the two calamitic wings (bending angle) is around 120°. In case of a benzene central

core, the mesogens are connected in 1 and 3 positions (i.e., meta position to each other). If the central core is a naphthyl, the two calamitic wings are connected in 2 and 7 positions.

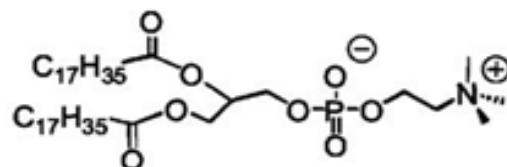


Lyotropic Liquid Crystals: Lyotropic liquid crystals are formanisotropic aggregates when combined with a solvent, like water. The phase behavior is dependent on the concentration and polarity of solvent and also on the temperature. Molecules which form lyotropic phases are usually amphiphilic, having non-polar, hydrophobic "tails" at one end with a polar, hydrophilic "head" at the other end. Some examples are sodium stearate (soap) and phospholipids. The concentration of material in the solvent and the response of the amphiphile to the solvent environment dictate the type of lyotropic phase formed. For example, in a polar solvent like water, micelles are formed in which the hydrophobic tails assemble together and the hydrophilic heads groups are presented to the solvent. When combined with a non-polar solvent such as hexane, an inverse micelle is formed where the hydrophobic tails shield the hydrophilic head groups from the non-polar environment. Under certain conditions, these micelles further aggregate to form more complicated assemblies, such as lamellar and hexagonal Phases, which generate lyotropic liquid crystal phases. Lamellar phases are particularly significant as they form the structural basis for biological membranes

Examples of Lyotropic liquid crystals and their phase structures

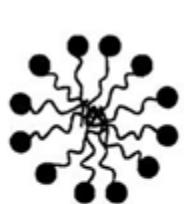


Sodium Sterate

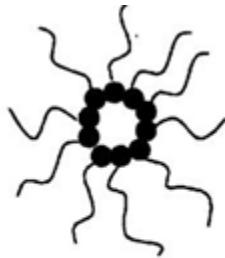


Phospholipid

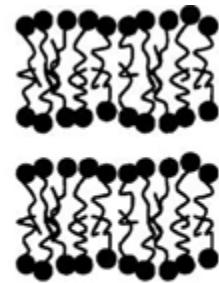
Micellar aggregates and phase structures formed by Lyotropic liquid crystals are shown below.



a.) micelle



b.) inverse micelle



c.) lamellar

6.3.2 Applications of liquid crystals:

Liquid crystal displays operate at low voltages (a few volts) and consume less power as compared to other displays and hence are used in:

1. Liquid crystal displays: Used in display devices such as watches, calculators, mobile telephones, laptop computers, and clocks.
2. Liquid crystal thermometers: Chiral nematic LCs reflect light and the color which is reflected is temperature dependent.

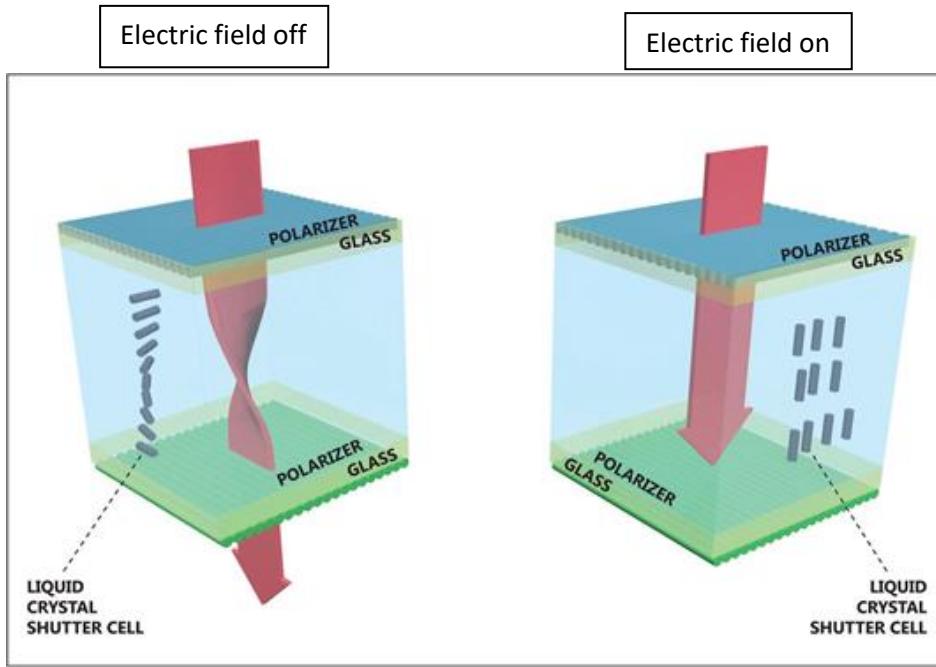
6.3.3 Liquid Crystals in Display systems

The electro-optic effect of liquid crystals controls the brightness/darkness of the light emerging from its elements and this is used in information displays. Information is passed on to the user using LCs which control the brightness/darkness of the parts of a display. Liquid Crystal Displays are available in many sizes and can be used to display numeric, alphanumeric and graphic images. The numeric display has seven segments whereas alphabets are displayed using fourteen segments. More complex graphic images are formed using pixels (picture elements) which are closely packed array of dots in two dimensions.

A numeric display consists of seven segments for each digit. Light from the area of each of the seven segments is controlled independently and is used to create any one of the ten digits. When an electric field is applied to a segment, the liquid crystal in that segment undergoes deformation (is activated) and when polarized light is incident, the light is modulated depending on the deformation in that segment.

In twisted nematic displays (TND), the nematic LC is sandwiched between two ITO coated glass plates with parallel (homogeneous) alignment of its molecular director with the glass walls.

However, the two glass plates are twisted by 90° relative to each other (as shown in the following figures).



In such geometry, the LC is forced to perform a 90° twist of the director resulting in a helical structure. The distance between the plates, hence the thickness of the LC film, is typically 6–10 μm . To complete the TND unit, a pair of crossed polarizers is placed on the outer side of the glass plates. In the absence of an external electric field, when linearly polarized light enters the device, the LC film rotates the polarization of the light by 90° . Thus, the light reaches the second polarizer with its polarization plane parallel to the polarizer axis and is transmitted. In this configuration, the display appears bright (off-state). However, when an electric field is applied (on-state), the 90° twist in the cell is lost and the LC molecules reorient in order to align the molecular director with the external electric field, causing the helical arrangement to be unwound. As a consequence, the light passing through the LC film is not guided through 90° and is not able to pass through the second polarizer. The display looks dark and the observer can see the black character on a silver gray background.

Ceramics

The term “ceramic” comes from (Gk. Keramos- burnt matter) indicating that desirable properties of these materials are generally achieved through a high-temperature heat treatment process called firing. Ceramics consist of a combination of non –metallic substances mostly silicates and metal oxides. It is used to indicate refractories, glass, enamels, porcelain, bricks and abrasive materials. For example, some of the typical ceramic materials include aluminum oxide, silicon dioxide, silicon carbide, silicon nitride and, also, the traditional ceramics are those composed of clay minerals as well as cement and glass. The chemical combination of different metallic and non-metallic elements gives rise to ceramic materials with a variety of properties. They could withstand a temperature of 1500 to 2000 $^{\circ}\text{C}$, but a particular application may require the metals to withstand the temperature up to 5000 $^{\circ}\text{C}$.

