

UNIT-I

ELECTRODE AND ENERGY SYSTEMS

ELECTROCHEMICAL CELLS:

An **electrochemical cell** is a device which converts chemical energy into electrical energy or electrical energy into chemical energy. Thus, there can be two types of electrochemical cells.

(i) **Electrolytic cells** are devices which convert electrical energy into chemical energy.

(ii) **Galvanic cells (or voltaic cells)** are devices which convert chemical energy into electrical energy. e.g. Daniel cell (Fig.1): The Daniel cell consists of two containers, one of which contains a zinc rod dipped in zinc sulphate solution and the other contains a copper rod dipped in copper sulphate solution. The solutions of two containers are connected by a salt bridge. The salt bridge is a U-tube, filled with either a jelly containing KCl or NH_4NO_3 , or saturated solution of KCl or NH_4NO_3 and both the ends of the U-tube are plugged with a porous material. The zinc and copper rods (electrodes) are connected externally through an ammeter or voltmeter by using a wire, the following changes are observed:

- Zinc starts to dissolve.
- Copper gets deposited on copper rod.
- The voltmeter indicates the flow of electrons from zinc to copper rod.
- The zinc sulphate solution becomes richer with Zn^{2+} ions.
- The copper sulphate solution becomes more dilute with respect to Cu^{2+} ions.

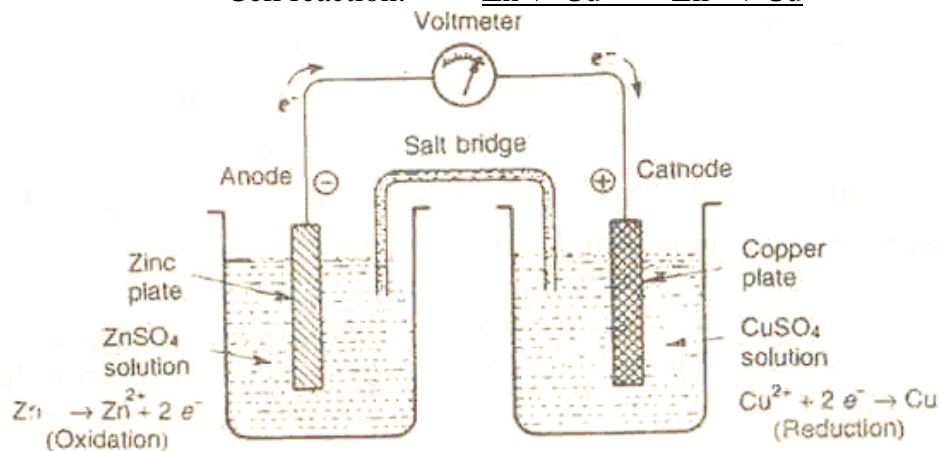
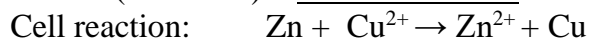
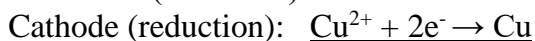
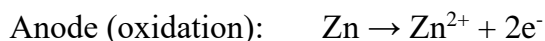


Fig.1. Daniel cell.

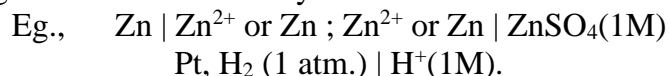
The flow of electrons from zinc electrode to copper electrode. Hence the flow of conventional current is from copper to zinc electrode.

Cell notation and convention:

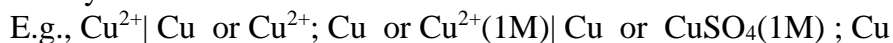
By convention, the electrode at which oxidation occurs is **anode** and the electrode where reduction occurs is **cathode**. Thus in the above cell zinc electrode acts as anode and copper electrode acts as cathode. In a galvanic cell anode is **negative** and cathode is **positive**. The reason, to this 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 the absorption of electrons by the reactant in the solution from the electrode, which thereby acquires a positive charge.

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

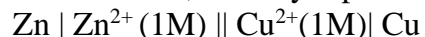
- (1) Anode is written on the left-hand side; while cathode is written on the right-hand side.
- (2) The electrode on the left (i.e., anode) is written by writing the metal (or solid phase) first and then the electrolyte. Two are separated by a vertical line or a semicolon. The electrolyte may be represented by the formula of the whole compound or by ionic species. Additional information regarding the concentration may also be mentioned in bracket.



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



- (4) A salt bridge is indicated by two vertical lines, separating the two half cells. Thus applying above considerations to Daniel cell, we may represent as:



Electromotive force of the cell (EMF): The difference in potential which causes a current to flow from an electrode of higher potential to that of lower potential is called the electromotive force (emf). The cell potential is represented by the E_{cell} .

$$E_{\text{cell}} = E_{\text{RHS}} - E_{\text{LHS}}$$

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

Standard emf of the cell is defined as the emf of the galvanic cell when the reactants and products of the cell reaction are at unit concentration or unit activity, at 298K and 1 atmosphere pressure. $E_{\text{cell}}^0 = E_{\text{RHS}}^0 - E_{\text{LHS}}^0$

Function of salt bridge:

In a galvanic cell, if the salt bridge is not used, then the two solutions should be either in contact with each other or separated by a porous membrane. In either case, positive and negative ions of the electrolytes will migrate across the junction in opposite directions as there is increase of positive and negative charges at anode and cathode respectively. Inside the cell the current is carried by ions, negative ions from cathode to anode and positive ions from anode to cathode. Because of the difference in the migration velocities of these ions, accumulation of charges across the junction occurs. This gives rise to the formation of an electrical double layer developing a potential called **liquid junction potential** across the junction. In such situations, the emf of the cell includes liquid junction potential also.

The use of salt bridge, however, avoids the liquid junction potential and provides the contact between the two solutions. It consists of saturated solution of a salt such as KCl or NH_4NO_3 , 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 avoiding liquid junction potential. During the cell reaction, either Cl^- diffuse from the salt bridge into the zinc half-cell or Zn^{2+} ions diffuse into the salt bridge to keep the zinc-half cell electrically neutral. At the same time, the copper half-cell is kept electrically neutral by the diffusion of either the positive (K^+) ions from the salt bridge to the copper cell or diffusion of SO_4^{2-} ions from the copper cell into the salt bridge. Without the salt bridge no electrical current would be produced by the galvanic cell since electrolytic contact must be maintained for the cell to function.

Single electrode potential (Reduction potential):

Electrode potential is defined as the potential developed on the electrode at the interface when it is in contact with a solution of its own ions. It is denoted by E. All single electrode potentials represent reduction potentials which is the measure of the tendency of an electrode to undergo reduction.

$$E = E^0 + \frac{RT}{nF} \ln [\text{M}^{n+}] \dots \dots \dots (1).$$

Equation (1) is mathematical representation for Nernst equation. E^0 is the electrode potential under standard conditions (for metal ion –metal electrodes, ion concentration is 1M and gas electrodes gas pressure is 1 atmosphere).

Substituting the values for R ($8.3143 \text{ JK}^{-1}\text{mol}^{-1}$), F (96500 Cmol^{-1}) at 298K, and converting natural logarithm to base 10, the Nernst equation reduces to

$$E = E^0 + \frac{0.0591}{n} \log [\text{M}^{n+}] \dots \dots \dots (2).$$

Standard electrode potential (E^0): **Standard electrode potential** is the potential developed when the electrode (metal) is in contact with solution of unit concentration (1M) at 298K.

- (i) It may be seen from equation (1) that $E = E^0$ where $[\text{M}^{n+}]$ is unity.
- (ii) If concentration of solution $[\text{M}^{n+}]$ is increased, the electrode potential increases and vice versa.
- (iii) If temperature is increased, the electrode potential increases and vice versa.

