UNIT-I
ELECTROCHEMISTRY

Electrochemistry deals with Chemical applications of electricity i.e., Chemical reactions produced by passing electric current through an electrolyte or production of electric curerent through a chemical reaction

Conductors: Material which allows free flow of electricity
Examples: All metals, graphite, fused salts, solution of electrolytes,

Non-conductors (Insulators): Materials which cannot conduct electrical current
Examples: wood, plastics, most of non metals

Types of conductors

   (i) **Metallic conductors :** All solid material, which conduct electric current due to the movement of electron from one end to the other end

   (ii) **Electrolytic conductors :** Conduct electric current due to the movement of ions

Differences between metallic conduction and electrolytic conduction

Metallic conduction	Electrolytic conduction
Involves flow of electrons	Involves movement of ions in a solution
Does not involve any transfer of matter	Involves transfer of electrolyte in the form of ions
Conduction decreases with increase in T	Conduction increases with increase in T
No change in the chemical properties of the conductor	Chemical changes occur aat the two electrodes

Types of electrolytic conductors
Strong electrolytes: Completely dissociate into ions in solution
Examples: HCl, NaOH, NaCl, KCl
Weak electrolytes: Which dissociate only to some extent in solution
**Non – electrolytes:** Do not ionise in solution

Cell Terminology

   i. **Current :** Flow of electrons through a conductor

   ii. **Electrode :** Electrode is a material (rod, bar, strip) which conducts electrons

   iii. **Anode :** Electrode at which oxidation occurs

   iv. **Cathode :** Electrode at which reduction occurs

   v. **Electrolyte :** Water soluble substance forming ions in solution and conducts electric current

   vi. **Anode compartment:** Compartment of the cell in which the oxidation half reaction occurs. Contains the anode

   vii. **Cathode compartment:** Compartment of the cell in which the reduction half reaction occurs. Contains the cathode

   viii. **Half – cell:** Part of the cell, which contains an electrolyte dipped in an electrolyte. If oxidation occurs in this half, then it is called the oxidation half cell. If reduction occurs at the cell, it is called the reduction half cell

   ix. **Cell:** Device consisting of two half cell. The two half cells are connected by a conductor
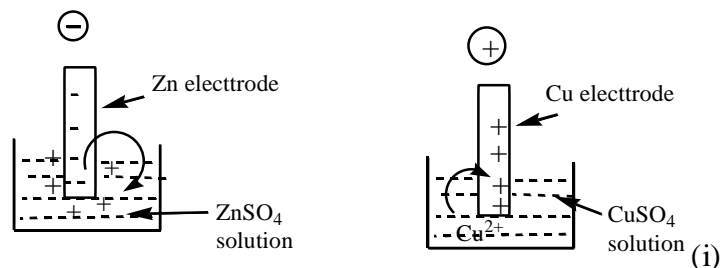
Electrode Potential

When a metal (M) is placed in a solution of its own salt (M^{n+}) one of the two processes are possible.

   (i)   +ve metal ions may pass into solution

$$M \longrightarrow M^{n+} + ne^- \text{ (Oxidation)}$$
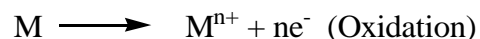
   (ii)   +ve metal ions from solution may deposit on the metal

$$M^{n+} + ne^- \longrightarrow M \text{ (reduction)}$$

When Zn electrode is dipped in $ZnSO_4$ solution, Zn goes into solution as Zn^{2+} ions.

   (iii)   When Cu electrode is dipped in $CuSO_4$ solution, Cu^{2+} ions from solution deposit on the metal.

A layer of + or – ve ions if formed on the metal, **Helmholtz electrical double layer** due to which a difference of potential is setup between the metal ions and the solution.

At equilibrium, the potential difference becomes a constant value **(Electrode potential of the metal).**

The tendency of the electrode to lose electrons is **Oxidation potential.**

Tendency of an electrode to gain electrons is **reduction potential.**

Single electrode potential (E): Tendency of a metallic electrode to lose or gain electrons when it is in contact with a solution of its own ions.

Standard electrode potential (E^0): Tendency of a metallic electrode to lose or gain electrons when it is in contact with a solution of its own ions of 1M Concentration.

Nernst Equation for Electrode Potential

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

For such redox reversible reactions, the free energy change (ΔG) and its equilibrium constant (K) are related by

$$\Delta G = -RT \ln K + RT \ln \frac{[\text{Pr}oduct]}{[\text{Re}ac\tan t]}$$

$$= \Delta G^0 RT \ln \frac{[\text{Pr}oduct]}{[\text{Re}ac\tan t]} \qquad (1)$$

ΔG^0 = Standard free energy change

The above equation is **Van't Hoff Isotherm**

In the cell, if the reaction involves the transfer of 'n' electrons, 'n' faraday of electricity will flow.

 If E is the emf of the cell, the total electrical energy produced will be

$$\Delta G = nEF \qquad \text{(or) } \Delta G^0 = nE^0 F \qquad (2)$$

Comparing (1) & (2) $- nEF = - nEF^0 RT \ln \dfrac{[M]}{[M^{n+}]}$ (3)

Dividing (3) by – nF and knowing that [M] = 1

$$E = E^0 - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]} \qquad \text{(or)} \quad E = E^0 + \frac{RT}{nF} \ln [M^{n+}]$$

$$E = E^0 + \frac{2.303RT}{nF} \log [M^{n+}] \qquad (4)$$

When,   R = 8.314 J/K/mole; F = 96,500 coloumbs, T = 298 K the above equation becomes

$$E = E^0 + \frac{0.0591}{n} \log[C]$$ (**Nernst equation for single electrode potential**)

Applications of Nernst equation
   i.   To calculate unknown electrode potentials
   ii.   Prediction of corrosion tendency of metals
   iii.   To construct emf series

Measurement of single electrode potential

It is not possible to evaluate the absolute value of a single electrode potential. Potential difference between two electrodes can be measured. For this purpose a **reference electrode** is used.
**Saturated hydrogen electrode (SHE)** is a common reference electrode whose potential is fixed as zero **(Primary reference electrode)**
The emf of the cell with SHE and the electrode under test as electrodes will be equal to the potential of the electrode
Setting up of SHE is difficult
Saturated calomel electrode is used as a secondary reference electrode

## Primary reference electrode: Saturated hydrogen electrode (SHE)
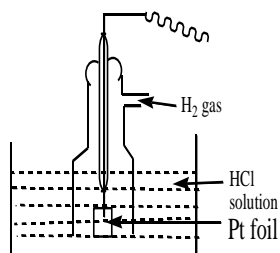
Construction: Hydrogen electrode consists of a Pt foil that is connected to a Pt wire sealed in a glass tube. Hydrogen gas is passed through the arm of the surrounding gas tube. The electrode dipped in 1N HCl and hydrogen is passed at 1 atm.is **SHE**
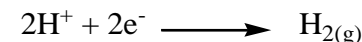
H₂ gas

HCl solution

Pt foil

$$\text{Pt , H}_2 \text{ (1atm) / H}^+\text{n(1M) ; E}^0 = 0\text{V}$$
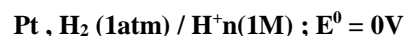
It is represented as
In the cell, when SHE acts as anode, the electrode reaction is

$$H_{2(g)} \longrightarrow 2H^+ + 2e^-$$

When it acts as cathode, the electrode reaction is

$$2H^+ + 2e^- \longrightarrow H_{2(g)}$$
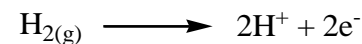
Limitations
   i.   requires hydrogen gas and is difficult to set up and transport
   ii.   requires large volume of test solution
   iii.   The solution may poison the surface of Pt electrode
   iv.   Potential of the electrode is dependent on atmospheric pressure.

Secondary reference electrode: Saturated calomel electrode (SCE)

Pt wire
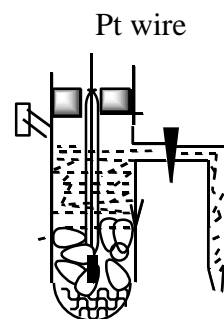
Construction: Calomel electrode consists of a glass tube containing Hg at the bottom over which mercurous chloride paste is placed. The tube is filled with a saturated solution of KCl. A Pt electrode is dipped in. The side tube is for making contact via a salt bridge. The electrode potential of this electrode is +0.2422 V. It is represented as:
Hg, Hg₂Cl₂(s), KCl (sat. solution)
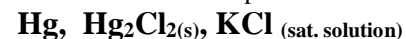
In the cell, when SCE acts as anode, the electrode reaction is

$$2Hg_{(l)} \longrightarrow Hg_2^{2+} + 2e^-$$

When it acts as cathode, the electrode reaction is

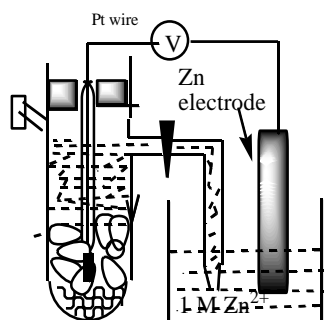$$Hg_2^{2+} + 2e^- \longrightarrow 2Hg_{(l)}$$
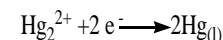
The electrode potential (cathode) is given by

$$E_{(calomel)} = E^0_{(calomel)} - \frac{RT}{2F} \ln a_{Cl^-}$$

The electrode potential depends on the activity of Cl^- and Temperature.

a $_{Kcl}$	emf	a $_{Kcl}$	emf (V)	a $_{Kcl}$	emf (V)
0.1	0.3338	1.0	0.2800	Saturated	0.2422

Values at 298 K

Measurement of single electrode potential of Zn using SCE

Zn electrode is coupled with calomel electrode. Since, the reduction potential of Zn electrode is less than E^0_{Cal} ; calomel electrode will act as cathode and the reaction

$$Hg_2Cl_{2(s)} \longrightarrow 2Hg_{(l)} + 2C\,l^-$$

$$E_{cell} = E^0_{right} - E^0_{left}; \quad E_{cell} = E^0_{cal} - E^0_{Zn}$$

$$E^0_{Zn} = E^0_{cal} - E_{cell} = +0.2422 - 1.0025 = -0.7603V$$

Electrode potentials of metals with respect to SHE (Electrochemical series (or) EMF series)

Definition:

When the various metals are arranged in the order of their increasing values of standard reduction potential on the hydrogen scale, the arrangement is called the electrochemical series

Electrochemical series

Electrode	Electrode reaction	E^0 (V)	Nature
Li^+/Li	$Li^+ + e \rightleftharpoons Li$	-3.01	Anodic
Mg^{2+}/Mg	$Mg^{2+} +2e \rightleftharpoons Mg$	-2.37	
Pb^{2+}/Pb	$Pb^{2+} +2e \rightleftharpoons Pb$	-1.12	
Zn^{2+}/Zn	$Zn^{2+} +2e \rightleftharpoons Zn$	-0.76	
Fe^{2+}/Fe	$Fe^{2+} +2e \rightleftharpoons Fe$	-0.44	
Sn^{2+}/Sn	$Sn^{2+} +2e \rightleftharpoons Sn$	-0.136	Pt-Reference:
H^+/H_2	$2H^+ + 2e \rightleftharpoons H_2$	0.00	
Cu^{2+}/Cu	$Cu^{2+} +2e \rightleftharpoons Cu$	+0.34	
Ag^+/Ag	$Ag^+ + e \rightleftharpoons Ag$	+0.80	
Au^+/Au	$Au^+ + e \rightleftharpoons Au$	+1.50	
½ F_2/F^-	½ $F_2 + e \rightleftharpoons F^-$	+2.87	Cathodic

Significance of emf series (or) Application of electrochemical series (or) Applications of Nernst equation

i. Calculation of standard emf of the cell
E^0 can be calculated if the standard electrode potential values are known

$$E_{cell} = E^0_{right} - E^0_{left}$$

ii. Relative ease of oxidation or reduction
Higher (+ve) value of standard reduction potential, greater is the tendency for reduction.
Metals on the top (- value) are more easily oxidized.

Fluorine has higher +ve value of standard reduction potential (+2.87V) and shows higher tendency for reduction.
Lithium has highest – ve value (-3.02V) and shows higher tendency towards reduction.

iii. Displacement of one element by the other
Metals which lie higher in the series can displace those which lie below them in the series.
Copper will displace silver from its solution.
Iron will displace copper from its solution.

iv. Determination of equilibrium constant (K) for a reaction

$$-\Delta G^0 = RT \ln K = 2.303RT \log K$$

$$\log K = \frac{-\Delta G^0}{2.303RT} = \frac{nFE^0}{2.303RT} \quad \left[\because -\Delta G^0 = nFE^0 \right]$$

From the value of E^0, the equilibrium constant for the reaction can be obtained

v. Hydrogen displacement behaviour
Metals with – ve reduction potential (metals placed above H_2) in emf series will displace hydrogen from acid solutions.
Zn will displace H_2 from dilute acids whereas, silver cannot.

vi. Predicting the spontaneity of redox reactions
If E^0 of a cell is +ve the reaction is spontaneous
If E^0 of a cell is -- ve the reaction is not possible

Galvanic series

Magnesium
Magnesium alloys
Zinc
Alluminium
Alluminium alloys
Copper
Copper – nickel alloys
Gold
Platinum

Oxidation potential of various metals alloys are measured by immersing them in sea water. SCE is used as the reference electrode. The values are arranged in decreasing order of activity and the series is **Galvanic series**

This series provide more practical information on the relative corrosion tendencies of different metals and alloys. The speed of corrosion depends on the difference in potential between the anodic and cathodic metals in contact.

Electrolytic cells
Chemical changes are brought about by using electrical energy in electrolytic cells
Electrolysis
Process of chemical decomposition of an electrolyte by passage of electricity
Example: Electrolysis of HCl
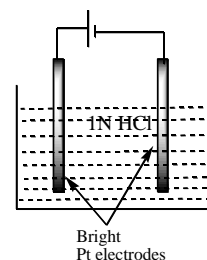
Mechanism
HCl will dissociate into H^+ and Cl^- in water
On passing electric current the following reactions occur at the electrodes

At anode: $2Cl^- \rightleftharpoons Cl_2 + 2e$ (oxidation)

At cathode: $2H^+ + 2e^- \rightleftharpoons H_2\uparrow$ (reduction)

1N HCl

Bright Pt electrodes

Electrochemical cells (Galvanic cells)

Chemical energy is converted to electrical energy in electrochemical cells
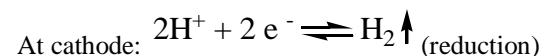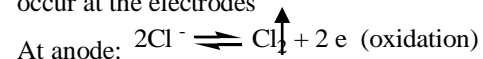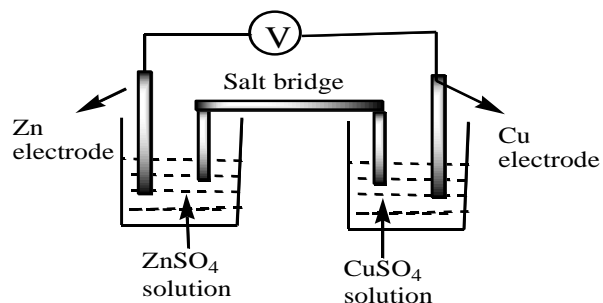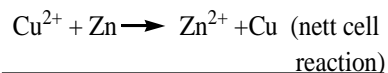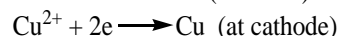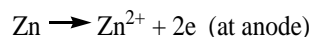
Example: Daniel Cell through the voltmeter.

Cell device (construction)

Consists of Zn electrode dipped in 1M $ZnSO_4$ solution and a Cu electrode dipped in 1M $CuSO_4$ solution. Each electrode is a half cell. The solutions are inter connected by salt bridge and the two electrodes are connected by wire

Reactions occuring in the cell

$Zn \longrightarrow Zn^{2+} + 2e$ (at anode)

$Cu^{2+} + 2e \longrightarrow Cu$ (at cathode)

$Cu^{2+} + Zn \longrightarrow Zn^{2+} + Cu$ (nett cell reaction)

At anode: oxidation takes place with the liberation of e^-.
At cathode: Reduction takes place by the acceptence of e^-.
The electrons liberated in oxidation reaction flow through external wire and are consumed by the copper ions at the cathode.

Salt bridge: It consists of a U-tube containing a saturated solution of KCl or $(NH_4)_2NO_3$ in agar – agar gel. It connects the two half cells.

Functions

i.   Eliminates liquid junction potential
ii. Provides a path for the flow of electrons between two half cells

Representation of a galvanic cell (Cell diagram)

i.   Galvanic cell consists of two electrodes, anode and cathode
ii. Anode is written on the LHS and cathode on RHS
iii. The anode is written with the metal first and then the electrolyte which are separated by a vertical line

Example: Zn/Zn^{2+} (or) $Zn/ZnSO_4$

iv. The cathode is written with the electrolyte first and then the metal **Example :** Cu^{2+}/Cu (or) $CuSO_4/Cu$
v.   The two half cells are separated by a salt bridge, which is indicated by two vertical lines.

Using the above representation, the galvanic cell is represented as

$$Zn/ZnSO_4 \,(1M) \,//) \,CuSO_4 \,(1M) \,/Cu$$
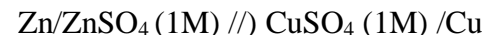
Differences between electrolytic cells and electrochemical cells

Electrolytic cell	Electrochemical cell
Electrical energy converted to chemical energy	Chemical energy converted to electrical energy
Anode carries +ve charge	Anode carries – ve charge
Cathode carries – ve charge	Cathode carries + ve charge
Electrons are supplied to the cell from an external source	Electrons are drawn from the cell
Amount of electricity is measured by coulometer	Emf produced is measured by potentiometer
Extent of chemical change is governed by Faraday's laws	The e.m.f of the cell depends on the concentration of the electrolyte and chemical nature of the electrode

Standard cell

Saturated soloution CdSO₄

CdSO₄.8/3H₂0 Crystals

Hg+Hg₂SO₄ paste

Hg

Cd - Hg amalgam
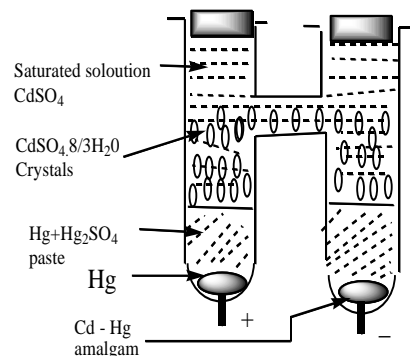
A standard cell is the one which gives constant emf. It is a souce of constant potential.
Weston cadmium cell consists of a H – shaped glass vessel. The bottom of the glass tubes are sealed with Pt wires.
+ve electrode (left arm) contains Hg over which a paste of Hg_2SO_4 is placed

The – ve electrode (right arm) contains Hg – Cd amalgam over which crystals or $CdSO_4.8/3H_2O$ is placed.
Remaining part of the cell is filled with a saturated solution of $CdSO_4$. The upper ends of the tubes are closed with corks.
The emf of the cell is 1.0807 V.

Representation

Cd in Hg/3CdSO₄.8H₂O // CdSO₄.Hg₂SO₄ / Hg

Concentration Cells

- The transport of ions due to concentration gradient of the electrolyte at both half-cells is accompanied by a fall in free energy.

The loss in free energy produces electrical energy

- electrolyte *(concentrated)* → electrolyte *(dilute)*
- No net chemical reaction.
- Concentration cell is made up of two half-cells having identical electrodes, identical electrolyte, except that the concentrations of reactive ions at two electrodes are different.

Cu*(s)* | CuNO₃*(C1M)(dilute)* || CuNO₃*(C2 M)(concentrated)* | Cu*(s)*⁺; *C1<C2*

$$\text{Cathode: } Cu^{2+}(C2\ M) + 2e^- \rightarrow Cu(s)$$

$$\text{Anode: } Cu(s) \rightarrow Cu^{2+}(C1M) + 2e^-$$

$$\text{Net: } Cu^{2+}(C2\ M) \rightarrow Cu^{2+}(C1\ M)$$

The transport of cupric ion from a region of higher oncentration to one of lower concentration.

- $E°$ for a concentration cell is always zero, since this would be the potential of a cell in which the electro active species are at unit activity in both compartment.

$$Ecell = \frac{0.0592V \log C2/C1}{n}$$

Ex: Oxygen concentration Cell (differential aeration corrosion).

Ion-Selective Electrodes (ISE)

- Electrodes possess certain selectivity towards certain ions.
- Ion Selective Electrodes (ISE) are membrane electrodes that respond selectively to ions in the presence of others
- The potential developed at the membrane surface is related to the concentration of the species of interest.
- The sensing part of the electrode is an ion-specific membrane which is permeable to specific ion and also known as a specific ion electrode (SIE).

Classification:

Depending upon the nature of membranes used

Polymer Membrane electrodes:

Consist of various ion exchange materials in an inert matrix such as PVC, polyethylene or silicone rubber. Electrodes of this type include Potassium, Calcium and Nitrate**.**

Solid State Electrodes:

Utilize relatively insoluble inorganic salts in a membrane. Potentials are developed at the membrane surface due to the ion exchange process. Examples of this type of electrode include silver / sulfide, chloride and fluoride.

Gas Sensing Electrodes:

Gas sensing electrodes are available for the measurement of ammonia, carbon dioxide, and nitrogen oxide. This type of electrode has a gas permeable membrane and an internal buffer solution. The pH of the buffer solution changes as the gas reacts with it. The change is detected by a combination pH sensor within the housing**.**

Glass Membrane Electrodes:

Glass membrane electrodes are formed by the doping of the silicon dioxide glass matrix with various chemicals. The most common of the electrode of this type is the pH electrode. Glass membrane electrodes are also used for sodium ions**.**

Advantages of ion selective electrodes:

- The cost of initial setup to make analysis is relatively low.
- ISE determinations are not subject to interferences such as color in the sample

Glass membrane electrodes: measurement of pH

- Glass membrane is the most essential component which is sensitive and permits the passage of hydrogen ions, but no other ionic species.

- When the electrode is immersed in a test solution containing hydrogen ions the external ions diffuse through the membrane until an equilibrium is reached between the external and internal concentrations
- Thus there is a build up of charge on the inside of the membrane which is proportional to the number of hydrogen ions in the external solution.
- The glass membrane functions as an ion exchange resin, and an equilibrium set up between Na^+ ions of the glass and H^+ ions in the solution.
- $E\ G = E0\ G - 0.0592VpH$

Construction:

- Ion Selective Electrodes are available as half-cells (mono) and combination electrodes where the reference is built into the same probe.
- *Combined electrode:* Both glass electrode and reference electrode are combined as a single electrode.

wires to pH meter

Combined Glass Electrode

filling hole

Ag/AgCl reference electrode

reference electrode internal solution (sat KCl)

AgCl covered silver wire

pH sensitive glass bulb

glass electrode internal solution [HCl(0.1M)]
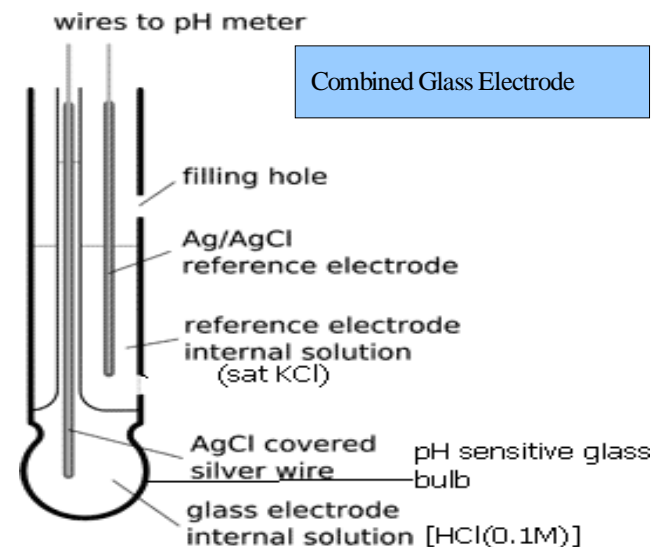
Mono electrodes

- Require the use of an additional reference electrode.
- If the membrane is attached to the end of a tube that contains an internal reference electrode like Ag/AgCl, the glass electrode acts as a internal reference electrode.

Ag | AgCl (s), HCl (0.1M)| Glass|test solution$^{+.}$

- Otherwise ion glass electrode acts as a simple half cell:

  Pt, 0.1 M HCl|Glass $^{+}$

- Silver/ silver chloride electrode or calomel electrode is used as second electrode. Since the potentials of the two reference electrodes are constant, any change in cell potential is due to change in potential across the membrane.
- **Cell configuration:**

Ag | AgCl (s), KCl (sat)||test solution^{+} |Glass| HCl (0.1M)|AgCl (s)|Ag

or

Pt|Hg|Hg$_2$Cl$_2$, KCl(sat)||test solution^{+} |Glass| HCl (0.1M)|AgCl (s)|Ag

- Ecell =Eleft- Eright

Glass Electrode-
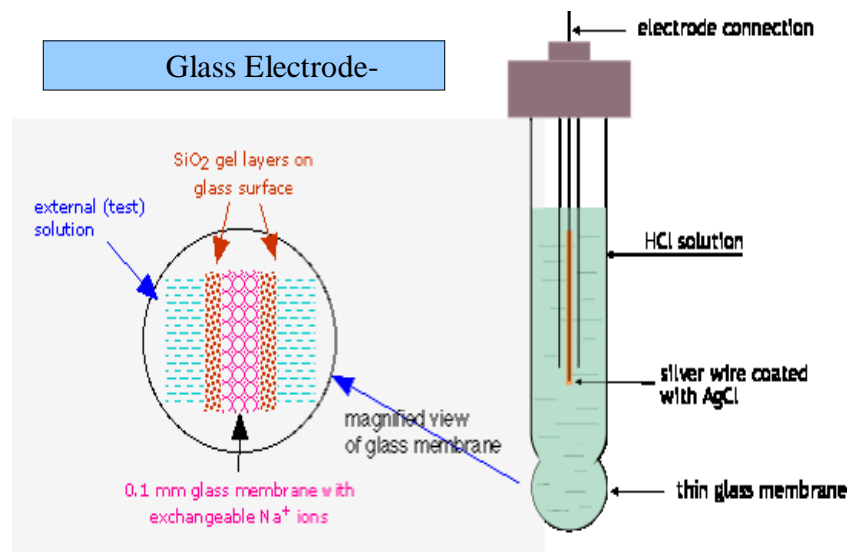
- pH = Ecell+E^{0}G -E$_{ref}$ /0.0592

Potentiometric titration

- Potentiometric titration is a volumetric method in which the changes in the emf between two electrodes (referent and indicator electrode) on the addition of titrant of known concentration (titrant) to a solution of unknown (analyte).
- The indicator electrodes is reversible with respect to one of the ions of analyte taking part in the titration reaction but does not take part in the reaction. They are inert electrode made up of Pt or Au.
- During the course of the titration, the concentration of active ion in the analyte changes thereby electrode potential of indicator electrode changes.
- Types of potentiometric titration for the determination of analytes in solutions include acid-base, redox, precipitation, and complexometric.

I) Redox Titration: Fe^{2+} against dichromate

- The concentration of an ion such as Fe^{2+} can be found by titrating with a strong oxidizing agent such as KMnO$_4$ (Mn^{7+}) or K$_2$Cr$_2$O$_7$ (Cr^{6+}).
- The titration is carried out in one side of a cell whose other half is a reference electrode: Calomel electrode, Pt| Hg | Hg $^{2+}$ (aq) | KCl ||

- Cell configuration:

Pt(s)/ Hg+ (aq)/Hg₂ Cl₂ (s) / KCl // Fe³⁺(aq)| Fe²⁺(aq)| Pt(s)

$Pt(s)/\ Hg+\ (aq)/Hg_2\ Cl_2\ (s)\ /\ KCl\ //\ Fe^{3+}(aq)|\ Fe^{2+}(aq)|\ Pt(s)$
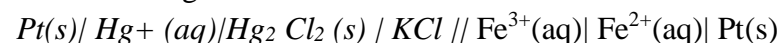
- $E_{meas} = E_{Ind} - E_{SCE}$
- Eind

$(E_{Fe3+/Fe2+}) = E_{0\ Fe3+/Fe2+} + 0.0591\ \log Fe^{3+}/Fe^{2+}$

where $E^0_{Fe3+/Fe2+} = 0.77V$

- Initially the left cell contains only Fe^{2+}. As the titrant is added, the ferrous ion is oxidized to Fe^{3+}
- according to the reaction.

$K_2Cr_2O_7 + FeSO_4 + 7H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 3\ Fe_2(SO_4)_3 + 7H_2O + K_2\ SO_4$

- Once the first drop of Cr^{6+} ($K_2Cr_2O_7$) titrant has been added, the potential of the indicator electrode is controlled by the ratio of oxidized and reduced iron which causes the potential to rise as more iron becomes oxidized.
- Near the end-point the ratio changes very rapidly since a small quantity of of added Mn^{7+} or Cr^{6+} removes considerable proportion of the few remaining Fe^{2+} ions.
- When the equivalence point is reached, the Fe2+ will have been totally consumed and the potential will then be controlled by the concentration ratio of cell couple Cr^{6+} / Cr^{3+}
- The end point is found not by measuring a particular cell voltage, but by finding what volume of titrant gives the steepest part of the curve.
- A titration curve has a characteristic sigmoid curve. The part of the curve that has the maximum change marks the equivalence point of the titration.
- The first derivative, $\Delta E/\Delta V$, is the slope of the curve, and the endpoint occurs at the volume, V', where $\Delta E/\Delta V$ has the maximum value.
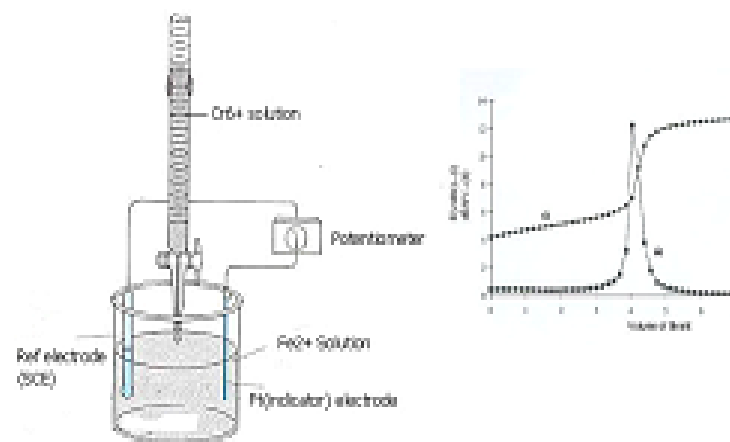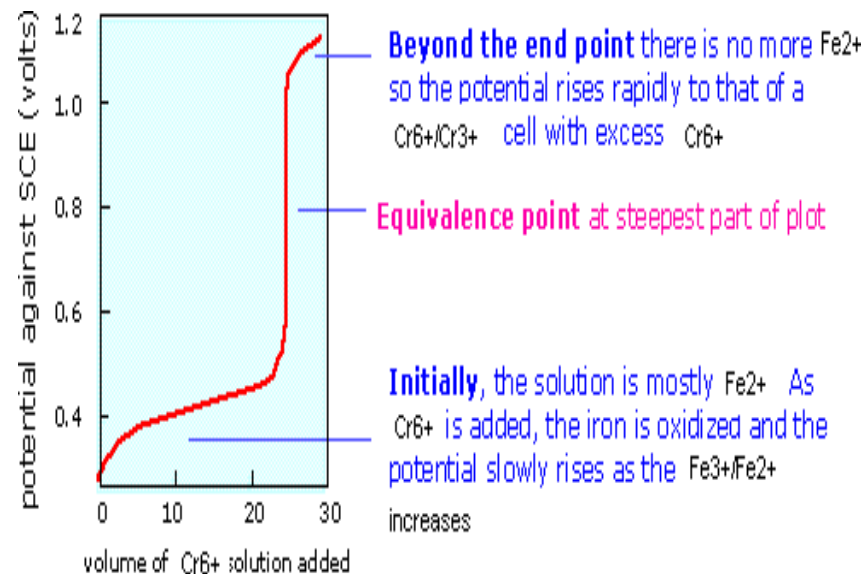
II) Precipitation Titration- Ag^+ Vs Cl^- titrants

- Titration involving precipitation can be followed potentiometrically by the use of active metal (Ag) electrode.
- For the measurement of Ag^+, Ag electrode dipping in unknown $AgNO_3$ solution is coupled with calomel electrode.
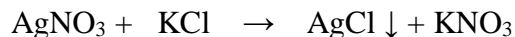- Cell configuration:

    $Pt(s)| Hg(| Hg^{2+} (aq) | KCl(sat)|| Ag^+(aq)|Ag(s)$
- $E_{meas} = E_{Ag+ / Ag} - E_{SCE}$

    $E_{meas} = E_{Ag+ / Ag} - 0.246$ V,

    $E_{Ag+ / Ag} = E^0_{Ag+ / Ag} + 0.0591 \log [Ag^+]$
- Initially the cellcontain excess Ag^+ ions. As the titrant KCl or NaCl is added, concentration of Ag^+ ion decreases due to the precipitation of Ag^+ ions as AgCl according to the equation

 $AgNO_3 + KCl \rightarrow AgCl \downarrow + KNO_3$
- The reduction potential of active electrode goes on decreasing progressively on the addition of KCl.
- At the end point the concentration change of Ag^+ is quite rapid and its concentration becomes very small due to slight solubility of AgCl.
- After the end point, further addition of KCl or NaCl does not affect the concentration of Ag^+ due to common ion effect .
- A titration curve has a characteristic sigmoid curve. The part of the curve that has the maximum change marks the equivalence point of the titration.
- The first derivative, $\Delta E/\Delta V$, is the slope of the curve, and the endpoint occurs at the volume,

    V', where $\Delta E/\Delta V$ has the maximum value

Advantages of potentiometric titration

- They are more accurate and precise.
- Can be used with colored or opaque solutions and ionic concentration down upto $10^{-3}N$
- No interference due to other ions.
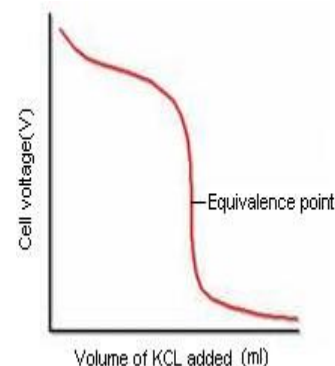
Conductometric Titrations

- Method of volumetric analysis based on the change in conductance of the solution at the equivalence point or end point during titration.
- Conductance (C) is the reciprocal of electrical resistance (R). [C = 1/R].It is a measure of the ability of a solution to conduct electricity.
- The conductance of a solution depends upon the number of free ions in the solution ion, the charge on the ions and the mobility of the ions. The conductance of a solution is the sum of the conductances of all of the ions that are in the solution. C = Ci
- The unit of conductance is the Siemens (S), which is the reciprocal of resistance Ω.
- Specific conductance (K) is the conductance of one cm cube of material and is usually measured with an alternating current between two identical, platinized platinum electrodes.
- Specific conductance is obtained by multiplying measured conductance by cell constant of the conductivity cell. K=cell constant x measured conductance
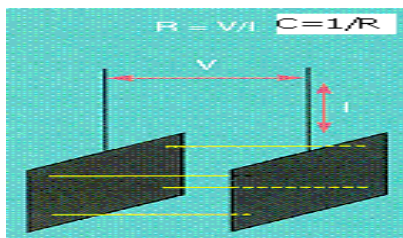
Conductivity Cell: Specially designed cells in which two plates of inert metal (Pt or Au) are provided to serve the flow in and flow out of electron.