For mechanical behavior, ceramic materials are relatively stiff and strong, very hard, brittle, highly susceptible to fracture, higher stability, and higher melting points. Most of these are insulators like other covalent materials. Some of the refractory materials are quite stable and are thus used as structural materials in structures where resistance to high temperature and oxidation are essential, as in furnaces for steel making and as glass making. About optical characteristics, Ceramics may be transparent, translucent, or opaque, and some of the oxide ceramics (e.g., Fe_3O_4) exhibit magnetic behavior. These new materials affect our lives; electronic, computer, communication, aerospace and a host of other industries rely on their use.

Classification of ceramic materials on the basis of application

1. *Glasses* - products of fusion rapidly cooled to a rigid condition without crystallization. They are noncrystalline silicates that contain other oxides. Optical transparency is the most desirable properties of these materials. The most common uses for these materials are as ovenware, tableware, oven windows because of their strength and excellent resistance to thermal shock. They also serve as electrical insulators and as substrates for printed circuit boards and heat exchangers and regenerators.

2. *Clay products*- structural clay products, whitewares

Clay is the principal component of the whitewares and structural clay products. Structural clay products include building bricks, tiles-applications in which structural integrity is essential. In the whiteware ceramics group are porcelain, pottery, china and sanitary ware. Feldspar and quartz may be added which influence the changes that occur during firing. Fireclays are hydrated aluminosilicates of composition $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$.

3. *Refractories* – fire clay, silica, basic, special materials :

The materials that are employed at elevated temperatures and often in reactive environments. By composition and application, the four main subdivisions are fireclay, silica, basic and special. Typical applications include furnace linings for metal refining, glass manufacturing, metallurgical heat treatment and power generation.

3a. *Acid refractories*

They consist of mostly acidic materials like alumina (Al_2O_3) and silica (SiO_2). They are not attacked or affected by acidic materials, but easily affected by basic materials. They include substances such as silica, alumina, and fire clay brick refractories. Fireclay bricks are used in

furnace construction to confine hot atmosphere and to insulate structures from excessive temperatures thermally.

3b. Neutral refractories

These are used in areas where slags and atmosphere are either acidic or basic and are chemically stable to both acids and bases. The principal raw materials belong to but are not confined to, the M_2O_3 group. The typical examples of these materials are alumina (Al_2O_3), chromia (Cr_2O_3) and carbon.

3c. Basic refractories

The refractories that are rich in periclase, or magnesia (MgO) are termed basic; they may also contain calcium, chromium, and iron compounds. These are used in areas where slags and atmosphere are basic; they are stable to alkaline materials but could react with acids. The steelmaking process used artificial periclase (roasted magnesite) as a lining material for the furnace.

4. Abrasive materials – metal oxides and nitrides:

The abrasives being hard and tough are used to cut, grind and polish other softer materials. Diamond, SiC, Tungsten carbide are typical examples. The abrasives may be employed in the form of loose grains, bonded to an abrasive wheel or coated on paper or fabric, used for sharpening knives and polishing wooden surfaces.

5. Cement – Portland cement:

When mixed with water, inorganic cement forms a paste that is capable of assuming just about any desired shape. The subsequent setting is a result of chemical reactions involving the cement particles and occurs at the ambient temperature. For Portland cement is the most common hydraulic cement, the chemical reaction is one of hydration. The produced mixture hardens into a solid mass on reacting with water and provides the water-resistant product.

6. Advanced ceramics - composite materials, engine rotors:

Many of our modern technologies use advanced ceramics because of their unique mechanical, chemical, electrical magnetic and optical properties and property combinations. Examples: ceramic ball bearings, piezoelectric ceramics.

Properties to be considered:

1. Glass-ceramic materials have relatively high mechanical strength; low coefficient of thermal expansion (to avoid thermal shock) and high-temperature capabilities, excellent dielectric properties and good biological compatibility, ease of fabrication. They serve as electrical insulators and as a substrate for printed circuit boards.
2. In refractories, porosity must be controlled. Strength, load bearing capacity and resistance to attack by corrosive materials all increase with porosity reduction. Any residual porosity will have a deleterious influence on both elastic properties and strength.

Mechanical properties of ceramics:

Mechanical properties of ceramics are inferior to Metals.

Energy absorption is low. Strength and melting temperature vary linearly. At low temperature, ceramics are brittle while close to its melting temperature, non-crystalline ceramics becomes ductile.

The processing method of ceramics decides the strength and are usually strong in compression than in tension. Ceramics have limited energy absorption, load carrying capacity.

Brittle fracture

When the tensile load is applied on crystalline or non-crystalline ceramics, fracture takes place, before any deformation sets-in. Brittle ceramic strength is lower than expected. Compressive strength is higher than tensile strength. Flaws in the ceramics behaves like stress magnifiers and forms the cracks. Fractures in ceramics sequentially take place. Fracture toughness is the ability of the ceramics to resist the fracture is directly proportional to applied stress and length of the crack.

Stress-strain behavior

As ceramics are brittle, they tend to fracture before it reaches plastic deformation state. As materials under consideration have diverse shapes, their tensile strength measurement is difficult. Instead, three-point bending apparatus to measure stress-strain behavior.

Flexural or fracture strength σ_{fs} is the stress at fracture is directly proportional to load at fracture and indirectly proportional to the thickness of the material.

Elastic behavior:

Elastic deformation is reversible deformation, while plastic deformation is permanent deformation. In reversible deformation, the material comes to its original configuration, (shape and size), when load/force are released. Elastic deformation can be due to tension / compression / shear force. Metals and ceramics usually have linear elastic behavior. The elastic modulus, like fracture strength, is directly proportional to load at fracture and indirectly proportional to the thickness of the material.

Composite materials

A composite material is a material system composed of two or more macro constituents that differ in shape and chemical composition. Many of our modern technologies require materials with proper combinations of properties that cannot be met by the conventional metal alloys, ceramics, and polymeric materials. This is especially true for structural materials that have low densities are strong, stiff and abrasion resistant and are needed for aerospace, underwater and transport applications. Other applications of these materials involve automotive, home appliance and sporting goods, industries.

Material property combinations and ranges have been extended by the development of composite materials. A composite is composed of two (or more) individual materials which come from the categories namely metals, ceramics, and polymers. Thus ***Composites are artificially produced multiphase materials having a desirable combination of the best properties of the constituent phases.*** Usually, one phase (the matrix) is continuous and surrounds the other (the dispersed phase). The properties of composites are a function of the properties of the constituent phases, their relative amounts and the geometry of the dispersed phase.

Some composites occur in nature. For example, wood consists of strong and flexible cellulose fibers surrounded and held together by a stiffer material called lignin. However, most are synthetic composites. One of the most common and familiar composites is fiberglass, in which small glass fibers are embedded within a polymeric material (epoxy or polyester). The glass fibers are relatively strong and stiff (but also brittle), whereas the polymer is ductile. The plastic matrix holds the glass fibers together and also protects them from damage by sharing out the forces acting on them. It is still widely used today for boat hulls, sports equipment, building panels and many car bodies.