Nernst equation for emf of cells: Nernst equation may also be used to calculate the emf of chemical cells

$$E_{\text{cell}} = E^0_{\text{cell}} - (0.0591/n) \log [\text{products}] / [\text{reactants}]$$

$$\text{or, } E_{\text{cell}} = E^0_{\text{cell}} + (0.0591/n) \log [\text{reactants}] / [\text{products}]$$

$$\text{or, } E^0_{\text{cell}} + (0.0591/n) \log [\text{species at cathode}] / [\text{species at anode}]$$

In Daniel cell, $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$

$$E_{\text{Danielcell}} = E^0_{\text{Danielcell}} + (0.0591/n) \log [\text{Cu}^{2+}] / [\text{Zn}^{2+}]$$

Electrochemical series:

When elements are arranged in increasing order of (down-wards) of their standard electrode potential, a series called electrochemical series (or emf series) is obtained. Such an arrangements of few elements is given in table 1

Table-1. Electrochemical seeries

M^{n+}/M	E^0 (V) at 298K
Li^+/Li	- 3.05 (Anode)
K^+/K	- 2.93
Ba^{2+}/Ba	- 2.90
Ca^{2+}/Ca	- 2.87
Na^+/Na	- 2.71
Mg^{2+}/Mg	- 2.37
Al^{3+}/Al	- 1.66
Zn^{2+}/Zn	- 0.76
Cr^{3+}/Cr	- 0.74
Fe^{2+}/Fe	- 0.44
Cd^{2+}/Cd	- 0.40
Ni^{2+}/Ni	- 0.23
Sn^{2+}/Sn	- 0.14
Pb^{2+}/Pb	- 0.13
H^+/H_2	0.00 (Reference)
Cu^{2+}/Cu	0.34
Ag^+/Ag	0.80
Hg^{2+}/Hg	0.85
Pt^{2+}/Pt	1.20
Au^{3+}/Au	1.38 (Cathodic)

Concentration cells (Fig.2): A concentration cell is an electrochemical cell made of two-half cells having identical electrodes, identical electrolyte, except that the concentrations of electrolyte solutions are different. Two half cells may be joined by a salt bridge. Eg:

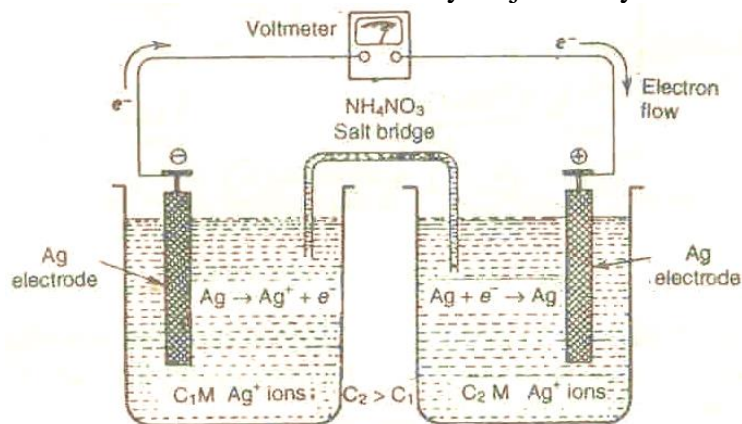


Fig.2. Concentration cell

The cell is represented by



The Ag electrode which is in contact with lower concentration (C_1) of the electrolyte acts as anode where oxidation occurs and enters into the solution. The Ag electrode which is in contact with higher concentration (C_2) of the electrolyte acts as cathode where reduction occurs and deposition of Ag occurs.

Electrode reactions: Anode : $\text{Ag (s)} \rightarrow \text{Ag}^+(\text{C}_1\text{M}) + \text{e}^-$

Cathode: $\text{Ag}^+(\text{C}_2\text{M}) + \text{e}^- \rightarrow \text{Ag (s)}$

Cell reaction: $\text{Ag}^+(\text{C}_2\text{M}) \rightarrow \text{Ag}^+(\text{C}_1\text{M})$

There is no net chemical reaction but only concentration change takes place. Evidently, the emf so developed is due to the mere transference of metal ions from the solution of higher concentration (C_2) to the solution of lower concentration (C_1).

Emf of the cell (E_{cell}) = $E_{\text{cathode}} - E_{\text{anode}}$

$$E_{\text{cell}} = [E^0 + \frac{RT}{nF} \ln \text{C}_2] - [E^0 + \frac{RT}{nF} \ln \text{C}_1]$$

$$E_{\text{cell}} = \frac{RT}{nF} \ln [\text{C}_2] / [\text{C}_1] \text{ -----(1)}$$

At 298K,

$$E_{\text{cell}} = \frac{0.0591}{n} \log [\text{C}_2] / [\text{C}_1] \text{ -----(2)}$$

Note: (i) When $\text{C}_1 = \text{C}_2$ (concentrations are equal), $\log [\text{C}_2 / \text{C}_1] = 0$ and hence no electricity flows (since $\text{emf} = 0$).

(ii) When $[\text{C}_2 / \text{C}_1] > 1$ (i.e., $\text{C}_2 > \text{C}_1$), $\log [\text{C}_2 / \text{C}_1]$ is positive. Thus, the direction of spontaneous reaction is from the more concentrated solution (C_2) to less concentrated solution (C_1).

Reference electrode: Any electrode of constant and reproducible potential, used to determine the potential of other electrode.

E.g., Standard hydrogen electrode.

Measurement of single electrode potential: The potential of a given electrode is measured using standard hydrogen electrode (SHE) whose potential is arbitrarily taken as zero volt at all temperatures and is the reference point for all potential measurements.

Note: It is impossible to measure the absolute value of single electrode potential. It is because a single electrode constitutes only a half cell. A half cell, not be lose or gain electrons by itself. The loss or gain of electrons can take place only in a complete circuit containing two half cells connected to each other. So, the electrode potential can only be measured by using some electrode as reference electrode.

Secondary reference electrodes: Because of the difficulties involved in the use of standard hydrogen electrode as reference electrode, some other electrodes constant electrode potential, referred to as secondary reference electrodes. Two such electrodes are (i) calomel electrode (ii) silver-silver electrode.

(i) Calomel electrode (mercury-mercurous electrode):

Construction: Mercury is placed at the bottom of glass tube. A paste of calomel (Hg_2Cl_2) and mercury is placed over the pool of mercury. The remaining part of the tube is filled either a saturated or standard (normal or decinormal) solution of potassium chloride. A platinum wire is fused in a glass tube is dipped into mercury is used for electrical contact. A salt bridge is used to couple with other half-cells (Fig. 3a).

The calomel electrode is represented as

$\text{Hg} \mid \text{Hg}_2\text{Cl}_2 (\text{s}) \mid \text{KCl} (\text{saturated or standard})$ or $\text{Hg}, \text{Hg}_2\text{Cl}_2 (\text{s}), \text{KCl} (\text{saturated or standard})$.

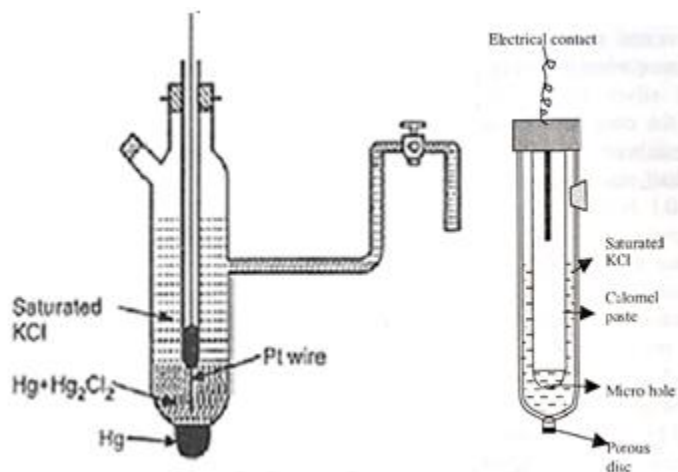
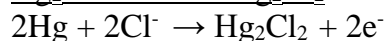
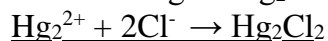


Fig.3. Calomel electrode

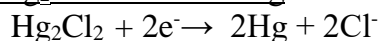
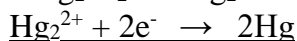
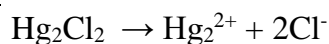
Working: Calomel electrode can act as anode or cathode depending on the nature of the other electrode of the cell.

The electrode reactions are represented as follows.

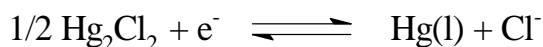
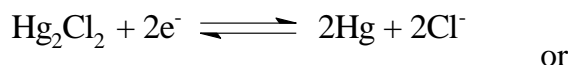
As anode:



As cathode:



The net reversible electrode reaction is



$$\text{Electrode potential } E = E^0 - \frac{2.303RT}{F} \log [\text{Cl}^-]$$

$$\text{At } 298\text{K}, E_{\text{cal}} = E^0_{\text{cal}} - 0.0591 \log [\text{Cl}^-]$$

Since the calomel electrode is reversible with respect to chloride ion its electrode potential depends on the concentration of KCl solution.