Titration of strong acid vs strong base (hydrochloric acid with sodium hydroxide)

- The reaction that takes place in the titration vessel is
  $$H^+ + Cl^- + Na^+ OH^- \rightarrow H_2O + Na^+ Cl^-$$
- Before the end point, H+ is removed from the solution by reaction with OH^-, and Na^+ is added to the solution.
- Since the relative conductance of H^+ is about seven times that of Na^+, the conductance of the solution decreases prior to the end point.
- After the end point, no H^+ is available to react, and the conductance of the solution increases as a result of the addition of Na^+ and OH^-.
- Consequently the titration curve has a V-shape as shown in the figure.
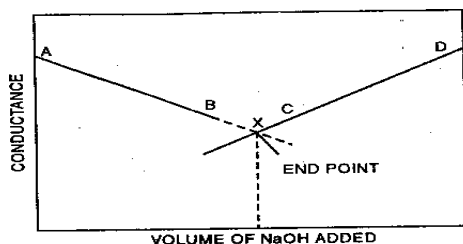
Fig. . Plot of conductance versus volume of NaOH.

- Na^+ OH^- The end point of the titration corresponds to the intersection of the extrapolated linear portions of the titration curve.

Titration of weak acid vs strong base (Acetic acid with NaOH)

- Since acetic acid is dissociated slightly (Ka = 1.8×10^{-5}) in aqueous solution, the conductance of the acetic acid solution is initially small.
- As sodium hydroxide is added, the hydroxide reacts with the acid to form water and acetate. $CH_3COOH + NaOH \rightarrow H_2O + Na^+ CH_3COO^- + H^+ + CH_3COO^-$
- The addition of CH_3COO^- and Na^+ ions to the solution causes the conductance of the solution to increase.
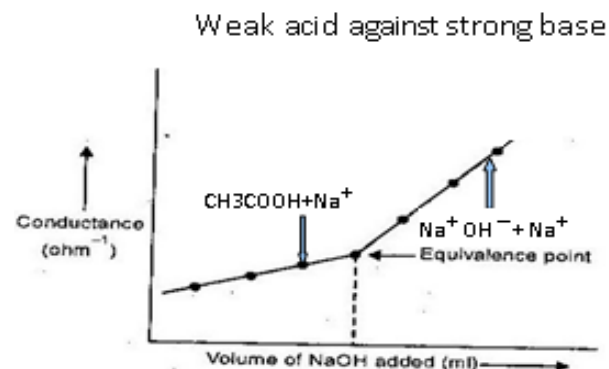
After the end point, Na^+ and OH^- are added to the solution. Since the relative conductance of OH^- is nearly five times that of $C_2H_3O_2^-$, the conductance of the solution after the end point increases more rapidly than it did before the end point.

- The end point corresponds to the intersection of the extrapolated linear portions of the curve.

Advantages of conductometric titration

- No special care is necessary near the end point as the end point is ascertained graphically**.**
- Colored solution which cannot be titrated by ordinary volumetric methods with the help of indicators can be titrated
- The titrations of weak acid against weak bases can be performed, they cannot be measured in volumetric titration because they do not produce sharp color change of indicators.
- Very dilute solutions can be titrated
- The method is very accurate in dilute solutions
- It can even be used in colored or turbid solution.

What is a sensor….?

A sensor is a device that detects events or changes in quantities and provides a corresponding output. The output is usually an electrical or an optical signal.

Examples:

- A mercury thermometer converts the measured temperature Into expansion and contraction of a liquid which can be visualized on the calibrated glass tube.
- A thermocouple converts temperature to an output voltage.
Types:

Physical sensors: A physical sensor is a device that provides information about a physical property of the system. Ex : pressure sensors, temperature sensors etc.

Chemical sensors: A chemical sensor is a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal. Ex: COD, methane , ions etc.

Classification of chemical sensors:

- Optical sensors
- Electrochemical sensors
- Electrical sensors
- Mass sensitive sensors
- Magnetic sensors
- Thermometric sensors
- Others – radiation detecting sensors

Electrochemical sensors : Sensors which transform the effect of the electrochemical interaction analyte – electrode into a useful signal are known as electrochemical sensors. Such effects may be simulated electrically or may result in a spontaneous interaction at the zero current condition.

Types:

1. Voltametric – Current is measured in the DC or AC.

2. Potentiometric - Potential is measured (reference electrode and working electrode).

3. CHEMFET – Chemically Sensitized Field Effect Transistor.

4. Potentiometric Solid Electrolyte Gas Sensors – These are different from potentiometric sensors because these work in high temperature solid electrolytes and are usually applied for gas sensing measurements.

Potentiometric sensors:

A potentiometric sensor is a type of chemical sensor that may be used to determine the analytical concentration of some components of the analyte gas or solution. These sensors measure the electrical potential of an electrode when no current is present.

Principle

The signal is measured as the potential difference (voltage) between the working electrode and the reference electrode. The working electrode's potential must depend on the concentration of the analyte in the gas or solution phase. The reference electrode is needed to provide a defined reference potential.

In potentiometric sensors, the zero-current potential (relative to a reference) developed at a selective membrane or electrode surface in contact with a sample solution is related to analyte concentration.

The main use of potentiometric transducers in biosensors is as a pH electrode.

$$E = Eo + RT/nF \ln[\text{analyte}]$$

- Eo is a constant for the system
- R is the universal gas constant
- T is the absolute temperature
- z is the charge number
- F is the Faraday number
- ln[analyte] is the natural logarithm of the analyte activity.

The best known potentiometric sensor is the Ion Selective Electrode (ISE).

Solvent polymeric membrane electrodes are commercially available and routinely used for the selective detection of several ions such as K^+, Na^+, Ca^{2+}, NH_4^+, H^+, CO_3^{2-} in complex biological matrices.

The antibiotics nonactin and valinomycin serve as neutral carriers for the determination of NH4+ and K+, respectively. ISEs used in conjunction with immobilised enzymes can serve as the basis of electrodes that are selective for specific enzyme substrates.

The two main ones are for urea and creatinine. These potentiometric enzyme electrodes are produced by entrapment the enzymes urease and creatinase, on the surface of a cation sensitive (NH_4^+) ISE.
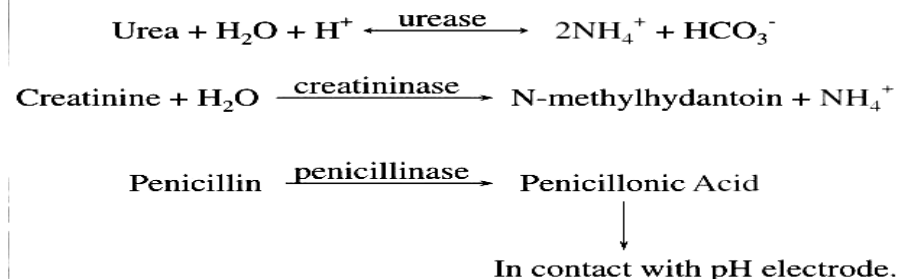
$$\text{Urea} + H_2O + H^+ \xleftarrow{\text{urease}} 2NH_4^+ + HCO_3^-$$

$$\text{Creatinine} + H_2O \xrightarrow{\text{creatininase}} \text{N-methylhydantoin} + NH_4^+$$

$$\text{Penicillin} \xrightarrow{\text{penicillinase}} \text{Penicillonic Acid}$$

In contact with pH electrode.

Chemical biosignals:

Signals providing information about concentration of various chemical agents in the body.

- Level of glucose (diabetes)
- Blood oxygen level (asthma, obstructive pulmonary disease, heart and kidney failure)
- Gases in blood and breathing airflow (anesthetic gases, carbon dioxide etc.)
- pH

Glucose sensor:

Same chemistry as the oxygen sensor, but monitors H_2O_2 + 6 O_2 (opposite chemistry to O_2 sensor).The H_2O_2 is formed from glucose, catalyzed by an immobilized enzyme, glucose oxidase, glucose + O_2 6 gluconic acid + H_2O_2 (different from glucuronic acid)

Device is similar to oxygen sensor, except that there is a double layered membrane. In a biological fluid, External polycarbonate membrane excludes proteins etc; glucose oxidase is bound to membrane, forms H_2O_2 with glucose in sample. Internal

membrane allows H_2O_2 to diffuse to the electrode (anode, in this case) where it is oxidized to O_2.
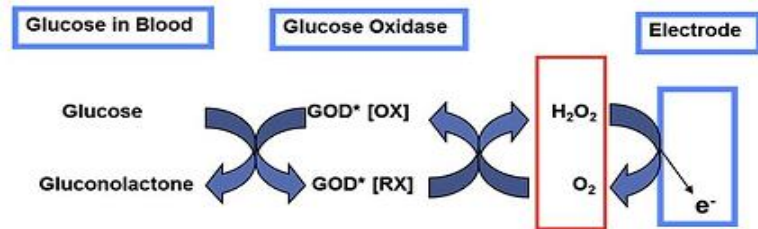
Gas sensors:

A gas sensor is a device which detects the presence of various gases within an area, usually as part of a safety system. This type of equipment is used to detect a gas leak and interface with a control system so a process can be automatically shut down. A gas sensor can also sound an alarm to operators in the area where the leak is occurring, giving them the opportunity to leave the area. Gas sensor measures the concentration of gas in its vicinity.

Most often, these are pH-sensing devices that are calibrated in the units of interest, such as ppbv of CO_2, ppbv of SO_2. Note that this means that they are not specific for a single gaseous analyte.

Types of gas sensor

CO_2, SO_2, NH_3 - Glass membrane, senses pH change

HCN, H_2S - Ag_2S membrane, senses pCN or pS

HF - LaF_3 membrane, senses pF

The gas sensor has a thin plastic membrane (often silicone rubber) to admit gas into the sensor. Only a very thin layer of aqueous solution is in contact with the gas, in order to keep response times short.

Some Applications of Gas Sensor:

- Process control industries
- Environmental monitoring
- Fire detection Alcohol breath tests
- Detection of harmful gases in mines
- Home safety

Blood oxygen level- pulse oximetry:

Pulse Oximeter used to measure oxygen saturation in the body i.e how much of the hemoglobin in the blood is carrying the oxygen. Oxygen enters the lungs and then is passed on into blood. The blood carries the oxygen to the various organs in our body. The main way oxygen is carried in our blood is by means of hemoglobin. Normal oxygen saturation values are 97% to 99% in a healthy individual on room air.

Working principle:

Pulse Oximetry consists of Red(R) and Infrared(IR) light emitting LEDs and a photo detector. Oxygenated and deoxygenated hemoglobin have different light absorption rate.

- Oxygenated hemoglobin absorbs more infrared light
- Deoxygenated hemoglobin absorbs more red light

Finger is placed in between the light source and the light detector. Non absorbed light by finger reaches at detector. Light is emitted from light sources which goes across the pulse oximeter probe and reaches the light detector. The amount of light absorbed depends on three physical properties:

1. concentration of the light absorbing substance.

2. length of the light path in the absorbing substance.

3. oxyhemoglobin and deoxyhemoglobin absorbs red and infrared light differently

Amount of light absorbed is proportional to the concentration of the light absorbing substance. Amount of light absorbed is proportional to the length of the light path. Oxyhemoglobin

absorbs more infrared light than red light & deoxyhemoglobin absorbs more red light than infrared light.Using this ratio, the pulse oximeter can then work out the oxygen saturation.

Uses:

- Operating rooms.
- ICU.
- Postanesthesia care units.
- Emergency departments and ambulances.
- Endoscopy suites.
- Sleep laboratories
- Cardiac catheterization laboratories.
- Delivery suites
- Wards.

UNIT-I
ELECTROCHEMISTRY
QUESTION BANK
PART A

01. Define an Electrochemical cell. Give one example.

A cell which converts chemical energy into electrical energy is known as electrochemical cell. Example: Daniel cell , Batteries.

02. What do you mean by re-dox reaction?

Both reduction and oxidation takes place simultaneously in a cell reaction then it is known as redox reaction of an electrochemical cell.

03. What is electrode potential?

It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with its own salt solution. It is denoted as "E"

04. Define an origin of electrode potential.

When a metallic electrode is placed in its own salt solution, two types of reaction takes place.
   a) +ve ions may pass into the solution. $M \rightarrow M^{n+} + ne^-$ (oxidation)
   b) +ve ions from the solution may deposit over the metal. $M^{n+} + ne^- \rightarrow M$ (reduction)

The above reaction takes place in an electrode then it is known as an origin of electrode potential.

05. Define oxidation potential and reduction potential.

Oxidation potential: The tendency of a metallic electrode to lose electrons, Reduction potential: The tendency of a metallic electrode to gain electrons

06. How an electrochemical is measured? Define EMF of an electrochemical cell.

It is measured by EMF.: "The difference of potential which causes flow of electrons from one electrode of higher potential to the other electrode of lower electrode potential".
$EMF = E_R - E_L$

07. What are the applications of electrochemical cell?
   - Determination of sparingly soluble salt.
   - Determination of the valency ion.
   - Determination of standard free energy change and K.
   - Potentiometric titrations can be carried out.,
   - Hydrolysis constant can be determined.

08. Define electrochemical series.

When various types of metallic electrodes are arranged in their increasing order of standard reduction potential on the basis of hydrogen scale is known as emf series.

09. Write the significance of electrochemical series.
   a) To calculate the standard emf of the cell.
   b) Relative ease of oxidation or reduction.
   c) Displacement of one element by the other.,
   d) Hydrogen displacement behavior.
   e) Determination of equilibrium constant (K) for the reaction.

10.Define Single and Standard electrode potential.

Single electrode potential: It is the ability of the electrode to gain or lose electrons, when it is dipped in its own salt solution. Standard electrode potential: It is the ability of the electrode to gain or lose electrons, when it is dipped in its own salt solution of 1M concentration at 25^0C.

11.Predict the following cell reaction is feasible or not.
$Zn/Zn^{2+}(1M)//Cu^{2+}/Cu$; Given that $E^o{}_{Cu2+/Cu}=0.34V$ and $E^o{}_{Zn2+/Zn}= -0.76V$.
We know that
$E^o cell = E^o right - E^o left$
$= 0.34- (-0.76)$
$= 1.1V$
Since, E^o of the cell is positive, and the cell reaction is feasible.

12.List any four applications of Nernst equation.
- It is used to calculate the emf of a given cell.
- Corrosion tendency of a metal can be predicted.
- Electrode potential of a given metal can be calculated.
- Feasibility of a given cell reaction can be predicted.

13. What is mean by Electrolysis.
Process of chemical decomposition of an electrolyte by passage of electricity.Example: Electrolysis of HCl.

14. Define Gas sensors.
A gas sensor is a device which detects the presence of various gases within an area, usually as part of a safety system.

15.write any four Applications of Gas Sensor.

- Process control industries
- Environmental monitoring
- Fire detection Alcohol breath tests
- Detection of harmful gases in mines
- Home safety

16. Discuss Potentiometric sensors.
A potentiometric sensor is a type of chemical sensor that may be used to determine the analytical concentration of some components of the analyte gas or solution. These sensors measure the electrical potential of an electrode when no current is present.

17. Define Chemical biosignals:
Signals providing information about concentration of various chemical agents in the body.

18. Blood oxygen level- pulse oximetry
Pulse Oximeter used to measure oxygen saturation in the body.

19. What is mean by Physical sensors.
A physical sensor is a device that provides information about a physical property of the system. Ex : pressure sensors, temperature sensors etc.

20. Define Chemical sensors.
A chemical sensor is a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal. Ex: COD, methane , ions etc.

21.Differences between metallic conduction and electrolytic conduction.

Metallic conduction	Electrolytic conduction
Involves flow of electrons	Involves movement of ions in a solution
Does not involve any transfer of matter	Involves transfer of electrolyte in the form of ions
Conduction decreases with increase in T	Conduction increases with increase in T
No change in the chemical properties of the conductor	Chemical changes occur aat the two electrodes

PART-B

1. What are electrochemical series? Give its applications.
2. Derive Nernst equation.
3. How Measurement of single electrode potential
4. Explain working method of Electrochemical cells (Galvanic cells)
5. Write Differences between electrolytic cells and electrochemical cells
6. Discuss briefly Glass membrane electrodes: measurement of pH
7. Explain Redox Titration: Fe^{2+} against dichromate
8. Explain Precipitation Titration- Ag^+ Vs Cl^- titrants
9. Explain Titration of strong acid vs strong base (hydrochloric acid with sodium hydroxide)
10. Discuss Titration of weak acid vs strong base (Acetic acid with NaOH)
11. Brief notes on Blood oxygen level- pulse oximetry.
12. Discuss in detail Gas sensors.

UNIT-I
ELECTROCHEMISTRY
CONTENT BEYOND THE SYLLABUS:

Bowl-shaped electrode that converts carbon dioxide into fuels:

Scientists have developed a bowl-shaped electrode which can efficiently convert carbon dioxide into fuels, helping combat the climate change threat posed by rising atmospheric CO_2. An electrode is an electrical conductor used to make contact with a nonmetallic part of a circuit, like air or electrolyte.

Researchers, including those from the University of Bath in the UK, believe the design will eventually allow the use of renewable electricity to convert CO_2 into fuels and chemicals without creating additional atmospheric carbon. Using this reaction, known as the reduction of carbon dioxide, has exciting potential, according to the study published in the Journal of Materials Chemistry A.

However, two major obstacles are poor conversion efficiency of the reaction and a lack of detailed knowledge about the exact reaction pathway. The new electrode addresses these challenges with higher conversion efficiency and sensitive detection of molecules created along the reaction's progress — thanks to its innovative shape and construction. The bowl shaped electrode works six times faster than standard planar — or flat — designs, researchers said.

The bowl-like shape of the design concentrates electric fields on its hot edges — the rim of the bowl — which then concentrates positively charged potassium ions on the active sites of the reaction, reducing its energy requirements. The Copper-Indium alloy electrode can also be useful to sensitively study the reaction process.

"There is evidence that CO_2 increases surface ozone, carcinogens, and particulate matter, thereby increasing death, asthma, hospitalisation, and cancer rates," said Professor Ventsislav Valev, from the University of Bath. "It is therefore crucial to keep researching new ways for lowering the CO_2 levels in the atmosphere," Valev said. The team wants to continue research to develop the most efficient catalyst to perform carbon reduction.

"CO_2 is causing climate change, making our planet warmer. By using clean electricity, we can convert CO_2 into chemical fuels, which can be used again," said Professor Liwu Zhang, from Fudan University in China. "This builds a cycle of CO_2, with no increment of CO_2 concentration and will help save our world," Zhang said. However, researchers said in order to improve the efficiency of transforming CO2 into chemical fuels, it is extremely important to know the reaction pathway, and find the most suitable catalyst.

Modified Electrodes Used for Electrochemical Detection of Metal Ions in Environmental Analysis:

Heavy metals (HMs) are persistent in the environment (waters and soils), which means that they cannot be degraded. HMs mainly come from anthropic activities such as mining, smelting, or different kinds of wastes. Keep in mind that, among HMs, although some are necessary for life (iron, selenium, cobalt, copper, manganese, molybdenum, zinc), unfortunately, many others are toxic. For example, mercury (Hg) enters the environment through not only coal burning but also through mining or industrial wastes, and is known to cause damage mainly to the nervous system; Lead (Pb) comes from automobile exhausts, old paints, mining wastes, incinerator ash or water from lead pipes

and is also known to causes damage to the nervous system; Cadmium (Cd), which causes kidney diseases, comes from the electroplating and mining industries; lastly, arsenic (As) comes from herbicides or, again, from the mining industry and causes damage to skin, eyes, and liver. Other major heavy metals are chromium, nickel, tin and thallium. For sanitary reasons, it has become necessary to detect and quantify HMs in soils or in waters. For example, French regulations set mercury contents in drinking water at 1 $\mu g \cdot L^{-1}$, silver or lead at 10 $\mu g \cdot L^{-1}$ and arsenic at 50 $\mu g \cdot L^{-1.}$

Traditional analytical methods are atomic absorption or emission spectroscopies (AAS, AES), inductively coupled plasma mass spectrometry (ICP-MS) or cold vapor atomic fluorescence spectrometry (CVAFS). They are extremely sensitive but are however expensive and require laborious pre-treatment processes. Therefore, in some cases, these methods may be replaced by more easy-to-use and inexpensive ones such as sensors, which may be based on either optical transduction (e.g., photonic crystal sensors) or on electrochemical transduction (ion-selective electrodes, polarography, potentiometry, amperometry, conductimetry) on which the review will more specifically focus. Other transduction methods have been extensively reviewed elsewhere.

Heavy metals are generally present under their cationic form (Hg^{2+}, Pb^{2+}, Cd^{2+}…), therefore, they can be electro reduced to the corresponding metal at an electrode; this corresponds with a pre-concentration step, because a large amount of metal can be deposited on the electrode even if the cation concentration is low, providing that the deposition (electro reduction) time is sufficiently long. In a second step, an anodic potential scan is applied, so that the metal is oxidized back to the corresponding cation. This electrochemical reaction is extremely fast, giving a strong current (proportional to the quantity of metal ion initially present in the medium) and providing high sensitivity; in addition, each metal is oxidized at a particular potential, which provides specificity. This method is called Anodic Stripping Voltammetry (ASV) and is extremely pertinent for HMs quantification. The first part of this review will be dedicated to this technique used on unmodified electrodes (mercury, bismuth or noble metals in the bulk form), or electrodes modified at their surface by nanoparticles, nanostructures (CNT, graphene) or other innovative materials such as boron-doped diamond.

Another way to functionalize electrodes is to use conducting polymers (polypyrrole, polythiophene, polyaniline, polynapthalene, *etc*.). One main reason for the interest in conducting polymers (CPs) is that small perturbations at their surface or in their bulk can generate strong changes in their electroactivity, which can be probed by amperometry or potentiometry. Another interest of CPs, beyond the simplicity they offer in modifying a conducting surface, is that they are easy to functionalize with additional chemical functions. The easiest way is to dope CPs with doping ions carrying the required function. The other way is to chemically modify the backbone of the CPs with the desired function. Additionally, it has been shown that some CPs are biocompatible, and therefore are convenient for binding biomolecules.

Biomolecules such as DNA, peptides or proteins have been reported to selectively bind HM ions. This allows for selective preconcentration of ions at an electrode surface before stripping voltammetry, therefore avoiding interferences between metals. Lastly, beyond the use of simple biomolecules, enzymes (generally phosphatase or urease) have been also employed for the detection of HMs, which interact with their active site and lower their activity (this phenomenon is called enzyme inhibition). However, isolated enzymes immobilized on electrodes are often unstable;

this is why whole cells such as microalgae or other micro-organisms, containing themselves active enzymes, have attracted much interest. All these items will be detailed in this review.

UNIT – II
CORROSION AND ELECTROCHEMICAL PROCESS

Corrosion

Corrosion is defined as the gradual deterioration of a metal or alloy by the chemical or electrochemical reaction with the environment.

Causes of corrosion

Metals occur in nature either in (i) native state (or) (ii) in combined state

i. Native state

Metal those occuring in nature in native (or) free (or) uncombined state are non – reactive with the environment. They are noble metals. They do not undergo corrosion. Example: Au, Pt, Ag

ii. Combined state

Except noble metals, all the other metals are reactive and react with the environment and form compounds such as oxides, sulphides, chlorides and carbonates by reaction with the environment. They exist in nature in the form of their stable compounds (ores). Example: Fe_2O_3, ZnO, PbS, $CaCO_3$

How and why corrosion occurs
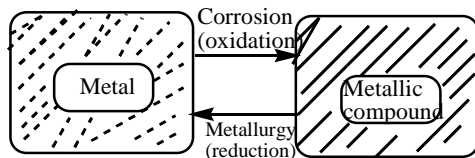
Metals are extracted from the ores by reduction. In pure metallic state these are unstable. The reverse

Process, oxidation resulting corrosion tames place.

When the metals are used in various environments, such as corrosive gases, moisture, the metal surface tends to decay, which is the reason for corrosion

Due to corrosion, some of the useful properties of metals such as electrical conductivity, ductility, malleability are lost

Consequences of corrosion

i.   Formation of corrosion parts on the machinary the efficiency will be lost
ii.   Products get contaminated
iii.   Results in plant failure
iv.   Necessity arises for overdesign
v.   Toxic products are released

Classification (Theories of corrosion)

Based on the environment, corrosion is classified into

(i) Dry (or) chemical corrosion   (ii) Wet (or) Electrochemical corrosion

Dry (or) Chemical corrosion

This process is due to the attack of metal surfaces by atmospheric gases such as O_2, H_2S, SO_2, NO_2

There are 3 main types of dry corrosion

i. Oxidation corrosion   ii. Corrosion by hydrogen iii. Liquid – metal corrosion

Mechanism of dry corrosion Oxidation corrosion

Oxidation corrosion is brought by the direct attack of oxygen at low or high T, on metal surfaces in the absence of moisture. Alkali metals and alkaline earth metals are rapidly oxidised at low T. At high T, almost all metals except Ag, Au and Pt are oxidised
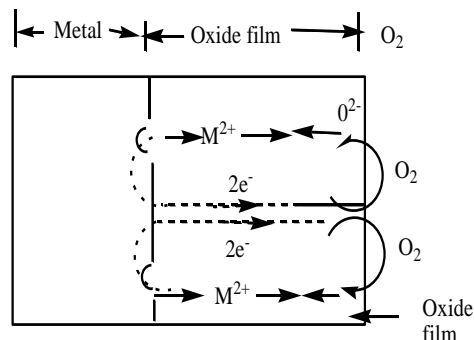
Mechanism of dry corrosion
Oxidation occurs first at the surface of the metal resulting in the formation of metal ion (M^+). Oxygen changes to ionic form (O^-) and reacts with metal ions for form oxide film. Once the metal surface

covered with a monolayer of metal oxide, for further corrosion, the metal ion diffuses outward through the metal – oxide barrier. Thus, the growth of the oxide film commenses perpendicular to metal surface

At the metal / oxide film interface $\quad M \longrightarrow M^{2+} + 2e^-$

At the oxide film / environment interface

$$\frac{1}{2} O_2 + 2e^- \longrightarrow O^{2-}$$
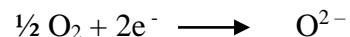
The overall reaction is $\quad M + \frac{1}{2} O_2 \longrightarrow M^{2+} + O^2 \equiv MO$ (oxide film)

Nature of metal oxide film

Nature of metal oxide film on the metal surface plays an important role in oxidation corrosion

i. Stable oxide layer : Stable oxide layer is a fine grained structure, and gets adsorbed tightly to the metal surface. Such layer is impervious and stops further oxygen attack. Such a film behaves as a protective coating and further corrosion is prevented

Examples: Oxides of Al, Sn, Pb, Cu form stable oxide layers

ii. Unstable oxide layer: Unstable oxide layer is formed on noble metals, which decomposes back into metal and oxygen

Examples: Oxides of Pt, Ag

iii. Volatile oxide layer: The oxide layer volatilizes as soon as it is formed leaving the fresh metal surface for further corrosion

Example : Molybdenum oxide

iv. Protective or non-protective oxide film: (Pilling – Bedworth ratio)

Ratio of the volume of the oxide formed to the volume of metal consumed is called as **Pilling – Bedworth ratio**

If the volume of the oxide layer formed is less than the volume of the metal, the oxide layer is porous and non protective. **Examples : Na, Mg, Ca**

If the volume of the oxide layer formed is is greater than the volume of the metal, the oxide layer is non porous and protective, **Examples : Pb, Sn**

Corrosion by hydrogen

i. Hydrogen embrittlement

Contact of metals with H_2S at ordinary T causes evolution of atomic hydrogen : $Fe + H_2S \longrightarrow FeS + 2H$

Atomic hydrogen diffuses into the metal and collects in the voids, where it recombines into molecular hydropgen.

$H + H \longrightarrow H_2 \uparrow$
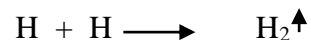
Collection of these gases in voids develop very high pressure, which causes cracks and blisters in the metal.

ii. Decarburisation

At higher T, atomic hydrogen is formed by the thermal decomposition of molecular hydrogen : $H_2 \longrightarrow 2H$

When steel is exposed to this environment, atomic hydrogen combines with carbon of steel to produce methane gas :

$C + 4H \longrightarrow CH_4$
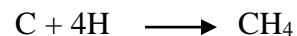
Accumulation of these gases leads to high pressure, which causes cracking. The process of decrease in carbon content of steel is called as **'decarburisation of steel'**

Liquid – metal corrosion

This is due to the flowing action of liquid metal at high T. Corrosion reaction involves

    i.   Dissolution of solid metal by liquid metal

    ii.   Liquid metal penetrating into solid metal

Wet corrosion (Electrochemical corrosion)

Conditions

i. When two dissimilar metals or alloys are in contact with each other in the presence of an aqueous solution or moisture

ii. When a metal is exposed to varying concentrations of oxygen or an electrolyte

Under these conditions, one part of the metal becomes anode and another part becomes cathode.

Mechanism of Wet corrosion

i. In the anodic part, oxidation (or) dissolution of metal occurs : M $\longrightarrow$ $M^{2+}+2e^-$

ii. In the cathodic part, reduction occurs, which depends on the nature of the corrosive environment

      (a) If the corrosion environment is acidic, hydrogen evolution occurs $2H^+ + 2e^- \longrightarrow H_2$

      (b) If the corrosive environment is slightly alkaline or neutral, hydroxyl ion is formed : $\frac{1}{2} O_2 + 2e^- + H_2O \longrightarrow 2OH^-$

The metal ions from the anodic part and non metallic ions from cathodic part diffuse towards each other through conducting medium and form a corrosion product between anode and cathode

(a) Hydrogen evolution corrosion

All the metals above hydrogen in the electrochemical series have a tendency to dissolve in acidic solutions with evolution of hydrogen gas

At anode : Iron undergoes dissolution to give Fe^{2+} ions with the liberation of e^-

Fe $\longrightarrow Fe^{2+} +2e^-$ (oxidation)

At cathode : Liberated electrons flow from anodic to cathodic part where H^+ is reduced to H_2

$2 H^+ \longrightarrow H_2$

(b) Adsorption of oxyge corrosion

The surface of iron is generally coated with a thin film of oxide. However, if the oxide film develops some crack, some anodic areas will be created on the surface and the remaining part acts as cathode

At anode : Iron dissolves with liberation of e^-

At cathode: Liberated e^- flow from cathodic to anodic part through metal, where they are taken up by dissolved oxygen to form OH^-.