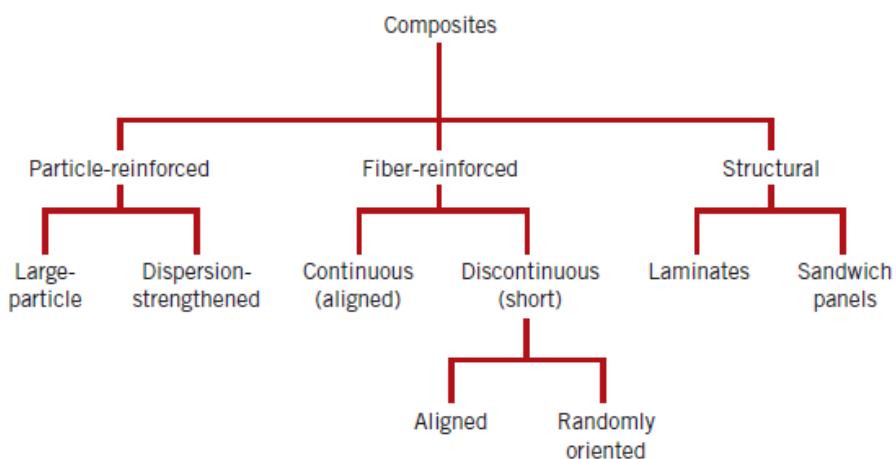
An optimum combination of properties is usually sought rather than one particular property, in selecting a composite material. For example, wings of an aircraft must be lightweight and be strong, stiff and sturdy. Several fiber-reinforced polymers possess this combination of properties. Adding significant amounts of carbon black to natural rubber increases its strength drastically. Properties of composite materials are determined by three factors.

- i) The materials used as component phases in the composite
- ii) The geometric shapes of the constituents
- iii) The manner in which the phases interact with one another.

Classification of composites

Composites are classified into various types based on different parameters. One such classification is based on the matrix material, and the reinforcement geometry (particles, fibers, layers) and the simple scheme of such classification are shown below consisting of three main divisions.

- I. Particle reinforced - Properties are isotropic
 - Large particle
 - Dispersion strengthened
- II. Fiber reinforced - Properties can be isotropic or anisotropic
 - Continuous (aligned)
 - Discontinuous(short) – Aligned and Randomly oriented
- III. Structural - Based on the build-up of sandwiches in layered form
 - Laminates
 - Sandwich panels

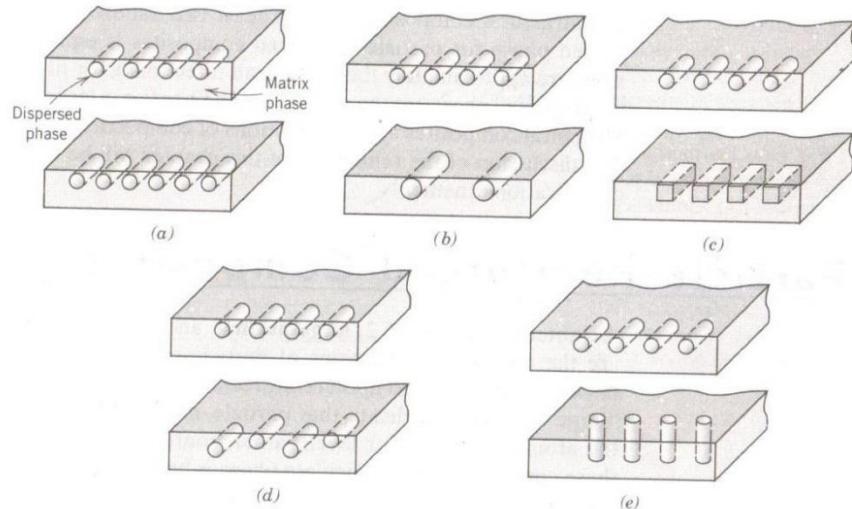


Particle reinforced:

The dispersed phase for particle reinforced composites is equiaxed (i.e., particle dimensions are approximately the same in all directions). Large particle and dispersion –strengthened composites fall within this category. The distinction between these is based upon reinforcement or strengthening mechanism.

For most of the large particle reinforced composites, the particulate phase is harder and stiffer than the matrix. In essence, the matrix transfers some of the applied stress to the particles, which bear the friction of the load.

For dispersion-strengthened composites, particles usually are much smaller. In this the matrix bears the major portion of an applied load, the small dispersed particles hinder the motion of dislocations. Thus plastic deformation is restricted such that yield and tensile strengths, as well as hardness improve.



Fiber reinforced:

The essential composites are those in which the dispersed phase is in the form of a fiber. The dispersed phase has the geometry of a fiber (large length to diameter ratio). Design goals of fiber reinforced composites often include high strength and /or stiffness on a weight basis. With these composites, an applied load is transmitted to and distributed among the fibers via the matrix phase. On the basis of diameter, fiber reinforcements are classified as whiskers, fibers, or wires.

Fiber orientation and concentration have a significant influence on the strength and other properties of fiber reinforced composites. With respect to orientation, two extremes are possible;

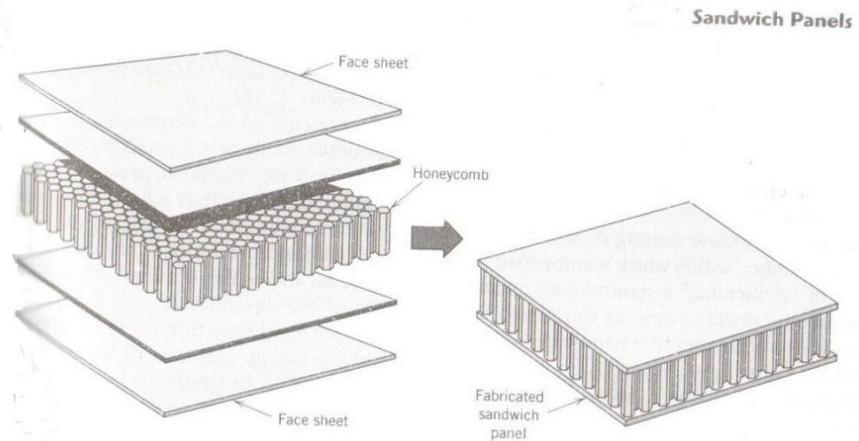
- i) a parallel alignment of the longitudinal axis of the fibers in a single direction and
- ii) a random alignment. Continuous fibers are generally aligned whereas discontinuous fibers may be aligned randomly oriented or partially oriented. Better overall composite properties are realized when the fiber distribution is uniform.

Structural:

Structural composites are combinations of composites and homogeneous materials, the properties of which depend not only on the properties of the constituent materials but also on the geometrical design of the various structural elements. Laminar composites and sandwich panels are two of the most common structural composites.

The properties of laminar composites are virtually isotropic in a 2-D plane. This is made possible with several sheets of a highly anisotropic composite, which are cemented onto one another such that the high strength direction is varied with each successive layer.

Sandwich panels consist of two strong and stiff faces that are separated by a core material or structure. These structures combine relatively high strengths and stiffnesses with low densities.



Influence of length, orientation, concentration, and elastic behavior of fibers

Influence of fiber length

The mechanical characteristics of a fiber-reinforced composite depend not only on the properties of the fiber but also on the degree to which an applied load is transmitted to the fibers by the matrix phase, which in most cases is at least moderately ductile. Significant reinforcement is possible only if the matrix – fiber bond is strong. On the basis of diameter, fiber reinforcements are classified as whiskers, fibers, or wires. Since reinforcement discontinues at the fiber extremities, reinforcement efficiency depends on fiber length. For each fiber – matrix combination, there exists some critical length; the length of continuous fibers dramatically exceeds this critical value, whereas shorter fibers are discontinuous.

For some glass and carbon fiber–matrix combinations, this critical length is on the order of 1 mm, which ranges between 20 and 150 times the fiber diameter.