At 298K, the electrode potentials as follows:

KCl concentration	0.1N	1N	Saturated
Electrode potential (V)	0.334	0.281	0.2422

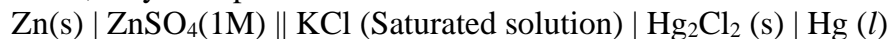
Advantages of calomel electrode (a secondary reference electrode):

1. It is very simple in construction.
2. The potential is reproducible and stable over a long period.
3. Its electrode potential will not vary with temperature.

- Applications:** (i) As secondary reference electrode for potential measurements.
(ii) Determination of pH of a solution

Determination of single electrode potential using calomel electrode: The test electrode (e.g., Zn^{2+}/Zn) is coupled with a saturated calomel electrode (Fig.4).

The cell, so formed, may be represented as



The calomel electrode is written on the right as reduction takes place at this electrode

The emf of this cell measured potentiometrically.

$$\begin{aligned} \text{Then } E_{\text{cell}} &= E_{\text{cathode}} - E_{\text{anode}} \\ &= E_{\text{cal}} - E_{\text{Zn}^{2+}/\text{Zn}} \\ &= 0.2422 - E_{\text{Zn}^{2+}/\text{Zn}} \\ \text{i.e., } E_{\text{Zn}^{2+}/\text{Zn}} &= 0.2422 - E_{\text{cell}} \end{aligned}$$

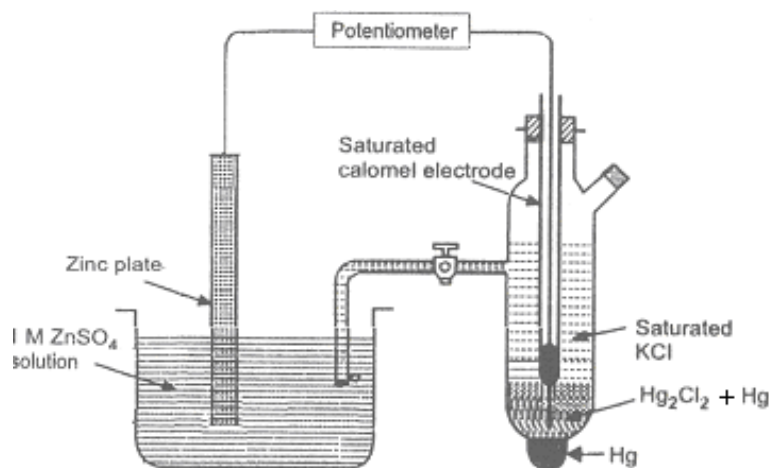
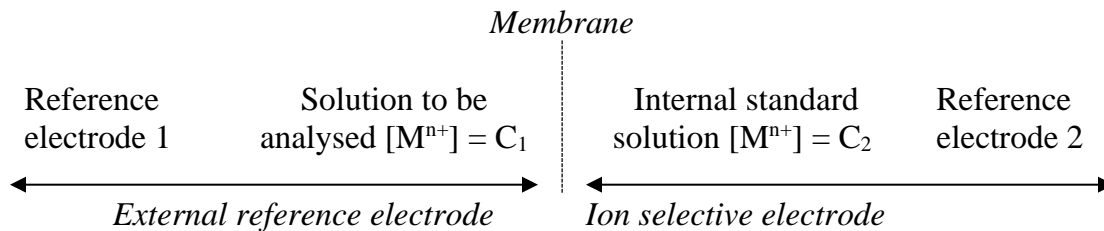


Fig.4. Determination of electrode potential of zinc electrode using calomel electrode as reference electrode.

Ion-selective electrodes: Ion-selective electrode is the one which selectively responds to a specific ion in a mixture and potential developed at the electrode is a function of concentration of that ion in the solution. The electrode generally consists of a membrane which is capable of exchanging the specific ions with the solution with which it is in contact. Therefore, these electrodes are also referred to as membrane electrodes



There are three types of membranes (Fig. 5):

(1) Glass membrane (e.g., glass electrode).

(2) Solid state membranes

(i) For fluoride (F^-) ions- lanthanum trifluoride crystal doped with europium difluoride.

(ii) For chloride (Cl^-) ions – pressed pellet of $Ag_2S + AgCl$. The electrode has a Teflon Body and crystal is held in position with epoxy resin.

(3) Liquid state membranes:

(i) For certain alkali and alkaline earth cations-neutral monocyclic crown ethers and phosphate diester.

(ii) For anions-iron phenanthrolic complexes. Liquid state membrane is usually obtained by absorbing the active molecules on an inert porous support such as porous polymer.

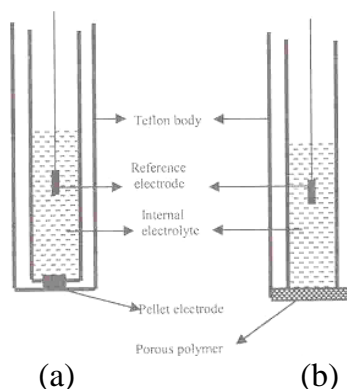


Fig.5. Ion selective electrodes with different types of membranes (a) solid state (b) liquid membrane on a porous polymer.

Applications: Ion selective electrodes are used in determining

- (i) The concentration of a number of cations such as H^+ , Li^+ , Na^+ , K^+ , Ag^+ , NH_4^+ , Cd^{2+} , Pb^{2+} , Cu^{2+} , Ca^{2+} and hardness [$Ca^{2+} + Mg^{2+}$];
- (ii) The concentration of anions such as F^- , NO_3^- , CN^- , S^{2-} and halide ions;
- (iii) The pH of a solution using glass electrode (H^+ ion-selective electrode) and
- (iv) The concentration of gas using gas sensing electrodes. For example, an electrode which measures the level of CO_2 in blood samples makes use of glass electrode in contact with a very thin CO_2 permeable silicone rubber membrane soaked in a dilute solution of sodium bicarbonate.

Glass electrode:

Construction: A glass electrode (Fig.5.) consists of a long glass tube with a thin walled glass bulb at one end. Special glass (Corning glass containing 22% Na_2O , 6% CaO and 72% SiO_2) of low melting point and high electrical conductance is used for the purpose. This glass can specifically sense hydrogen ions up to a pH of about 9. The bulb contains 0.1 M HCl and a $Ag/AgCl$ electrode (as internal reference electrode) is immersed into the solution and connected by a platinum wire for electrical contact. The electrode is represented as,
 $Ag | AgCl(s) | HCl(0.1M) | glass.$

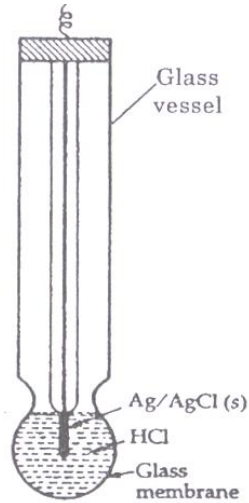
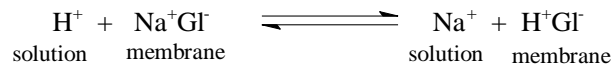


Fig.5. Glass electrode

Electrode potential of glass electrode (E_g):

Principle: If a thin walled glass bulb containing an acid is immersed in another solution, the membrane undergoes an ion exchange reaction; Na^+ ions on the glass are exchanged for H^+ ions. The potential is developed across the glass membrane (Fig.6).



The potential difference, E_b at the interface also referred to as the boundary potential is the result of difference in potential ($E_2 - E_1$) developed across the gel layer of glass membrane between the two liquids.