Nett corrosion reaction is $Fe^{2+} + OH^- \longrightarrow Fe(OH)_2$

If enough oxygen present

$4 Fe(OH)_2 + O_2 + H_2O \longrightarrow 4 Fe(OH)_3$ (rust)
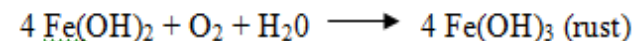
Types of electrochemical corrosion:

i. Galvanic corrosion

When two metals are in contact with each other in presence of an aqueous solution or moisture, galvanic corrosion occurs

Moree active metal (more –ve electrode potential) acts as cathode

Less active metal (less –ve electrode potential) acts as cathode

(a) Zn – Fe couple : Zn is more active and dissolves in preference to Fe

(b) Fe – Cu couple: Iron is more active than Cu and undergoes corrosion in preference to Cu

Other examples

Steel screw in brass marine hardware corrodes

      Galvanic corrosion can be prevented by providing an insulating material between the two metals

(ii) Differential aeration (Concentration cell corrosion)

This type of corrosion occurs when a metal is exposed to varying concentration of oxygen or any electrolyte on the surface of the base metal

Example: Metals partly immersed in water or conducting solution (**Water line corrosion)**
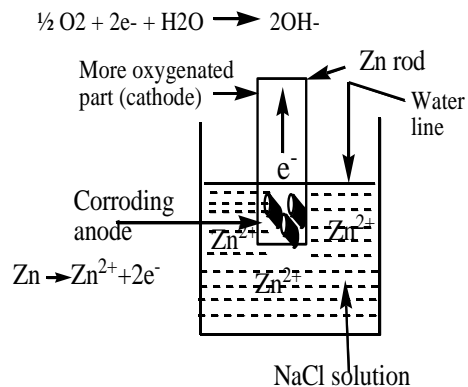
If the metal is partially immersed in the conducting solution, the metal part above the solution is more aerated and hence becomes cathode. The metal part inside the solution is less aerated and thus, become acidic and suffers corrosion

1. Pitting corrosion

      Pitting is localised attack, resulting in the formation of a hole around which the metal is relatively unattacked cathode due to high oxygen concentration.

The rate of corrosion will be more, when the area of cathode is larger and the area of anode is smaller. A amll pit is formed at the surface of the metal
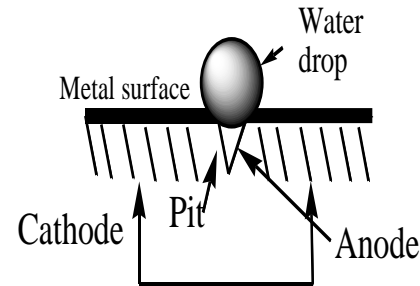
Consider a drop of water or aqueous NaCl resting on a metal surface. The area covered by the drop acts as an anode due to less oxygen concentration and suffers corrosion Uncovered area acts as
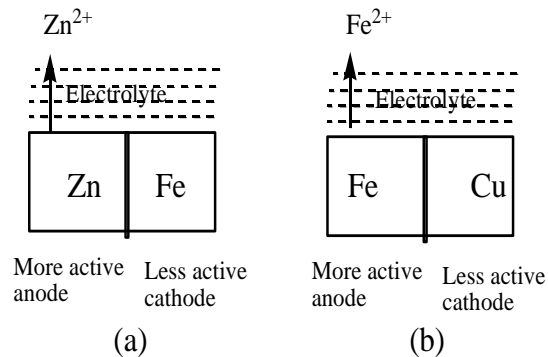
2. Intergranular Corrosion (IGC)

- This type of corrosion occurs along the grain boundaries. When a metal is solidified the solidification starts at a number of randomly distributed nuclei within the molten mass.

- Each of them grows in a regular pattern or atomic array to form grains. Because of random distribution of the nuclei, the planes of atoms in adjacent grains do not match and these mismatched areas between grains are known as grain boundaries.

- Certain compounds precipitate along the grain boundaries. The precipitated compounds as well as the grain centers behave as cathode, whereas the grain boundaries behave as anode.

- Owing to the precipitation of certain compounds at the grain boundaries the solid metal solution adjacent to the boundary becomes depleted in those constitutents. Thus, a potential difference is created leading to the corrosion at the anodic grain boundaries.

It is common in stainless steel and other heat treated alloys

The presence of **mismatching of grains** leads to highly active grain boundaries.

Due to this high activity along the boundaries, the Cr and C present in SS react to give Chromium Carbide, which precipitates along the boundary. This decreases the % of Cr at

the boundary and hence the **boundary becomes anodic** with respect to the bulk of the grain, resulting of corrosion at boundary.
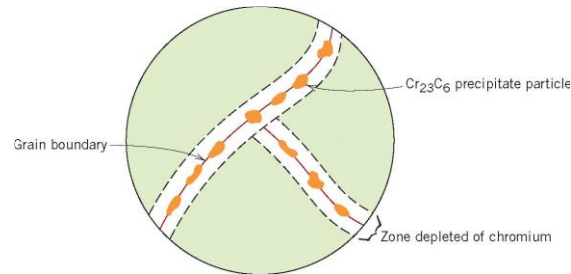
Adopting proper and controlled heat treatment methods can minimize IGC.

3. Stress Cracking Corrosion

It occurs because of the combined effect of

- Static tensile stress and
- Corrosive environment near the metal

The metal develops internal stress during manufacture process like fabrication, heat treatment, rolling insufficient annealing etc.

Thermodynamically, areas under stress are at higher energy level. Therefore, they have high electrode potential and act as anode. The stress-free areas are at lower electrode potential and act as cathode. The difference in potential of these two is quite low and corrosion is concentrated in small path that is anodic. The anodic area

become highly reactive and is attacked even by a mild corrosive environment resulting in the formation of a crack.

The corrosive agents are very specific like

- Caustic alkalies and strong nitrate solution for mild steel
- Brass undergoes corrosion easily in the presence of traces of NH3.
- Acid chloride for stainless steel.
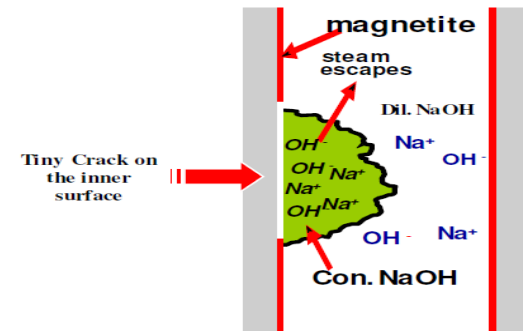
For example caustic embrittlement is a type of SCC occurring in boilers. In high pressure boilers, Na_2CO_3, used for treating hard water is converted to NaOH.

Na2CO3 + H2O → 2NaOH + CO2
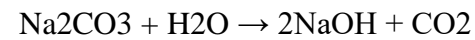
High pressure

Due to the repeated heating and cooling, the walls of the boiler contain lot of tiny cracks.

The NaOH formed as above, enters these cracks and evaporates. Thus the cracks contain higher concentration of NaOH and attack the surrounding area, dissolving iron of boiler

forming sodium ferroate. This causes embrittlement of boiler parts, particularly stressed parts like bends, joints, and rivets.

Another example is the corrosion of brass in presence of NH_3.

Prevention Methods:

i. Adopting **Phosphate Conditioning** as an alternative to Carbonate conditioning

ii. By **sealing the hair line cracks** with Sodium sulphate , Tannin, Lignin etc. (can be done easily by adding a little amount of sealants in water)

Other examples

i.   Corrosion occurs under metal washers, where oxygen cannot diffuse easily.

ii.   Lead pipeline passing through clay to cinders undergo corrosion. The pipeline under cinders is more aerated.

Difference between chemical and electrochemical corrosion

Chemical corrosion	Electrochemical corrosion
Occurs only in dry condition	Occurs in the presence of moisture or electrolyte
Due to direct chemical attack of the metal by environment	Due the setting up of large number of anodic and cathodic areas
Even a homogeneous metal surface gets corroded	Heterogeneous surface (or) bimetallic contact is necessary
Corrosion products accumulate in the same place where corrosion occurs	Corrosion occurs at the anode, while product formed elsewhere
Self controlled	Continuous process
Follows adsorption mechanism	Follows electrochemical reaction

Factors influencing the rate of corrosion:

i. Nature of the metal   ii. Nature of the environment

 Nature of the metal

(a) Position in the emf series:

Extent of corrosion depends on the position of the metal in the emf series.   Metals above hydrogen in the series get corroded vigorously.

Lower is the reduction potential, greater is the rate of corrosion

When two metals are in contact, the more active metal undergoes corrosion

Greater is the difference in their positions in the emf series, faster will be the corrosion rate

(b) Relative area of anode and cathode

Rate of corrosion will be more when the cathodic area is large.

When the cathodic area is larger, the demand for electrons will be more and results in the increased rate of corrosion in the anodic area

(c) Purity of the metal

100% pure metal will not undergo any corrosion.

Presence of impurities will create heterogeneity and galvanic cells are setup.

Effect of impurites on the rate of corrosion of Zn

% purity of Zn	99.999	99.99	99.95
Corrosion rate	1	2650	5000

(d) Overvoltage (Over potential)

Hydrogen over voltage will be reduced to 0.33 by the addition of small impurity like $CuSO_4$ to H_2SO_4. This results in the increased rate of corrosion

Nature of the environment

(a) Temperature

Rate of corrosion $\propto$ T, as the rate of chemical reaction and the rate of diffusion of the ions increases with increase in T

(b) Humidity:
 Rate of corrosion will be more when the humidity of the environment is high
Moisture acts as the solvent for oxygen in air, to produce the electrolyte essential for corrosion

(c) Presence of corrosive gases
Acidic gases like CO_2, SO_2, H_2S and fumes of HCl produce electrolytes, which are acidic and increases electrochemical corrosion

(d) Presence of suspended particles
Particles like NaCl, $(NH_4)_2SO_4$ along with moisture act as powerful electrolytes and accelarate electrochemical corrosion

(e) Effect of pH
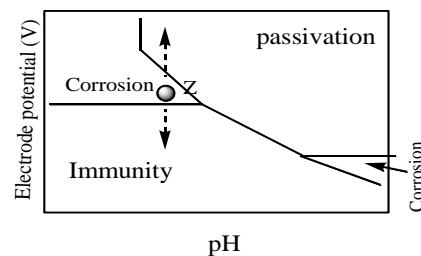
Pourbaix Diagram
Explains the possibility of corrosion with respect to pH and the electrode potential of the metal
Pourbaix diadgram for iron in water clearly shows the zones of corrosion, immunity and passivity. In the diagram Z is

the point at pH = 7 and electrode potential = - 0.4 V. It is in the corrosion zone, indicating that iron rusts in water under this condition.
The rate of corrosion can be altered by shifting the point Z into immunity and passivity zones, if the potential is changed to – 0.8 V by applying an external current

On the other hand, corrosion of iron can be reduced by moving into the passivity region by applying +ve potential
Rate of corrosion will be maximum, when the environment is acidic.

Electroplating:
Electroplating is the process of deposition of a metal on a metal, non-metal or alloy by passing electric current through an electrolytic solution containing soluble salt of the coating metal.
In this method, the base metal to be coated or electroplated is made the cathode and the coating metal is made the anode.
The process of electroplating consists of two steps.
(i) Surface preparation: In this step, the surface of the metal to be electroplated is cleaned by several chemical and mechanical methods.
(ii) Electrodeposition: In this step, the coating metal is electroplated over the base metal.
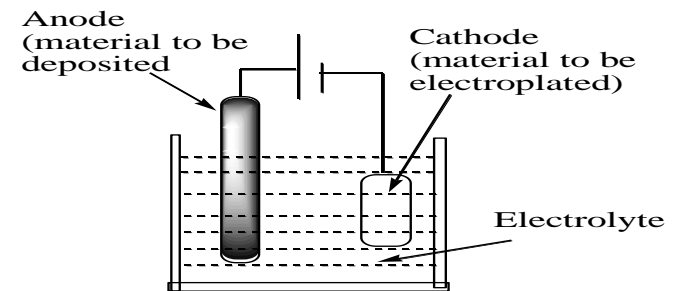
Electroplating of Copper:
For copper plating, the anode is made of copper and the cathode is the material to be electroplated. The electroplating bath may be acidic or alkaline.

(a) **Acidic bath**: Also called sulphate bath, it consists of 200-250 g/l $CuSO_4$, 50-75 g/l H_2SO_4 and rest water. The additives are gelatin or dextrin, sulphur containing brightener and sulphonic acid. The operating temperature is 20-40^{0}C. The pH is low and the current density is about 20-50 mA/cm2.

This bath is used for coating in printed circuit boards (PCB) and is not suitable for electroplating iron and its alloys.

(b) **Alkaline bath**: It is also called cyanide bath. The composition per liter of the bath is as follows: CuCN: 40-50g. KCN: 20-30g, 10g K_2CO_3 and rest water. Brighteners like Al_2O_3 and thiosulphate are also added to the electrolytic bath. The pH is maintained between 12 and 13, current density used is 10-40 mA/cm2 and the temperature of the bath is 40-50^{0}C.

This bath finds application in the coating of printed circuit boards and is also suitable for plating iron and its alloys. It is used as an undercoating for chromium plating.

If during electrolysis, the anode is made of the coating metal itself, concentration of the electrolyte remains unchanged, as the metal ions deposited from the bath are replaced continuously from the anode

Example:

If $CuSO_4$ solution is used as an electrolyte, it ionizes as

$$CuSO_4 \rightleftharpoons Cu^{2+} + SO^{2-}_4$$

On passing current, Cu^{2+} ions get deposited at the cathode

$$Cu^{2+} + 2e^- \longrightarrow Cu \text{ (at cathode)}$$

The free SO_4^{2-} ions migrate to the copper anode and dissolve an equivalent amount of Cu from $CuSO_4$:

$$Cu^{2+} + SO^{2-}_4 \longrightarrow Cu\ SO_4 + 2e^- \quad \text{(At anode)}$$

$CuSO_4$ formed gets dissolved in the electrolyte. Thus, there is a continuous replenishment of electrolyte during electrolysis.

Process:

The article to be plated is cleaned with dilute acid. The article made cathode in the electrolytic cell. The anode is the coating metal. When dc current is passed from battery, coating metal ions migrate to the cathode and get deposited. A thin layer of coating metal is obtained on the article to be coated. To get strong, adherent smooth deposit, certain additives (glue, gelatin) are added to the bath. Optimum conditions for plating (T, current density and concentration of electrolyte) are maintained.

Electroless plating:

In electroless plating, a noble metal (less reactive metal) is deposited on a less noble metal (more reactive metal) without the passage of electric current. It involves a redox reaction catalyzed by the metal of the alloy being deposited; hence it is also termed as autocatalytic coating. The method employs a suitable reducing agent to bring about the reduction of metal ions to metal that gets deposited over catalytically active surface.

Metal ions + reducing agent $\rightarrow$ Metal + Oxidised product
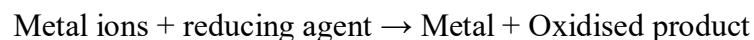
This technique has been used for manufacturing mirrors by the reduction of a complexed metal with the help of a mild reducing agent like formaldehyde.

Advantages:
1. Electrical energy is not used
2. It helps in coating non-conducting objects, non-metallic surfaces like plastic, semiconductors.
3. The throwing power is unlimited.
4. No excess deposit at joints.

5. Edges, inside holes, irregular objects and objects of complex geometries and shapes can easily be coated evenly. It is difficult to coat these surfaces by electroplating.

6. Hydrogen gas is not trapped in the blind holes.

7. Resulting deposits have unique physical, chemical, mechanical and magnetic properties.

8. Coating is harder and less porous than regular coating.

Disadvantages

1. Process is expensive as the chemicals used cost high.

2. Rate of deposition is rather slow.

3. A careful analytical control of the bath is required.

Electroless plating of Nickel

Surface to be plated	Chemical used for activation
Al, Cu, Fe, brass, Au, Ag, Pt, Rh and Co	No activation required and nickel is plated directly on their surface
Stainless steel	By dipping in hot solution of 50% dilute H2SO4
Magnesium alloy	Thin coating of Zn and Cu over it
Non-metallic articles like plastics, glass or quartz	They are first dipped in SnCl2, solution containing HCl followed by dipping in palladium chloride so that a thin activating surface layer of Pd is formed on their surface.

Bath

The coating bath contains the following

- Coating solution – 20 g/l of $NiCl_2$
- Reducing agent – 20 g/l of sodium hypophosphite
- Complexing agents cum exhalant – 15 g/l sodium succinate
- Buffer – 10 g/l of sodium acetate

The pH of the bath is maintained at 4.5 and temperature is 93^0C.

Following reactions take place when the activated surface is dipped in the bath

At cathode : $Ni^{2+} + 2e^- \longrightarrow Ni$
At anode : $H_2PO_2^- + H_2O \longrightarrow H_2PO_3^- + 2H^+ + 2e^-$

Net reaction: $Ni^{2+} + H_2PO_2^- + H_2O \longrightarrow Ni + H_2PO_3^- + 2H^+$
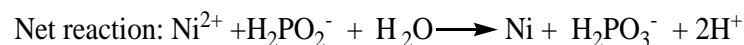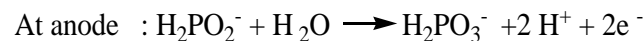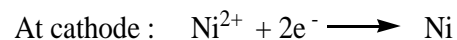
As seen above H+ ions are liberated in the reaction hence the pH of the bath goes down which adversely affects the quality of the plating. Consequently continuous addition of the buffer is essential to maintain the pH. $NiCl_2$ and hypophosphite are also consumed and need to be replenished continuously. In addition to the above reactions there may be formation of phosphorous which results in Ni-P alloy deposition.

Applications

1. Owing to excellent throwing power, this method is applied for coating objects with complex geometrical shapes and also on the internal diameter of tubular parts that are otherwise difficult to access.

2. It is used for plating several components like pistons, fasteners, pipes, valves, shafts and hydraulic systems, fuel injection assemblies.

3.Electroless nickel plating finds use in jewellery, electroless nickel plating on acrylonitrile butadiene styrene polymer is used in decorative items.

4. In electrical industry electroless Ni-P coating is used in making magnetic components.

Electrochemical machining :

Electrochemical machining is a process of a selective dissolution of the anodically connected work piece material submerged in an electrolyte together with an anodically connected tool.

Principally electrochemical machining is similar to Electro polishing where the work piece surface roughness decreases due to the conversion of the atoms into ions and their removal from the surface as a result of a passage of an electric current. Electrochemical machining is generally opposite to electroplating where the metallic ions traveling through the electrolyte solution deposit on the surface of the cathodically connected work piece.

The electrochemical reactions occurring in the electrochemical machining process are as follows:

At the anode the iron atoms covert into the iron ions (cations):

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

The electrons lost by the iron atoms travel to the cathode through the DC power supply.

At the cathode the electrons react with water molecules forming gaseous Hydrogen and hydroxyl ions (anions) according to the reaction:

$$H_2O + 2e^- \rightarrow H_2 + 2OH^-$$
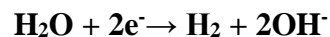
The cations and the anions react in the aqueous solution and create insoluble ferrous hydroxide:

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

The insoluble hydroxide is taken away by the flowing electrolyte and then it precipitates at the tank bottom forming the sludge.

The principle scheme of electrochemical process is presented in the figure below.

Electrochemical machining process
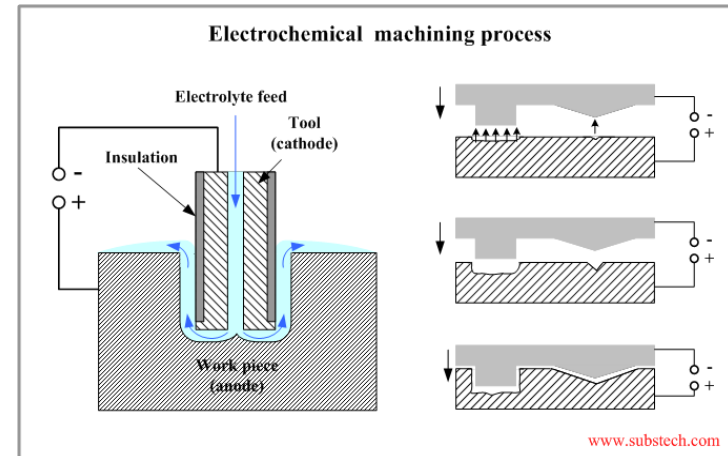
The work piece is mounted in a fixture electrically isolated from the tank and other machine parts. The work piece is connected to the positive terminal (anode) of the Power Supply. The tool is connected to the negative terminal (cathode).

The electrolyte is continuously flowing through a hole in the tool to the gap between the work piece and the tool surfaces.

The tool is moving towards the work piece at a constant speed of about 0.05"/min (1.25 mm/min). The gap between the tool and the work piece is kept constant. Stable behavior of the process is a result of a control of the power supply voltage.

The final shape of the work piece formed as a result of the electrochemical machining process conforms the shape of the tool.

Electrolytes used in electrochemical machining:

- Sodium chloride (**NaCl**) at the concentration of 20% - for ferrous alloys(e.g. Steels and cast irons and cobalt alloys.
- Sodium nitrate (**NaNO₃**) - for ferrous alloys.
- Hydrochloric acid (**HCl**) - for Nickel alloys.
- A mixture of sodium chloride (**NaCl**) and sulfuric acid (**H₂SO₄**) - for nickel alloys.
- A mixture of 10% hydrofluoric acid (**HF**), 10% hydrochloric acid (**HCl**), 10% nitric acid (**HNO₃**) - for Titanium alloys.
- Sodium hydroxide (**NaOH**) - for tungsten carbide (**WC**).
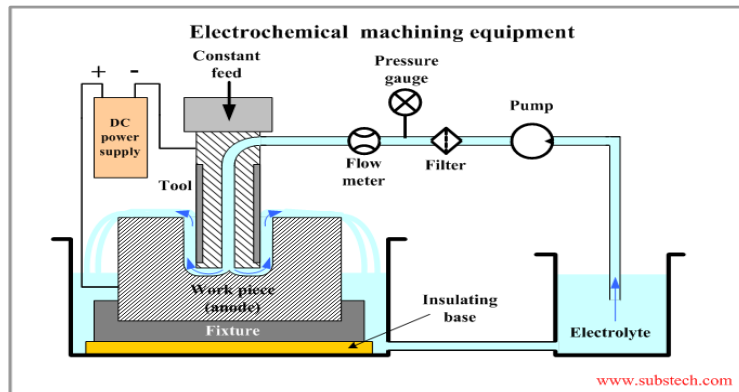
Applications of electrochemical machining
- Machining of hard materials. The process parameters and the tool life time do not depend on the hardness of the work piece therefore electrochemical machining is often used for machining hard materials. Turbine blades and rifle barrels are fabricated by electrochemical machining.
- Producing holes and cavities which cannot be obtained by conventional machining methods.
- Die sinking. Electrochemical machining is often used as an alternative to the cavity type electric discharge machining (EDM).
- Fabrication of thin walled parts. Electrochemical machining does not produce surface stress in the work piece therefore even very brittle and easily deformed materials may be machined in thin walled shapes.
- Grinding of a work piece by a rotating wheel, which performs grinding operation through an electrolyte. The wheel is conductive and cathodically connected. Non-conductive hard particles are set on the wheel surface. The particles provide a constant gap through which an electrolyte is continuously fed. Hard and brittle materials are ground by the method.

Advantages of electrochemical machining:
- The rate of machining does not depend on the hardness of the work piece material.
- The tool does not wear. Soft materials (e.g., copper) may be used for tool fabrication.
- No stresses are produced on the work piece surface.
- No burrs form in the machining operation.
- High surface quality may be achieved.
- High accuracy of the machining operation.

Disadvantages of electrochemical machining:
- Higher cost.
- Electrolyte may cause corrosion of the equipment.
- Large production floor is required.
- Only electrically conductive materials may be machined.
- Not environmentally friendly process.

Electropolishing:

Electropolishing is an electrochemical process in which the atoms of a work piece submerged in an electrolyte convert into ions and are removed from the surface as a result of a passage of an electric current.

In electropolishing the metallic work piece dissolves in the electrolyte in contrast to Electroplating where the metallic ions traveling through the electrolyte solution deposit on the work piece surface.

In an electropolishing cell (see the figure below) the work piece is anode. It is connected to the positive terminal of the direct current power supply. The negative terminal is connected to a cathode plate commonly made of stainless steel, copper or lead. The anode and the cathode are immersed into an electrolyte solution.

Principally electropolishing is similar to Electrochemical machining where the work piece material is removed due to the conversion of the atoms into ions, formation of an insoluble precipitate and its transfer from the surface. The DC power supply, the anodically connected work piece, the electrolyte and the cathode form an electric circuit.
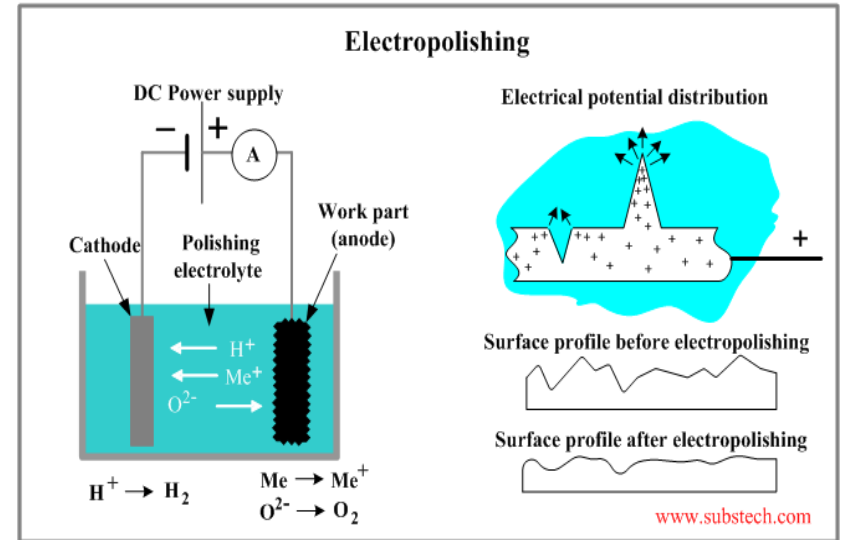
According to Faraday's law the amount of the removed material is directly proportional to the amount of electric charge, passed through the circuit. The amount of electric charge $Q=I*t$ (I – electric current, t – time).

The amount of the metal removed from the work piece surface in an electropolishing process varies from 0.1 to 2.5 mil (2.5-64 μm).

The important feature of the electropolishing process is its ability to dissolve asperities (peaks) on the work surface much faster than the material in "micro-valleys". Such selective dissolution is a result of different values of the electrical potential of the peaks and valleys. The positive charge of the anodically connected work piece is concentrated in the peaks where the current density is higher than average which causes a selective dissolution of the peaks and smoothening the surface.

Brightening:

- Brightening is an effect of lower surface roughness produced by electropolishing operation.
- The surface of the parts produced by metalworking operations (cutting, Rolling, stamping, Drawing) is relatively rough and has to be improved by a polishing operation.
- One of the polishing techniques is a mechanical polishing. However mechanical polishing produces scratches, debris and may leave the abrasive particles on the work surface. Additionally mechanical polishing causes a formation of residual stresses in the surface layer.
- In contrast to mechanical polishing electropolishing produces a surface free of both mechanical defects and residual stresses.
- Surface roughness is a parameter of the surface quality commonly measured as the average deviation of the surface profile from the mean line.
- Electropolishing reduces the profile peaks resulting in smootheningthesurface.

    The improvement of the surface roughness achieved by electropolishing is commonly a half of the original roughness value.

Deburring:

The selective dissolution of prominent point (peaks) on the work surface in the electropolishing process is utilized in deburring operation.

Small burrs (up to 0.5 mil/13 μm) produced in some various metalworking operations may be effectively removed by electropolishing.

Like in the peaks on the surface the density of the electric current passing through burrs is higher than the average value therefore the burrs material is removed much faster. The resulting surface is electropolished and free of burrs.

In contrast to mechanical deburring (e.g. vibratory deburring) electropolishing does not produce scratches and residual stresses on the work surface.

Passivating:

Passivation is a chemical process of a restoration of the corrosion resistance of a contaminated stainless steel part.

The contaminant particles embedded into the surface disturb the protecting layer of chromium oxide and allow oxidation of iron (rust formation).

In the conventional passivation process the contaminants are removed by a treatment in 20% nitric acid.

The contaminating particles may also be removed by electropolishing. Additionally electropolishing produces higher surface concentration of chromium due to the preferential dissolution of iron and nickel atoms. In contrast to the treatment by nitric acid the passivation by electropolishing does not produce distortion and does not cause hydrogen embrittlement.

Stress relieving:

Tensile stresses concentrated in the part surface reduce its Fatigue.

The stresses may be induced in various fabrication stages: metalworking operations (stamping, Rolling, Drawing, grinding), heat treatment, vibratory deburring, Electroplating. The thickness of the layer with the surface stresses is about 1 mil (25 μm).

Electropolishing allows to remove the stressed surface skin from the work piece.The fatigue strength is additionally improved due to smoothening the surface of electropolishing. The surface

defects such as scratches, foreign particles embedded into the surface, tool produce notch effect decreasing the fatigue limit.

Defects free electropolished surface provides an increased fatigue strength.

Benefits of electropolishing:
- Bright appearance;
- Absence of abrasive scratches;
- Improved fatigue strength due to stress relieving and defects free surface;
- Lower coefficient of friction due to smoother surface (reduced microasperities);
- Better corrosion resistance;
- Allows processing fragile and delicate parts.

Disadvantages of electropolishing:
- Rough surface defects cannot be removed;
- Electropolishing multiphase alloys may cause roughening due to selective dissolution of different phases.

Electrophoretic deposition EPD

Electrophoretic deposition EPD is a method of coating a conductive part with particles suspended in a fluid dispersion under the influence of an electric field applied between the work part and the counter electrode.

Similar to Electroplating coating electrophoretic deposition utilizes electrically charged particles moving between two electrodes (an anode and a cathode) immersed in a liquid media. However in contrast to conductive electrolytes used in electroplating, the fluids of electrophoretic dispersions are dielectric.

In addition the electroplating coatings are built from metallic ions converted into atoms when discharged at the cathode, whereas in electrophoretic process the coating is formed by a deposition of relatively large powder particles which may be polymeric, ceramic or metallic.

The following characteristic features define electrophoretic deposition:
- There is a stable dispersion of particles in a solvent (a colloid).
- The particles gain a surface charge as a result of an electrostatic interaction with the molecules of the solvent.
- The particles are capable to move in the suspension towards the work part under the influence of a voltage imposed between the work part and the counter electrode (the phenomenon called electrophoresis).
- A rigid deposition composed of condensed particles is built up on the work part surface in contrast to dip coating - a painting process in which the concentration of particles in the layer adhered to the work part is the same as the concentration of the particles in the bulk suspension.
- The deposited coating is adhered to the surface of the work part.

When a voltage is applied between the electrophoretic electrodes the charged particles start to migrate towards the electrode with the opposite electric polarity. The particles are deposited first of all at the surface areas with the highest electric potential. The formed coating decreases the potential of such areas and equalizes the potential distribution over the part surface. As a result a uniform and even film forms over the whole part surface including the surface of cavities, edges and corners. The coating thickness is determined by the voltage value which is typically 25-400 V. After a coating of a certain thickness is built the deposition process stops.

If the electrophoretic dispersion is aqueous, the voltage applied between the immersed electrodes immersed causes water molecules to decompose.

At the anode Oxygen is generated according to the oxidation reaction:

$$2 H_2O \rightarrow O_2 + 4 H^+ + 4e^-$$
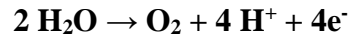
The reduction reaction at the cathode results in a formation of Hydrogen:

$$H_2O + 2e^- \rightarrow H_2 + 2 OH^-$$
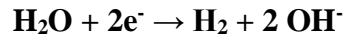
As a result of electrolysis the solution surrounding the anode becomes acidic and in the cathode region - alkaline. Changes of the solution PH destabilize the colloid causing the particles to coagulate and deposit on the electrode surface.

Polarity of electrophoretic deposition. The electric charge of the dispersed particles may be either positive or negative. The positively charged particles are attracted to the cathode. The process of a deposition of positively charged particles is classified as cathodic electrophoretic coating in contrast to anodic electrophoretic coating related to the deposition of negatively charged particles.

Anodic electrophoretic process: is less expensive. It produces coatings of good aesthetic appearance. However the anode metal slightly dissolves in the solvent producing metallic ions which are incorporated in the coated film. The metallic contamination of anodic coatings decreases their corrosion resistance. Therefore anodic electrophoretic coatings are mostly used in indoor applications.

Cathodic electrophoretic process: results in a deposition of coatings with very low metallic contamination. Cathodic coatings are characterized by high corrosion resistance and durability in both indoor and outdoor applications.

Electrophoretic coating process: The industrial applications of electrophoretic deposition are referred to as e-coating, electrocoating, electrophoretic painting or electrophoretic coating.