Influence of fiber orientation and concentration

The arrangement or orientation of the fibers relative to one another, the fiber concentration, and the distribution all have a significant influence on the strength and other properties of fiber-reinforced composites. Concerning orientation, two extremes are possible: (1) a parallel alignment of the longitudinal axis of the fibers in a single direction, and (2) a random alignment. Continuous

fibers are normally aligned (Figure 6a), whereas discontinuous fibers may be aligned (Figure 6b), randomly oriented (Figure 6c), or partially oriented. Better overall composite properties are realized when the fiber distribution is uniform.

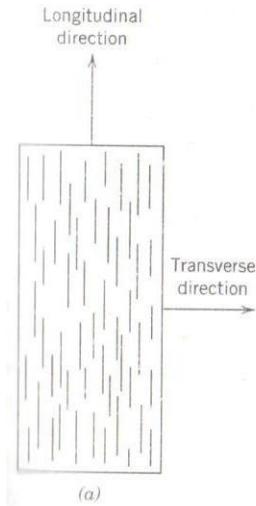


Figure 6a

Figure 6b

Figure 6c

Fiber arrangements are also crucial relative to composite characteristics. The mechanical properties of continuous and aligned fiber composites are highly anisotropic. In the alignment direction, reinforcement and strength are a maximum; perpendicular to the alignment they are minimum.

For short and discontinuous fibrous composites, the fibers may be either aligned or randomly oriented. Significant strengths and stiffness are possible for aligned short-fiber composites in the longitudinal direction. Despite some limitations on reinforcement efficiency, the properties of randomly oriented short fiber composites are isotropic.

Elastic Behavior—Longitudinal Loading

When the load is applied on the composite in the direction of the orientation of continuous fiber, then its modulus of elasticity is equal to the summation of the products of the modulus of elasticity (E) and volume fraction (V) of the respective phases.

i.e., Modulus of elasticity of composite, $E = (EV)_{matrix} + (EV)_{fiber}$

When the load is applied on the composite perpendicular to the orientation of continuous fiber, the inverse of the modulus of elasticity is equal to the summation of the ratio of volume fraction (V) and modulus of elasticity (E) of the respective phases.

i.e., $1/E = (EV)_{matrix} + (EV)_{fiber}$

$$\frac{1}{E} = \left(\frac{V}{E}\right)_{matrix} + \left(\frac{V}{E}\right)_{fiber}$$

Polymer – Matrix Composites

Polymer-matrix composites (PMCs) consist of a polymer resin as the matrix, with fibers as the reinforcement medium. These materials are used in diverse composite applications, as well as in the largest quantities, due to their room-temperature properties, ease of fabrication, and cost.

Polymer matrix materials:

The matrix materials used in composites are polyesters, vinyl esters, epoxies, polyetheretherketone (PEEK), polyphenylene sulfide (PPS), and polyetherimide (PEI). PEEK, PPS and PEI are the polymeric resins with potential aerospace applications.

The fibers, which are the reinforcing materials generally used are - Glass fibers, carbon fibers or aromatic polyamides (or aramids). Accordingly, they are classified into three categories.

- i) Glass Fiber-Reinforced Polymer (GFRP) Composites,
- ii) Carbon Fiber-Reinforced Polymer (CFRP) Composites, and
- iii) Aramid Fiber-Reinforced Polymer Composites.

The fiber is embedded in the matrix to make the matrix stronger. Fibre reinforced composites impart two important properties: (i) often stronger than steel (ii) less weight. This means that composites can be used to make automobiles lighter, and thus making them more fuel efficient.

Advantages of polymer composites: Polymer composite materials are preferred to conventional metals and materials for the following advantageous properties;

- Lightweight.
- High strength to weight ratio.
- More durable than conventional materials like steel and aluminum.
- Good corrosion resistance.
- High fatigue strength.
- High-temperature resistance.

Applications:

- Composites of phenolic resins and nylon are used in heat shields for space crafts.
- Automotive and railway applications.
- As the structural material in construction industries.

i) Glass Fibre Reinforced Plastic (GFRP):

Glass Fibre Reinforced Plastic is a typical polymer composite in which the reinforcing material is fiberglass. Its matrix is made by reacting a **polyester with carbon-carbon double bonds** in its backbone and **styrene** - a mix of the styrene and polyester over a mass of glass fibers.

The styrene and double bonds in the polyester react by free radical polymerization to form a cross-linked resin. The glass fiber is trapped inside, where they act as a reinforcement. The matrix adds toughness to the composite, while fibers have good tensile strength. The matrix gives compressional strength to the composite. Fiber reinforced composites are used in applications like car engine components, airplane parts.

ii) Carbon Fiber Reinforced Polymer (CFRP) Composite:

Carbon is a high-performance fiber material that is most commonly used reinforcement in advanced polymer matrix composites. The reasons for this are as follows:

1. Carbon fibers have the highest specific modulus and specific strength of all reinforcing fiber materials.
2. They retain their high tensile modulus and high strength at elevated temperatures; high-temperature oxidation, however, may be a problem.
3. At room temperature, carbon fibers are not affected by moisture or a wide variety of solvents, acids, and bases.
4. These fibers exhibit a diversity of physical and mechanical characteristics, allowing composites incorporating these fibers to have specific engineered properties.
5. Fiber and composite manufacturing processes have been developed that are relatively inexpensive and cost-effective.

Use of the term “carbon fiber” may seem perplexing since carbon is an element. Carbon fibers are not totally crystalline, but are composed of both graphitic and noncrystalline regions; these areas of non-crystallinity are devoid of the three-dimensional ordered arrangement of hexagonal carbon networks that is characteristic of graphite. Manufacturing techniques for producing carbon fibers are relatively complex and will not be discussed. However, three different organic precursor materials are used: rayon, polyacrylonitrile (PAN), and pitch. Processing technique will vary from precursor to precursor, as will also the resultant fiber characteristics.

Carbon-reinforced polymer composites are currently being utilized extensively in sports and recreational equipment (fishing rods, golf clubs), filament-wound rocket motor cases, pressure vessels, and aircraft structural components—both military and commercial, fixed wing and helicopters (e.g., as a wing, body, stabilizer, and rudder components).

iii) Aramid Fiber-Reinforced Polymer Composite:

Aramid fibers are high-strength, high-modulus materials that were introduced in the early 1970s. They are especially desirable for their outstanding strength-to-weight ratios, which are superior to metals. Chemically, this group of materials is known as poly(paraphenylene terephthalamide). There are some aramid materials; trade names for two of the most common are KevlarTM and NomexTM.

Kevlar composites:

Kevlar is an aromatic polyimide (or aramid). The chemical composition of Kevlar is poly(para phenyleneterephthalamide). They belong to the family of nylons. Common nylons, such as nylon-6,6 do not have very good structural properties, so the incorporation of para-aramids improve the properties. The aramid ring gives Kevlar its thermal stability, while the para structure gives it high strength and modulus. Kevlar is used as matrix material whereas many fibers like carbon fiber or glass fiber are used as the reinforcing agent.

Advantages:

- Lightweight, high strength, Thermally Stable
- Resistant to impact and abrasion damage. It can be used as a protective layer on graphite laminates.

- Can be mixed with graphite to provide damage resistance and to prevent failure.

Disadvantages:

- Fibers themselves absorb moisture, so Kevlar composites are more sensitive to the environment than glass or graphite composites.
- Poor compression resistance.

Biomaterials

Biomaterials is an exciting and rapidly developing interdisciplinary field involving elements of materials science, engineering, biology, chemistry, and medicine. The biomaterials topic is designed to provide a broad basis in the fundamentals of biomaterials science and engineering.

Definition

Biomaterial - Any material of natural or synthetic origin that comes in contact with tissue, blood or biological fluids, and intended for use in prosthetic, diagnostic, therapeutic or storage application.