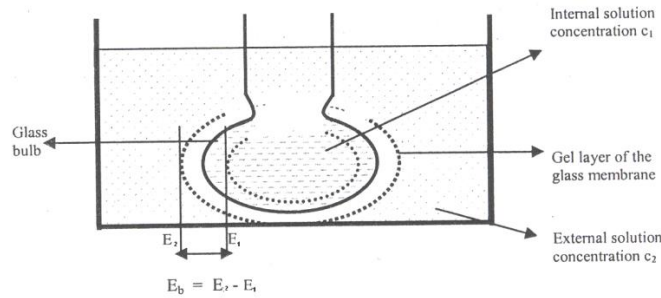


Fig.6. Glass membrane

E_b can be related to the difference in the hydrogen ion concentration of the two solutions by

the relation, $E_b = E_2 - E_1 = \frac{RT}{nF} (\ln C_2 - \ln C_1)$ (1)

Where C_1 is the concentration of H^+ ions of acid solution inside the glass bulb and C_2 is the concentration of the acid solution into which the glass bulb is dipped.

$$E_b = -\frac{RT}{nF} \ln C_1 + \frac{RT}{nF} \ln C_2 \quad \text{.....(2)}$$

If the concentration C_1 of the solution inside the glass bulb is constant, then the first term on the R.H.S. of equation (2) is constant. Therefore

$$E_b = \text{Constant} + \frac{RT}{nF} \ln C_2$$

Substituting the value of R and F at 298K

$$E_b = L + 0.0591 \log C_2 \quad \text{.....(3)}$$

Where L is a constant which depends primarily on the pH of the solution taken in the bulb and glass electrode assembly. Since $C_2 = [H^+]$ of the solution, Equation (3) written as,

$$E_b = L - 0.0591 \text{ pH} \dots\dots\dots(4)$$

The boundary potential established is mainly responsible for the glass electrode potential E_g and is given by

$$E_g = E_b + E_{Ag/AgCl} \dots\dots\dots(5)$$

From equation (1), $E_b = 0$ when $C_1 = C_2$. But in practice, it has been observed that even when $C_1 = C_2$, a small potential is developed. This is called asymmetric potential (E_{asy}). Hence, Equation (5) can be written as

$$E_g = E_b + E_{Ag/AgCl} + E_{asy}$$

$$E_g = L - 0.0591 \text{ pH} + E_{Ag/AgCl} + E_{asy}$$

$$E_g = E_g^0 - 0.0591 \text{ pH} \dots\dots\dots(6)$$

Where E_g^0 is a constant equal to $L + E_{Ag/AgCl} + E_{asy}$

Determination of pH using glass electrode:

The glass electrode is immersed in the solution, the pH of which is to be determined. It is combined with a reference electrode such as a calomel electrode through a salt bridge (Fig.7).

The cell assembly is represented as,

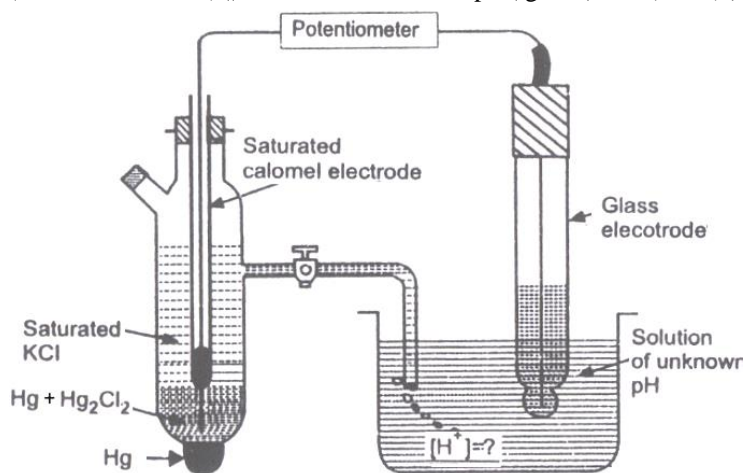
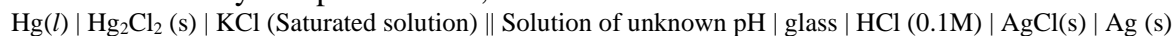


Fig.7. Determination of pH using glass electrode

The emf of the above cell, E_{cell} is measured using an electronic voltmeter with a null type potentiometer circuit (or a pH meter) (An ordinary potentiometer with a low resistance of the galvanometer is not used because of high internal resistance of the glass electrode). E_{cell} measured is the difference between the calomel electrode (E_{cal}) and E_g .

$$E_{cell} = E_g - E_{cal}$$

$$= [E_g^0 - 0.0591 \text{ pH}] - E_{cal}$$

$$\text{Therefore, } \text{pH} = \frac{E_g^0 - E_{cal} - E_{cell}}{0.0591}$$

Advantages of glass electrode:

- (i) Glass electrode can be employed in the presence of strong oxidizing or reducing substances and metal ions.
- (ii) It is not poisoned easily.
- (iii) Accurate results are obtained between pH range 1-9. However, by using special glass electrodes, pH 1-13 can be measured.
- (iv) It is simple to operate, can be used in portable instruments and therefore extensively used in chemical, industrial, agricultural and biological laboratories.

Limitations of glass electrode:

- (i) In strongly acidic solutions of $\text{pH} < 1$, the salt effect due to anions is observed.
- (ii) It can be used up to a pH of 13 but being sensitive to Na^+ ions above a pH of 9, the linear relationship between glass electrode altered. So an alkaline error is introduced beyond a pH of 9, which should be taken into consideration.
- (iii) It does not function properly in some organic solvents like pure alcohol.

BATTERY TECHNOLOGY

Battery is a device consisting of two or more galvanic cells connected in series or parallel or both, that can store chemical energy in the form of active materials and on demand convert it into electrical energy through electrochemical redox reaction. Batteries can thus generate power and can act as portable sources of electrical energy.

Introduction:

The basic electrochemical unit in a battery is a galvanic cell. The components of such a cell are shown schematically in Fig. 1. In common usage, the term battery is often applied to a single cell.

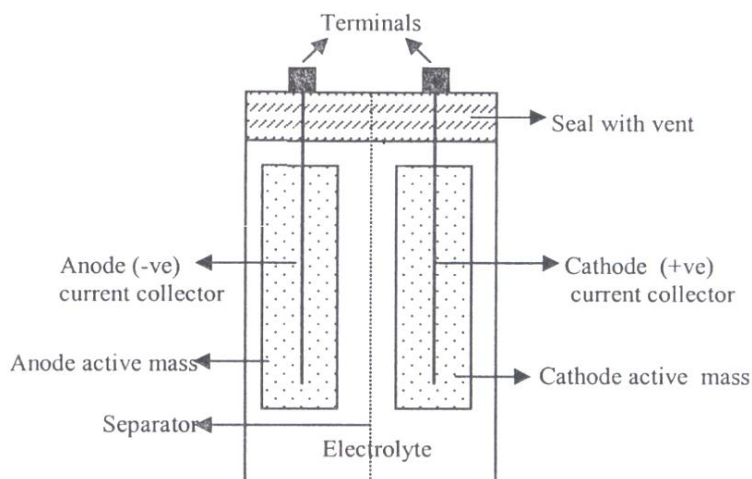


Fig.1. Principal components of a battery

The principal components of a battery are:

1. **The anode or negative electrode**- it gives out electrons to the external circuit by undergoing oxidation during electrochemical reaction.
2. **The cathode or positive electrode**-it accepts electrons from the external circuit and reduction of active species occurs.
3. **The electrolyte-an ionic conductor**: The electrolyte (active mass in the anode and cathode compartments) is commonly a solution (or a slurry) of an acid, alkali or salt having high ionic conductivity. Solid electrolytes with appreciable ionic conductivity at the operating temperature of the cell are also used.
4. **The separator**- The material that electronically isolates the anode and the cathode in a battery to prevent internal short circuiting is referred to as a separator. It is permeable to the electrolyte so as to maintain the desired ionic conductivity. Thus the main function is to transport ions from anode compartment to the cathode compartment and vice versa. Fibrous forms of regenerated cellulose, vinyl polymers and polyolefins, cellophane and nafion membranes are commonly used as separators.

The battery components are selected based on the following properties.

Anode material: (i) ease of oxidation (low reduction potential) (ii) capacity to deliver high coulombic output (iii) good conductivity (iv) high stability and (v) ease of fabrication. The anodes are usually low cost materials. Zinc is predominantly used as anode since it has the

properties mentioned above. Lithium, the lightest metal is also used as an anode in the modern batteries.

Cathode material: (i) capacity to facilitate reduction of active species in the medium (ii) resistance to electrolyte.

Electrolyte: (i) good ionic conductivity but poor electrical conductivity to prevent internal short circuit (ii) resistance to the electrode materials (iii) safety during handling.

Separator: (i) permeability for passage of ions from anode to cathode compartment and vice versa during discharging and charging (ii) capacity to prevent mixing of active masses in the two components (iii) high ionic conductivity but electronically insulating (iv) high strength flexibility (v) resistant to the active materials.

The cell is designed such that the electrodes are surrounded by the active mass; the electrodes are electrically separated by a suitable separator so as to prevent internal short-circuiting. The cells are built in many shapes and configurations-cylindrical, button, flat plates and prismatic. The cell components are designed according to the desired cell shape of the cell. The cells are sealed by different methods to prevent leakage and drying out.