The deposition process includes the following stages:
- Hanging the work parts
- Alkaline cleaning
- Rinsing
- Acid cleaning
- Immersion in adhesion promoter (wetting agent)
- Electrphoretic deposition
- Rinsing and dispersion recovery
- Rinsing in de-ionized water
- Dehydration oven
- Curing

The most popular applications of electrophoretic deposition are cathodic coating of automotive parts with epoxy, acrylic and polyurethane films.

The coatings have excellent scratch resistance and corrosion resistance. Acrylic and polyurethane coatings are also resistant against ultra-violet light.

Etching:

Etching PCB is to use the materials of chemical reactions or physical impact of technologies that are removed. Etching techniques can be divided into wet etching and dry etching, chemical solution used in wet etching through chemical reactions in order to achieve the purpose of etching, dry etching is usually a plasma etching, its effect may be the impact chips by plasma surface physics, or possibly a plasma activated chemical reaction between base and surface atoms, or even role may be a composite of the two.

PCB Etching:

Currently used for print circuit board etching of solvents are iron (Ferric Chloride), cupric chloride (Cupric Chloride), alkaline ammonia (Alkaline Ammonia), sulfuric acid hydrogen peroxide (Sulfuric Acid + Hydrogen Peroxide) etching fluid, ammonium persulfate, sulfuric acid – chromic acid etching solution. Like the PCB manufacturing in Fusion PCB of Seed. Etching liquid are mainly copper chloride solution, ferric chloride liquid, alkaline etching, acid/hydrogen peroxide (hydrogen peroxide) etching.

Chloride copper etched liquid by chloride copper ($CuCl_2$ Castle, $2H_2O$) + hydrochloride (HCl) + hydrogen peroxide (H_2O_2) + water (H_2O) composition; three ferric chloride etched liquid is by three ferric chloride ($FeCl_3$) + hydrochloride (HCl) + water (H_2O) composition of; alkaline etched liquid of main components has copper ammonia complex ion; sulfuric acid/hydrogen peroxide (hydrogen peroxide) etched liquid to sulfuric acid and hydrogen peroxide (hydrogen peroxide) mainly components.

PCB etching process and copper chloride and ferric chloride market, PCB manufacturers some 95% using copper chloride ($CuCl_2$), IC substrate maker about 80% using ferric chloride ($FeCl_3$), 20% using copper chloride ($CuCl_2$). You can try etching PCB at home.

UNIT – II
CORROSION AND ELECTROCHEMICAL PROCESS
QUESTION BANK
PART - A

1.Define corrosion

Corrosion is defined as the gradual destruction of a metal or alloy by the chemical or electrochemical reaction with its environment.

2. Why do metals undergo corrosion?

Most of the metals (except noble metals) naturally exist in combined form. During metallurgy metals are extracted from the ores by reduction. In pure metallic state these are unstable and considered to be in the excited state. So these metals have a tendency to attain stable state, which is known as corrosion.

3. What are the types of corrosion?

Based on the environment, corrosion is classified into
(i) Dry (or) chemical corrosion   (ii) Wet (or) Electrochemical corrosion.

4. What are the consequences of corrosion?

- The efficiency of machine will be lost due to the loss of useful properties of metals.
- Products get contaminated due to corrosion
- Increase in maintenance and production cost.
- Preventive maintenance like metallic (or) Organic coating is required.
- Toxic products are released

5. What is Pilling bedworth rule?

The ratio of the volume of the metal oxide formed to the volume of metal is known as Pilling – Bedworth rule. According to this, If the volume of the oxide layer formed is less than the volume of the metal, the oxide layer is porous and non protective.
Examples: Na, Mg, Ca

If the volume of the oxide layer formed is greater than the volume of the metal, the oxide layer is non porous and protective.
Examples: Pb, Sn

6. What is H_2 embrittlement?

When metals comes in contact with H_2S at ordinary temperature causes evolution of atomic hydrogen .This atomic hydrogen diffuses into the metal and collects in the voids, where it recombines into molecular hydrogen developing very high pressure, which causes cracks and blisters in the metal. This is known as hydrogen embrittlement.

7. Comment on liquid-metal corrosion.

Liquid-metal corrosion is due to the chemical action of flowing liquid metal at high temperature on solid metal or alloy. The corrosion reaction involves,

    i.   either dissolution of solid metal in liquid metal [or]

    ii.   internal penetration of the liquid metal in to the solid metal. This causes weakening of the solid metal.

Example: Devices used for nuclear power plant.

8. Write the elemental reactions involved during electrochemical corrosion.
i. In the anodic part, oxidation (or) dissolution of metal occurs

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

ii. In the cathodic part, reduction occurs, which depends on the nature of the corrosive environment

      (c) If the corrosion environment is acidic, hydrogen evolution occurs

$$2H^+ + 2e^- \longrightarrow H_2$$

      (d) If the corrosive environment is slightly alkaline or neutral, hydroxyl ion is formed

$$\tfrac{1}{2}\, O_2 + 2e^- + H_2O \longrightarrow 2OH^-$$

9. What type of corrosion takes place when a Zinc rod dipped in HCl solution?

Hydrogen evolution corrosion takes place. Since Zinc displaces hydrogen easily from acids.

10. State two conditions for wet corrosion to take place.

This type of corrosion occurs in moist environment. It occurs
(i) When the conducting liquid is in contact with metal
(ii) When two different metals are immersed or dipped partially in the solution.

11. Differentiate chemical and electrochemical corrosion

Chemical corrosion	Electrochemical corrosion
Occurs only in dry condition	Occurs in the presence of moisture or electrolyte
Due to direct chemical attack of the metal by environment	Due the setting up of large number of anodic and cathodic areas
Corrosion products accumulate in the same place where corrosion occurs	Corrosion occurs at the anode, while the product gathered at cathode
Self controlled	Continuous process
Follows adsorption mechanism	Follows electrochemical reaction

12. What is galvanic corrosion? Discuss

When two different metals are in contact with each other in presence of an aqueous solution or moisture, galvanic corrosion occurs.The more active metal (more negative electrode potential) acts as anode and less active metal (positive electrode potential) acts as cathode.
Example:
(a) Zn – Fe couple : Zn(- 0.76V) is more active and dissolves in preference to Fe(- 0.44V)
(b) Fe – Cu couple: Iron (- 0.44V) is more active than Cu (+0.34V) and undergoes corrosion in preference to Cu.

13. Iron corrodes faster than aluminium, even though iron is placed below aluminium in the emf series. Why?

This is because aluminium forms a non-porous, very thin, tightly adhering protective oxide film on its surface and this film does not permit corrosion to occur.

14.How can you minimize galvanic corrosion?

Galvanic corrosion can be minimized by
    a. providing an insulating material between the two metals
    b. providing smaller area for cathode and larger area for anode

15. Rusting of iron is quicker in saline water than in ordinary water. Why?

The presence of sodium chloride in water leads to increased conductivity of water layer in contact with the iron surface, thereby corrosion current increases and rusting is speeded up.

16. Copper equipment should not possess a small steel bolt. Give reason.

Iron (- 0.44V has negative electrode potential) acts as anode and while copper equipment (+ 0.34 V has positive electrode potential) acts as cathode resulting a galvanic corrosion. Since anodic area is very small, it is completely corroded in due course of time and the action of bolt is finished, i.e., the equipment loses its bolt after sometime.

17. In a structure, dissimilar metals should not be allowed to come in contact with each other. Why?

When two dissimilar metals comes in contact with each other,it leads to galvanic corrosion, metal having negative electrode potential undergoes corrosion.

18. Bolt and nut made of the same metal is preferred in practice. Why?

Bolt and nut made of the same metal is preferred, because such a combination will not permit galvanic corrosion to take place.

19. What is differential aeration (concentration cell)corrosion?

This type of corrosion occurs when a metal is exposed to different concentrations of Oxygen. The part of metal which is more exposed to oxygen (air) act as cathode and unaffected. The other part of the metal, which is less, exposed to oxygen(air) act as anode and undergoes corrosion.

20. What is pitting corrosion? Why is it severe?

Pitting is localised attack, resulting in the formation of a hole around which the metal is relatively unaffected. Pitting corrosion is dangerous because the formation of small anodic and large cathodic areas results in severe corrosion of the anode region.

Example: Metal covered by a drop of water or aqueous NaCl, sand, dust.. The area covered by the drop acts as an anode due to less oxygen concentration and suffers corrosion Uncovered area acts as cathode

21. How does purity of a metal influence corrosion?

100% pure metal will not undergo any corrosion,presence of impurities will create heterogeneity resulting galvanic cells.

Effect of impurites on the rate of corrosion of Zn

% purity of Zn	99.999	99.99	99.95
Corrosion rate	1	2650	5000

22. What are the objectives of electroplating?

   (i)   To increase the resistance to corrosion
   (ii)   To improve the hardness and appearance
   (iii)   To increase the decorative value
   (iv)   To increase the chemical attack
   (v)   To improve the surface properties

23. What is the need for preliminary treatment of metal surfaces?

Generally metal surfaces are covered with impurities like rust, scale, oil and grease. Presence of these impurities will produce porous and discontinuous coatings.

In order to obtain uniform, smooth, cohesive and adherent coating, these impurities must be removed from the metalsurfaces to be coated

24. What is electroless plating?

Electroless plating is a technique of depositing a noble metal (noble metal salt solution) on a catalytically active surface of the
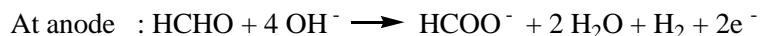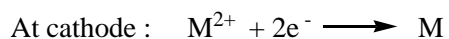
base metal by using a suitable reducing agent without electric current.

The reducing agent reduces the metal ions to metal, which gets plated over the catalytically activated surface giving a uniform coating.

25. Bring out the reactions taking place during electroless plating

The object to be plated, is immersed in the bath containing the salt of the metal and reducing agent. The metal ion from the solution will be reduced to the corresponding metal and gets plated over the surface of the object

Reactions

At cathode : $M^{2+} + 2e^- \longrightarrow M$

At anode : $HCHO + 4\,OH^- \longrightarrow HCOO^- + 2\,H_2O + H_2 + 2e^-$

Net reaction: $M^{2+} + HCHO + 4\,OH^- \longrightarrow HCOO^- + 2\,H_2O + H_2$

26. What are the advantages of electroless plating?
    i.   No electricity is required
    ii.   Can be easily plated on insulators
    iii.   Complicated parts can be easily electroplated
    iv.   coating possess unique mechanical, chemical and magnetic features

27. What is electrophoretic coating?

Electrophoretic deposition EPD is a method of coating a conductive part with particles suspended in a fluid dispersion under the influence of an electric field applied between the work part and the counter electrode.

28. What is electrochemical machining?

Electrochemical machining is a process of a selective dissolution of the anodically connected work piece material submerged in an electrolyte together with an anodically connected tool.

PART-B
    1. Explain the rusting of iron with the help of electrochemical theory of corrosion.
    2. Explain chemical corrosion. Also explain the intensity of corrosion varying with the nature of oxide layer of formation over metal.
    3. Explain galvanic corrosion with an example.
    4. State and also explain the various factors that influences the rate of corrosion
    5. Write notes on (i) Intergranular corrosion and (ii) Stress corrosion.
    6. What is electroplating? Discuss the plating composition, mechanism and application of electroplating of copper.
    7. What is electroless plating? Write a short notes on electroless nickel plating and discuss its applications.
    8. Discuss the various process involved in electropolishing.
    9. Describe the electrophoretic coating process in detail.
   10. Write notes on electrochemical machining process.

UNIT – II
CORROSION AND ELECTROCHEMICAL PROCESS
CONTENT BEYOND THE SYLLABUS

Corrosion control

Control of corrosion by modifying metal

1. **By selection of the metal :** Noble metals are used in ornaments and surgical instruments
2. **By using pure metal :** Pure metals have high corrosion resistance
3. **By alloying :** Stainless steel containing Cr produces a coherent oxide film, which protects steel
4. **By proper design :**

(i) Avoid galvanic corrosion

poor design   Good design
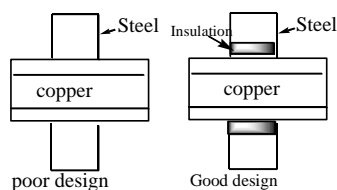
: If two metals are , galvanic corrosion occurs. Galvanic corrosion can be prevented by

(a) Selecting metals as close as possible in the emf series

(b) Providing smaller area for cathode

(c) Inserting an insulating material between two metals

(ii) Drainage affects corrosion

poor design   good design
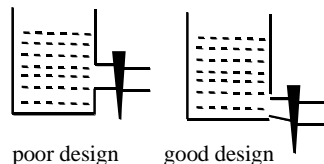
Tanks and other containers must be designed in such a way that the whole of the liquid be drained off completely

(iii) Avoid sharp corners and edges

(iv) Avoid crevices

Welded joints should be preferred to riveted joints

5. By cathodic protection

The metal is forced to behave like cathode

Sacrificial anodic protection method

The metallic structure to be protected is made cathode by connecting it with more active metal

Corrosion will be concentrated only on more active metal

The artificial anode gets oxidised protecting the original metallic structure

Hence, this process is called Sacrificial anodic protection

Al, Zn and Mg are used as sacrificial anodes

This method is used for the protection of ships and boats

Applications

i.   Protection of underground pipelines
ii.   Insertion of Mg sheets in boilers to prevent formation of rust
iii. Ca metal is used to reduce engine corrosion

Corrosion inhibitors

Corrosion inhibitor is a substance which reduces the corrosion of a metal, when it is added to corrosive environment

Types of inhibitors

1. Anodic inhibitors :

Examples : Chromates, nitrates and tungstates if transition metal ions with high oxygen content

Anodic inhibitors are those that prevent corrosion occuring at the anode by forming an insoluble compound with the metal ions.

These precipitates get adsorbed on to the metal surface forming a protective film and hence reduce corrosion

2. Cathodic inhibitors :

In electrochemical corrosion, the cathodic reactions are of two types, depending on the environment

(a) In an acidic solution :

Examples : Organic inhibitors like amines, mercaptans, thiourea, heavy metal soaps

In the acidic solution, the cathodic reaction is evolution of H_2

The corrosion can be reduced in 2 ways

(i) By slowing down the diffusion of H^+ to the cathode. This is done by organic inhibitors

(i) By increasing the overvoltage of H_2 evolution. This can be done by adding antimony or arsenic oxides, which deposit adherent film of metallic As or Sb at the cathodic areas.

(b) In neutral solution:

Example : Sodium sulphite, hydrazine

Corrosion can be reduced by

i.   By eliminating oxygen from neutral solution using a reducing agent

ii.   Eliminating OH^- by adding Mg, Zn or Ni salts.

III. Vapour phase inhibitors

Examples : Dicyclohexyl ammonium nitrate, benzotriazole

Vapour phase inhibitors readily vaporise and form a protective layer on the metal surface.

These are used in storage containers, packing materials, sophisticated instruments

UNIT III
BATTERIES AND FUEL CELLS

"*Man's brain may be compared to an electric battery...a group of electric batteries will provide more energy than a single battery.* "
Napoleon Hill .

3.1 INTRODUCTION

Batteries are the storehouses of electrical energy. They provide well contained energy conversion devices which greatly contributed to the needs of mankind. Zero emission vehicles of the future will be battery powered only. Many non-polluting energy conversion devices such as photovoltaic systems require the concomitant use of rechargeable batteries for energy storage.

In 1799, Alessandro Volta developed the first electrical battery. This battery, known as the Voltaic Cell, consisted of two plates of different metals immersed in a chemical solution. Faraday was the first to use the word "electrode" as a general term for a pole of a battery, 'anode' = negative electrode and 'cathode' = positive electrode of a battery.

3.1.1 BASIC COMPONENTS OF A BATTERY

Anode

Anode is the electrode where oxidation takes place. Here electrons are released to the external circuit. It is marked negative as it is relatively more negative when compared to the other electrode. During recharging, this acts as cathode. Anode material should undergo oxidation easily. Lithium, Zinc, Cadmium, Lead, etc. are widely used as anode.

Cathode

Cathode accepts the electrons produced at anode and the active pieces gets reduced. It is the positive terminal of the cell. During recharging, this acts as the anode. Cathode material should be stable and must facilitate reduction reaction. Graphite, Lead, Nickel etc. are widely used as cathode materials.

Electrolyte

Electrolyte is an ionic conductor that provides connectivity between anode and cathode of the battery. The electrolytes used are acids, bases or salts having high ionic conductivity. Sometimes, solids are also used as electrolytes. It allows electronic movement between the electrodes during charging and discharging.

Separator

Direct contact of anode and cathode produces internal short circuit. These are insulating membrane that prevents or isolates anode and cathode electrically to prevent short circuit. Rubber, cellulose, vinyl polymers etc are widely used as seperators.

A battery is an electrochemical cell or many electrochemical cells connected in series, to be used as a source of direct electric current at a constant voltage". A battery is a device which converts chemical energy into electrical energy through various chemical reactions.

A cell consists of an anode, cathode and an electrolyte. A battery consists of number of anodes, cathodes and electrolytes or a combination of two or more cells.
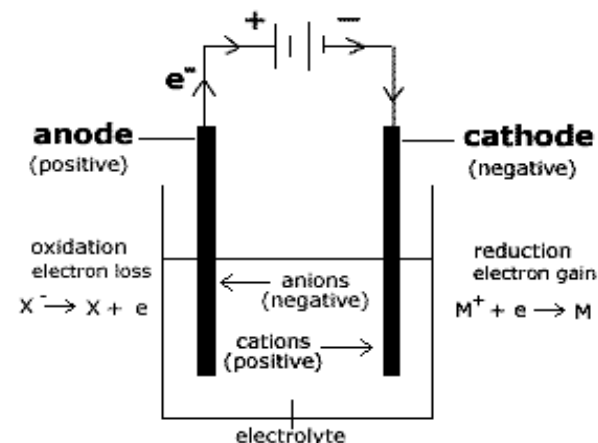
Fig 3.1 **Electrochemical cell**

Requirements of a battery

- It should have more storage capacity.
- It should be light and compact.
- It should provide power for longer time period.
- It should be capable of recharged.
- It should give constant voltage
- It should be resistance to self-discharge.
- It should be cheaper.

3.1.2 CHARACTERISTICS OF BATTERY

1. Voltage
2. Current
3. Capacity
4. Energy Efficiency
3. Power Density
6. Discharge& Discharge Rate
6. Cycle Life
7. Self Life

Voltage (Cell Potential)

Voltage of a battery is an electromotive force or difference of potential between any two electrodes and it is denoted by (V_C - V_A).

The theoretical standard cell voltage can be determined using E^0 values:

E^0cell = E^0 cathode – E^0 anode

The theoretical cell voltage is modified by the Nernst equation,

$E_{cell} = E^0_{cell} + (2.303RT)/nF \log[P/R]$

(where, P=product, R=reactant)

If the difference in the standard electrode potential is more, higher is the emf of the cell.

Current

Current is a measure of how many electrons are flowing through a conductor. Current is usually measured in amperes (A) and is the amount of charge flowing per second.

Current(I) = q/t, with units of A=Cs^{-1}

Current flow over time is defined as ampere-hours (amp-hours or Ah), a product of the average current and the amount of time it flowed.

Capacity

The energy stored in a battery, is called the battery capacity. It is a measure of the charge stored by a battery, determined by the amount of electrical energy the battery can deliver over certain period and is measured in Ampere-hour (Ah), capable of being provided by a battery during discharge.

Its value depends upon the size of the battery and is given by Faraday's relation,

$$C = \frac{wnF}{M}$$

Where, W = mass of active material and M = molar mass of the active material

It is the number of moles of the electro active material associated with the complete discharge of the cell.

Energy Efficiency

It is defined as the ratio of useful energy output to the total energy input.

$$\% \text{ Energy efficiency} = \frac{\text{Energy released during discharge}}{\text{Energy required during discharge}} \times 100$$

Energy efficiency is using less energy to provide the same service. There are other definitions is a good operational one.

Power Density or Specific Power

Storage density of electricity: It is the amount of electricity in Ampere per unit mass, which the storer can hold. In other words, it is the capacity per unit mass of the battery.

Energy density: It is the amount of energy stored in a given system or region of space per unit volume.

Power density (W/Kg or W/lit) is the power of the battery per unit weight that represents the speed at which the energy can be delivered to the load.

Power density = Energy density / Time

In energy transformers including batteries, fuel cells, motors etc., and also power supply units or similar, power density refers to a volume. It is then also called volume power density, which is expressed as W/m^3.

Discharge

Discharge is the conversion of chemical energy stored within a cell to electrical energy and subsequent withdrawal of this electrical energy into a load.

Discharge rate: An expression of the speed which a battery is being discharged, at a specific point in time.

Capacity Retention / Stability / Cycle Life

Capacity retention is derived from the number of cycles that the cell undergoes charge-discharge processes. Although factors like electrolyte stability, temperature, etc, influence the capacity of degradation, phase stability of the electrode is the prime component in determining the cycle life of a cell/ battery.

The actual operating life of the battery is affected by the rate and depth of cycles and by other conditions such as temperature and humidity. The higher the (Depth of Discharge) DOD, the lower the cycle life.

Self-Life (Expiration Date)

Self-life is the period of time a battery can be stored without significant deterioration. Aging is subject to storage temperature and state of charge. While primary batteries have a self life up to 10 years, lithium-based batteries are good for 2 to 3 years, nickel-based batteries are good for 3 years, etc.

3.2 TYPES OF BATTERIES

Batteries are classified into three categories depending upon the recharging capacities:
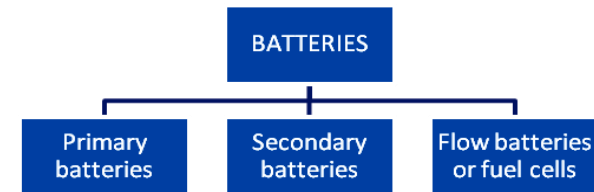
1. Primary battery or Primary cells

These are cells in which the electrode reactions cannot be reversed by passing an external current. The reactions are possible only once and the battery will be dead after use. Hence it is non - rechargeable battery.

Eg: Daniel cell, Leclanche cell, Mercury cell.

2. Secondary battery or Secondary cells

These are cells in which the electrode reactions can be reversed by passing an external current. Thus a secondary battery may be used through a large number of cycles of charging and discharging. Hence it is a rechargeable battery.

Eg: Lead acid battery, Ni-Cd battery.

3. Fuel cell or flow battery

It is a device which converts chemical energy of the fuel directly into electrical energy. The chemicals used are usually very simple ones such as H_2 and O_2.

Eg: H_2-O_2 fuel cell, Methanol fuel cell etc.

Table 3.1   Differences between Primary and Secondary batteries

Primary Batteries	Secondary batteries
Primary batteries are used only once	Secondary batteries can be used for several cycles.
Irreversible battery	Reversible battery
They are cheap.	They are expensive.
Initial cost is low.	Initial cost is very high.
Disposable.	Periodic recharging and regular maintenance is required.

3.3 PRIMARY BATTERIES

DRY CELL (*Leclanche Cell*)

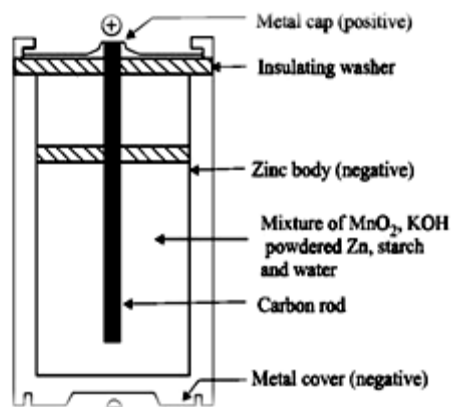- This is the most familiar type of dry cell. It consists of a zinc container as anode, and graphite rod as cathode.

Fig 3.2 **Dry Cell**

- The electrodes are separated by electrolyte mixture i.e., graphitised manganese dioxide and a paste of NH$_4$Cl and ZnCl$_2$.
- The MnO$_2$ is mixed with graphite powder to increase the conductivity.

- Starch is added to the electrolyte (NH$_4$Cl, ZnCl$_2$ and MnO$_2$) to make it into a thick paste.
- To reduce leakage the cell is enclosed in polypropylene cylinder.
- The cell can be represented as:
$$Zn/Zn^{2+}, NH_4^+ / MnO_2/C$$
- The cell reactions are:

At Anode: $Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$

At Cathode: $2MnO_{2(s)} + H_2O + 2e^- \longrightarrow Mn_2O_{3(s)} + 2OH^-_{(aq)}$
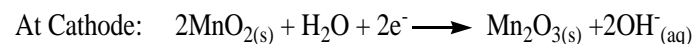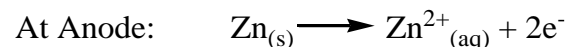
- However, an acid base reaction between OH$^-$ and NH$_4^+$ (derived from NH$_4$Cl

  evolves NH$_{3(g)}$ which disrupts the current flow.

$NH_4^+_{(aq)} + OH^-_{(aq)} \longrightarrow NH_{3(g)} + H_2O_{(l)}$
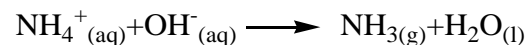
- This is prevented by a reaction of NH$_{3(g)}$ with Zn^{2+} (from ZnCl$_2$) to form the

  complex ion [Zn (NH$_3$)$_2$]Cl $_{(s)}$. Hence the reactions at two electrodes are:

$2MnO_{2(s)} + 2NH_4^+_{(aq)} + 2e^- \longrightarrow [Zn(NH_3)_2]Cl_{2(s)}$

$Zn_{(s)} + 2NH_4^+_{(aq)} + 2Cl^-_{(aq)} + 2MnO_{2(s)} \longrightarrow Mn_2O_{3(s)} + [Zn(NH_3)_2]Cl_{2(s)} + 2H_2O$
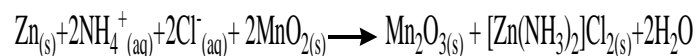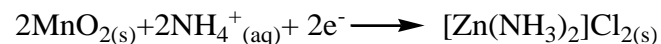
- Thus, the reduction reaction occurs within the moist paste comprised of NH$_4$Cl and MnO$_2$. The NH$_3$ which is liberated reacts with Zn^{2+} from ZnCl$_2$ to form the complex [Zn (NH$_3$)$_2$]Cl $_{(s)}$.
- The dry cell 'couple' produces about 1.3 volts.

Disadvantages

- When current is drawn rapidly from it, products build up on the electrodes thereby causing drop in voltage.
- Acidic NH$_4$Cl slowly corrodes the zinc container of the dry cell, even when the cell is not in use. Hence, dry cell becomes dead after a long time, even it is not used.

Uses

Dry cell finds applications in flash-lights, transistor radios, calculators, etc.

3.4 SECONDARY STORAGE BATTERIES
3.4.1 Lead-Acid Battery

- A lead-acid battery is a storage battery which can operate both as a voltaic cell and as an electrolytic cell. When it act as voltaic cell it supplies electrical energy, on recharging, it acts as an electrolytic cell.
- It consists of lead (Pb) as the anode , lead dioxide (PbO_2) as the cathode and
  sulphuric acid of density 1.30 gm/ml acts as electrolyte.
- Six lead-acid electrochemical cells connected in series are placed in polypropylene container.
- The cell may be represented as: $Pb/PbSO_4$ // H_2SO_4 (aq) / PbO_2 / Pb
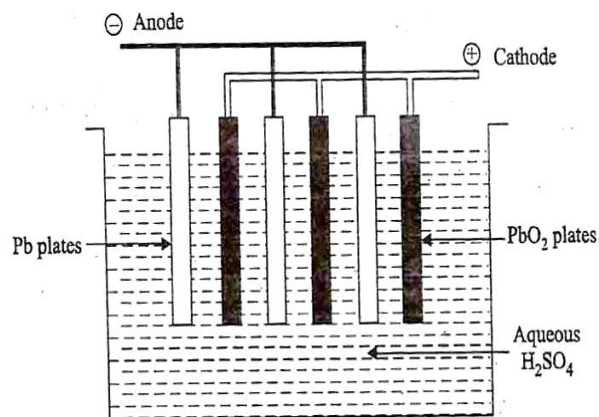
Fig 3.3 **Lead acid battery**

Working
Discharging

When the lead-acid storage battery operates, the following reaction occurs.

At anode*:* Lead is oxidized to Pb^{2+} ions, which further combines with SO_4^{2-} forming insoluble $PbSO_4$.

$$Pb_{(s)} \longrightarrow Pb^{2+}(aq) + 2e^-$$
$$Pb^{2+}_{(aq)} + SO_4^{2-}_{(aq)} \longrightarrow PbSO_{4(s)}$$
$$\overline{Pb_{(s)} + SO_4^{2-}_{(aq)} \longrightarrow PbSO_{4(s)} + 2e^-}$$
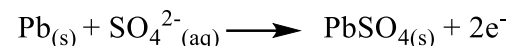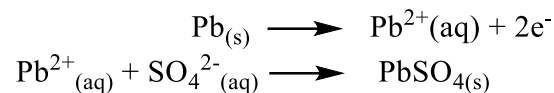
At cathode*:* PbO_2 is reduced to Pb^{2+} ions, which further combines with SO_4^{2-} forming insoluble $PbSO_4$.

$$PbO_{2(s)} + 4H^+ + 2e^- \longrightarrow Pb^{2+}_{(aq)} + 2H_2O$$
$$Pb^{2+}_{(aq)} + SO_4^{2-}_{(aq)} \longrightarrow PbSO_{4(s)}$$
$$\overline{PbO_{(s)} + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_{4(s)} + 2H_2O}$$
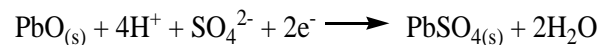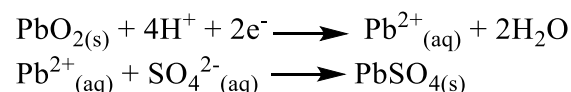
Overall cell reaction
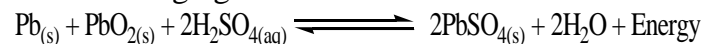
discharging
$$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightleftharpoons 2PbSO_{4(s)} + 2H_2O + Energy$$
charging

From the above cell reactions, it is clear that $PbSO_4$ is precipitated at both the electrodes and H_2SO_4 is used up. As a result, the concentration of H_2SO_4 decreases and hence the density of H_2SO_4 falls below 1.2 gm/mol. Therefore, the battery needs recharging.

Charging

The cell can be charged by applying electric current across the electrodes that is slightly higher than the cell current in the opposite direction. The electrode reaction gets reversed. As a result, Pb is deposited on anode and PbO_2 on the cathode. The density of H_2SO_4 also increases.

The net reaction during charging is :

$$2PbSO_{4(s)} + 2H_2O + Energy \underset{\text{discharging}}{\overset{\text{charging}}{\rightleftharpoons}} Pb_{(s)} + PbO_{2(s)} + 2H_2SO_4$$
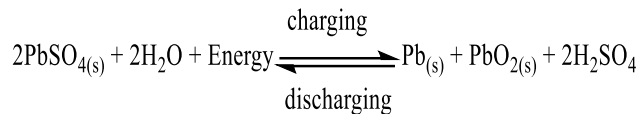
Advantages

- It produces very high current.
- It is made easily.
- Six cells can make a car battery.
- Internal resistance is low.
- It is expected to function effectively for 300-330 cycles.

Disadvantages of lead-acid batteries

- Very large in size and heavy weight.
- Possibility of leakage as electrolyte is liquid.
- The self-discharging rate is low when compared to other rechargeable batteries.
- The performance of the battery at low temperatures is poor as sulphuric acid becomes viscous, therefore flow of current gets reduced.
- Recycling of the battery causes environmental hazards.
- Mechanical strain and normal bumping reduces battery capacity.
- The lead acid battery has the lowest energy density, making it unsuitable for handheld devices that demand compact size.

Uses

- Lead storage cell is mainly used in automobiles like cars, buses and trucks.
- It is used in gas engine ignition, telephone exchanges, hospitals and power stations.
- It is also used in Uninterrupted Power Supply (UPS), as a power system which provides current constantly without a break.

3.4.2 Nickel-Cadmium (NICAD) battery

- A Nickel-Cadmium battery is a type of alkaline storage battery. It is a portable rechargeable cell and its cell voltage is fairly constant about 1.4 volt.
- In a Ni-Cd cell, the anode is cadmium and the cathode is nickel oxide (NiO_2). The electrolyte is a solution of KOH. The electrode and electrolytes are enclosed in a sealed container.