Factors that govern biomaterial choice

- Bulk properties: The use of biomaterial in particular applications is often dictated by bulk properties; Mechanical (Eg. modulus, strength & toughness for load-bearing applications, wear resistance for articulating surfaces, flexibility & compliance for vascular and soft tissues.), Chemical (Eg. degradation) and Optical (Eg. whiteness, clarity) matched to those of natural organs.
- Ability to Process

Requirements of Biomaterials

A biomaterial should broadly satisfy the following requirements;

- Biocompatibility - the ability of a material to perform with an appropriate host response in a specific application. The biomaterials must neither degrade in its properties within the body (unless this is wanted), nor biomaterials/devices (and any degradation product) must cause any adverse reaction within the host's body. Biocompatibility is strongly determined by the primary chemical structure of the material.
- Biofunctionality - The material must satisfy its design requirements. Eg: Articulation to allow movement (e.g. artificial knee joint), load transmission and stress distribution etc.
- Inert or specifically interactive
- Mechanically and chemically stable - tensile strength, yield strength, elastic modulus, corrosion and fatigue resistance, surface finish, creep, and hardness.
- Processable (for manufacturability) - should be machinable, moldable and extrudable
- Sterilizable

Types of Biomaterials

The biomaterials are divided into four classes: – Metals, Ceramics (including glasses), Composites and Polymers. The properties and safety of materials must be carefully assessed with respect to the specific application. Metals are susceptible to degradation by corrosion, a process that can release by-products that may cause adverse biological responses. Ceramics are attractive as biological implants for their biocompatibility. The availability of a wide range of polymers significantly influenced the growth of tissue engineering and controlled drug delivery technologies. Innovations in the composite material design and fabrication processes are raising the possibility of realizing implants with improved performance.

1. *Metals and alloys*

Metals are widely used as biomaterials due to their favorable mechanical properties like strength and toughness, especially fracture toughness and fatigue strength. The type of bonding (closely packed crystal structure) in metals and metal alloys render them valuable exclusively for load-bearing implants, such as hip and knee prostheses and fracture fixation wires, pins, screws, and plates. Their properties depend on the processing method and purity of the metal. When processed suitably they contribute high tensile, fatigue and yield strengths; low reactivity and good ductility. Although pure metals are sometimes used, alloys frequently provide an improvement in material properties, such as strength and corrosion resistance. The main considerations in selecting metals and alloys for biomedical applications are their excellent electrical and thermal conductivity, biocompatibility, appropriate mechanical properties, corrosion resistance, and reasonable cost.

The human body is an aggressive medium for inducing corrosion in metals: water, dissolved oxygen, proteins, chloride and hydroxide. The biocompatibility of the metallic implant is of considerable concern because these implants can corrode in an *in vivo* environment. The corrosion of the implant material will weaken the implant, and the corrosion products induce a toxic effect on the surrounding tissues and organs. Hence to avoid corrosion, the composition of the biological environment (ions, pH, oxygen pressure, etc.) should be considered. Choice of appropriate metals, avoiding implantation of dissimilar metals and minimizing pits and crevices on the metal surface can reduce corrosion. Three material groups dominate biomedical metals: Stainless steel, titanium and titanium alloys and cobalt-chromium-molybdenum alloy.

Stainless steel (most common 316L) used in orthopedics (Eg. Joint replacements, screws) and dental implants has 60-65% Fe, 17-19% Cr, 12-14% Ni, > 0.030% C and minor amounts of N, Mn, Mo, P, Si, and S. The low carbon content enables better resistance to *in vivo* corrosion,

chromium for corrosion resistance by formation of surface oxide and nickel improves strength. Due to the potential long-term release of Ni^{2+} , Cr^{3+} and Cr^{6+} restricted to temporary devices.

Ti alloys due to the combination of its excellent characteristics such as high strength, low density, lightweight, high specific strength, good resistance to corrosion, complete inertness to body environment, enhanced biocompatibility, good mechanical properties are a suitable choice for implantation. TiO_2 layer provides good corrosion resistance to stress corrosion cracking and corrosion fatigue in body fluids. But, titanium has unsatisfactory wear. Eg. heart pacemakers, artificial heart valves, Bone and Joint Replacements

Co-Cr-Mo alloy- Cobalt-based alloys are highly resistant to corrosion even in chloride environment due to spontaneous formation of passive oxide layer within the human body environment. The thermal treatments used to Co-Cr-Mo alloys modify the microstructure of the alloy alters the electrochemical and mechanical properties of the biomaterial. The corrosion products of Co-Cr-Mo are more toxic than those of stainless steel 316L.

2. Ceramics

Inorganic polycrystalline compounds that contain metallic and non-metallic elements. High oxidized state and inter-atomic ionic/covalent bonding in ceramics make them resistant to oxidation, increasingly stable and non-conducting. Ceramic biomaterials have been used less extensively than either metals or polymers. The bioceramics are highly chemically inert in the body, hard, possess excellent corrosion resistance, high wear resistance, high modulus (stiffness) & compressive strength and fine aesthetic properties (for dental applications), but they are difficult to fabricate. Ceramics are used in several areas like dentistry, orthopedics, and as medical sensors. Eg: Alumina, Zirconium, Calcium phosphate, Silica, hydroxyapatite

Bioceramics are of three basic types: bioinert, bioactive and bioresorbable ceramics.

- i) Bioinert refers to a material that retains its structure in the body after implantation and does not induce any immunologic host reactions.

Eg. Alumina (Al_2O_3) is used in loadbearing hip prostheses and dental implants, because of its combination of excellent corrosion resistance, good biocompatibility, high wear resistance and high strength. These properties are attributed to ionic bonding/electrostatic interactions with the charges on the proteins. The reasons for the excellent wear and friction behavior of alumina are associated with the surface energy and surface smoothness of this ceramic.

- ii) *Bioactive* refers to materials that form direct chemical bonds with bone or even with the soft tissue of a living organism.

Eg. Bioglass and glass-ceramics widely used for filling bone defects permit modification of the surface that occurs upon implantation. Bonding to bone is due to specific amounts of ionic network formers: SiO_2 and P_2O_5 and network modifiers: Na_2O and CaO . They are partially soluble *in vivo*, which facilitates direct chemical bond with bone, which includes a slight solubility of the glass ceramic and a solid state reaction between the stable apatite crystals in the glass ceramic and the bone. The porosity of bioglass is beneficial for resorption and bioactivity.

- iii) *Bioresorbable* refers to materials that degrade by a hydrolytic breakdown in the body, while they are being replaced by regenerating natural tissue; the chemical byproducts of the degrading materials are absorbed and released via metabolic processes of the body.

Eg. Calcium phosphate ceramics have ideal pore size similar to that of spongy bone, and hence bond to living the bone-like apatite layer on their surface.

Ceramics typically fail due to little plastic deformation, and they are sensitive to the presence of cracks or other defects, has low tensile strength and poor fatigue resistance. They are brittle and relatively difficult to process.

3. Polymers

Polymers are the most widely used materials in biomedical applications. The unique properties of the polymeric biomaterials compared to metal or ceramic materials are flexibility, ease of manufacture to produce various shapes (latex, film, sheet and fibers), ease of secondary processability, surface modification, reasonable cost, resistance to biochemical attack, good biocompatibility, light weight, availability in a wide variety of compositions with tailorable physical and mechanical properties. But they are leachable, absorb water and proteins, allows surface contamination, wear and tear and difficult to sterilize.

Eg: Polymethylmethacrylate (PMMA) is used as intraocular lenses due to its high refractive index, easily processability, environmental stability (relatively inert) and good mechanical properties.