Lithium-ion battery (Fig. 2):

Li-ion battery has a four layer structure. The **anode** (negative electrode) is made of lithium, intercalated (included between the layers) in graphite (C_6), has a current collector of thin Copper foil. The **cathode** (positive electrode) is made up from lithium liberating compounds such as Lithium cobalt oxide (or Lithium manganese oxide or Lithium Nickel-oxide), has a current collector of thin Aluminium foil. An **electrolyte** is made with lithium-salt ($LiPF_6$, $LiBF_4$, or $LiClO_4$) and organic solvents (ethylene carbonate or dimethyl carbonate). The electrolyte provides conductivity medium for lithium ions to move between the electrodes. A **separator** is a fine porous polymer film such polyethylene or polypropylene.

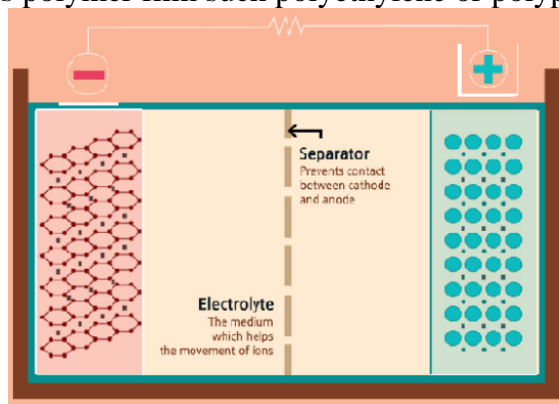


Fig. 2. Li-ion battery

Working: During discharge Li ions are dissociated from the anode and migrate across the electrolyte and are inserted into the crystal structure of cathode. At the same time electrons travel through external circuit from negative to positive terminals powering external device to balance the reaction.

At the anode: $Li_xC \rightarrow C + xLi^+ + x e^-$

At the cathode: $Li_{1-x}CoO_2 + x Li^+ + x e^- \rightarrow LiCoO_2$

Overall reaction: $Li_xC + Li_{1-x}CoO_2 \rightarrow C + LiCoO_2$

During charging: Lithium in cathode electrode material is ionized and moves from cathode to anode and gets inserted into the anode. Electrons are pumped by the charger from the cathode to the anode terminals.

It gives an overall voltage of 4 V, more than twice that of a standard alkaline battery. This gives much **better energy density than** other rechargeable batteries.

Applications: They are used to operate laptop computers, mobile phones, telecommunication equipments, portable radios and TVs, pagers and aerospace applications.

Advantages:

Special properties of Li metal that make it advantageous to use an electrode material:

i) Light weight, (ii) low electrode potential (-3.05V), (iii) Highly reactive and (iv) high electrical conductivity.

FUEL CELLS

Fuel cells are defined as galvanic cells in which chemical energy of a fuel is directly converted into electrical energy by means of redox reactions involving fuels and oxidants.

Like any other electrochemical cell, the fuel cell has two electrodes and an electrolyte. However, the fuel and the oxidizing agents are continuously and separately supplied to the two electrodes of the cell, at which they undergo reactions. These cells are capable of supplying current as long as they are supplied with reactants.

A fuel cell essentially consists of the following arrangement:

Fuel / electrode/ electrolyte /electrode / oxidant

At anode, fuel undergoes oxidation: $\text{Fuel} \rightarrow \text{Oxidation product} + n\text{e}^-$

At the cathode, the oxidant gets reduced: $\text{Oxidant} + n\text{e}^- \rightarrow \text{Reduction products}$.

The electrons liberated from the oxidation process at the anode can perform useful work when they pass through the external circuit to the cathode.

Difference between a fuel cell and a battery:

	Fuel cell	Battery
1.	Fuel cells need constant supply of reactants and the products are removed constantly.	Batteries are not be supplied with reactants constantly.
2.	They do not store chemical energy	They store chemical energy
3.	They are more efficient and not rechargeable	Some are rechargeable.

Advantages of fuel cells:

- (i) High efficiency of energy conversion process (75%).
- (ii) They are eco-friendly as the products of the overall reactions are not toxic and hence pose no pollution problems.
- (iii) They can produce direct currents for long periods at a low cost.

Methanol-Oxygen fuel cell:

Methanol is one of the most electroactive organic fuels in the low temperature range. It is mainly because, (i) It has low carbon content. (ii) It possesses a readily oxidisable OH group and (iii) It has high solubility in aqueous electrolytes.

A typical methanol-oxygen fuel cell is shown in Fig. 3.

Methanol containing some sulphuric acid (3.7M) is circulated through the anode chamber. Pure oxygen is passes through the cathode chamber and sulphuric acid (which is electrolyte), is placed in the central compartment. Both the electrodes are made of platinum. A membrane is inserted adjacent to the cathode on the inner side to minimize diffusion of methanol into the cathode thereby reducing the concentration of methanol near the cathode. In the absence of a membrane, methanol diffuses through the electrolyte into the cathode and undergoes oxidation.

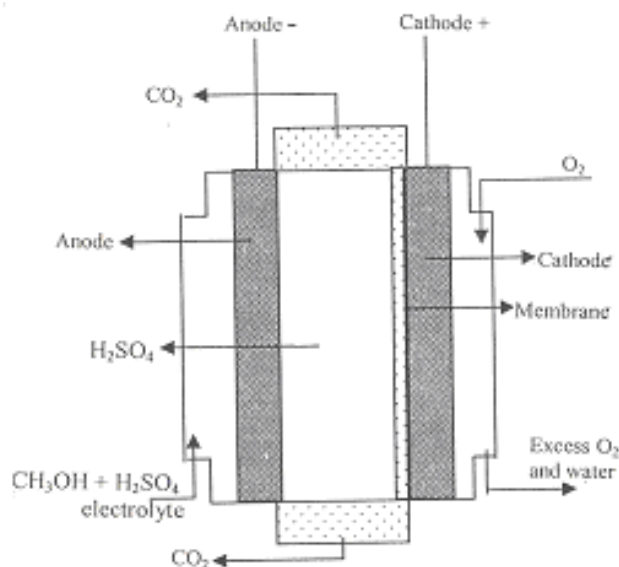


Fig.3. Methanol-oxygen fuel cell

Electrode reactions:

At anode: $\text{CH}_3\text{OH} (\text{l}) + \text{H}_2\text{O} (\text{l}) \rightarrow \text{CO}_2 (\text{g}) + 6\text{H}^+ (\text{aq}) + 6\text{e}^-$

At cathode: $3/2 \text{O}_2 (\text{g}) + 6\text{H}^+ (\text{aq}) + 6\text{e}^- \rightarrow 3\text{H}_2\text{O} (\text{l})$.

Cell reaction: $\text{CH}_3\text{OH} (\text{l}) + 3/2 \text{O}_2 (\text{g}) \rightarrow \text{CO}_2 (\text{g}) + 2\text{H}_2\text{O} (\text{l})$.

The emf the cell is 1.20V at 25⁰C. An advantage of the use of an acid electrolyte is that the CO₂, a product of the reaction can be removed easily. The use of alkali as electrolyte presents problems. The CO₂ produced is absorbed by the electrolyte and the electrolyte gradually converted into carbonate. This decreases the efficiency because of the increasing concentration polarization at the electrode surface and decreasing the conductivity of the electrolyte.

Applications: It is used in military applications and in large scale power production.

POLYMERS

INTRODUCTION:

Polymer (Greek poly = many; mers = units or parts): A polymer is a macromolecule (giant molecule of high molecular mass) built-up by the linking together of a large number of simple molecules (monomers).

Example: Polythene is formed by linking a large number of ethene molecules together.



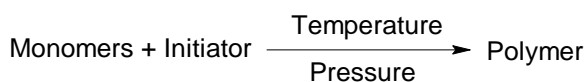
Monomer: A monomer is a simple molecule having two or more bonding sites through which each can link to other monomers to form a polymer chain. Monomers are often called building blocks of a polymer chain.

Functionality: The total number of functional groups or bonding sites present in a monomer molecule is called the functionality of the monomer. For a substance to act as a monomer, it must have at least two reactive sites or bonding sites (*bifunctional*).

Functionality of some commercial monomers:

Sl. No.	Monomers	Functional group Reactive centres	Functionality
1.	Vinyl compounds	Two reactive centres at the double bond	Two
2.	Ethylene glycol	Two alcoholic -OH groups	Two
3.	Glycerol	Three alcoholic -OH groups	Three
4.	Adipic acid	Two -COOH groups	Two
5.	Hexamethylene diamine	Two -NH ₂ groups	Two
6.	Phenol	Three active centres at ortho and para positions	Three
7.	Formaldehyde	Two active centres	Two
8.	Bisphenol-A	Two phenolic -OH groups	Two
9.	Diisocyanate	Two isocyanate groups	Two

Polymerization: The chemical process by which the monomers (low molecular weight) are converted into polymers (high molecular weight) is called polymerization. All polymerization reactions need suitable initiators.