It is represented as: Cd / Cd(OH)$_2$ // KOH / NiO$_2$ / Ni

Working
Discharging

The NICAD battery operates when cadmium is oxidised to Cd^{2+} ions and insoluble Cd (OH)$_2$ is formed. Ni^{2+} ions then combine with OH$^-$ ions to form Ni (OH)$_2$.
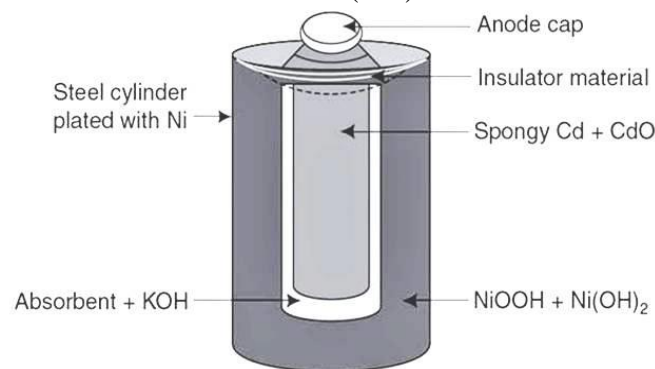
Fig 3.4 **NICAD Battery**

At anode : Cd is oxidized to Cd2+ and combines with OH- to form Cd(OH)2

$$Cd_{(s)} + 2OH^- \rightleftharpoons Cd(OH)_{2(s)} + 2e^-$$
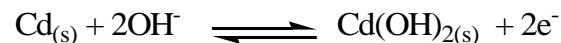
At cathode: NiO2 gains electrons (Ni undergoes reduction from +4 to +2) Ni2+ then combines with OH- to form Ni(OH)2.

$$NiO_{2(s)} + 2H_2O_{(l)} + 2e^- \rightleftharpoons Ni(OH)_{2(s)} + 2OH^-$$

Overall Reaction

$$Cd(s) + NiO_2 + 2H_2O \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}}$$

$$Cd(OH)_{2(s)} + Ni(OH)_{2(s)} + Energy$$
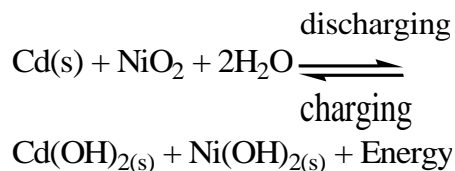
Charging

The cell can be recharged by passing an excess current in the opposite direction to that of the cell current, the electrode reactions get reversed. During charging Cd gets deposited on the anode and NiO_2 on the cathode.

The net reaction during discharging and recharging is:

$$Cd(OH)_{2(s)} + Ni(OH)_{2(s)} \underset{\text{discharging}}{\overset{\text{charging}}{\rightleftharpoons}}$$

$$Cd_{(s)} + NiO_2 + 2H_2O$$
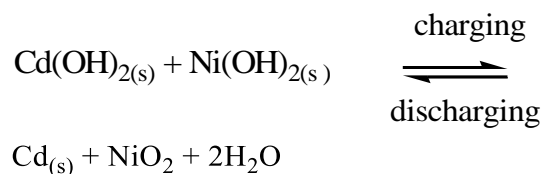
From the above reactions, it is clear that

- No gaseous products are formed.
- Cd(OH)2 and Ni(OH)2 formed adhere well to the surfaces, which can be removed by recharging the cell.

Advantages

- It has longer life than lead storage cell.
- Available in a wide range of sizes, high number of charge/discharge cycles.
- Possess good load performance and allows recharging even at low temperatures.
- It is compact and lighter and used in high current applications.
- It is smaller and lighter.

- Like a dry cell, it can be packed and sealed.
- It is the lowest cost battery in terms of cost per cycle.

Disadvantages

- It is very expensive.
- Cadmium is highly toxic.
- Relatively low energy density, low capacity when compared to other rechargeable syatems.
- Has relatively high self-discharge and need to be recharged after storage.

Uses

- It is used in emergency power applications and communication equipments.
- It is used in electronic calculators, electronic flash units, transistors and other battery powered small tools.
- Due to low temperature performance it is widely used in aircraft and space satellites.

3.4.3 Lithium Battery

Lithium is the lightest among all metals and it can float on H_2O. The electrochemical properties of lithium are excellent and it is a highly reactive material. These properties gives lithium the potential to achieve very high energy and power densities in high density battery applications such as automotive and standby power.

Lithium battery is a solid state battery because instead of liquid or a paste electrolyte, solid electrolyte is used.

Construction

- The Lithium battery consists of a lithium anode and a TiS_2 cathode.
- A solid electrolyte allows the passage of ions but not electrons.
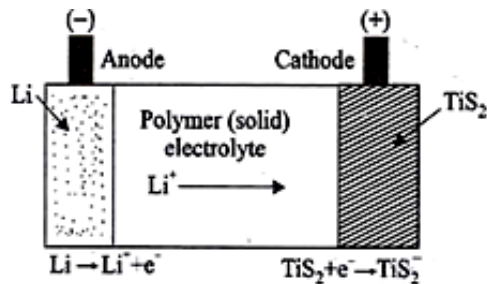
Fig 3.3 Solid state lithium battery

Working

Discharging

When the anode is connected to cathode Li^+ ions move from anode to cathode. The cathode receives Li^+ ions and electrons.

At Anode: $Li(s) \longrightarrow Li^+ + e^-$

At Cathode: $TiS_{2(s)} + e^- \longrightarrow TiS_2^-$

Overall cell reaction: $Li_{(s)} + TiS_{2\,(s)}^- \longrightarrow Li^+ + TiS_2^- \longrightarrow LiTiS_2$
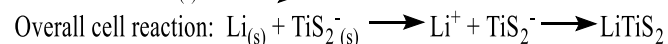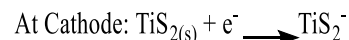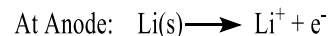
Charging

The Lithium battery is recharged by suppling an external current which drives the

Li^+ ions back to the anode. The net reaction is:

$LiTiS_2 \longrightarrow Li^+ + TiS_2^-$

Hence the cell is rechargeable. It gives high voltage 3.0 volts

Advantages of Li battery

- It generates a high voltage upto 3.0volt.
- Since Li is a light-weight metal, only 7g of lithium produces 1 mole of electrons.
- Since Li has the most negative E^0 value, it generates a higher voltage than the other types of cells.
- It can be made in different shapes and sizes.
- There is no risk of leakage from the battery, since all its constituents are solid.

- It posses high energy density.

Disadvantage

Li battery is more expensive than other batteries.

Uses

- Button sized Li batteries are used in calculators, electronic flash units, transistors,
- Head phones and cordless appliances.

3.4.4 Lithium ion Battery (or) LIB

A Lithium ion battery is a type of rechargeable battery in which lithium ions move from the negative electrode (anode) to the positive electrode (cathode) during discharge and back when charging.
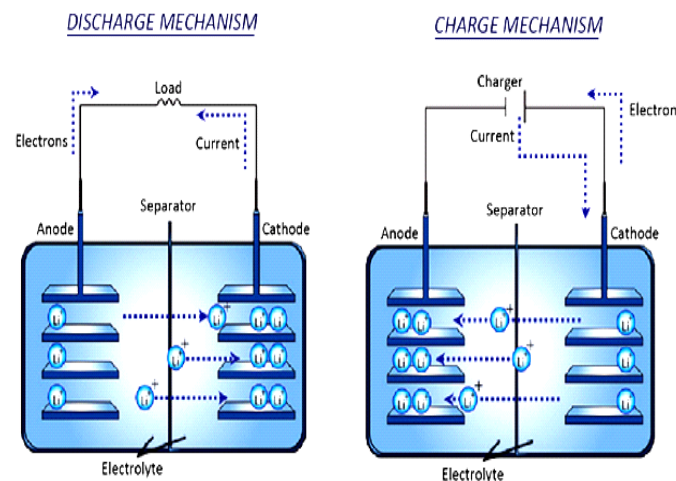
Fig 3.6   Lithium Ion Battery

Construction:

- A positive electrode is made with lithium cobalt oxide $LiCoO_2$ or Lithium manganese oxide $LiMn_2O_4$ has a current collector made of thin aluminium foil.

- A negative electrode made with special carbon usually graphite (C_6) has a current collector of thin copper foil.
- A separator is a fine porous polymer film.
- An electrolyte is made with lithium salt in an organic solvent.
- Eg. $LiPF_6$, $LiBF_4$ or $LiClO_4$ in ether.

Working

- The traditional batteries are based on galvanic action but Lithium ion secondary battery depends on an intercalation mechanism.
- Intercalation is the reversible inclusion or insertion of a molecule into materials with layered structure.
- During discharge Li ions are dissociated from the anode and migrate across the electrolyte and are inserted into the crystal structure of the host compound of cathode.
- Electrons also flow from the negative electrode to the positive electrode through the external circuit.

Discharging

At Anode: $Li_xC_6 \longrightarrow xLi^+ + xe^- + 6C$

At Cathode: $xLi^+ + xe^- + LiCoO_2 \longrightarrow Li_{1+x}CoO_2$
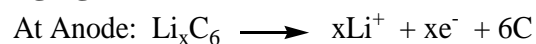
Advantages

- A typical Li ion battery can store 130 watt-hours electricity in 1 kilogram of battery as compared to lead acid batteries which can store only 23 watt-hours of electricity in one kilogram.
- All rechargeable batteries suffer from self-discharge when stored or not in use.
- In LIB, there will be a three to five percent of self discharge for 30 days of storage.

- They have high energy density than other rechargeable batteries.
- They are less weight.
- They produce high voltage of about 4volt.
- They have improved safety i.e., more resistance to overcharge.
- Fast charge but slow discharge rate.

Disadvantages

- They are expensive.
- They are not available in standard cell types.

Applications

- LIB is used in cameras, calculators.
- They are used in cardiac pacemakers and other implantable device.
- They are used in telecommunications, equipments, instruments portable radios, TVs and pages.
- They are used to operate laptop computers, mobile phones and aerospace application.

"Like a battery, the human mind and body must be fully discharged to stretch their capacity." — *Haresh Sippy.*

3.4.5 SUPERCAPACITORS

In response to the changing global landscape, energy has become a primary focus of the major world powers and scientific community. As the concern grows over fossil fuel usage, in terms of global warming and resource depletion, there will be a progressive swing to renewable energy. This will necessitate the development of improved methods for storing electricity when it is available and retrieving when it is needed. There has been great interest in developing and refining more efficient energy storage devices. One of such devices is the supercapacitor.

Definition

Super capacitors can be defined as a energy storage device that stores energy electro statically by polarising an electrolytic solution. Unlike batteries no chemical reaction takes place when energy is being stored or discharged and so super capacitors or ultra capacitors can go through hundreds of thousands of charging cycles with no degradation. Ultra capacitors are also known as double-layer capacitors or super capacitors.

These supercapacitors have the following characteristics:

- Greater density of stored energy
- High power discharge; rapid charge and discharge
- Long useful life
- Start quickly, accelerate quickly, climbing powerfully
- The capacitance is 30 times as the lead acid batteries, it is the most important characterisitic of the electrical automobile.

Types of super capacitor
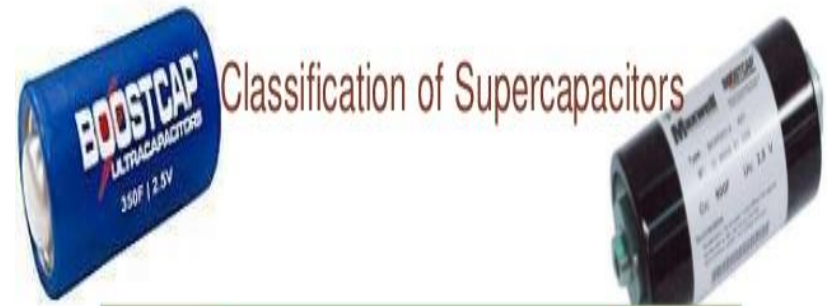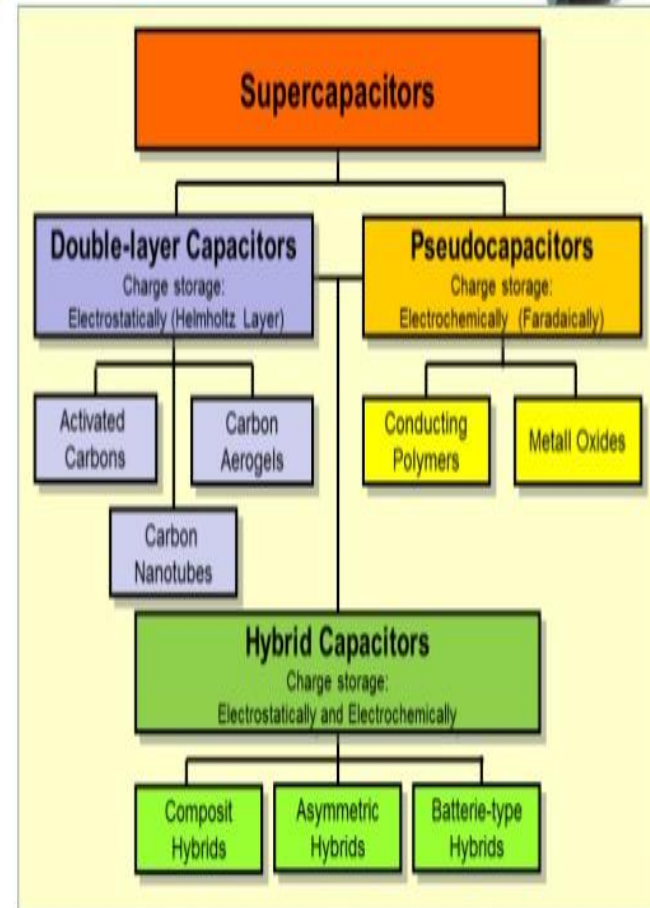
Electrochemical double layer capacitor
Principle, construction and working

Principle Energy is stored in supercapacitor by polarizing the electrolytic solution. The charges are separated via electrode – electrolyte interface.
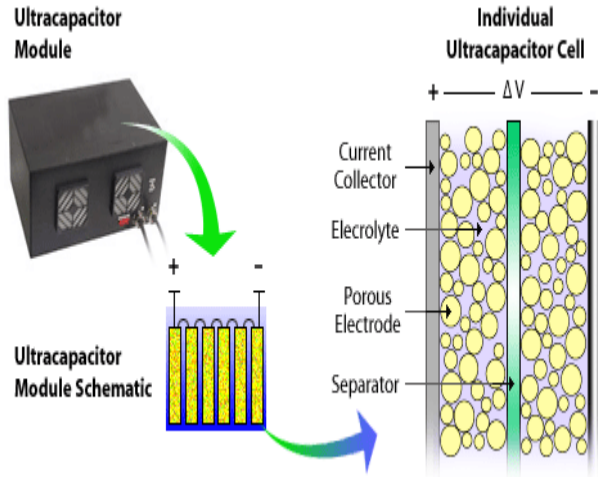
Construction

Super capacitor consist of a porous electrode, electrolyte and a current collector (metal plates). There is a membrane, which separates, positive and negative plated is called separator. The following diagram shows the ultracapacitor module by arranging the individual cell.

Working

There are two carbon sheet separated by separator. The geometrical size of carbon sheet is taken in such a way that they have a very high surface area. The highly porous carbon can store more energy than any other electrolytic capacitor. When the voltage is applied to positive plate, it attracts negative ions from electrolyte. When the voltage is applied to negative plate, it attracts positive ions from electrolyte.

Therefore, there is a formation of a layer of ions on the both side of plate. This is called 'Double layer' formation. For this reason, the ultracapacitor can also be called Double layer capacitor. The ions are then stored near the surface of carbon. The distance between the plates is in the order of angstroms. According to the formula for the capacitance,

$$\text{Capacitance} = \frac{\text{dielectric constant of the medium} \times \text{area of the plate}}{\text{distance between the plates}}$$

Ultracapacitor stores energy via electrostatic charges on opposite surfaces of the electric double layer. They utilize the high surface area of carbon as the energy storage medium, resulting in an energy density much higher than conventional capacitors. The purpose of having separator is to prevent the charges moving across the electrodes. The amount of energy stored is very large as compared to a standard capacitor because of the enormous surface area created by the (typically) porous carbon electrodes and the small charge separation (10 angstroms) created by the dielectric separator
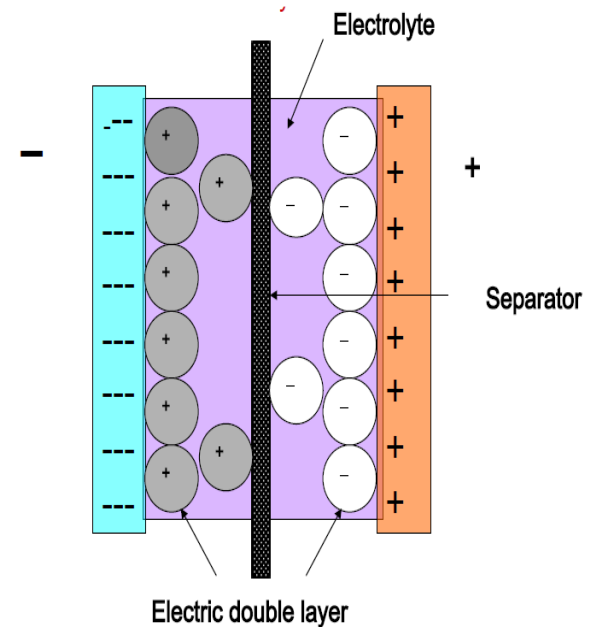
Advantages

- Long life: It works for large number of cycle without wear and aging.
- Rapid charging: it takes a second to charge completely
- Low cost: it is less expensive as compared to electrochemical battery.
- High power storage: It stores huge amount of energy in a small volume.
- Faster release: Release the energy much faster than battery.

Disadvantages

- They have Low energy density Individual cell shows low voltage
- Not all the energy can be utilized during discharge
- They have high self-discharge as compared to battery.
- Voltage balancing is required when more than three capacitors are connected in series.

Applications

- They are used in electronic applications such as cellular electronics, power conditioning, uninterruptible power supplies (UPS),
- They used in industrial lasers, medical equipment.
- They are used in electric vehicle and for load leveling to extend the life of batteries.
- They are used in wireless communication system for uninterrupted service.
- There are used in VCRs, CD players, electronic toys, security systems, computers, scanners, smoke detectors, microwaves and coffee makers.

Activated carbons

Activated carbon is the most commonly used electrode material in EDLCs. The activated carbon possesses a higher surface area than other carbon-based materials and is less expensive. It can be observed that the activated carbon can be obtained in different complex porous structures of miropores (<20A wide) to macropores (>500A) to achieve their high surface areas.

There is an empirical relationship between the distribution of pore sizes, the energy density and power density of the device. Larger pore sizes correlate with higher power densities and smaller pore sizes correlate with higher energy densities. As a result, the pore size distribution of activated carbon electrodes is a major area of research in EDLC design.

Carbon aerogels

Carbon aerogels are also beng used as an electrode materials for EDLCs. Carbon aerogels are formed from a continuous network of conductive carbon nanoparticles with interspersed mesopores (mesopore(20-500A). Due to this continuous structure and their ability to bond chemically to the current collector, carbon aerogels do not require the application of an additional adhesive binding agent. As a binderless electrode, carbon aerogels have been shown to have a lower ESR (equivalent series resistance) than activated carbons. This reduced ESR, which yields higher power, is the primary area of interest in supercapacitor research involving carbon aerogels.

3.3 FUEL CELL

A voltaic cell involves oxidation-reduction reaction. All ordinary combustion reactions are redox reactions. However, when a fuel is burned, the electron exchange takes place only when the atoms of the oxidizing agent (oxygen or air) come in direct contact with the atoms of the substance being oxidized (the fuel). The energy is released principally as heat.

In a fuel cell, electric energy is obtained without combustion from oxygen and a gas that can be oxidized. Hence, a fuel cell converts the chemical energy of the fuels directly to electricity. The essential process in a fuel cell is:

$$\text{Fuel} + \text{Oxygen} \longrightarrow \text{Oxidation products} + \text{Electricity}$$

3.3.1 Characteristics of fuel cell

- They do not store chemical energy
- Reactants are to be supplied constantly while products are removed constantly. In this respect, a fuel cell resembles an engine more than does a battery.
- The efficiency of a fuel cell is about twice that of a conventional power plant.
- Fuel cell generators are free of noise, vibration, heat transfer, thermal pollution.
- They do not run down like batteries as the reactions take place under nearly reversible conditions and the efficiency is higher in producing more useful work.

3.6 TYPES OF FUEL CELL

Fuel cells are distinguished on the basis of the type of electrolyte.

1. Hydrogen-Oxygen or Alkaline Fuel Cells (AFC)
2. Molten Carbonate Fuel Cells (MCFC)
3. Phosphoric Acid Fuel Cells (PAFC)
4. Solid Oxide Fuel Cells (SOFC)
5. Proton Exchange Membrane Fuel Cells (PEMFC)
6. Bio Fuel Cells (BFC)
7. Methanol Oxygen Fuel Cells (MOFC)

3.6.1 Hydrogen Oxygen fuel cell (or) Alkaline Fuel Cell

Construction

- One of the simplest and most successful fuel cell is hydrogen-oxygen fuel cell.

- The alkaline fuel cell or hydrogen-oxygen fuel cell was designed and first demonstrated publicly by Francis Thomas Bacon in 1939.
- It consists of porous carbon electrodes impregnated with suitable catalyst like finely divided platinum, or a 73/23 alloy of palladium and silver or nickel.
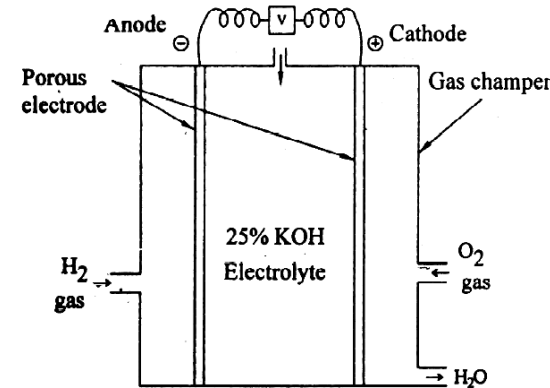
Fig 3.7 **Hydrogen-Oxygen fuel cell**

- Concentrated KOH or NaOH solution is placed between the electrodes to act as electrolyte. For low-temperature operating fuel battery (-34^0C to 72^0C), potassium thiocyanate dissolved in liquid ammonia is employed.
- The electrodes used here must be: (i) good conductors, (ii) good electron – sources or sinks and (iii) not be consumed or deteriorated by the electrolyte heat or electrode reactions.

Working

- Hydrogen and oxygen gases are bubbled through the anode and cathode compartment respectively.
- H_2 get oxidised in presence of Pt (electro catalyst) to form H^+. The electrons from anode is absorbed by O_2 at cathode which reacts with water from electrolyte to form OH^- ions.

The two ions (H^+ and OH^-) combine in the electrolyte medium to form H_2O.

Anode : $\qquad 2H_{2\,(g)} + 4OH^-_{\,(aq)} \longrightarrow 4H_2O_{(l)} + 4e^-$

Cathode : $\qquad O_{2\,(g)} + 2H_2O_{\,(l)} + 4e^- \longrightarrow 4OH^-_{\,(aq)}$

Overall reaction $\qquad 2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$
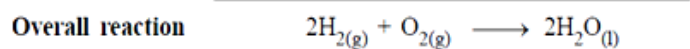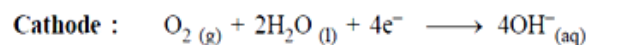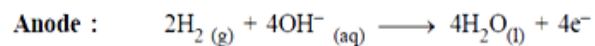
- The standard emf of the cell, $E^0 = E^0_{\,ox} + E^0_{\,red} = 0.83\ V + 0.40\ V = 1.23\ V$. In actual practice, the emf of cell is 0.8 to 1.0V.
- It may be noted that the only product discharged by the cell is water.
- A large number of these cells are stacked together in series to make a battery, called fuel cell battery or fuel battery.

Advantages
- It has high efficiency.
- It is portable and easy to maintain.
- It does not produce any harmful exhaust.
- Water produced from hydrogen-oxygen fuel cells can be used for drinking purpose.
- It can be used as a source in space flights.
- No noise and thermal pollution.

Disadvantages
- The corrosiveness of the electrolytes used.
- It needs to be stored in high tanks.
- It is difficult to predict the life time of fuel cells accurately.
- High cost of pure hydrogen and the catalyst needed for the electrode reactions

(Ex. Pt, Pd, Ag etc.,)
- Problem of handling gaseous fuels at low temperature or high pressure.

Applications
- Fuel cells are ideal for power generation.
- They are used for powering buses, boats and trains.
- Hospitals use fuel cells to provide electricity.
- All major auto makers are working to commercialise a fuel cell car.
- Fuel cells are used in smart phones, laptops and tablets.
- Hydrogen-oxygen fuel cells are uses as auxiliary energy source in space vehicles, submarines or other military-vehicles.
- The product water proved to be a valuable source of fresh water by the astronauts.

3.6.2 PROTON EXCHANGE MEMBRANE FUEL CELL (PEMFC)

A polymer electrolyte membrane fuel cell is one of the best candidates as a portable power source for commercial applications primarily because of its light weight, high energy high power, non emission and low temperature operation. It offers an order of magnitude higher power density than any other fuel cell system, which can operate on reformed hydrocarbon fuels with pre treatment and air.

Construction
- Proton exchange membrane fuel cells (PEMFC) also known as Polymer electrolyte membrane (PEM) fuel cells are consisted of a proton conducting electrolyte in solid polymer form.
- Electrodes (anode & cathode) are made of porous carbon containing a platinum or ruthenium catalyst.
- The electrolyte is a polymer membrane, which is an electronic insulator, but an excellent conductor of hydrogen ions.

- The most commonly used membranes are based on per fluorosulfonic acid (PFSA) and Nafion (Tetrafluorethylene copolymer containing sulphonic acid group) the proton of which are free to migrate through the membrane.
- The electrolyte membrane is sandwiched between the anode and cathode to produce a single "membrane electrode assembly" (MEA),which is less than millimeter thickness.
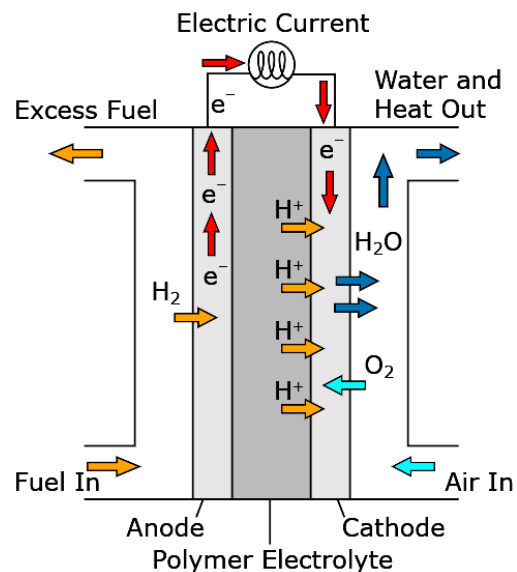
Fig 3.8 **Proton Exchange Membrane Fuel Cell**

The essential requirements of polymer electrolyte membranes include

- High proton conductivity.
- Low electronic conductivity.
- Impermeability to fuel gas or liquid.
- Good mechanical toughness in both the dry and hydrated states.

- High oxidative and hydrolytic stability.
- Chemical and thermal stability.
- Low water drag and low methanol crossover.

Working

- Pressurized hydrogen gas (H_2) enters cell on anode side, which is forced through catalyst. When H_2 molecule contacts platinum catalyst, it splits into H^+ ions and electrons.
- Electrons from anode are conducted through the external circuit and return to the cathode side of the fuel cell.
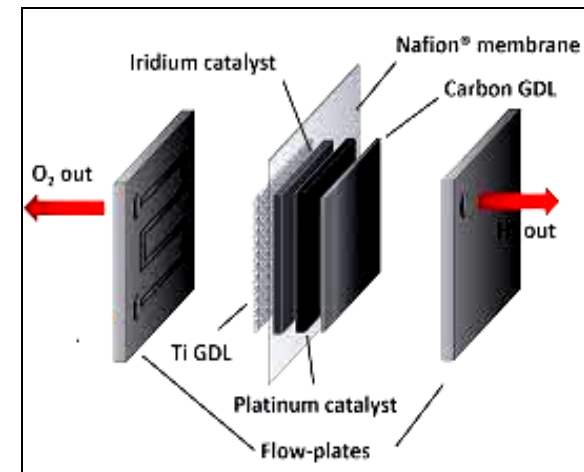
Fig 3.9 **Membrane Electrode Assembly**

- On the cathode side, oxygen gas (O_2) is forced through the catalyst forms oxide ion.
- The oxide ion attracts the H^+ ions through the membrane to form a water molecule (H_2O).

$$\text{Anode} \quad H_2 \longrightarrow 2H^+ + 2e^-$$

$$\text{Cathode} \quad 1/2\,O_2 + 2H^+ + 2e^- \longrightarrow H_2O$$

$$\text{Overall} \quad H_2 + 1/2\,O_2 \longrightarrow H_2O$$
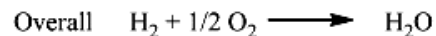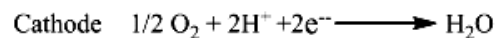
Advantages

- Use of solid polymer electrolytes eliminates the corrosion and safety concerns associated with liquid electrolyte fuel cells.
- Its low operating temperature $173^\circ C$ provides instant start up and requires no thermal shielding to protect personnel.
- Has high power density.
- It offers an order of magnitude higher power density than any other fuel cell system, which can operate on reformed hydrocarbon fuels with pre treatment and air.
- Offers the advantage of low weight and volume.

Disadvantages

- High cost,
- High methanol permeability.
- Environmental incompatibility with other materials.
- Expected life of PEMFC is very short and not suitable for DG (distributed generation).
- The most commonly used catalyst (Pt) is very expensive.
- Sensitive to fuel impurities (CO poisoning diminishes the efficiency of the cell).
- Hydrogen generation and storage is a significant problem.

3.6.3 METHANOL-OXYGEN FUEL CELL (DMFC)

The Direct Methanol Fuel Cell is relatively new technology. Like, PEM fuel cell the DMFC uses polymer electrolyte. But DMFC used liquid methanol or alcohol as fuel instead of reformed hydrogen fuel.

Construction

- The fuel cell consists of two electrodes.
- The anode consists of porous nickel electrode impregnated with a Pt/Pd catalyst.
- The cathode is nickel electrode coated with silver catalyst (oxygen electrode).
- The electrolyte KOH is placed in between the two electrodes.
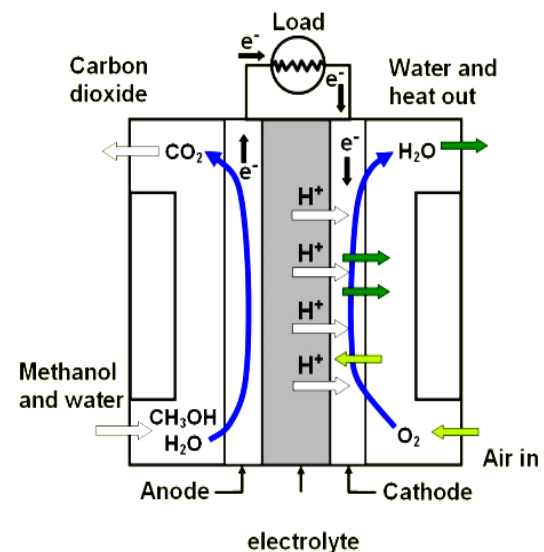
Fig 3.10   Methanol Oxygen Fuel Cell

Working

- Air is allowed to bubble on the catalyst surface.
- 33 ml methanol of water is added at the anode.
- During chemical reactions the negative electrode draws hydrogen by dissolving liquid methanol

(CH_3OH) in water in order to eliminate the need of external reformer.

- At the positive electrode the recombination of the positive ions and negative ions takes place to produce water as a by product.

$$Anode \quad CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$$

$$Cathode \quad 3/2\ O_2 + 6H^+ + 6e^- \longrightarrow 3H_2O$$

$$Overall \quad CH_3OH + 3/2\ O_2 \longrightarrow CO_2 + 2H_2O$$
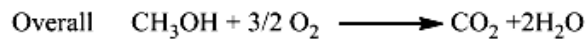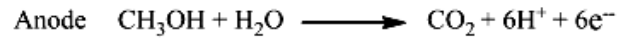
- The protons produced migrate through the polymer electrolyte to the cathode where they react with oxygen to produce water.
- During the cell operation CO_2 and water vapour are liberated around the electrodes.
- Normally a single DMFC can supply only 0.3-0.3V under loaded conditions.

Advantages

- Easy transportation and handling.
- Readily available, relatively lesser cost.
- Stable at all atmospheric conditions.
- Negative electrode catalyst draws the hydrogen from the methanol and reduces overall cost due to the absence of reformer.

Disadvantages

- Methanol is very toxic and highly flammable.
- Methanol is made from non-renewable fossil fuels.
- It's of low efficiency because methanol can pass through the available membrane materials.

Applications

- All kinds of portable, automotive and mobile applications like powering laptop, computers, cellular phones, digital cameras.
- Fuel cell vehicles.
- Space craft applications.

3.6.4 SOLID OXIDE FUEL CELL (SOFC)

Solid oxide fuel cells (SOFCs) are best suited for large-scale stationary power generators that are able to provide electricity for factories and towns. SOFC use a hard non porous ceramic compound as electrolyte (calcium oxide or zirconium oxide),which operates extremely at high temperature 1000^oC.

SOFC differ in many respects from other fuel cell technologies.