Surfaces of materials are high-energy regions and thereby facilitate chemical reactions that influence the performance of biomaterials. Eg. Some biopolymers are susceptible to chemical reactions that lead to degradation through hydrolysis. However, in some cases, a polymer is specifically chosen for its ability to degrade *in vivo*.

Polymer hydrolysis involves the scission of susceptible molecular groups by reaction with H₂O, catalyzed by acid, base or enzyme.

Molecular and structural factors influencing hydrolysis are

- a) Bond Stability - Susceptible linkages at bonds where resonance stabilized intermediates are possible.
- b) Hydrophobicity: ↑ hydrophobicity ⇒ ↓ hydrolysis
- c) MW & architecture: higher MW ⇒ ↓ hydrolysis
- d) Morphology: crystallinity ↓ hydrolysis
 - crystallinity ↓ solubility
 - porosity ↑ hydrolysis
- e) Tg: less mobility ⇒ ↓ hydrolysis

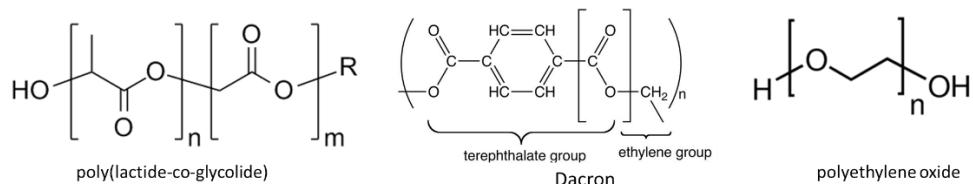
Rates of Hydrolysis: anhydride > ester > amide > ether

Esters: R-COO-R' + H₂O → R-COOH + HO-R'

An amorphous poly(lactide-co-glycolide) with rapid degradation property is used as bioresorbable sutures, controlled release matrices, tissue engineering scaffolds etc. Whereas, semicrystalline polyethylene terephthalate (Dacron) with very slow hydrolysis property find application in vascular grafts, arterial patches, heart pumps etc.

Ethers: R-O-R' + H₂O → R-CH₂-OH + HO-CH₂-R'

Semicrystalline polyethylene oxide (PEO) used for protein resistant coatings and hydrogels is flexible, hydrolyzable, water soluble and bioinert. These properties are derived from both primary and strong secondary H-bonding.



However, some olefins (e.g., Ultrahigh molecular weight polyethylene-UHMWPE: joint cup liners), halogenated hydrocarbons (e.g., PVC: catheters; PTFE: vascular grafts), siloxanes (e.g., PDMS: soft tissue prostheses) and sulfones (e.g., PSF: renal dialysis membranes) exhibit stable polymer chemistry

4. Composites

Natural biocomposites include bone, wood, dentin, cartilage, and skin. Bone achieves most of its mechanical properties as a natural composite material composed of calcium phosphate ceramics in a highly organized polymeric collagen matrix. Biocomposites are composite materials composed of a biodegradable matrix and biodegradable natural fibers as reinforcement in order to obtain properties that improve every one of the components. Composite materials allow a flexible design since their structure and properties can be optimized and tailored to specific applications. Eg. fiberglass with a polymeric matrix is used in the current synthetic casting materials. The use of composite materials for biomedical applications offers many new options and possibilities for implants design. The implant structure and its interactions with the surrounding tissues can be optimized by varying the constituents, the type, and distribution of the reinforcing phase and adding coupling agents. The composite materials and components can be designed to obtain a wide range of mechanical and biological properties.

Thin films

A thin film in general, refers to films with thickness ranging from 0.1 μm to about 300 μm . Coatings such as paint or varnish are typically much thicker. Thin film coatings have unique properties and hence make them desirable for a variety of reasons including materials conservation and design flexibility. A large number of materials which are used for coatings today range from the naturally occurring oxide layer (which protects the surfaces of many metals such as aluminum, titanium, and stainless steel), to those with very deliberate and controlled alloying additions to the surface to produce specific properties as follows;

- Chemically stable in the environment where it is used
- Adhere well to the substrate
- Uniform thickness
- Chemically pure or of controlled chemical composition
- The low density of imperfections
- Optical or magnetic properties, insulator or semiconductor as required for particular applications

As the film is inherently fragile, the bonding between the thin film and substrate provides the structural support. The bonding forces may be primary chemical in nature. Eg. The oxide lattices of the metal oxide and the glass blend at the interface forming a thin zone of intermediate composition. The bonding energies are in the range of 250 - 400 kJ/mol. In some cases, the bonds are based on intermolecular van der Waals and electrostatic forces. The energies are in the range of 50-100 kJ/mol. Eg. Deposition of polymer film on a metal surface

Uses of thin films

They are used as conductors, resistors and capacitors. They are widely used as optical coatings on lenses to reduce reflection and to protect the softer glass against scratching. Thin metallic films have been used as protective coatings on metals. Eg. Silver plating, chrome plating. Metal tool surfaces are coated with ceramic thin films to increase their hardness. The top of the drill bit is normally coated with a thin film of tungsten carbide to impart hardness and wear resistance. The films are applied to the glass to reduce scratching and abrasion and to increase lubricity.

Formation of thin films

The process of applying a thin film to a surface is known as thin-film deposition or fabrication. It is the technique for depositing a thin film of material onto a substrate or onto previously deposited layers. Thin films are formed by different techniques such as physical vapor deposition (PVD) or chemical vapor deposition (CVD). In PVD there is no change in the chemical nature of the source and coated material whereas in CVD due to chemical reactions occurring, the chemical identity of the source and the coated thin film materials are different.

Physical vapor deposition

PVD processes are atomistic deposition processes in which material is vaporized to form a solid or liquid source in the form of atoms or molecules, transported as vapor through a vacuum or low pressure gaseous (or plasma) environment to the substrate where it condenses. The material to be deposited is placed in an energetic, entropic environment so that particles of material escape its surface. Facing this source is a cooler surface which draws energy from these particles as they arrive, allowing them to form a solid layer. The whole system is kept in a vacuum deposition chamber, to allow the particles to travel as freely as possible. Since particles tend to follow a straight path, films deposited by physical means are commonly directional, rather than conformal.

Typically, PVD processes are used to deposit films with thicknesses in the range of a few nanometers to thousands of nanometers. The substrates can range in size from very small to very large, in shape from flat to complex geometries. The source-substrate geometry influences the ultimate film uniformity. Two principal methods for optimizing film uniformity over large areas involve varying the geometric location of the source and interposing static as well as rotating shutters between evaporation sources and substrates. The chemical purity of evaporated films depends on the nature and level of impurities that (1) are initially present in the source, (2) contaminate the source from the heater, crucible, or support materials, and (3) originate from the residual gases present in the vacuum system. Typical PVD deposition rates are 10-100 Å/s.

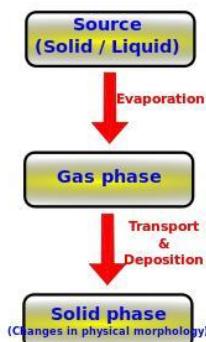


Fig. PVD: Process flow diagram

Vacuum evaporation is one of the important methods for depositing thin films using PVD technique.

Vacuum deposition: This method is used to form thin films of substances that can be vaporized without destroying their chemical identities. Eg. Optical lenses are coated with inorganic materials such as MgF_2 , Al_2O_3 and SiO_2 . During evaporation, a target consisting of the material to be deposited is bombarded by a high energy source such as a beam of electrons or ions in a high vacuum chamber with a pressure of 10^{-5} torr or less. This dislodges atoms from the surface of the target, ‘vaporizing’ them. Vaporized atoms from the target move in a straight path to the substrate to be coated. Finally, the metal atoms get deposited on the substrate surface mounted at an appreciable distance away from the evaporation source. Uniformity is obtained by rotating the substrate to be coated.