Degree of polymerization (DP): The number of repeating units (n) in a polymer chain is called degree of polymerization. There may be hundreds or thousands or tens of thousands or more monomer molecules linked together in a polymer molecule.



Where 'n' is the degree of polymerization.

The DP can be used to calculate the molecular weight of a polymer.

Molecular weight of polymer = DP × molecular weight of repeat unit.

If the DP of polyethylene is 1,000, then Mol. wt = DP × Mol. wt. of ethylene

$$= 1,000 \times 28$$

$$= 28,000$$

High polymers: The polymers with high degree of polymerization (10,000 to 1,00,000) and high molecular masses (10,000 to 10,00,000) are called high polymers.

MOLECULAR WEIGHT OF POLYMERS:

Several properties of polymers depend on the size of the polymer chains. The length of the polymer chain can be conveniently expressed in terms of molecular mass of the polymer. The molecular mass (M) of a homopolymer is related to the degree of polymerization (DP) by the equation

Molecular weight of polymer (M) = DP × molecular weight of repeat unit.

The molecular mass of the heteropolymer is the sum of the products of molecular weight of repeat unit. The polymer product is a mixture of chains of different lengths but of definite molecular weight. The polymers are in reality polydispersed materials. The molecular weights of such polymers are expressed in terms of 'average value'. There are many statistical methods for calculating the average molecular weights of polymers. The principal averaging methods are:

(a) Number average molecular weight

(b) Weight average molecular weight

(a) Number average molecular weight

The number average molecular weight (M_n) is calculated by dividing the sum of the molecular weight contribution from the individual molecules by the number of molecules. The details of calculations are as shown below:

Let a polymer sample consist of 'n' polymer chains of which n_1 of M_1 mol. wt., n_2 of M_2 mol. wt. till n_i of M_i molecular weight.

Total number of molecules = $n_1 + n_2 + n_3 + \dots + n_i = \sum n_i$.

The number fraction of n_1 species = $\frac{n_1}{\sum n_i}$

Molecular weight contribution from n_1 species = $\frac{n_1 M_1}{\sum n_i}$

The molecular weight contribution from other species, computed in similar fashion, yields

$$\frac{n_2 M_2}{\sum n_i}, \frac{n_3 M_3}{\sum n_i}, \dots, \frac{n_i M_i}{\sum n_i}$$

Therefore, $\bar{M}_n = \frac{n_1 M_1}{\sum n_i} + \frac{n_2 M_2}{\sum n_i} + \frac{n_3 M_3}{\sum n_i} + \dots + \frac{n_i M_i}{\sum n_i}$

$$\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i}$$

(b) Weight average molecular weight:

Weight average molecular weight is of significant when polymer property depends not just on the number of polymer but on size or weight of each molecule. Compared to number average molecular weight, weight average molecular weight takes into account the molecular weight of a chain in determining contributions to molecular weight average.

The weight of n_1 species = $W_1 = n_1 M_1$.

Similarly, the weights of n_2, n_3, \dots, n_i species are, $n_2 M_2, n_3 M_3, \dots, n_i M_i$, respectively.

Total weight of the polymer = $W = \sum n_i M_i$.

The weight fraction of n_1 species = $\frac{n_1 M_1}{\sum n_i M_i}$

Molecular weight contribution from n_1 species = $\frac{W_1 M_1}{W} = \frac{n_1 M_1 \times M_1}{\sum n_i M_i} = \frac{n_1 M_1^2}{\sum n_i M_i}$

Similarly molecular weight contributions from other species are

$$\frac{n_2 M_2^2}{\sum n_i M_i}, \frac{n_3 M_3^2}{\sum n_i M_i}, \dots, \dots, \dots, \frac{n_i M_i^2}{\sum n_i M_i}$$

The weight average molecular weight is given by the expression,

$$\bar{M}_w = \frac{n_1 M_1^2}{\sum n_i M_i} + \frac{n_2 M_2^2}{\sum n_i M_i} + \frac{n_3 M_3^2}{\sum n_i M_i} + \dots + \frac{n_i M_i^2}{\sum n_i M_i}$$

$$\bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$

Example:

A polymer sample contain 5 molecules having a molecular weight of 2000, 4 molecules having a molecular weight of 3000 and 3 molecules having a molecular weight of 4000. Calculate number average and weight average molecular weight.

Solution:

The number average molecular weight is given by $\bar{M}_n = \frac{\sum n_i M_i}{\sum n_i}$

$$\bar{M}_n = \frac{5 \times 2000 + 4 \times 3000 + 3 \times 4000}{5 + 4 + 3}$$

$$\bar{M}_n = 2833.33$$

The weight average molecular weight is $\bar{M}_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$

$$\bar{M}_w = \frac{5 \times (2000)^2 + 4 \times (3000)^2 + 3 \times (4000)^2}{5 \times 2000 + 4 \times 3000 + 3 \times 4000}$$

$$\bar{M}_w = \frac{(1000)^2 [5 \times (2)^2 + 4 \times (3)^2 + 3 \times (4)^2]}{5 \times 2000 + 4 \times 3000 + 3 \times 4000}$$

$$\bar{M}_w = 3058.8235$$

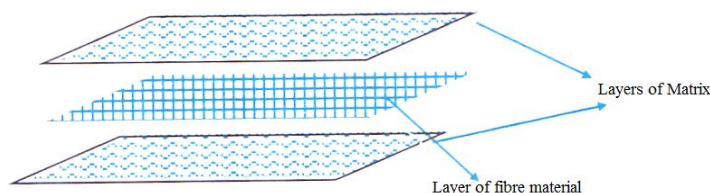
POLYMER COMPOSITES:

Introduction: Structural materials required in various industries such as aircraft industry, should have properties such as, (i) low density (ii) high strength and stiffness (iii) abrasion and impact resistance and (iv) corrosion resistance. No single metal, alloy, ceramic or polymeric material is known which can offer the combination of aforesaid property. This is because a strong material is relatively dense and an increase in stiffness generally results in a decrease in impact strength. The search for materials possessing the above properties has led to the development of composite materials.

Definition: A combination of two or more distinct components to form a new class of material suitable for structural applications is referred to as composite materials. When one of the components is a polymer, the resulting composite is called a polymer composite.

While each component retains its identity, the composite material displays macroscopic properties superior to its parent constituents, particularly in terms of mechanical properties.

Polymer composites are generally made of two components, namely (i) matrix and (ii) fibre. The fibre is embedded in the matrix in order to make the matrix stronger. The matrix is usually a thermoset material such as epoxy resin or a polyamide and it holds the fibres together. Fibre is most often glass but sometimes may be a **carbon fibre**, polyethylene or Kevlar.



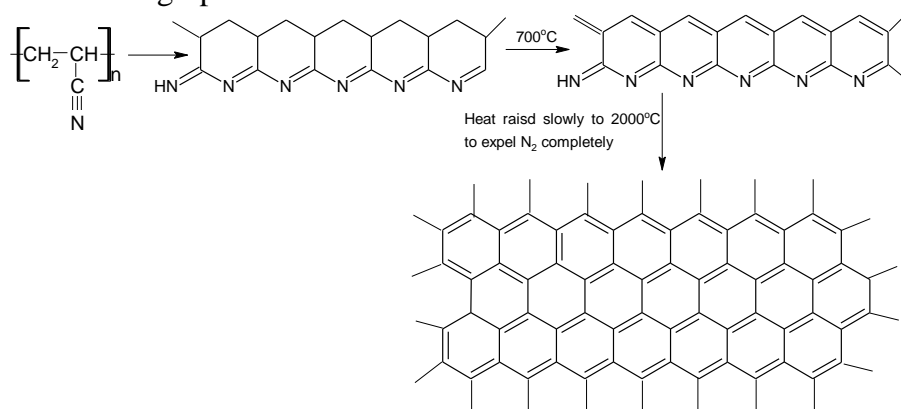
Fibre-reinforced composites are strong and light. They are often stronger than steel, but weigh much less and hence these composites can be used to make automobiles lighter, achieving more fuel efficiency and less pollution.

A common fibre-reinforced composite is fiberglass. Its matrix is made by mixing a polyester and a styrene pouring the mixture over a mass of glass fibres. The styrene and the double bonds in the polyester react by free radical vinyl polymerization to form a cross-linked resin. The glass fibres are trapped inside where they react as reinforcement. The composite may be made stronger by lining up all the fibres in the same direction. When the composite is pulled in the direction of the fibres it shows high strength. If the fibres used are in more than one direction (such as in a woven fabric), the resulting composite will be strong in all directions.