- The anode, cathode and electrolyte are all made of ceramic substance
- Because of the ceramic make up the cells can operate at temperature as high as $1000\ ^oC$.
- The cells can be configured either as rolled tubes or as flat plates and manufactured using many of the technique now employed by the electronics industry.
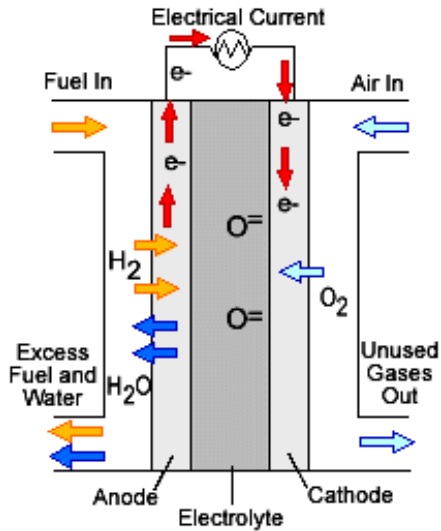
Fig 3.11 **Solid Oxide Fuel Cell**

Construction

- It consist of two porous electrodes separated by a dense oxygen ion conducting electrolyte (solid ceramic oxides)
- The anode used is highly porous, electronically conducting Ni/ yettria-stabilised zirconia cermets (Ni/YSZ)
- The cathode is based on a mixed conducting pervoskite lanthanum manganite ($LnMnO_3$)
- Yettria-stabilised zirconia is used as the oxygen conducting electrolyte. To improve the conductivity of electrolyte, Scandium-doped zirconium oxide can be used instead of YSZ but high cost of scandium limits the use of latter.
- SOFC use a hard non porous ceramic compound as electrolyte (calcium oxide or zirconium oxide),

which operates extremely at high temperature 1000 $^\circ$C

- The fuels used may be gas (natural gas, biogas, hydrogen) or liquid (methanol, diesel and gasoline).

Requirements of electrolyte

- Ions conductive -oxygen ion transport.
- Chemically stable (at high temperatures as well as in reducing and oxidizing environments).
- Gas tight/free of porosity.
- Uniformly thin layer.

Working

- It consists of two porous electrodes separated by a dense, oxide ion conducting electrolyte.
- Oxygen supplied at the cathode (air electrode) reacts with incoming electrons from the external circuit to form oxide ions.
- These ions migrate to the anode (fuel electrode) through the oxide ion conducting electrolyte.
- At the anode, oxide ions combine with hydrogen (and/or carbon monoxide) in the fuel to form water (and/or carbon dioxide), liberating electrons.
- Electrons (electricity) flow from the anode through the external circuit to the cathode, where oxygen in gas phase reduced to oxide ion.

When hydrogen is the fuel the reactions are:

$$\text{Anode} \quad H_2 + O^{2-} \longrightarrow H_2O + 2e^-$$

$$\text{Cathode} \quad 1/2\ O_2 + 2e^- \longrightarrow O^{2-}$$

$$H_2 - 1/2\ O_2 \longrightarrow H_2O + \text{Electrical energy} + \text{heat}$$
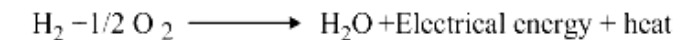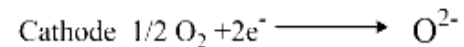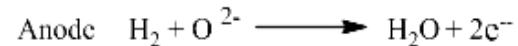
When carbon monoxide is the fuel the reactions are:

$$\text{Anode} \quad CO + O^{2-} \longrightarrow CO_2 + 2e^-$$
$$\text{Cathode} \quad 1/2\ O_2 + 2e^- \longrightarrow O^{2-}$$
$$\text{Overall} \quad CO + 1/2\ O_2 \longrightarrow CO_2$$
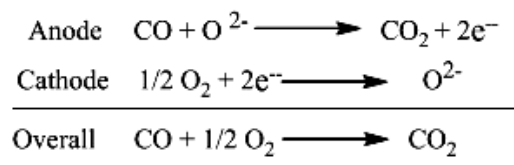
Advantages

- They can run on a wide Variety of fuels (gas or liquid).
- Precious metal (Pt) catalyst is not required.
- Long-term stability.
- They operate at high temperature (1000^0C)
- They are not sensitive to CO poisoning.
- They have a relatively low cost.
- They have a relatively high efficiency about 30-60%
- Waste heat can be recycled to make additional electricity, which improves efficiency (upto 83%).
- They have a fast start up.
- The electrolyte has a relatively high resistance.
- The compact size and cleanliness of SOFCs make them especially attractive for urban area.

Disadvantages

- High operating temperature which results in mechanical and chemical compatibility issues.

Uses

- Solid oxide fuel cells (SOFCs) are best suited for large-scale stationary power generators that are able to provide electricity for factories and towns.

3.6.4 BIOFUEL CELL

Biofuel cell is a device that converts chemical energy into electrical energy by the catalytic reaction of microorganisms or enzymes.
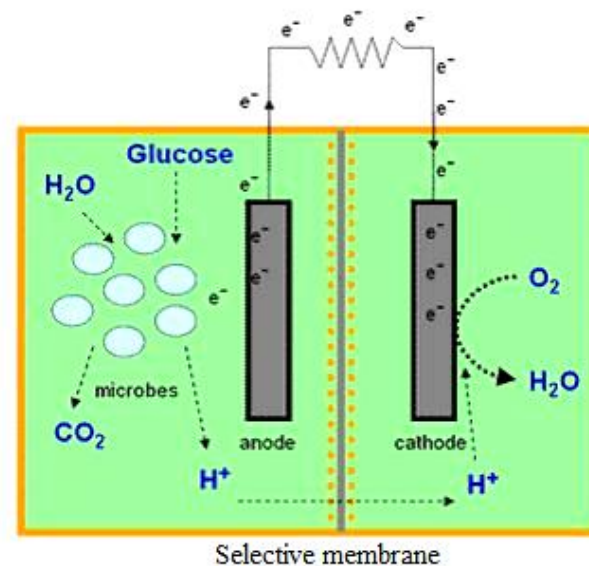
Fig 3.12 **Bio Fuel Cell**

Construction

- Microorganisms are able to convert enormous amounts of energy from an incomparable range of chemical substrates.
- Bio-fuel cells are a subset of fuel cells that employ biocatalysts such as a microbe, enzyme or even organelle interacting with an electrode surface. The main types of biofuel cells are defined by the type of biocatalyst used.

- Microbial fuel cells employ living cells to catalyze the oxidation of the fuel, whereas enzymatic fuel cells use enzymes for this purpose.
- Like other cells, Biofuel cells require porous anode and cathode structures and a polymer electrolyte membrane or a salt bridge to separate the electrodes.
- It consists of organic substrate (Glucose or Urea) which acts as a fuel which is oxidized by living organisms.
- Bio anode: It contains fuel oxidizing enzymes like glucose oxidase, alcohol hydrogenase, glucose dehydrogenase.
- Bio cathode: It contains oxygen reducing enzymes like laccase, bilirubin oxidase, ascorbate oxidase.
- Fuel: Organic substrate like Glucose or Urea.

Working

- At the anode, microorganisms or enzymes oxidize organic matter and produce CO_2, proton (H^+) and electron.

$$C_6H_{12}O_6 + 6H_2O \longrightarrow 6CO_2 + 24H^+ + 24e^-$$
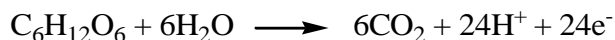
- At the cathode, either living organisms (microbes) or enzymes act as catalysts for oxidant reduction and accept electrons, the same principle as the conventional fuel cells.

$$24H^+ + 24e^- + 6O_2 \longrightarrow 12H_2O$$

- Overall Reaction

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$$
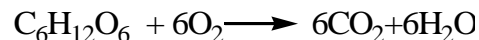
- Some microorganisms cannot transfer the electron to the anode, and therefore mediators such as thionine, methyl viologen, etc have to be used to facilitate the electron transfer.

- However, recent development has shown that there exist electrochemically active bacteria (such as: Shewanellaputrefaciens, Aeromonashydrophila) which can transfer electron directly to the electrode without mediators.

Advantages

- More efficient than turbine (~23%) or solar (~13%) electricity generation.
- Does not require substrate to be combustible.
- Does not require the use of toxic and expensive heavy metals or metalloids.
- Is not limited by the reactivity of the electron donor.
- Do not produce toxic end products.

Disadvantages

- Its current output was generally very low 10^{-3} to 10^{-6} A
- Raw materials like vegetable and fruit extracts, petroleum extracts and human waste should be available in plenty.

Potential Applications

- Powering monitoring devices in remote locations.
- Decentralized domestic power source.
- Conversion of waste organic matter to electricity instead of methane.
- Conversion of renewable biomass to electricity instead of ethanol.
- Bioremediation of environmental contaminants.

"It is my conclusion that the human mind and body is essentially a single cell rechargeable battery that is charged from the atmospheric DC voltage and the Earth."

— Steven Magee, Health Forensics.

UNIT III
BATTERIES AND FUEL CELLS
QUESTION BANK
PART A

1.What are the important requirements of a battery?

- It should have more storage capacity.
- It should be light and compact.
- It should provide power for longer time period.
- It should be capable of recharged.
- It should give constant voltage
- It should be resistance to self-discharge.
- It should be cheaper

2.What is a primary battery? Give an example.

These are cells in which the electrode reactions cannot be reversed by passing an external current. The reactions are possible only once and the battery will be dead after use. Hence it is non - rechargeable battery.

Eg: Daniel cell, Leclanche cell, Mercury cell.

3.Mention the differences between primary battery and secondary battery.

Primary Batteries	Secondary batteries
Primary batteries are used only once	Secondary batteries can be used for several cycles.
Irreversible battery	Reversible battery
They are cheap.	They are expensive.
Initial cost is low.	Initial cost is very high.
Disposable.	Periodic recharging and regular maintenance is required.

4.Why does a dry cell become dead after a long time, even it has not been used?

Acidic NH_4Cl slowly corrodes the zinc container of the dry cell, even when the cell is not in use. Hence, dry cell becomes dead after a long time, even it is not used

5.What are secondary cells?

These are cells in which the electrode reactions can be reversed by passing an external current. Thus a secondary battery may be used through a large number of cycles of charging and discharging. Hence it is a rechargeable battery.

Eg: Lead acid battery, Ni-Cd battery.

6.State the reaction when a lead storage battery is recharged.

$$PbO_{2(s)} + 4H^+ + 2e^- \longrightarrow Pb^{2+}_{(aq)} + 2H_2O$$
$$Pb^{2+}_{(aq)} + SO_4^{2-}_{(aq)} \longrightarrow PbSO_{4(s)}$$

$$PbO_{(s)} + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_{4(s)} + 2H_2O$$
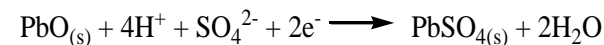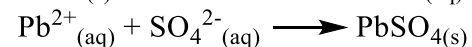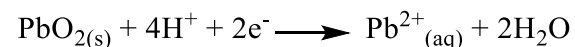
7. What are the applications of lead acid storage cell?

- Lead storage cell is mainly used in automobiles like cars, buses and trucks.
- It is used in gas engine ignition, telephone exchanges, hospitals and power stations.
- It is also used in Uninterrupted Power Supply (UPS), as a power system which provides current constantly without a break.

8.Write the cell representation of NICAD battery.

It is represented as:

$Cd / Cd(OH)_2 // KOH / NiO_2 / Ni$

9.Give the advantages and disadvantages of NICAD battery?

Advantages

- It has longer life than lead storage cell.
- Available in a wide range of sizes, high number of charge/discharge cycles.
- Possess good load performance and allows recharging even at low temperatures.
- It is compact and lighter and used in high current applications.
- It is smaller and lighter.
- Like a dry cell, it can be packed and sealed.
- It is the lowest cost battery in terms of cost per cycle.

Disadvantages

- It is very expensive.
- Cadmium is highly toxic.
- Relatively low energy density, low capacity when compared to other rechargeable syatems.
- Has relatively high self-discharge and need to be recharged after storage.

8. List out the advantages of Li battery.

- It generates a high voltage upto 3.0volt.
- Since Li is a light-weight metal, only 7g of lithium produces 1 mole of electrons.
- Since Li has the most negative E^0 value, it generates a higher voltage than the other types of cells.
- It can be made in different shapes and sizes.

- There is no risk of leakage from the battery, since all its constituents are solid.
- It posses high energy density.

9. What is Energy density?

It is the amount of energy stored in a given system or region of space per unit volume.

10. What is power density?

Is the power of the battery per unit weight that represents the speed at which the energy can be delivered to the load.

Power density = Energy density / Time

11.What is capacity retention?

Capacity retention is derived from the number of cycles that the cell undergoes charge-discharge processes. Although factors like electrolyte stability, temperature, etc, influence the capacity of degradation, phase stability of the electrode is the prime component in determining the cycle life of a cell/ battery.

12. Mention the advantages of fuel cells.

- It has high efficiency.
- It is portable and easy to maintain.
- It does not produce any harmful exhaust.
- Water produced from hydrogen-oxygen fuel cells can be used for drinking purpose.
- It can be used as a source in space flights.
- No noise and thermal pollution.

13.State the limitations of fuel cells?

- The corrosiveness of the electrolytes used.
- It needs to be stored in high tanks.
- It is difficult to predict the life time of fuel cells accurately.

- High cost of pure hydrogen and the catalyst needed for the electrode reactions
- (Ex. Pt, Pd, Ag etc.,)
- Problem of handling gaseous fuels at low temperature or high pressure.

14. Write the characteristics of fuel cells.
- They do not store chemical energy
- Reactants are to be supplied constantly while products are removed constantly. In this respect, a fuel cell resembles an engine more than does a battery.
- The efficiency of a fuel cell is about twice that of a conventional power plant.
- Fuel cell generators are free of noise, vibration, heat transfer, thermal pollution.
- They do not run down like batteries as the reactions take place under nearly reversible conditions and the efficiency is higher in producing more useful work.

15. Write down the reactions occur in Methanol Oxygen fuel cell.

Anode $CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$

Cathode $3/2\ O_2 + 6H^+ + 6e^- \longrightarrow 3H_2O$

Overall $CH_3OH + 3/2\ O_2 \longrightarrow CO_2 + 2H_2O$
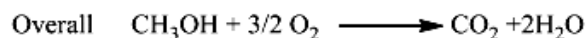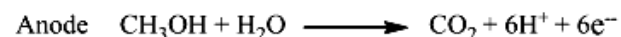
16. Write down the reactions of Solid Oxygen Fuel Cell.

Anode $H_2 + O^{2-} \longrightarrow H_2O + 2e^-$

Cathode $1/2\ O_2 + 2e^- \longrightarrow O^{2-}$

$H_2 - 1/2\ O_2 \longrightarrow H_2O + Electrical\ energy + heat$
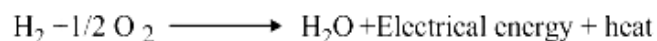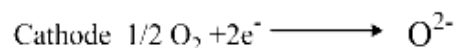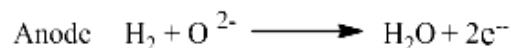
17. What are the requirements for SOFC electrolyte?
- Ions conductive -oxygen ion transport.
- Chemically stable (at high temperatures as well as in reducing and oxidizing environments).
- Gas tight/free of porosity.
- Uniformly thin layer.

18. What are the drawbacks of biofuel cells?
- Its current output was generally very low 10^{-3} to 10^{-6} A
- Raw materials like vegetable and fruit extracts, petroleum extracts and human waste should be available in plenty.

19. Give two examples for electrochemically active bacteria.
- Shewanellaputrefaciens,
- Aeromonashydrophila

PART B

1. Discuss the principles and working of Hydrogen Oxygen fuel cell.
2. Explain the construction and working of methanol oxygen fuel cell.
3. What is SOFC? Explain its working. What are its advantages?
4. Describe the principles involved in Proton Exchange Membrane fuel cell.
5. Write an informative note on Biochemical fuel cells.
6. Construct and explain primary battery (Dry cell) with neat diagram.
7. Explain the principle, working of lead acid battery.
8. Discuss the construction and working of NICAD battery.
9. What are lithium batteries? Explain the construction and working of lithium ion batteries. Mention its advantages over other types of batteries.
10. Write a note on Lithium battery.

UNIT III
BATTERIES AND FUEL CELLS
CONTENT BEYOND SYLLABUS

X-ray Absorption under Operating Conditions for Solid-Oxide Fuel Cells Electrocatalysts: The Case of LSCF/YSZ

Solid-oxide fuel cells (SOFC) represent a forefront theme in materials research, since they allow the production of electrical energy from hydrogen or hydrocarbon fuels with very high thermodynamic efficiency. SOFC electrodes act as catalysts (for oxidation of the fuel at the anode, and for reduction of oxygen at the cathode), and as mixed electron/ion conductors. Although a great deal of performance testing is routinely carried out on a wide variety of electro catalysts to optimize their composition and microstructure, advanced structural characterization studies have been relatively uncommon so far.

In this paper, we studied, under operating conditions (at high temperature and under an external electrical potential), the atomic and electronic structure of $La0.6Sr0.4Co0.8Fe0.2O_3$ (LSCF), which is a technologically relevant electrode material for high-temperature and intermediate-temperature SOFC.

This material has been the subject of a large number of studies in the last several decades. Kawada et al. reported on the chemical stability of LSCF, ultimately concluding that it is stable at high temperatures and under different atmospheres. However, cation segregation on one surface was observed when an oxygen partial pressure gradient was applied to LSCF, which resultedin Co-rich and Sr-rich precipitates on the surface exposed to higher $P(O_2)$.

In general, few examples of characterization in operating conditions have been reported in the literature to date, regarding both in-house and large-scale facilities techniques. Among the few studies in the literature on this topic, Baumann et al. observed a strong activation for the oxygen reduction reaction in an LSCF/YSZ model system, associated with a steep decrease of the resistivity of LSCF, due to an applied electrical potential (either cathodic or anodic) of the order of several volts. This effect was found to last for several hours after the polarization, which suggests a more profound transformation rather than a simple change of oxidation state. X-ray photoelectron spectroscopy (XPS) performed on films subject to different treatments were found to be enriched with Sr and Co on the surface.

An ever-increasing interest is developing at synchrotrons around the world to improve in situ/operando experimental setups in order to control the chemical/physical environment and the electrical loading applied to the sample under the beam. This allows for accurately monitoring the chemical changes in technologically relevant materials under service conditions. This approach was used, for instance, to study several SOFC cathode-electrolyte-air triple boundary surfaces using photoelectron microscopy under polarization . More recently, Nenning et al. examined the electrochemistry and XPS spectra of lanthanum strontium ferrite (LSF) and lanthanum strontium cobaltite (LSC) thin film electrodes over YSZ, during polarization (around 0.5 V either cathodic or anodic) and in different atmospheres (H_2 or O_2). Given the surface-sensitive conditions of such an XPS investigation, a pronounced difference was found in the behavior of cobalt compared to all other elements, which was attributed by the authors to the higher reducibility of the Co ions. In fact, in an earlier soft X-ray absorption spectroscopy study of LSCF under different oxygen partial pressures at 800 _C, it was already found that the Co absorption edge is modified by the oxygen non-stoichiometry, while the Fe edge is not .

Among synchrotron techniques, X-ray absorption spectroscopy allows one to obtain information about the atomic and electronic structure of the samples, so that it is particularly

suited for SOFC electrode materials, often constituted by variable valence elements that can modify their oxidation state and the local structure in dependence of reaction environment and applied potential.Regarding this concern, the development of reliable experimental protocols is essential to obtain significant information on SOFC materials. Among the issues addressed by the above cited authors, Lai et al. investigated catalyst poisoning, arguing that deactivation of an LSCF cathode by CO_2 is enhanced under a cathodic bias. Skinner et al. observed that cathodes constituted by Ruddlesden-Popper phases did not undergo significative redox phenomena under polarization. Irvine et al. studied the processes occurring at the electrode-electrolyte interface, and, in particular, assessed the reversible exsolution phenomena occurring during the operation.

We have recently developed an electrochemical cell for the X-ray structural characterization of SOFC electrocatalysts under operating conditions: high temperature (up to 800 _C), controlled atmosphere, and electrical loading. To this aim, we modified a thermochemical cell for in-situ X-ray spectroscopy with an electrically insulating quartz sample holder, and current collectors in order to impose a voltage bias on the sample.

In this paper, we present our first results with this setup on a LSCF/YSZ cathode/electrolyte half-cell. By applying an external voltage bias, ranging from -1 V to +1 V, and employing X-ray absorption spectroscopy at a high temperature, we were able to investigate the different role of iron and cobalt concerning the oxidation state and structural rearrangement, as a function of time, temperature, and electrical polarization in operating conditions.

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UNIT-IV
ADVANCED MATERIALS

Introduction: Plastic

The word, plastic, was derived from the word 'Plastikos' meaning 'to mould' in Greek. *Plastics* are polymers which can be moulded into any desired shape or form, when subjected to heat and pressure in the presence of a catalyst. They undergo permanent deformation under stress termed as plasticity.

Plastics are obtained by mixing a resin with other ingredients to impart special engineering properties.

Fossil fuels have compounds containing hydrogen and carbon (hydrocarbon) which act as building blocks for long polymer molecules .These building blocks are known as monomers, they link together to form long carbon chains called polymers. Depending on physical properties, plastics are divided into two types: Thermoplastic and thermosetting.

Thermoplastics

The material that softens when heated above the melting temperature and becomes hard after cooling is called thermoplastics. Thermoplastics can be reversibly melted by heating and solidified by cooling in limited number of cycles without affecting the mechanical properties.

The important properties of the thermoplastics are high strength and toughness, better hardness, chemical resistance, durability, self lubrication, transparency and water proofing.
With the application of heat, thermoplastic softens and it can be molded into desired shapes.
Example: PVC, nylon, polythene, etc.

Thermosetting:

Plastics which cannot be softened again by heating once they are molded are called thermosetting plastics. The property of material becoming permanently hard and rigid after cooling. The transformation from the liquid state to the solid state is irreversible process. It means that the thermosets can't be recycled. Heavily cross-linked polymers come under the category of thermosetting plastics. The mechanical properties like tensile strength, compressive strength, and hardness are not temperature dependent. Hence thermosets are generally stronger than the thermoplastics.

Example: Bakelite, melamine, etc. Bakelite is used for making electrical switches whereas melamine is used for floor tiles.

Differences between thermo and thermosetting plastics:

S.No	Thermoplastics	Thermosetting plastics
1	They are formed by addition Polymerization	They are formed by condensation polymerization.
2	Adjacent polymer chains are held together by week Vander Waals forces	Adjacent polymer chains are held together by strong covalent bonds called crosslink.
3	They soften on heating and stiffen on Cooling	They do not soften on heating.
4	They can be remoulded	They cannot be remoulded and reused.
5	They are week, Soft and less brittle	They are strong, hard and more brittle.
6	They are soluble in organic solvents	They are insoluble in organic solvents.
7	They have very low molecular weights Ex : Polyethylene ,polypropylene	They have high molecular weights. Ex : Bakelite

POLYPROPYLENE (PP)

This polyolefin is readily formed by polymerizing propylene with suitable catalysts, generally alkyl aluminum and titanium tetrachloride.

Polypropylene is produced by the chain-growth polymerization of propene.

Monomère de propylène   Polymère de polypropylène
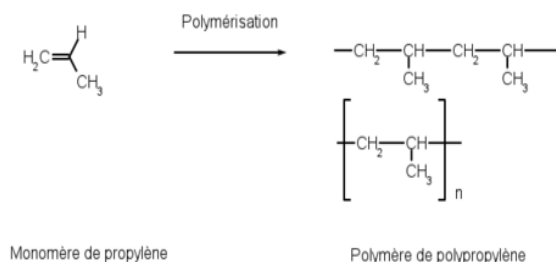
Polypropylene properties vary according to molecular weight, method of production, and the copolymers involved. Polypropylene has been very successfully applied to the forming of fibers due to its good specific strength which is why it is the single largest use of polypropylene. Polypropylene also happens to be one of the lightest plastics available with a density of 0.905 g/cm².

APPLICATIONS:

Polypropylene is widely used in Automotive Appliances, Household Goods, Film, Containers, Packaging, Electrical/Electronic Appliances and for general purpose.

Polyvinyl chloride

PVC is the world's third-most widely producedsynthetic plastic polymer,after polyethylene and polypropylene. About 40 million tonnes of PVC is produced per year. Pure polyvinyl chloride is a white, brittle solid. It is insoluble in alcohol but slightly soluble in tetrahydrofuran.

Preparation

Polyvinyl chloride is produced by polymerization of the vinyl chloride monomer
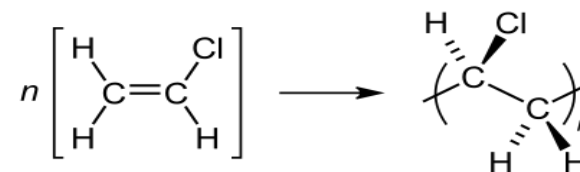
Applications

Economical, versatile polyvinyl chloride is used in a variety of applications in the building and construction, health care, electronics, automobile and other sectors, in products ranging from piping and siding, blood bags and tubing, to wire and cable insulation, windshield system components and more.

Polyurethanes

Polyurethanes are made by the exothermic reactions between alcohols with two or more reactive hydroxyl (-OH) groups per molecule (diols, triols, polyols) and isocyanates that have more than one reactive isocyanate group (-NCO) per molecule (diisocyanates, polyisocyanates). For example a diisocyanate reacts with a diol:
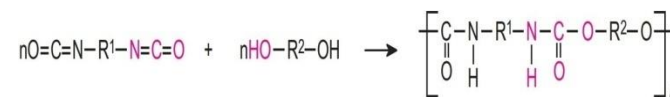
The group formed by the reaction between the two molecules is known as the 'urethane linkage'. It is the essential part of the polyurethane molecule.

Applications:

Without polyurethane, many products that consumers use every day would be less comfortable, less efficient and not perform as well. Because of its versatility, polyurethane adds value and provides solutions for many products and application types.
Polyurethanes are combined with nylon to make more lightweight and stretchable garments .

Polyurethane rigid foams are widely used as insulation in refrigerators and freezers.

Polyurethanes are used extensively in cars to help reduce weight, increase fuel economy while providing comfort and safety.

Polyurethane makes several types of highly efficient insulation materials, sealants and adhesives for homes and buildings.

Polyurethanes are also used as protective coatings on floors, making them easy to clean and maintain.

Polyamides

The polymers having an amide linkage between their monomers are called polyamides. Typical polyamide polymers are described below.

(a) Nylon-66. It is obtained by condensing adipic acid with hexamethylenediamine with the elimination of water molecule. The chain length depends upon the temperature and time for which the process is carried out.
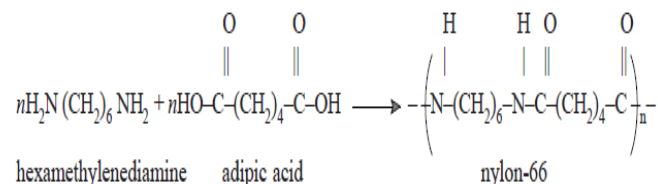
The polyamides are identified by numbers. These numbers refer to the number of carbon atoms in diamine and in the dibasic acid. As in the above case, the carbon atoms are 6 in each case, therefore, the product is described as nylon-66.

Uses : Nylon-66 is a linear polymer, and has very high tensile strength. It shows good resistance to abrasion. Nylon-66 is usually fabricated into sheets, bristles for brushes and in textile. Crinkled nylon fibres are used for making elastic hosiery.

POLYACRYLATES

Preparation

Acrylic esters are derived from acrylic acid ($CH_2=CHCO_2H$). Acrylic acid is "esterified" by reacting it with alcohols such as ethanol (ethyl alcohol) or methanol. The resultant methyl acrylate or ethyl acrylate is given the generic formula ($CH_2=CHCO_2R$), with R representing the organic group.

Properties:

Polyacrylates are an important class of polymers that are soft, tough and rubbery. Their glass transition temperature is well below room temperature. They are known for their high transparency; good impact toughness and elasticity, and have fairly good heat resistance.

Applications:

Major applications are coatings, paints, textiles, leather finishing, automotive products, tape adhesives, and oil-resistant and high-temperature-resistant elastomers. They are also used as comonomers to increase the plasticity of rigid and brittle plastics.

Silicone rubber

The silicones are a group of organosilicon polymers. They have a wide variety of commercial uses.

Preparation

The complete hydrolysis of $SiCl_4$ yields silica SiO_2, which has a very stable three-dimensional structure. The fundamental research of F.S. Kipping on the hydrolysis of alkyl-substituted chlorosilanes led, not to the expected silicon compound analogous to a ketone, but to long-chain polymers called silicones.
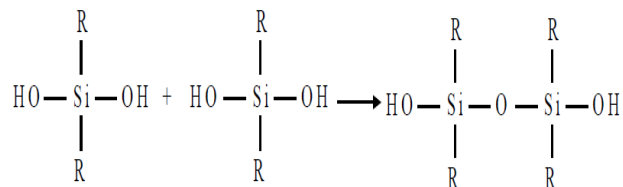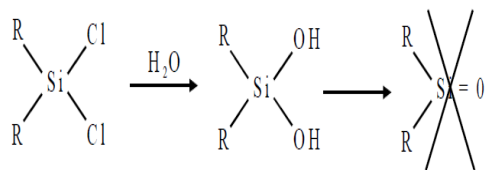
The starting materials for the manufacture of silicones are alkyl-substituted chlorosilanes. Thus the hydrolysis of trialkylmonochlorosilane R_3SiCl yields hexaalkylsiloxane.
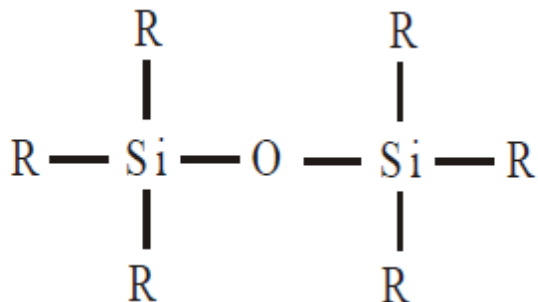
The dialkyldichlorosilane R2SiCl2 on hydrolysis gives rise to straight chain polymers and, since an active OH group is left at each end of the chain, polymerisation continues and the chain increases in length.

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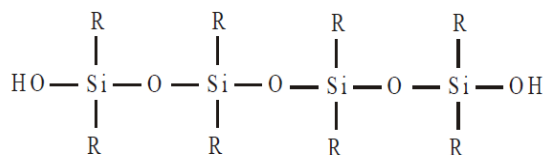
The hydrolysis of alkyl tricholorosilane RSiCl3 gives a very complex crosslinked polymer.
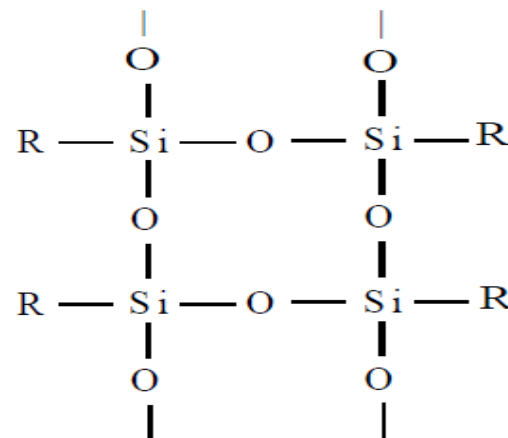
Applications

1) Silicones act as excellent insulators for electric motors and other appliances
as they can withstand high temperatures.
2) Straight chain polymers of 20 to 500 units are used as silicone fluids. They
are water repellent because of the organic side group. These polymers are
used in waterproofing textiles, as lubricants and as polish.
3) Silicone rubber retain their elasticity even at low temperatures and resist
chemical attack. They are mixed with paints to make them damp-resistant.
4) Silicone resins, a cross-linked polymer used as non-stick coating for pans
and are used in paints and varnish.
5) Silicone oils are highly stable and non-volatile even on heating. Hence used
for high temperature oil bath, high vacuum pump etc.

Biodegradable Polymer

These are those polymers which can decompose under aerobic or anaerobic conditions, as a result of the action of microorganism/enzymes. The materials develop it like starch, cellulose, and polyesters. . Some common examples of biodegradable polymers are PGA and PLA.

An estimated 86% of all plastic packaging mostly made of conventional polymers are used only once before it is discarded, producing a stream of waste that persists in waterways and landfill, releases pollutants and harms wildlife.

In contrast, biodegradable polymers (BPs) can be disposed of in prepared bioactive environments to undergo degradation by the enzymatic actions of microorganisms (bacteria, algae and fungi).

Their polymer chains may also be broken down by nonenzymatic processes such as chemical hydrolysis. Biodegradation converts them to CO_2, CH_4, water, biomass, humic matter, and other natural substances. BPs are thus naturally recycled by biological processes

Biodegradable polymers contain polymer chains that are hydrolytically or enzymatically cleaved, resulting in soluble degradation products. Biodegradability is particularly desired in biomedical applications, in which degradation of the polymer ensures clearance from the body and eliminates the need for retrieval or explant.