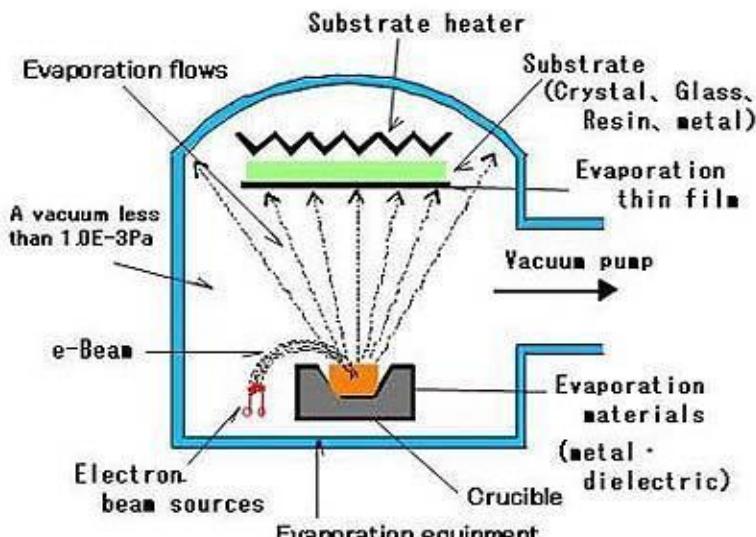


Fig. Schematic diagram of vacuum deposition

The vacuum environment may serve the following purposes by providing low pressure plasma environment, a means for controlling gas and vapor composition and a means for mass flow control into the processing chamber. And reducing the particle density of undesirable atoms and molecules (contaminants) so that the mean free path for collision is long

Advantages:

- PVD coatings are harder and more corrosion resistant than coatings applied by the electroplating process.
- Most coatings have high temperature and good impact strength, excellent abrasion resistance

- More environmentally friendly than traditional coating processes such as electroplating and painting.
- It is possible to change the target material without disturbing the system so that multilayer films can be formed.

Disadvantages:

- It is extremely difficult to coat undercuts and similar surface features
- High capital cost
- Some processes operate at high vacuums and temperatures, require skilled operators
- Processes involving a large amount of heat requires appropriate cooling systems
- The rate of coating deposition is usually quite slow

Chemical Vapor Deposition (CVD)

In this method, the surface is coated with a volatile, stable chemical compound at a temperature below the melting point of the surface. It involves the dissociation and /or chemical reactions of gaseous reactants in an activated (heat, light, plasma) environment, followed by the formation of a stable solid product. The deposition involves homogenous gas phase reactions, which occur in the gas phase, and/or heterogeneous chemical reactions which occur on/near the vicinity of a heated substrate leading to the formation of powders or films, respectively. It has been used to produce ultrafine powders and thin films.

In general, the CVD equipment consists of three main components:

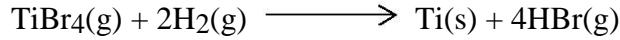
- (a) Chemical vapor precursor supply system: to generate vapor and deliver to the reactor.
- (b) CVD reactor component: consists of a reaction chamber equipped with a load-lock for the transport and placement of the substrate into the chamber, a substrate holder, and a heating system with temperature control. The main function is to heat the substrate to the deposition temperature.
- (c) Effluent gas handling system: This component consists of a neutralizing part for the downstream gases, and /or a vacuum system to provide the required reduced pressure for the CVD process.

Process principles and deposition mechanism: CVD process involves the following key steps:

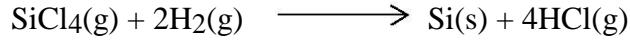
1. Generation of active gaseous reactant species

2. Transport of these gaseous species into the reaction chamber.
3. Gaseous reactants undergo gas phase reactions forming intermediate species.
 - (a) At a high temperature above the decomposition temperatures of intermediate species inside the reactor, homogeneous gas phase reaction can occur where the intermediate species undergo subsequent decomposition and/or chemical reaction.
 - (b) At temperatures below the dissociation of the intermediate phase, diffusion/convection of the intermediate species across the heated substrate surface occur. These intermediate species subsequently undergo steps (4-7)
4. Adsorption of gaseous reactants on to the heated substrate and the heterogeneous reaction occurs at the gas-solid interface (i.e. heated substrate) which produces the deposit and by-product species.
5. The deposits will diffuse along the heated substrate surface forming the crystallization center and growth of the film takes place.
6. Gaseous by-products are removed from the boundary layer through diffusion or convection.
7. The unreacted gaseous precursors and by-products will be transported away from the deposition chamber.

Examples: Titanium tetrabromide is evaporated and the gaseous TiBr₄ is mixed with hydrogen. The mixture is then passed over a substrate heated to about 1300 °C, such as silica or alumina. The metal halide undergoes reaction with hydrogen to form a thin film of titanium metal



Films of silicon are formed by decomposing SiCl₄ in the presence of H₂ at 1200 °C.



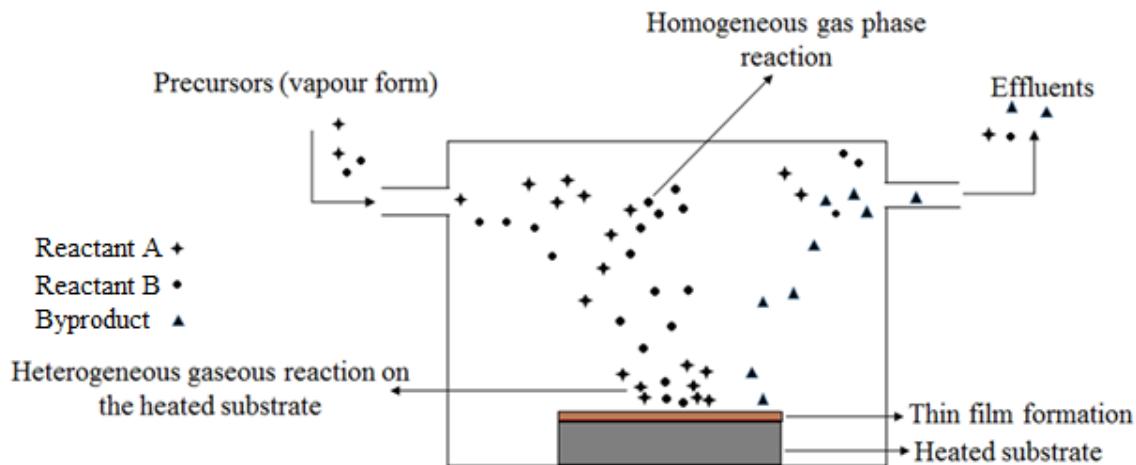


Fig. Schematic diagram of simplified CVD reactor

Advantages

- Capable of producing highly dense and pure materials without carbon or oxygen impurities.
- Produces uniform films with good reproducibility and adhesion at reasonably high deposition rates.
- Has good throwing power and hence can be used to uniformly coat complex shaped components and deposit films.
- Able to control crystal structure, surface morphology and orientation of the products by controlling the process parameters.
- Deposition rate can be adjusted readily. The low deposition rate is favored for the growth of epitaxial thin films for microelectronic applications. The deposition of thick protective coatings is favored by a high deposition rate.
- Reasonable processing cost using the CVD technique.
- The flexibility of using a wide range of chemical precursors such as nitrides, borides, organometallics which enable the deposition of a large spectrum of materials including metal carbides, nitrides, oxides and sulfides.