Carbon fibre: Carbon fibre is a fibre made up of carbon. Carbon fibre is very thin strands of carbon even thinner than human hair. When bound together with plastic polymer resin with heat, pressure or vacuum, a composite material is formed that is both strong and light weight. The strength of carbon fibre depends on the weave. The more complex the weave the more durable the composite will be.

Preparation: Carbon fibre is made by heating polyacrylonitrile (PAN) carefully and slowly when the polymer cyclizes through the cyano groups to form a polycyclic chain. The resulting solid is heated gradually so that hydrogen is expelled and rings become aromatic. It is then

roasted at 600-700°C when the adjacent chains join together losing more hydrogen gas. Then the temperature is gradually raised to 2000°C to get wider ribbon-like mass. The temperature is maintained around 2000°C till all the nitrogen is expelled leaving behind wider ribbon-like pure carbon fibre in the graphite form.



Properties:

i) Carbon fibre reinforced composites are very strong and are often stronger than steel but lighter. ii) Good corrosion resistance. iii) Very low coefficient of thermal expansion. iv) Low impact resistance.

Applications: i) In aerospace and automotive fields, as well as in sailboats. ii) In modern bicycles and motorcycles. ii) In consumer goods such as laptops, tripods, finishing rods, golf clubs, tennis rackets etc.

CONDUCTING POLYMERS:

Conducting polymers are generally obtained by doping an oxidizing or a reducing agent into organic polymers with conjugated backbone consisting of alternating double and single carbon-carbon bonds.

Mechanism of conduction in polyacetylene: The neutral polymer would have band model identical to that of an insulator. The polymer may be transformed into a conductor by doping it with an electron donor (reductive dopant such as sodium naphthalide) or an electron acceptor (oxidizing dopant such as iodine, AsCl_3 , FeCl_3). This resembles doping of Si with As or Ga. However, this doping would not produce donor level close to the conduction band and acceptor level close to the valence band as in the case of Si with As or Ga. In doped conjugated polymers, there are two types of π -electron energy bands- the π -bonding MOs constitute the valence band, while π^* -anti-bonding MOs form the conduction band.

The oxidative doping of a polyacetylene, (Fig. 1) leads to the removal of an electron from π -system of the backbone producing free radical and a positive charge. This combination of charge site and a radical is referred to as polaron, which could be a radical cation. This would create new localized electronic states in the forbidden gap being occupied by a single unpaired electron. Upon further oxidation, the free radical of the polaron is removed, creating a new defect called bipolaron (solitons). Due to the formation of soliton, a new localized electronic state appears in the middle of the energy gap. When doping is high,

several charged solitons form soliton band. This can later merge with edges of valence and conduction bands exhibiting conductivity.

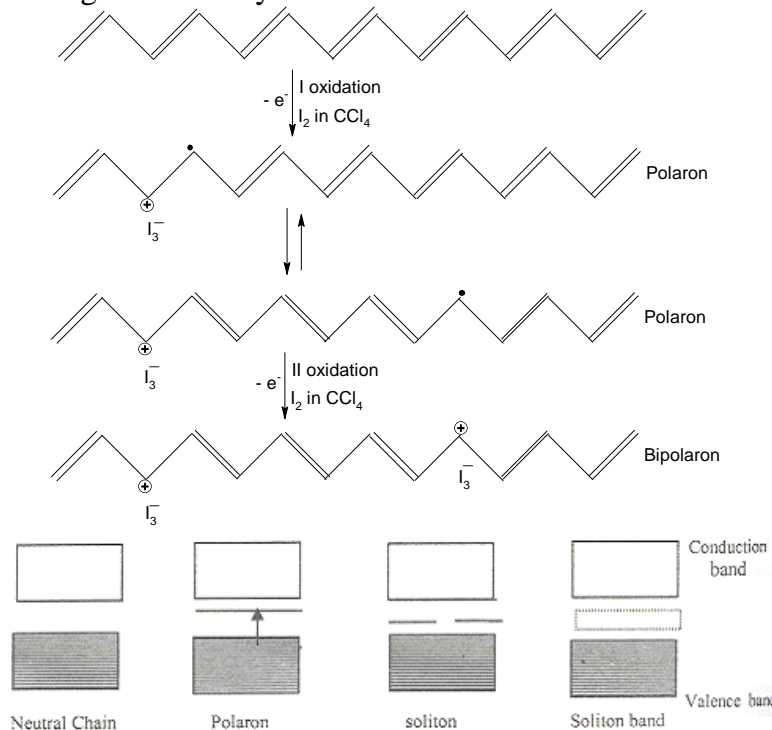


Fig.1. Band diagram of polyacetylene as the amount of oxidative dopant is increased

Polyaniline: Polyaniline is considered as one of the most useful conducting polymers because of its ease of preparation, its stability under aqueous conditions and the facility to fine-tune electrical, optical and chemical properties through substituent effects. It shows a conductivity of greater than $10^5 \text{ s}^{-1} \text{ m}^{-1}$. As a comparison Teflon has a conductivity of $10^{-16} \text{ s}^{-1} \text{ m}^{-1}$ and that of copper is $10^8 \text{ s}^{-1} \text{ m}^{-1}$.

Applications: Conducting polymers are highly promising materials to be used in electric and electronic applications. Some of the applications are

- (i) As electrode material for rechargeable batteries, for higher power to weight ratio (coin type materials).
- (ii) As conductive tracks on printed circuit boards.
- (iii) As sensor- humidity sensor, gas sensor, radiation sensor, biosensor for glucose, galactose etc.
- (iv) In electrochromic display windows. (v) In information storage devices.
- (vi) As film membranes for gas separations. (vii) In light emitting diodes.
- (viii) In fuel cells as the electrocatalytic materials

ANALYTICAL TECHNIQUES

Analytical technique is a method used to determine a chemical or physical property of a chemical substance, chemical element, or mixture. There is a wide variety of techniques used for analysis. Eg: Conductometry, Potentiometry etc.

CONDUCTOMETRY:

Conductometry is an electrochemical method of analysis based on measuring the resistance of an electrolytic solution.

Theory: Electrolytic conductivity is a measure of the ability of a solution to carry an electric current. Electrolytic solutions conduct current by the migration of ions under the influence of an electric field. Like a metallic conductor, they obey Ohm's law, $E = IR$

Where, E is the applied potential, I is the current and R is the resistance, which is the measure of hindrance caused for the flow of current under the potential applied.

The reciprocal of the resistance is called the conductance, $C = 1/R$.

The resistance of any conductor is directly proportional to the length and inversely proportional to the area of cross section of the conductor.

$R = \rho (l/a)$ Where ρ is the resistivity or specific resistance of the conductor.

Therefore, conductance, $C = 1/R = (1/\rho) (a/l)$

$$C = \kappa.(a/l)$$

Where, κ is the specific conductance or conductivity of the electrolyte solution. When $a=1$, $l=1$, $C = \kappa$. Or. **Specific conductance** is the conductance of an electrolyte solution kept between two electrodes of 1 m^2 cross sectional area at 1 m apart. It is the conductance of a meter cube of the solution. The unit of κ in SI units is Sm^{-1} .

In electrolytic solutions, the ion concentration is an important variable. It is usual to relate the electrolyte conductance in terms of equivalent conductance or molar conductance.

Equivalent conductivity is defined as the conductance of a solution containing one- gram equivalent weight of the electrolyte.

Molar conductance is defined as the conductance of a solution containing one mole of an electrolyte. Conductance of an electrolyte is directly proportional to (i) mobility of ions and (ii) number of ions present in unit volume. Measurement of conductance can be employed to determine the end point in acid-base titrations. In conductometric titrations, there is a change in conductance of the solution at the equivalence point. The principle underlying conductometric titrations is the substitution of ions of one mobility by ions of another mobility of ions. The equivalence point is determined graphically by plotting conductance (ordinate) against titre values (abscissa).

Instrumentation (Fig.1):

It consists of a conductivity cell made up of two platinum electrodes and a conductivity meter. The two electrodes have unit area of cross section and are placed unit distance apart. The analyte is taken in the beaker and titrant is added from micro burette. Magnetic stirrer is used to stir the solution.