Biodegradable polymers have applications in:
- Controlled/sustained release drug delivery approaches
- Tissue engineering scaffolds
- Temporary prosthetic implant

Poly (glycolic acid)
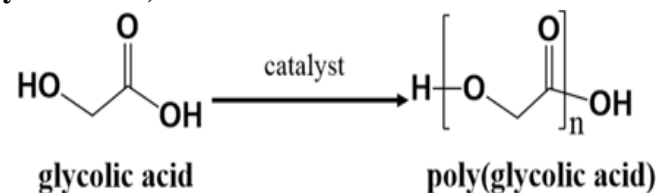
PGA is biodegradable thermoplastic polyester characterized by aliphatic ester bond that are responsible of its hydrolytic instability. The high crystallinity of PGA (45-55%) leads to remarkable mechanical properties. Carbonyl groups of PGA can be cleaved under hydrolytic or enzymatic conditions. PGA is fully biodegraded by the organism within 4 months but its mechanical properties almost disappeared after 6 weeks.
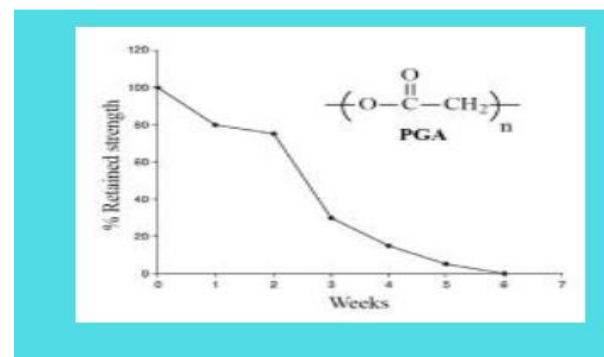
Poly (lactic acid)
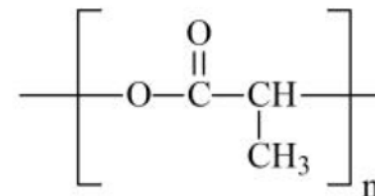
PLA is a thermoplastic, high-strength, high-modulus polymer. Biomedical use of PLA can be limited by its hydrophobicity which is responsible of low water sorption and thus relatively slow hydrolytic degradation. PLA mechanical properties remain quite high during the first months in physiologic conditions. Compared to PGA, 10 months are needed to reach a full biodegradation in the case of PLA.

Polylactic Acid (PLA)
- Highly versatile thermoplastic polymer
- Made 100% from renewable resources
- Lactic Acid is derived from various sources(Corn- Sugar Beets- Wheat)
- It is a biodegradable and bioactive polyester made up of lactic acid building blocks.

Preparation:
- It is can be produced by fermentative or chemical synthesis. The most popular route is fermentation, in which sugars and starches are converted into lactic acid by bacterial fermentation using an optimized strain of Lactobacillus.
- From lactic acid it is produced by direct polycondensation or ring opening polymerization of lactic acid cyclic dimmer, known as lactide.
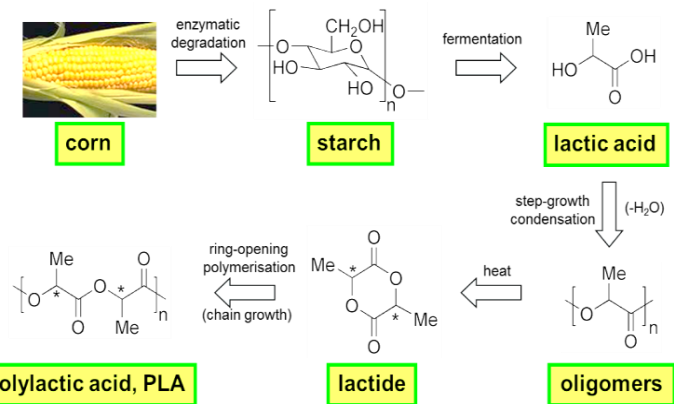
Properties:
- The PLA is a semi-crystalline polymer
- Its glass transition temperature around 55 to 59°C and melting point is 174-184 ° C.
- It shows a good mechanical strength, high Young's modulus, thermal plasticity and has good processability
- It is biodegradable and biocompatible
- It is insoluble in water and soluble in chlorinated solvents, hot benzene, tetrahydrofuran, and dioxane.

Advantages :
- It is derived from renewable resources.
- It is biodegradable nature and used to make ecofriendly plastics.
- Degradation time is weeks or months depending on the conditions
- Emission of greenhouse gases during its production is lower.
- The solid waste generated during its production is very low to a decrease in overall solid waste.
- Recyclable (can be converted back to monomer)

Disadvantages:

- It is unsuitable for high temperature applications
- It may show signs of getting soft or deforming on a hot summer day.

Applications:

- Single-use items like plates, cups, film wrap
- Plastic bottling and fast-food companies
- Textile industry
- Paper coatings, Clothing fibers, Compost bags
- Medical implants such as sutures, screws, rods, pins and mesh have been made due to its ability to degrade into non-toxic lactic acid and eliminating the need for further surgery.
- Polylactic acid injections for skin rejuvenation
- PLA fibers have been used to manufacture casual sports apparel, upholstery material, hygiene products, and diapers.
- PLA as material for food packaging due to increased aesthetics, better printability, good resistance to grease and oils, and reduced issues in taste and odor transfer.
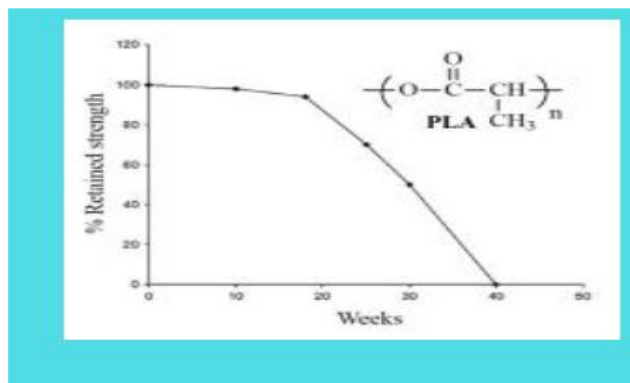
polylactic acid, a biodegradable plastic derived from corn starch, tapioca or the like.

Applications of biodegradable polymers

Biodegradable polymers are often used for drug encapsulation and other medical applications, food and cosmetics packaging are embracing biodegradable plastics. Apparently, many packaging films are made from starch-based and biodegradable plastics.

Biodegradable polymers have applications in:

- Controlled/sustained release drug delivery approaches
- Tissue engineering scaffolds
- Temporary prosthetic implant

Examples of cutlery made from biodegradable plastic

Conducting polymer

In general many organic polymers are used as electric insulators. (Ex: polyethylene, PVC, Teflon etc.). The main reason for non-conducting nature of organic polymers is due to the absence of conjugation in the backbone or absence of conductingingredients.

But due to the extensive research work in this area, scientists are able to synthesize conducting polymers. **Polyacetylene** is the first example of conductingpolymer.

Conducting polymers have backbones of continuous sp^2 hybridized carbon centers. One valence electron on each center

resides in a p_z orbital. The electrons in these delocalized orbitals have high mobility. The conducting properties for a polymer can be accomplished by doping with suitable species.

Examples of conducting polymers are

Polyphenylenevinylene, polyacetylene, polythiophene $(X = S)$ and polypyrrole $(X = NH)$, polyaniline $(X = N, NH)$ and polyphenylene sulfide $(X=S)$.

(X = NH/N, S)   (X = NH, S)
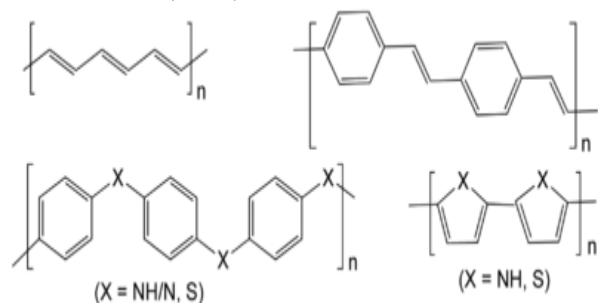
Nobel Prize in chemistry for the year 2000 was combinely awarded to Alan Heeger (University of California, Santa Barbara), Alan MacDiarmid (University of Pensylvania, USA) and Hideki Shirakawa (University of Tokyo &University of Kuba, Japan) for the pioneering work in the field of conducting polymers.

Applications:

- Conducting polymers are useful in discharging large quantities of static electricity in computer industries and in chemical industries. This can be accomplished by coating the conducting polymer over an insulating surface. Hence conducting polymers are used as antistatics.
- Conducting polymers can absorb harmful electromagnetic radiation. So these can be used to coat on the cases of computer monitors and cell phones.
- Printed circuit boards are used in electrical and electronic instruments. They contain copper coated epoxy resins which are expensive and have less adhesive nature. But polymer sheets coated with conducting polymers are inexpensive and have better adhesive properties.
- These are useful in the preparation of artificial nerves i.e., biocompatible conductive polymers can be used for transmitting electrical signals in the body.
- Artificial intelligent materials: These are also called as smart materials. The interesting aspects of these materials are that they can remember configuration and can confirm when exactly same stimulus is given. This property can be utilized in generating pass words where high security is required.
- The conducting polymers can undergo oxidation and reduction depending upon the reagent with which they react. This property can be utilized in detecting the gases. For example, the resistance of poly pyrrole increases on contact with NH_3 (reducing gas) while the resistance decreases in presence of NO_2(oxidizing gas).
- Polymer rechargeable batteries: Repeated oxidation and reduction of polymeric back bone constitutes the principle of polymer rechargeable batteries. For example, in poly pyrrole lithium cell is useful rechargeable battery compared to conventional Ni-Cd cell. So, these are environmentally safe and non toxic.
- These are useful as corrosion inhibitors.
- These can applied in Flat Panel Displays (less than 2 mm thick) which are thinner than liquid crystals displays or plasma displays
- These are also useful as Flexible Display Devices for mobile phones.

Poly aniline:

Polyaniline (PANI) is a conducting polymer of the semi-flexible rod polymer family. Amongst the family of conducting polymers and organic semiconductors, polyaniline has many attractive processing properties. Because of its rich chemistry, polyaniline is one of the most studied conducting polymers of the past 50 years

It can be synthesized by the oxidative polymerization of aniline in presence of ammonium persulphate dissolved in 1M HCl.
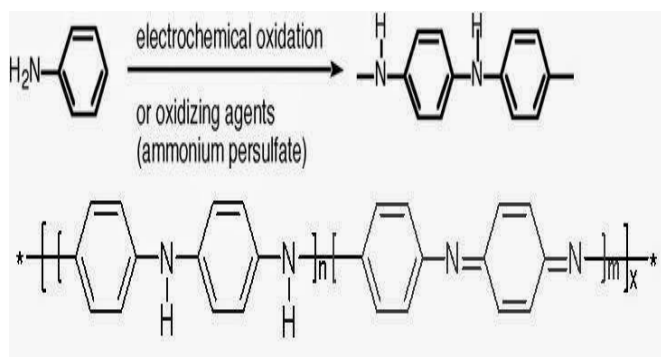
The major applications are printed circuit board manufacturing: final finishes, used in millions of m² every year, antistatic and ESD coatings, and corrosion protection.Polyaniline and its derivatives are also used as the precursor for the production of N-doped carbon materials through high-temperature heat treatment.

Metallic and ceramic implant materials

Ceramics are refractory, polycrystalline compounds, usually inorganic, including silicates, metallic oxides, carbides, and various refractory hydrides, sulfides, and selenides. Oxides such as Al_2O_3, MgO, SiO_2, etc. contain metallic and nonmetallic elements. Ionic salts (NaCl, CsCl, ZnS, etc.) can form polycrystalline aggregates, but soluble salts are not suitable for structural biomaterials. Diamond and carbonaceous structures like graphite and pyrolized carbons are covalently bonded. The important factors influencing the structure and property relationship of the ceramic materials are radius ratios (§2.2.2) and the relative electronegativity between positive and negative ions. Recently ceramic materials have been given a lot of attention as candidates for implant materials since they possess some highly desirable characteristics for some applications. Ceramics have been used for some time in dentistry for dental crowns by reason of their inertness to body fluids, high compressive strength, and good aesthetic appearance in their resemblance to natural teeth. Some carbons have also found use as implants, especially for blood interfacing applications such as heart valves. Due to their high specific strength as fibers and their biocompatibility, they are also being used as a reinforcing component for composite implant materials and tensile loading applications such as artificial tendon and ligament replacements. Although the black color can be a drawback in some dental applications, this is not a problem if they are used as implants. They have such desirable qualities as good biocompatibility and ease of fabrication.

Metals are used as biomaterials due to their excellent electrical and thermal conductivity and mechanical properties. Some metals are used as passive substitutes for hard tissue replacement such as total hip and knee joints, for fracture healing aids as bone plates and screws, spinal fixation devices, and dental implants because of their excellent mechanical properties and corrosion resistance. Some metallic alloys are used for more active roles in devices such as vascular stents, catheter guide wires, orthodontic archwires, and cochlea implants.

The first metal alloy developed specifically for human use was the "vanadium steel" which was used to manufacture bone fracture plates (Sherman plates) and screws. Most metals such as

iron (Fe), chromium (Cr), cobalt (Co), nickel (Ni), titanium (Ti), tantalum (Ta), niobium (Nb), molybdenum (Mo), and tungsten (W) that were used to make alloys for manufacturing implants can only be tolerated by the body in minute amounts. The biocompatibility of the metallic implant is of considerable concern because these implants can corrode in an in the hostile environment of the body.

The consequences of corrosion are the disintegration of the implant material , which will weaken the implant, and the harmful effect of corrosion products on the surrounding tissues and organs.

Stainless Steels

The first stainless steel utilized for implant fabrication was the 18-8, which is stronger and more resistant to corrosion than the vanadium steel. Vanadium steel is no longer used in implants since its corrosion resistance is inadequate in vivo. Later 18-8Mo stainless steel was introduced which contains a small percentage of molybdenum to improve the corrosion resistance in chloride solution (salt water), make them more resistant to physiological saline in human body . This alloy became known as type 316 stainless steel. The inclusion of molybdenum enhances resistance to pitting corrosion in salt water.

Compositions of 316L Stainless Steel

Element	Composition (%)
Carbon	0.03 max
Manganese	2.00 max
Phosphorus	0.03 max
Sulfur	0.03 max
Silicon	0.75 max
Chromium	17.00–20.00
Nickel	12.00–14.00
Molybdenum	2.00–4.00
Iron	34.00-41.00

Properties

316, 316 L stainless steel, which are widely used in implants are non magnetic and possess better corrosion resistance even in saline conditions. The nickel stabilizes the austenitic phase (a metallic, non-magnetic allotrope of iron with an alloying element) at room temperature and enhances corrosion resistance.

Applications

Steels are mainly used in orthopedic implants. The major uses include fracture fixation and joint replacement, Hip joints, ankle joints, knee joints, bone plates, screws etc.

Disadvantages

Even the 316L stainless steels may corrode inside the body under certain circumstances in a highly stressed and oxygen depleted region, such as the contacts under the screws of the bone fracture plate. Thus, these stainless steels are suitable for use only in temporary implant devices such as fracture plates, screws, and hip nails. Surface modification methods such as anodization and passivation are widely used in order to improve corrosion resistance, wear resistance, and fatigue strength of 316L stainless steel.

Titanium based alloys

Titanium alloys, because of their excellent mechanical, physical and biological performance, are finding ever-increasing application in biomedical devices. Titanium's lightness (4.5 g/cm^3) and good mechanochemical properties are salient features for implant application.

Titanium alloy (Ti6Al4V) is widely used to manufacture implants. The main alloying elements of the alloy are aluminum (5.5~6.5%) and vanadium (3.5~4.5%). The addition of alloying elements to titanium enables it to have a wide range of properties: (1) Aluminum tends to stabilize the α -phase,that is increase the transformation temperature from α – to β -phase (Fig. 1.4); (2)

vanadium stabilizes the β -phase by lowering the temperature of the transformation from α to β.

Properties
- Superior biocompatibility
- Excellent corrosion resistance because of the thin surface oxide layer
- Good mechanical properties
- Low density

Applications

They are widely used as hard tissue replacements in artificial bones, joints and dental implants.

Cobalt Chromium Alloys

The two basic elements of the Co Cr alloys form a solid solution of up to 65% Co and 35% of Cr. Molybdenum is added to produce finer grains which results in higher strengths after casting or forging. Chromium enhances corrosion resistance as well as strengthening of the alloy.

At the present time only two alloys are used extensively in implant fabrications, the castable CoCrMo and the wrought CoNiCrMo alloy.

Chemical Compositions of CoCr Alloys CoCrMo

Element	CoCrMo	CoNiCrMo
Cr	27.0	19.0
Mo	5.0	9.0
Ni	--	33.0
Co	68.0	39.0

Applications
- Co-Cr alloys are most commonly used to make artificial joints including knee and hip joints due to high wear-resistance and biocompatibility. Co-Cr alloys tend to be corrosion resistant, which reduces complication with the surrounding tissues when implanted, and chemically inert that they minimize the possibility of irritation, allergic reaction, and immune response. Co-Cr alloy has also been widely used in the manufacture of stent and other surgical implants as Co-Cr alloy demonstrates excellent biocompatibility with blood and soft tissues as well.
- The alloy is a commonly used as a metal framework for dental partials
- Due to mechanical properties such as high corrosion and wear resistance, Co-Cr alloys (eg. Stellites) are used in making wind turbines, engine components, and many other industrial/mechanical components where high wear-resistance is needed.
- Co-Cr alloy is also very commonly used in fashion industry to make jewellery, especially wedding bands.

Ceramics

Ceramics are refractory, polycrystalline compounds, usually inorganic, including silicates, metallic oxides, carbides and various refractory hydrides, sulfides, and selenides. Oxides such as Al_2O_3, MgO, SiO_2, and ZrO_2contain metallic andnonmetallic elements and ionic salts, such as $NaCl$, $CsCl$, and ZnS.

Ceramics in the form of pottery have been used by humans for thousands of years. In recent years, humans have realized that ceramics and their composites can also be used to augment or replace various parts of the body, particularly bone. Thus, the ceramics used for the latter purposes are classified as *bioceramics* Their relative inertness to the body fluids, high compressive strength, and aesthetically pleasing appearance led to the use of ceramics in dentistry as dental crowns. Some carbons have found use as implants especially for blood interfacing applications such as heart valves. Due to their high specific strength as fibers and

their biocompatibility, ceramics are also being used as reinforcing components of composite implant materials and for tensile loading applications such as artificial tendons and ligaments.

Ceramics used in fabricating implants can be classified as nonabsorbable (relatively inert), bioactive Or surface reactive (semi-inert) , and biodegradable or resorbable (non-inert) . Alumina, zirconia, silicone nitrides, and carbons are inert bioceramics. Certain glass ceramics and dense hydroxyapatites are semi-inert (bioreactive), and calcium phosphates and calcium aluminates are resorbable ceramics.

Hydroxy apatite:

Chemical formula
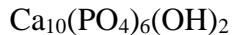
$$Ca_{10}(PO_4)_6(OH)_2$$

Hydroxyapatite (HAp) is a calcium phosphate similar to the human hard tissues in morphology and composition. Particularly, it has a hexagonal structure and a stoichiometric Ca/P ratio of 1.67, which is identical to bone apatite.

An important characteristic of hydroxyapatite is its stability when compared to other calcium phosphates. Thermodynamically, hydroxyapatite is the most stable calcium phosphate compound under physiological conditions as temperature, pH and composition of the body fluids.

Due to its outstanding properties such as, Biocompatibility, Bioactivity , Non toxicity and non inflammatory nature, hydroxyapatite bioceramic has got a variety of applications. Titanium and stainless steel implants are often covered with hydroxyapatite coatings to trick the body and reduce the implant rejection rate. Hydroxyapatite can also be used in instances where there are bone voids or defects. This process is carried out through powders, blocks or beads of the material being placed in the affected areas of bone.

Due to its bioactivity, it encourages the bone to grow and restores the defect. It typically results in healing times shorter than those observed if hydroxyapatite was not used.

Membranes for plasma separation and blood oxygenation

The application of membranes for the separation of solids from liquids is quite common in industrial processes and has had a major impact on biomedical processes. Within the past decade membranes have been applied in the separation of plasma from whole blood. The membranes for plasma separation and fractionation may be distinguished from conventional dialysis membranes and high-flux membranes used in hemofiltration by their very high or select passage of plasma proteins. Membrane techniques are simple and safe to apply and can be competitive to other separation technologies. Studies of membranes in the separation of components from the complex mixture of blood is particularly useful in extending the applications of membranes in bioseparations.

Over the years, tens of millions of lives have been saved and many more have been eased with the help of membranes for blood oxygenation and plasma separation.

Membranes as biomaterials form the basis for the procedures of lung substitution and plasma separation. These membranes are readily available and look very simple: white capillaries, wound to bundles or finished with rather basic textile technologies. But it is not as simple as that: they represent the highest standards of biomedical technology

Bio membranes posses the following characteristics

1. They are impermeable topolar molecules or ions.

2. They have adapted flexibility in shape and size.

3. They are durable

4. They contain proteins that are not simply structural in nature , but have a variety of enzymatic activities.

Examples of memebranes used for blood oxygenation and plasma separation

Polypropylene (PP)

Disposable syringes, blood oxygenator membrane, suture, nonwoven fabric, and artificial vascular grafts

Polymethylmetacrylate (PMMA)

 Blood pump and reservoirs, membrane for blood dialyzer

Membranes for plasma separation
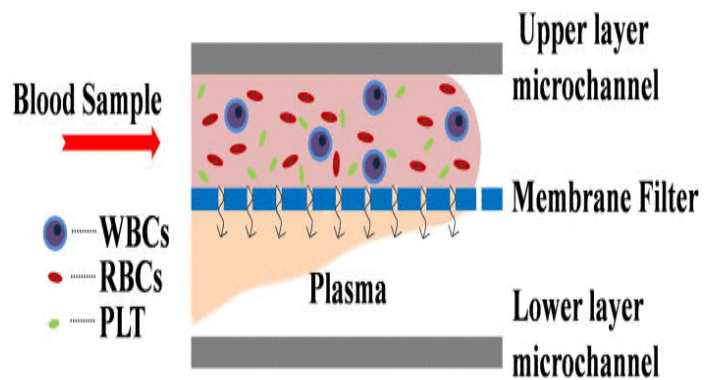
Membrane for blood oxygenation
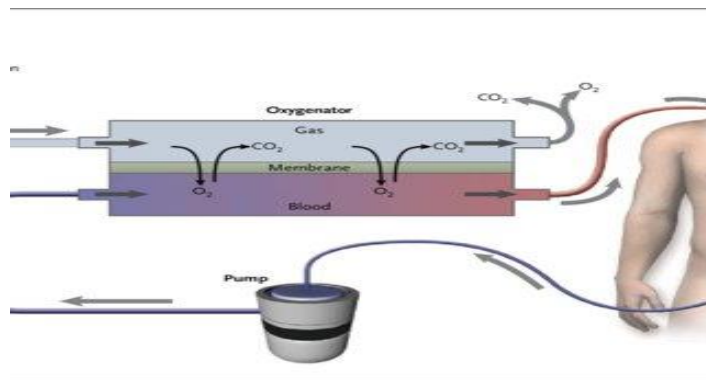
8 Ways-ceramic is used in modern day to day life

Do you think you come into contact with ceramic in your day-to-day life? We've put together a list of 8 ways ceramic is used in modern life, the obvious and the not so obvious.

Take a read and you might just be surprised!

THE OBVIOUS

1. Tiles

Our roofs, bathrooms and kitchens are covered in ceramic tiles. Ceramic can be glazed with different colours and printed with any design, so tiles can be tailored to different people's tastes. They are tough and easy to wipe clean once glazed which is perfect for use in the kitchen or bathroom!

2. Cookware

Majority of crockery and pots are made from ceramic. From unglazed to glazed, mortar and pestles to the mug that holds your tea, ceramic is a staple material in the kitchen. Ceramic knives have also become common, they are one of the hardest knives you can buy yet are extremely lightweight!

3. Brick

Our homes are made from brick and are held together by cement, both of which are types of ceramic. Without ceramic, what would we use instead to create the four walls of our homes?

4. Toilets

Sanitary ware such as toilets, sinks and bath tubs are made from ceramic. Ceramic can be glazed and fired so that it becomes non-porous, perfect for sanitary ware which gets used every day and is, of course, in contact with lots of water!

THE NOT-SO OBVIOUS

5. Space

NASA's Space Shuttle had thousands of heat-resistant tiles protecting its exterior from overheating due to friction generated by Earth's atmosphere. Future reusable space planes are expected to use a new, slimline ceramic material that will enable it to be both more aerodynamic and withstand temperatures up to 2400°C. Composite ceramics are also used to create the nose cones of spacecraft!

6. Cars

Ceramic can help to decrease pollution and capture toxic materials. Today's catalytic converters are made with ceramic and help convert harmful fumes into non-toxic gases, therefore having a huge benefit on the environment. Ceramic components can be found in almost every aspect of a vehicle and are a major contributor to advances in hybrid and eco-friendly vehicles.

7. Artificial Bones and Teeth

Toughened ceramic is used in hip replacements and is designed to be porous so that it can stimulate natural bone growth around the artificial joint. You will also find ceramic fillings for your teeth where the ceramic is chemically bonded to your tooth making it extremely strong.

8. Electronic Devices

Televisions contain ceramic insulators, computers have silicon chips and the electric motors in your vacuum cleaner or blender are also made using ceramic!

Some people say that ceramic is an outdated material and it is often described as 'old fashioned'. In reality, ceramic is the key to many of our new technologies and is used day to day by us all.

With ceramic, we have the capability to do things that we may only have dreamed of once. So next time you're wondering what material would be good for your product, why not think ceramic?

UNIT-IV
ADVANCED MATERIALS
QUESTION BANK
PART - A

1. Define plastics.

Plastics are polymers which can be moulded into any desired shape or form, when subjected to heat and pressure in the presence of a catalyst. They undergo permanent deformation under stress termed as plasticity.

2. Differentiate thermo and thermosetting plastics

S.No	Thermoplastics	Thermosetting plastics
1	They are formed by addition Polymerization	They are formed by condensation polymerization.
2	Adjacent polymer chains are held together by week Vander Waals forces	Adjacent polymer chains are held together by strong covalent bonds called crosslink.
3	They soften on heating and stiffen on Cooling	They do not soften on heating.
4	They can be remoulded	They cannot be remoulded and reused.
5	They are week, Soft and less brittle	They are strong, hard and more brittle.
6	They are soluble in organic solvents	They are insoluble in organic solvents.
7	They have very low molecular weights Ex : Polyethylene ,polypropylene	They have high molecular weights. Ex : Bakelite

3. How is polypropelene prepared?

Polypropelene is readily formed by polymerizing propylene with suitable catalysts, generally alkyl aluminum and titanium tetrachloride.

Polypropylene is produced by the chain-growth polymerization of propene.

Monomère de propylène   Polymère de polypropylène
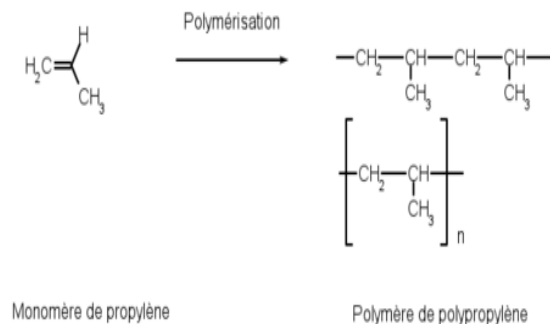
4. What are the uses of PVC?

Economical, versatile polyvinyl chloride is used in a variety of applications in the building and construction, health care, electronics, automobile and other sectors, in products ranging from piping and siding, blood bags and tubing, to wire and cable insulation, windshield system components and more.

5. What are polyamides? Give an example.

The polymers having an amide linkage between their monomers are called polyamides. Eg. Nylon66

6. How is Nylon66 obtained?

It is obtained by condensing adipic acid with hexamethylenediamine with the elimination of water molecule. The chain length depends upon the temperature and time for which the process is carried out.

hexamethylenediamine   adipic acid   nylon-66
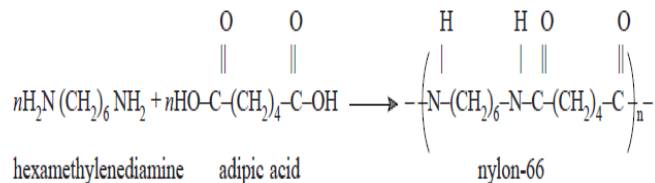
7. What are the properties of polyacrylates?

Polyacrylates are an important class of polymers that are soft, tough and rubbery. Their glass transition temperature is well below room temperature. They are known for their high transparency; good impact toughness and elasticity, and have fairly good heat resistance.

8. What are biodegradable polymers? Give examples.

These are those polymers which can decompose under aerobic or anaerobic conditions, as a result of the action of microorganism/enzymes. Some common examples of biodegradable polymers are PGA and PLA.

9. Give examples for conducting polymers. Examples of conducting polymers are

Polyphenylenevinylene, polyacetylene, polythiophene (X = S) and polypyrrole (X = NH), polyaniline (X = N, NH) and polyphenylene sulfide (X=S).

10. How is polyaniline synthesized?

It can be synthesized by the oxidative polymerization of aniline in presence of ammonium persulphate dissolved in 1M HCl.
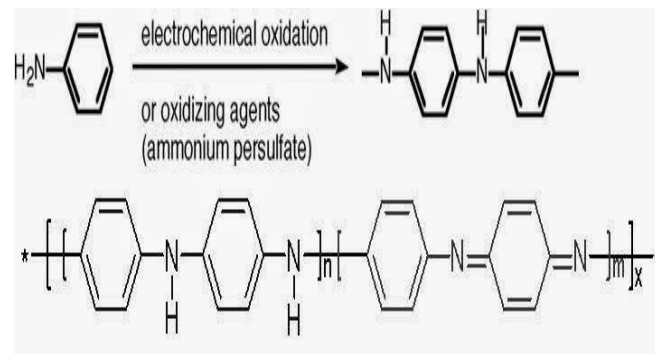
11. Why are metals used as biomaterials? Give examples.

Metals are used as biomaterials due to their excellent electrical and thermal conductivity and mechanical properties. Some metals are used as passive substitutes for hard tissue replacement such as total hip and knee joints, for fracture healing aids as bone plates and screws, spinal fixation devices, and dental implants because of their excellent mechanical properties and corrosion resistance.

12. Give the composition of 316 stainless steel

Element	Composition (%)
Carbon	0.03 max
Manganese	2.00 max
Phosphorus	0.03 max
Sulfur	0.03 max
Silicon	0.75 max
Chromium	17.00–20.00
Nickel	12.00–14.00
Molybdenum	2.00–4.00
Iron	34.00-41.00

13. What are ceramics?

Ceramics are refractory, polycrystalline compounds, usually inorganic, including silicates, metallic oxides, carbides, and various refractory hydrides, sulfides, and selenides.

14. What are the purposes of adding Al and V?

(1) Aluminum tends to stabilize the α -phase,that is increase the transformation temperature from α – to β -phase (Fig. 1.4); (2) vanadium stabilizes the β -phase by lowering the temperature of the transformation from α to β.

15. Give the composition of Co Cr alloys?

The two basic elements of the Co Cr alloys form a solid solution of up to 65% Co and 35% of Cr.

16. What are the disadvantages of using stainless steel as biomaterial?

Even the 316L stainless steels may corrode inside the body under certain circumstances in a highly stressed and oxygen depleted region, such as the contacts under the screws of the bone fracture plate. Thus, these stainless steels are suitable for use only in temporary implant devices such as fracture plates, screws, and hip nails.

17. Why are ceramics used in dentistry?

Their relative inertness to the body fluids, high compressive strength, and aesthetically pleasing appearance led to the use of ceramics in dentistry as dental crowns.

18. What is hydroxyl apatite? Give its formula.

Hydroxyapatite (HAp) is a calcium phosphate similar to the human hard tissues in morphology and composition. Its Chemical formula is $Ca_{10}(PO_4)_6(OH)_2$

19. What are the characteristics of biomembranes?

They are impermeable topolar molecules or ions.
2. They have adapted flexibility in shape and size.
3. They are durable
4. They contain proteins that are not simply structural in nature, but have a variety of enzymatic activities.

20. Give examples of memebranes used for blood oxygenation and plasma separation.

Polypropylene (PP), Polymethylmetacrylate (PMMA)

PART B

1. What are silicones? Give their preparation and applications.
2. Give the preparation properties and applications of Poly lactic acid.
3. Explain the applications of conducting polymers.
4. Explain the membranes for plasma separation and blood oxygenation.
5. Give the preparation and applications of PVC, Nylon 66 and polyurethanes.
6. What are stainless steels? Explain the composition, properties and applications of stainless steel as biomaterials.
7. What are conducting polymers? Give the preparation, properties and applications of polyaniline.
8. Explain the reasons for using metals and ceramics as implant materials? Give examples.