Drawbacks

- Chemical and safety hazards caused by the use of toxic, corrosive, flammable and/or

explosive precursor gases.

- Difficult to deposit multicomponent materials with well-controlled stoichiometry using multisource precursors because different precursors have different vaporization rates.
- The use of more sophisticated reactor and /or vacuum system by CVD variants such as low pressure or ultrahigh vacuum CVD, plasma-assisted CVD and photo-assisted CVD tends to increase the cost of fabrication.

Applications:

- Production of high-quality optical fibers suitable for long distance applications.
- Diamond thin films: They are used as heat sinks for microelectronics and optoelectronics, sensors, microwave devices, coatings for IR windows in nuclear detectors, UV imaging, cold cathodes. The potential applications of diamond films involve speaker diaphragms which are coated with thin films of diamond to provide improved acoustic properties.

Comparison between PVD & CVD

Features	PVD	CVD
Mechanism of deposition	Thermal energy	Chemical reaction
Deposition rate	High	Moderate
Deposited species	Atoms & ions	Precursor molecules dissociate into atoms
Energy of deposited species	Low (0.1-0.5 eV)	Low; can be high with plasma-assisted CVD
Throwing power	Poor	Good

Nano-materials

Nanoscience and nanotechnology deal with objects that have dimensions in the range from 1

nm to about 100 nm. Nano-materials are materials which have at least one of their dimension in the nanometer ($1 \text{ nm} = 10^{-9} \text{ m}$) range. The physical and chemical properties of nano-materials differ significantly from those of their bulk counterparts. The new properties are the result of an increase in the ratio of surface area to volume. This will change the surface effects such as those that give rise to catalysis, adsorption, adhesion and photonic effects. The reason for this is that the electrons in nanomaterials are confined within such a small volume that quantum effects now dominate optical and electronic behavior. Nano-fibers, nano-wires, nano-scale particles, Nano-channels and nano-tubes are some of the important nanostructures. The nano-science field is progressing so rapidly that it is probably hard to find any technical areas that are not useful.

The most important aspects of this field are connected with four issues;

- i) The way in which nanoparticles interact with their neighbors in solid arrays or with the second phase in composite materials.
- ii) Miniaturization of electronic circuits below the micro-scale to pack an increasing number of features into an integrated array.
- iii) Development of methods to produce nano-fibers that are of interest in geological tissue engineering, advanced textiles and filtration technology.
- iv) Use of micelles with diameters in the nano range for controlled drug delivery.

Classification

(a) Based on origin

- (i) *Natural nanomaterials*
- (ii) *Artificial nanomaterials*

Natural nanomaterials are those which are obtained naturally. Examples:- Carbon-nanotubes and fibers. Artificial nanomaterials are those which are synthesized artificially Examples:- Au/Ag nanoparticles, Polymeric nano-composites.

(b) Based on dimension

This classification is based on the number of dimensions which are not confined to the nanoscale range (<100nm). They may be amorphous or crystalline, single crystalline or polycrystalline, made up of one or more elements, metallic, ceramics or polymers.

(i) *Zero-dimensional*: Materials wherein all the dimensions are within the nanoscale range are called zero-dimensional nanomaterial. Eg: quantum dots.

(ii) *1 dimensional*: Here two dimensions are at the nanoscale range, another dimension is not. This leads to needle-like nanomaterials. Eg: nanotubes, nanorods, nanowires.

(iii) *2 dimensional*: Here one dimension is at the nanoscale range, the other two dimensions are not. They exhibit plate-like shapes. Eg: nanocoatings, nanofilms

(iv) *3 dimensional*: These materials are not confined to the nanoscale in any dimension. These are characterized by having three arbitrarily dimensions above 100 nm. They are also known as bulk nanomaterials. 3-D nanomaterials can contain dispersions of nanoparticles, bundles of nano wires/nanotubes as well as multilayers. Eg: Nanocrystalline materials, nanospheres.

There are other types of classifications based on their field of application, shapes, properties, structures, manufacturing process and morphologies.

Preparation of nanomaterials:

Nanomaterials can be synthesized by two different approaches. They are “Bottom-up” and “Top-down methods”. Top-down methods start with micro – or macro scale materials, which are then broken down chemically or physically to nanoparticles. Methods that are used include ball milling, chemical etching, electrospinning and the vaporization of metals using plasmas. They are slow, not cheap, and not suitable for large-scale production. Bottom-up methods involve the assembly of very small units (atoms, molecules or small nanoparticles) to create larger nanomaterials and systems. The fabrication is much less expensive.

“Bottom-up” Approach:

Sol-gel method

The sol-gel process is a wet-chemical technique used primarily for the fabrication of materials starting from a chemical solution which acts as the precursor for the preparation of gel by either discrete particles or network polymers. The process usually consists of five steps:

1. *Preparation of a precursor solution*: The desired colloidal particles are dispersed in a liquid to form a sol. Typical precursors are metal alkoxides, which undergo various forms of hydrolysis and polycondensation reactions. The formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution.

2. *Deposition of the sol onto a substrate*: The sol solution is coated on a substrate by spraying, dipping or spinning.
3. *Formation of gel*: The particles in the solid state are polymerized through the removal of the stabilizing components. This can be done either by heating the sol at a low temperature or allowing it to stand for a certain duration. This results in the formation of a gel.
4. *Drying process*: Removal of the remaining liquid (solvent) phase requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification.
5. *Heat Treatment*: After drying, a thermal treatment, or firing process, is often necessary to favor further poly-condensation reaction and enhance mechanical properties, structural stability of the gel.

The sol-gel approach is a cheap and low-temperature technique that allows for the fine control of the product's chemical composition. Even small quantities of dopants, such as organic dyes and rare earth elements, can be introduced in the sol and end up uniformly dispersed in the final product. It can be used as a means of producing very thin films of metal oxides for various purposes. Examples include Gallium based nano-materials, Dye-doped gel Glasses, Glass dispersed liquid crystals, Synthesis of glass-metal nano-composite, Metal-silica and Metal oxide-silica nanocomposites.

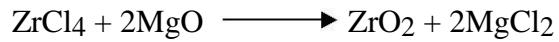
“Top Down” Approach:

Ball Milling

In this process, small balls are allowed to rotate around the inside of a drum and drop with gravity force on to a solid enclosed in the drum. The significant advantage of this method is that it can be readily implemented commercially. The grinding of ceramics can reduce them to a fine powder with each individual particle having nanoscale dimensions. It is difficult to avoid contamination of the nanoparticles by the materials used in the abrasion process and the particle sizes are not uniform. Polymers cannot be reduced to nanoparticles by grinding because of their molecular structure and their impact resistance. Ball milling can be used to make a variety of new carbon types, including carbon nanotubes. It is useful for preparing other types of nanotubes, such as boron nitride nanotubes and a wide range of elemental and oxide powders. For example, iron with grain sizes of 13-30 nm can be formed. Ball milling is the preferred method for preparing metal oxides.

To successfully prepare metal oxides, it is important to keep the crystallites from reacting and to

have an understanding of the kinetic energy transferred during crushing. However, a by-product can sometimes be useful. In the production of nanocrystalline Zirconia (ZrO_2), zirconium chloride is treated with magnesium oxide during milling to form zirconia and magnesium chloride:



The by-product, magnesium chloride, acts to prevent the individual nanocrystallites of zirconia agglomerating. It is washed out at the end of the process.