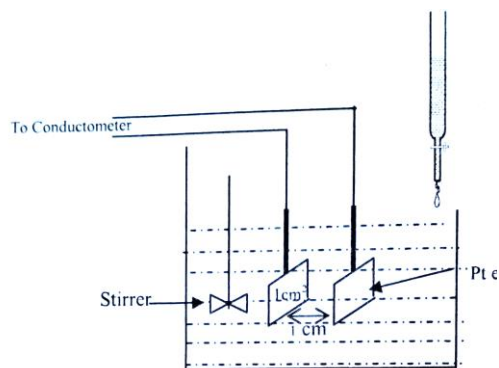
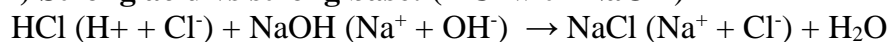


Fig.1. Conductometric titration unit

i) Strong acid vs strong base: (HCl with NaOH)



In the case of strong acid and strong base, the conductance 1st falls, due to the replacement highly mobile H^+ ion by less mobile Na^+ ions. After the equivalence point, the conductance rapidly rises with further addition of strong base and is due to increase in the concentration of the high mobile OH^- ions.

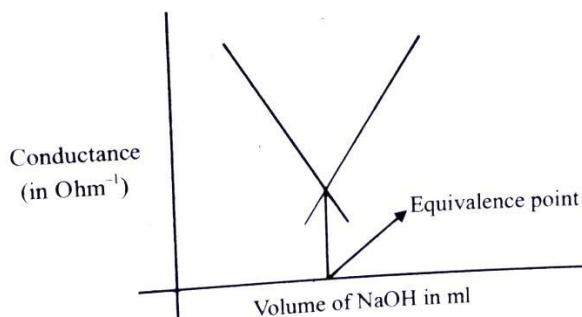


Fig.1. Conductometric titration curve of strong acid (HCl) with NaOH

(ii) Weak acid Vs strong base (CH₃COOH with NaOH)

Weak acid partially dissociated in aqueous solution the conductance of the acid will be initially low due to poor dissociation. When a strong base is added to the acid, the salt formed (CH_3COONa) is highly ionized and conductance increases on complete neutralization of the acid, addition of base lead to an increase in the number of more OH^- ion and hence conductance increase sharply.

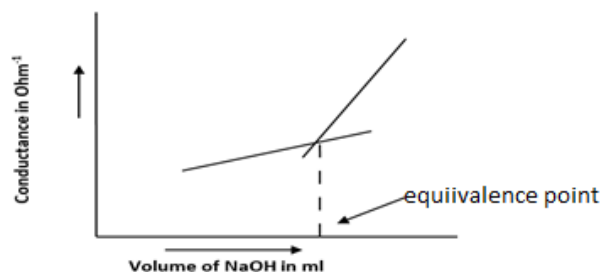


Fig.2. Conductometric titration curve of weak acid (CH_3COOH) with NaOH

Advantages:

(i) Mixtures of acids can be titrated. (ii) Accurate in dilute solutions. (iii) Very weak acids which can't be titrated potentiometrically but it can be titrated conductometrically.

POTENTIOMETRY:

Potentiometry is an instrumental method of analysis used to determine the concentration of a substance in a solution by measuring the potential difference between reference and indicator electrodes dipped in the solution and combined to form a galvanic cell.

Theory: The potential of an electrode is given by Nernst equation,

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

Where, E is the electro potential, E^0 is standard electrode potential, depends on the concentration of the ion $[M^{n+}]$. E can be measured by combining the electrode with a reference electrode and measuring the emf of the cell. The concentration can be calculated, provided E^0 of the electrode is known.

Instrumentation: The Potentiometer consists of a reference electrode, an indicator electrode and potential measuring device. The indicator electrode response rapidly to the changes in the concentration of analyte i.e the solution under study. A simple arrangement of potentiometric titration is depicted in the fig. A is the reference electrode (saturated calomel electrode), B is the indicator electrode (Platinum) and C is a mechanical stirrer. The solution to be titrated is taken in the beaker. A known volume of analyte is taken in the beaker and its potential is determined. The titrant is added in increments of 0.5cm^3 and emf is measured each time. At the approach of equivalence point, the ef tends to increase rpidly, few reading are taken beyond the end point. Thus, changes in potential at different volumes of titrant are recorded.

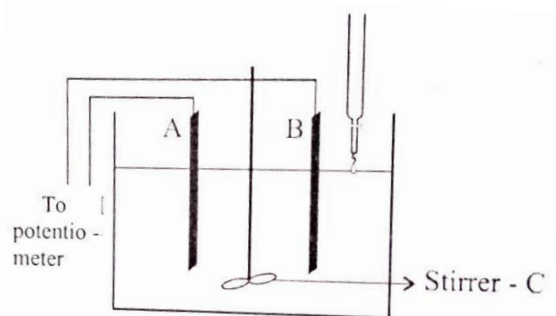


Fig.3. Potentiometric titration unit.

Applications:

Oxidation-reduction reactions: Oxidation reduction titration can conveniently be carried out as potentiometric titrations. For example, in the titration of Mohr's salt solution with potassium dichromate solution, calomel electrode is used as the reference and an inert platinum foil is used to pick up the potential of indicator electrode, which is actually the oxidation reduction electrode involving the redox species present in the solution. Before the titration is started, the solution contains only ferrous ions in the solution. When a

small volume of the dichromate solution is added, equivalent small quantity of Fe^{2+} ions are converted into Fe^{3+} ions. In the process, the Cr^{6+} ion in dichromate is reduced to Cr^{3+} ion.



The presence of Fe^{2+} and Fe^{3+} ions in the solution gives rise to an oxidation reduction electrode, the potential of which can be picked up by the platinum electrode dipped in the solution ($\text{Pt} / \text{Fe}^{3+}, \text{Fe}^{2+}$). The electrode potential of the so formed electrode is given by,

$$E = E^0 - 0.0591 \log \left\{ \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right\} \text{ at } 298\text{K}$$

The electrode potential of the indicator electrode depends upon the ratio of the concentrations of reduced and oxidized species in the solution. As the titration proceeds, the concentration of Fe^{3+} goes on increasing and that of Fe^{2+} goes on decreasing. As a result, the ratio in the expression for electrode potential goes on increasing and the increase in the value of the ratio becomes very large near the end point. This results in the large increase in the electrode potential and in turn, in the measured emf of the cell.

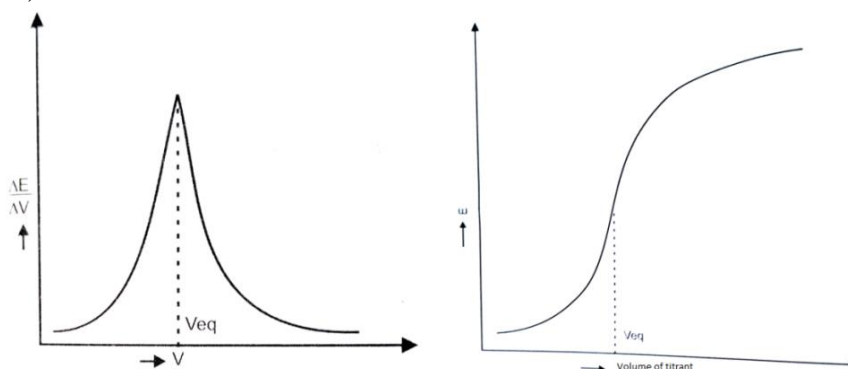


Fig.4. Potentiometric titration curves.

At the equivalence point, all the Fe^{2+} ions are converted into Fe^{3+} ions, the $\text{Pt} / \text{Fe}^{3+}, \text{Fe}^{2+}$ electrode ceases to exist. But addition of a slight excess of dichromate solution introduces Cr^{6+} ions into the solution, which along with the Cr^{3+} ions in the solution (formed during the oxidation of Fe^{2+}) form a new oxidation reduction electrode, $\text{Pt} / \text{Cr}^{6+}, \text{Cr}^{3+}$. This change over of indicator electrode at the end point also contributes to the large increase in potential at the end point, as E^0 of the two electrodes differ by a large value. After the end point, therefore it is $\text{Pt} / \text{Cr}^{6+}, \text{Cr}^{3+}$ acting as the indicator electrode.

Advantages of Instrumental method of analysis over chemical analysis:

(i) Chemical methods are time consuming procedures. It requires large time for analysis but instrumental methods are much faster. (ii) Chemical methods require large amount of the analyte (sample) but instrumental method requires very small amount of sample like ppm level. (iii) They are wide applications in industries. (iv) The analytical process can be automated.

Disadvantages: The instruments are expensive. (ii) An initial or continuous calibration is required using a sample of material of known composition (iii) The concentration range is limited. (iv) Specialized training is needed for the operation of certain sophisticated instruments.