UNIT –V
NANO MATERIALS

INTRODUCTION

The world of materials is rapidly progressing with new and trendiest technologies, and obviously novel applications. Nano technology is among these modern and sophisticated technologies, which is creating waves in the modern times. Actually, nano technology includes the concept of physics and chemistry of materials. It beckons a new field coming to the limelight. So, nano technology is an interesting but emerging field of study, which is under constant evolution offering a very wide scope of research activity.

Nanoscience

Nanoscience is the study of the phenomena and manipulations of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at larger scales.

Nano chemistry

Nano chemistry is a relatively new branch of chemistry concerned with the unique properties associated with assemblies of atoms or molecules in nano dimension (approximately 1 to 100 nm). It also deals with the synthesis, characterization, properties and applications of these nanomaterials.

Nano-technology

Nano-technology is the design, fabrication, characterization and applications of materials at nano-level (1-100 nm) and converting them into useful devices.

Why Nano Technology ?

In the materials world, particularly in ceramics, the trend is always to prepare finer powder for the ultimate processing and better sintering to achieve dense materials with dense fine-grained microstructure of the particulates with better and useful properties for various applications. The fineness can reach up to a molecular level (1 nm – 100 nm), by special processing techniques. More is the fineness, more is the surface area, which increases the 'reactivity' of the material. So, the densification or consolidation occurs very well at lower temperature than that of conventional ceramic systems, which is finally 'cost-effective' and also improves the properties of materials like abrasion resistance, corrosion resistance, mechanical properties, electrical properties, optical properties, magnetic properties, and a host of other properties for various useful applications in diverse fields.

Nanoparticles

Nanoparticles are the simplest form of structures with the sizes in nm range. In principle, any collection of atoms bonded together with a structural radius of <100nm can be considered as a nanoparticle..

Nanomaterials

Nanometre is one billionth of a metre.

$1nm = 1x10^{-9}m$

The properties of a bulk material will be different from its nanosized particle.

The unique properties of nanosized particles is mainly due to

i) The smaller particles having a relatively larger surface area compared with their volume, making them chemically more reactive.

ii) When this size is below 100nm, quantum effects can change the optical, electronic or magnetic qualities of materials.

Nanocrystal

Nanocrystal is a material particle having one dimension lesser than 100nm and composed of atoms in either a single or polycrystalline arrangement.

Quantum dot

Quantum dot is a nanocrystal made of semiconductor materials.

Polymeric Nanoparticles

Polymeric nanoparticles are prepared from polymers. They are considered as potential drug delivery devices due to applications in drug targeting to particular organs and tissues.

Dendrimers

Dendrimers is one kind of polymeric nanoparticles constructed by the successive addition of layers of branching groups. The properties of dendrimers are dominated by the functional groups on the molecular surface. It finds its applications as solubilizing agents imaging agents, sensors, drug delivery, Gene therapy, detecting agents such as a dye molecule.

CLASSIFICATION OF NANOMATERIALS

The main classification of nanomaterials is based on the dimensions of their structural elements.

(i) **Zero-dimensional (0D) nanomaterials:** Nanomaterials having diameter less than 100nm.

Example: Nanoparticles, nanoclusters and nanocrystals.

(ii) **One-dimensional (1D) nanomaterials:** Nanomaterials having one dimension in the nanometer scale. It includes nanofibers, nanorods and nanotubes.

(iii) **Two-dimensional (2D) nanomaterials:** Nanomaterials having two dimensions in the nanometer scale. It includes nanofilms, nanowires, nanolayers and nano coatings.

(iv) **Three-dimensional (3D) nanomaterials:** Nanomaterials having three dimensions in the nanometer scale. It includes powders, fibrous, multilayer and polycrystalline materials.

Table:-1 Distinction between molecules,nano particles and bulk material

Property	Atoms /Molecules	Nanomaterials	Bulk Materials
Size	Few amstrongs(10^{-10}m)	Nanometres(10^{-9}m)	Microns to higher(10^{-6}m)
No.of constituent particles	One atom to few/many atoms	Few atoms to several thousand of atoms	Infinite/ of the order of Avogadro number
Electronic structure	Confined	Confined	Not confined (continous)
Mechanical properties	NA	Properties depend on particle size	Properties independent of particle size
Wave nature	Applicable	Applicable	Applicable to limited extend
Random motion	Present	Present (Brownian)	Not Present
Stability	Stable	Can be stable or unstable depending on surface energy	Stable
Examples	NaCl , CO_2	Carbon nanotube	Gold bar, silver bar

Table:2 Bulk gold materials Vs nanosized gold

Gold bulk	Nanosized gold
Shiny (metallic)	Insulator
Yellow	red (~10 nm particles absorb green light)
noble metal	excellent catalysts (2–3 nm nanoparticles)
fcc structure	icosahedral symmetry
non-magnetic	Magnetic
melts at 1064°C	Much lower melting temperature (sizes depending)
constant physical Properties. regardless of its size	size-dependent properties

SIZE DEPENDENT PROPERTIES OF NANO MATERIALS

The nano materials have different properties when compared to bulk due to the following reasons

- Large surface area can make nano materials more chemically reactive and affect their strength or electrical properties.
- Quantum effects can begin to dominate the behavior of matter at nanoscale, which affects several properties such as melting point, boiling point, band gap,optical properties, mechanical properties and magnetic properties.

Nanomaterials are composed of grains resulting a significant increase in the volume fraction of grain boundaries or interfaces, resulting defect configurations. Hence the mechanical and chemical properties of nanomaterials are significantly altered due to defect dynamics.

The elastic property of nanomaterials are different from that of bulk alloys due to the presence of increased fraction of defects

Example

1. Nanocrystalline ceramics are tougher and stronger than those with coarse grains
2. Nano-sized metals exhibit significant decreases in toughness and yield strength increases

1. Thermal properties (Melting points)

Nano-materials have a significantly lower melting point or phase transition temperature than bulk materials. This is due to

 i. reduced lattice spacing between atoms.

 ii. due to huge fraction of surface atoms in the total amount of atoms.

- Nano crystal size decreases $\rightarrow$ surface energy increases $\rightarrow$ Melting point decreases
- Example:- Melting point of 3nm CdSe – 700K,
  Bulk CdSe --1678 K.

2. Optical properties (absorption and scattering of light)

- Nano materials exhibit different optical properties due to quantum confinement of electrons within the nano particles increases the energy level spacing.
- Optical properties depend on size, shape, surface characteristics, interaction with surrounding environment etc.

Example:

Bulk gold –yellow in colour.

Nano gold can be orange (80 nm) red (20 nm) or purple depending on particle size.

The optical absorption peak of a semiconductor nano particles shifts to a short, wavelength, due to an increased band gap

The colour of metallic nano particles may change with their sizes due to surface   plasma resonance

3. Magnetic properties

Magnetic properties of nano particles are different from that of the bulk materials. Ferro-magnetic behavior of bulk materials disappear, when the particle size is reduced and transfer to super- para magnetic. This is due to the huge surface area.

Example:

Material	Bulk	Nano scale
Fe,Co and Ni	Ferromagnetic	Super paramagnetism
Na,K	Paramagnetic	Ferromagnetic

4. Mechanical properties

The nano materials have less defects compared to bulk materials, which increases the mechanical strength. As nano-materials are stronger, harder and more wear resistant and corrosion resistant, they are used in spark plugs

Example:

Nano-crystalline carbides are much stronger, harder and wear resistant, which   are used in micro drills.

5. Electrical   properties

Electrical conductivity decreases with a reduced dimension due to increased surface scattering. However, it can be increased, due to better ordering in micro-structure

Nano-crystalline materials are used as very good separator plates in batteries, because they can hold more energy than the bulk materials.

Example:

Nickel-metal hydride batteries made of nanocrystalline nickel and metal hydride, require far less frequent recharging and last much longer.

NANO PARTICLES:

- Nanoparticles are the simplest form of structures with sizes in the nm range. In principle any collection of atoms bonded together with a structural radius of <100nm can be considered as a nanoparticle.
- Nanoparticles are very similar to nanoclusters but it contains larger aggregates containing 10^3 or more atoms.
- Nanoparticles may exhibit size-related properties that differ significantly from those observed in fine particles or bulk materials.   These are made of metals, semiconductors, or oxides and they show good mechanical, electrical, magnetic, optical , chemical, thermal, diffusion properties.
- The properties of materials change as their size approaches the nanoscale and as the percentage of atoms at the surface of a material becomes significant.

NANOCLUSTERS:

- Nano clusters constitute an intermediate state of matter between molecules and bulk materials.
- These are fine aggregates of atoms or molecules.
- A nanocluster is a nanometer sized particle made up of equal subunits. These subunits can be atoms of a single element, molecules or even combinations of atoms of several elements in subunits with equal stoichiometries

Example: Na_n, $(SF_6)_n$,$(H_2O)_n$, $(Cu_3Au)_n$, $(TiO_2)_n$ etc.

- The size of nanocluster ranges from sub-nanometer to 10 nm in diameter.
- It has been found that clusters of certain critical size (clusters with a certain number of atoms in the group) are more stable than others. Nanoclusters consisting of upto a couple of hundred atoms, but larger aggregates containing 103 or more atoms are called nanoparticles.

- Nanoclusters can be classified based on the nature of bonding present between the atoms of the aggregate.
  They are (a) vanderwaals cluster   (b) ionic cluster
            (c) metallic cluster and   (d) network cluster.
  (a) **Vander Waals cluster**: Here the interaction between the constituents of the cluster is weak vanderwaals forces (strength of bond is 0.3eV per atom or less). Weak binding leads to weak melting and boiling points.
   Example: Molecular clusters like $(SF_6)_n, (I_2)_n$
  (b)Ionic cluster: Here the force of attraction between the species is electrostatic force
   (strength of the bond is 2-4 eV per atom).
  Example: $(NaCl)_n$
  (c) Metallic cluster: Atoms are held together by metallic bonds. The force of attraction in metal clusters can range from moderate to strong ($0.3 – 3$ eV per atom).
  Example: $(Na)_n, (Cu_2 Au)_n$
  (d) Network cluster: Covlent bonding can result in the formation of atomic network. Bonds in clusters are usually strong($1-4$eV per atom).
   Example: C_{60} fullerene
 Production:

Aggregates of atoms
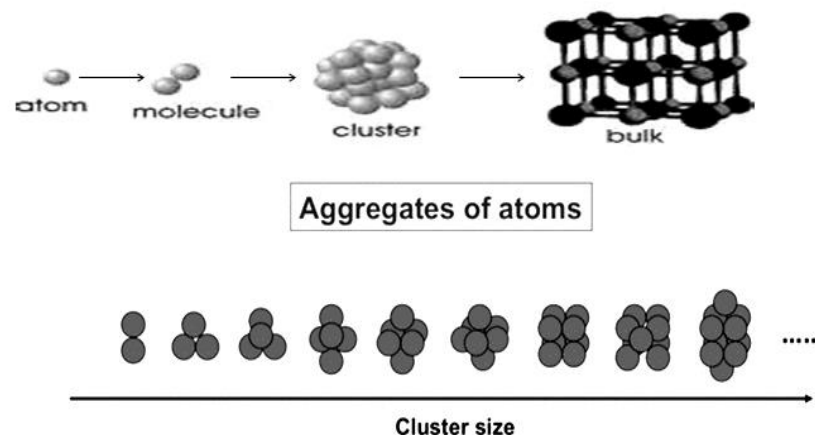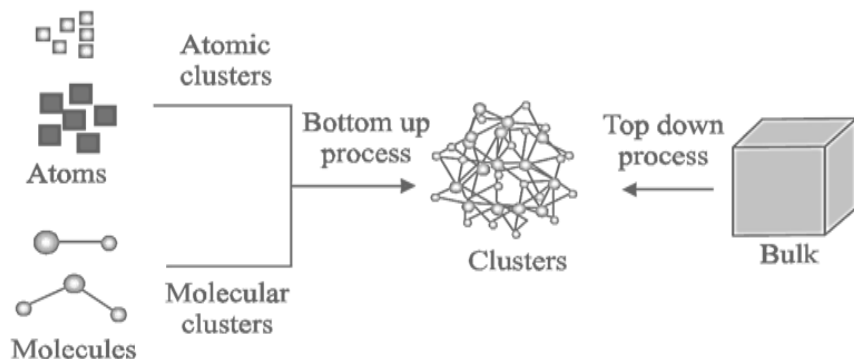
Cluster size

- Atomic clusters are formed by the nucleation of atoms.
- Molecular clusters are formed by the nucleation of molecules.

Properties of nano clusters:
- **Magic number:** Number of atoms present in the clusters of critical sizes with higher stability.
- Clusters containing transition metal atoms have unique electronic, chemical and magnetic properties.
- These properties vary with
  (a) The number of constituent atoms.
  (b) The type of element
  (c) The net charge on the cluster.
- The reactivity of nanoclusters are decreased due to their decrease in size.
- The melting point of nanoclusters are lower than the bulk materials due to high surface to volume ratio.
- The electronic structure of the nanocluster is more confined than the bulk materials.

Applications of nanocluster

1. It is used as catalysts in many reactions.
2. It is used in nano based chemical sensors.
3. It is also used as a light emitting diode in quantum computers.

3.2.3.NANO WIRES:

Nanowire is a two dimensional cylindrical solid material having an aspect ratio i.e, length to width ratio greater than 20. Diameter of the nanowire ranges from 10-100 nm.

Different types of nanowires are

S.No	Types of nanowires	Examples
1.	Metallic nanowires	Au, Ni, Pt
2.	Nanowires of semiconductors	InP, Si, GaN
3.	Nanowires of insulators	SiO_2, TiO_2
4.	Molecular nanowires	DNA

Synthesis of nanowires

1. Template-assisted synthesis

Template assisted synthesis of nanowires is a simple way to fabricate nanostructures. These templates contain very small cylindrical pores or voids within the host material and the empty spaces are filled with the chosen material to form nanowires.
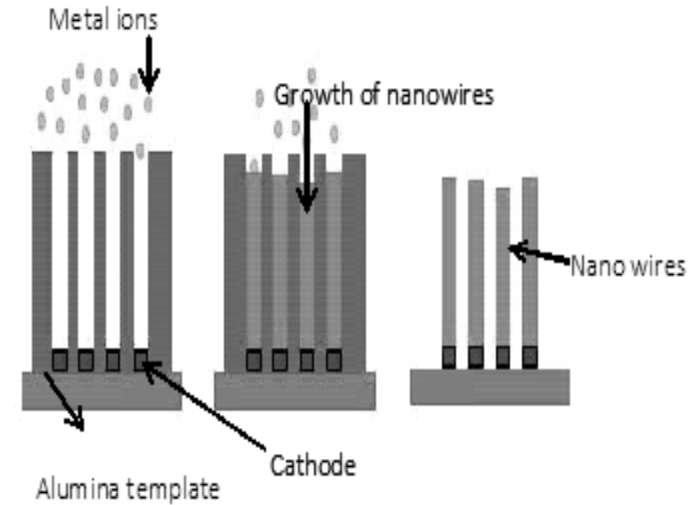
2. VLS (Vapour-Liquid-Solid)method

- Source material (Gas phase) is absorbed by the catalyst (liquid phase).
- Upon super saturation of the liquid alloy, a nucleation event generates a solid precipitate (Solid phase).
- This seed serves as a preferred site for further deposition of material at the interface of the liquid droplet.
- And promotes the elongation of the seed into a nanowire.

Reactant + Catalyst $\longrightarrow$ Nanoparticles
(Gas phase)   (Liquid phase)   (Solid phase)

(Source material)
Gas flow
(Liquid phase)
Catalyst
Substrate
(Seeding)
Nucleation
Growth direction
(Nano wire)
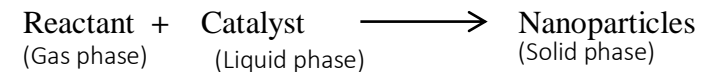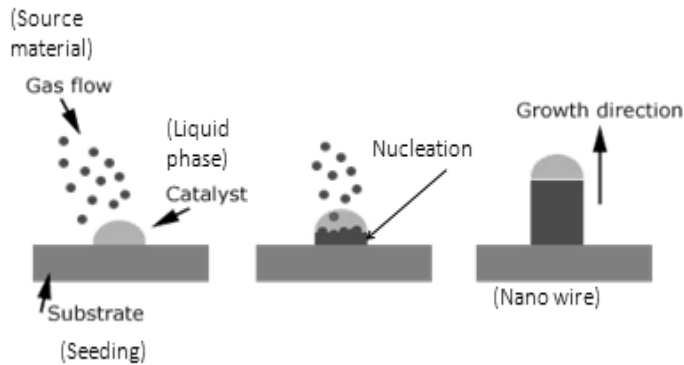
Properties of nanowires

- Nanowires are two-dimensional material.
- Conductivity is less than that of bulk materials.
- Due to its large surface area it exhibits different optical, chemical, thermal and Electric properties.
- Silicon nanowires show strong photoluminescence characteristics.

Applications of nanowires

- Used to enhance mechanical properties of composites.
- Used to prepare active electronic components like *p-n* junction and logic gates.
- Semiconductor nanowire crossings are used in digital computing.
- It is used in high-density data storage either as magnetic heads or as patterned storage media.
- It replaces conventional coppers in computers, televisions etc.,
- Used to link tiny components into very small circuits.

NANO RODS:

Nanorods are one dimensional nanostructures, shaped like long sticks rods. One dimension is in nanometre, which produces quantum confinement and alters the properties of the material. Usually, diameter is in the nanoscale. If the ratio of length to width is 1-20, it called a nanorod.

Eg: Zinc oxide, admium sulphide, Gallium nitride nano rods.

- It is a two-dimensional cylindrical solid material.
- Length to width ratio < 20.
- **Examples:** ZnO, CdS nanorods etc.,

Synthesis of nanorods:

- It is produced by direct chemical synthesis.
- Combination of ligands is required to control the shape of the nanorods.
- Ligands bond to different facets of the nanorod with varying strengths.
- Thereby, elongated Nano rods grow with desired shape.

Properties:

- Two dimensional materials.
- It exhibits optical and electrical properties.

Applications of nanorods

- Nanorods find application in display technologies.
- It is also used in the manufacturing of micro mechanical switches.
- Nanorods are used in an applied electric field, micro electro mechanical systems etc.,
- Nanorods along with noble metal nanoparticle function as theragnostic agents.
- They are used in energy harvesting and light emitting devices.
- Used as cancer therapeutics.

NANO TUBES:
- Nano-tubes are one of the most widespread studied and used materials, consists of tiny cylinders of carbon and other materials like boron nitride.
- Nano-tubes of carbon and inorganic compounds with structures comparable to the layered structure of graphite have been prepared. Studies on carbon nano-tubes are quite extensive.

Carbon Nanotubes (CNT)
- Carbon nanotubes are allotropes of carbon with a nanostructure having a length-to-diameter ratio greater than 1,000,000.
- When graphite sheets are rolled into a cylinder, their edges joined and form carbon nanotubes
- Nanotubes naturally align themselves into "ropes" and held together by vanderwaals forces. But each carbon atoms in the carbon nanotubes are linked by the covalent bond.
- Their unique molecular structure results in extraordinary macroscopic properties, including high tensile strength, high electrical conductivity, high ductility, high heat conductivity and relative chemical inactivity.
- It has potential applications in electronic industry.

Types of carbon nanotubes

Carbon nanotubes are lattice of carbon atoms, in which each carbon is covalently bonded to three other carbon atoms. Depending upon the way in which graphite sheets are rolled, two types of CNTs are formed.

1. Single - walled nanotubes (SWNTs).
2. Multi – Walled nanotubes (MWNTs)

1. Single - walled nanotubes (SWNTs)
- SWNTs consist of one tube of graphite. It is one-atom thick having a diameter of 2 nm and a length of 100

- SWNTs are very important, because they exhibit important electrical properties.
- It is an excellent conductor.

Three kinds of nanotubes are resulted, based on the orientation of the hexagon lattice.
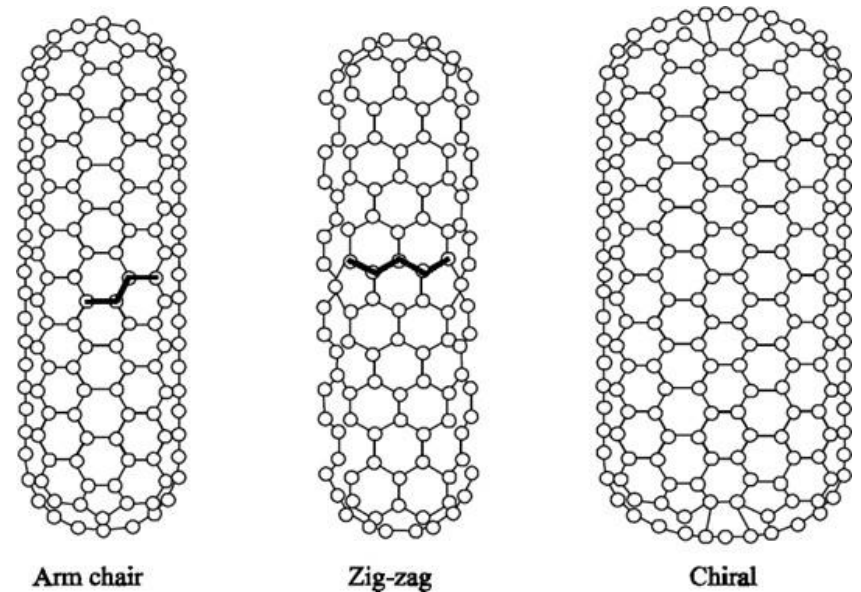
Fig :- Structure of Single walled carbon nanotubes

(a) Arm-chair structures: The lines of hexagons are parallel to the axis of the nanotube.

(b) Zig-zag structures: The lines of carbon bonds are down the centre.

(c) Chiral nanotubes: It exhibits twist or spiral around the nanotubes.

It has been confirmed that arm-chair carbon nanotubes are metallic while zig-zag and chiral nanotubes are semiconducting.

2. Multi - walled nanotubes (MWNTs)

MWNTs (nested nanotubes) consist of multiple layers of graphite rolled in on themselves to form a tube shape. It exhibits both

metallic and semiconducting properties. It is used for storing fuels such as hydrogen and methane.
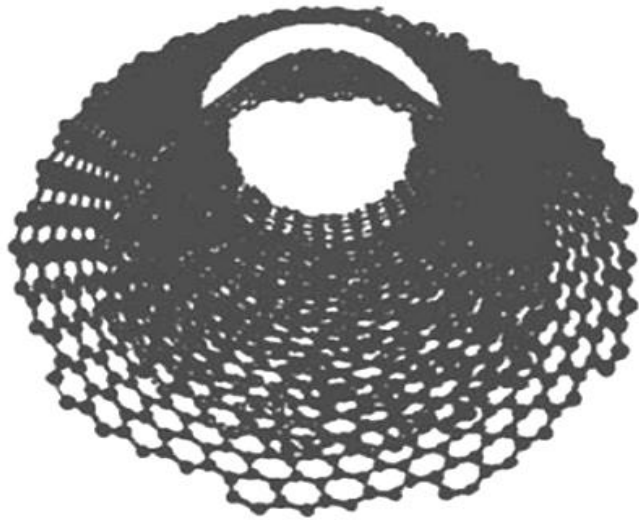
Fig :- Structure of Multi walled carbon nanotubes

Properties of CNTs

- CNTs are very strong, withstand extreme strain in tension and posses elastic flexibility.
- The atoms in a nano-tube are continuously vibrating back and forth.
- It is highly conducting and behaves like metallic or semiconducting materials.
- It has very high thermal conductivity and kinetic properties.

Applications of CNTs

- It is used in battery technology and in industries as catalyst.
- It is also used as light weight shielding materials for protecting electronic equipments.
- CNTs are used effectively inside the body for drug delivery.
- It is used in composites, ICs.

SYNTHESIS OF NANOPARTICLES
CHEMICAL METHODS
i).Metal Nanocrystals by Reduction

(a)Precipitation:
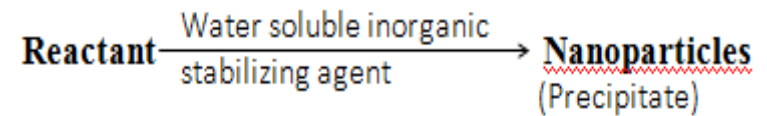
Examples: Precipitation of BaSO₄ Nanoparticles:
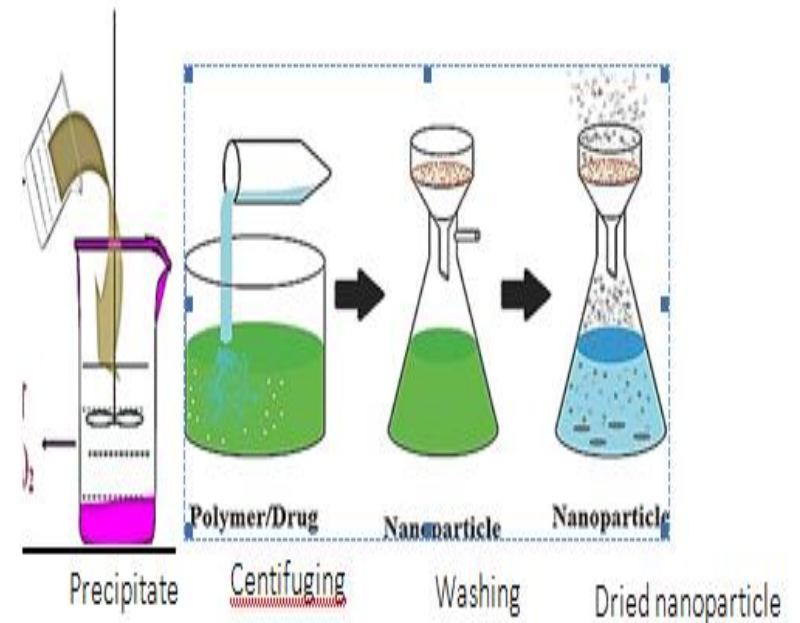
Procedure:

10 gm of Sodium hexameta-phosphate (stabilizing agent)

+ 80 mL distilled water/250ml beaker

↓ i.Dissolve it

ii.Add 10 mL of 1M Sodium sulphate solution
+ 10 mL of 1M Barium nitrate solution

Stir it for 1 hour

↓

Precipitate is obtained

↓

Centrifuge, wash with distilled water and dry it in vacuum drier

Reaction:

$$Ba(NO_3)_2 + Na_2SO_4 \xrightarrow{\text{Stabilizing agent}} BaSO_4\downarrow + NaNO_3$$
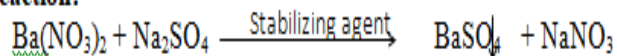
In the absence of stabilizing agent, Bulk $BaSO_4$ is obtained.

(b) Precipitation by reduction: This method involves reduction of metal salts in appropriate solvents with variety of *reducing agents*.

Metal salt $\xrightarrow[\text{Reduction}]{}$ Metal atom $\xrightarrow{\text{Stabilizing agent}}$ Nanoparticles
(Nucleation centre) (Atomic clusters)
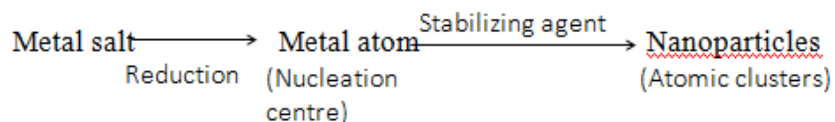
Clusters are surrounded by stabilizing molecule to prevent agglomeration.

Example-1:

Reduction of chloroaurate ions in aqueous solution by citric acid or sodium borohyd ride gives gold hydro sol (particle size in the range of 10-640 °A).

Reduction :

Chloro aurite ions + Sodium boro hydride $\xrightarrow{\text{Reduction}}$ Gold hydrosol
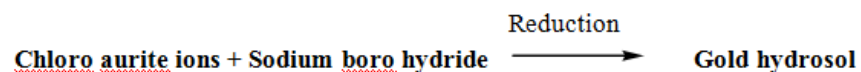
Alcohol, glycol, metal borohydride, Phosphonium chloride are some of the reducing agents involved in this method.

Sols of metals and semiconductor nano particles are stabilized by the presence of ligand or stabilizing agent(Long chain amines, thiol or polymers)

Ex: PVA-PVP which prevent the aggregation of the particle

Nano crystal of CdS, CdSe, Zno, Zns, HgTe, Pbs, Cus, Cu_2 S, AgI and TiO2 were prepared by this method.

Example-2:

$$3MoCl_2 + 6 NaBH(C_2H_5)_3 \xrightarrow[\text{Room temperature}]{\text{Stabilizing agent}} 3 Mo + 6NaCl + 3H_2 + 6B(C_2H_5)_3$$

(Dissolved in (Reducing
Toluene) agent)
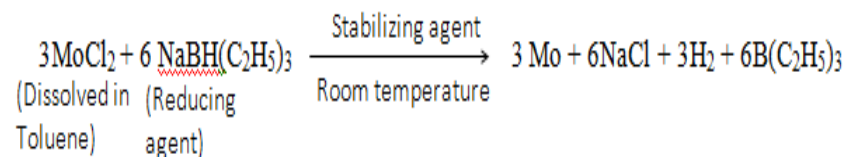
ii. Thermolysis

It is the process of making nano particles by the decomposition of solids at high temperature having metal cations and molecular anions (or) metal organic compounds.

(eg)- Lithium nano particles are produced by the decomposition of Lithium azide(LiN_3) at 400 °C.

Decomposition

$$\text{LiN}_3 \xrightarrow[\text{400 °C}]{\text{Decomposition}} \text{Li-nano particle}$$
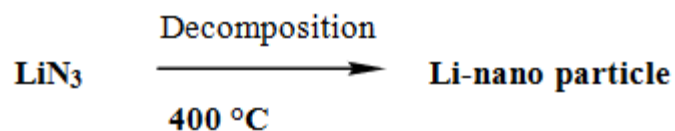
This method is of two types

    a.Hydrothermal process

    b.solvo thermal process

(a)Hydrothermal synthesis
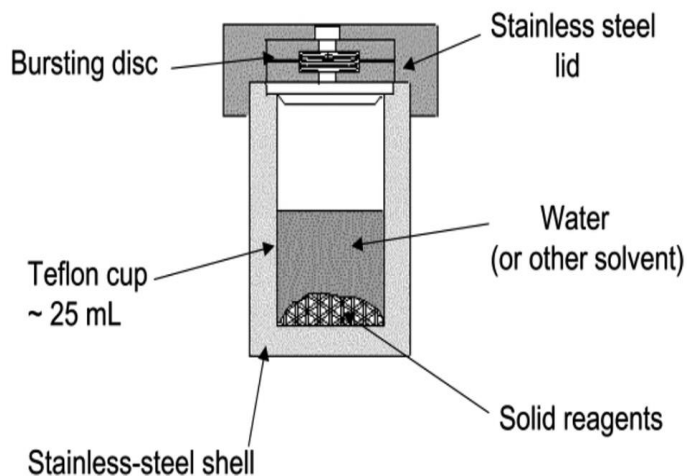
- Hydrothermal synthesis is carried out in an autoclave under autogenous (high) pressure and below the supercritical temperature of water (374 °C).
- These conditions are favorable for the crystallization of products.
- pH of the medium tobe maintained, pH is generally made alkaline to increase the solubility of the reactants.

Example-Synthesis of ZnO nanoparticles

- This process is carried out in teflon lined sealed stainless steel autoclave at the temperature range of 100 – 200 °C for 6 – 12 hrs under autogenous pressure.
- The stock solution of $Zn(CH_3COO)_2.H_2O$ (0.1M) was prepared in 50ml methanol under stirring.
- 25 ml of NaOH(0.2 – 0.5M) solution prepared in methanol was added to maintain PH (8-11),Finally at the end of the reaction white ZnO nano particles are formed.

$$Zn(OH)_2 \longrightarrow Zn^{2+} + 2OH^-$$
$$Zn^{2+} + 2OH^- \longrightarrow ZnO + H_2O$$
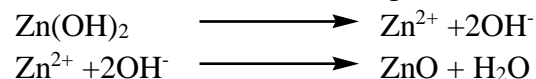
- Metal oxides, Carbon nanotubes etc. can be prepared this way.

Advantages

- Solvent used is water.
- Rate of the reaction is much faster at high temperature and pressure.
- Ability to synthesize large crystals of high quality.
- Reagents and solvents can be regenerated.
- Used to prepare nanomaterials of different morphology (powder, rod, wire, tube, single crystals and nanocrystals).

Disadvantages:

- High cost of equipment.
- Sometimes, it is difficult to predict the morphology of the product.

(b)Solvothermal synthesis

A "solvothermal reaction can be defined as a chemical reaction (or a transformation) between precursor(s) in a solvent (in a close

system) at a temperature higher than the boiling temperature of this solvent and under high pressure".

The Solvothermal method is identical to the hydrothermal method except that a variety of solvents other than water can be used for this process. This method has been found to be a versatile route for the synthesis of a wide variety of nanoparticles with narrow size distributions, particularly when organic solvents with high boiling points are chosen

It is a method for preparing a variety of materials such as metals, semiconductors, ceramics, and polymers.

- Solovothermal are usually thick walled steel cylinders with hermetic seal which must withstand high temperature and pressure for prolonged periods of times.
- The autoclave material must be inert with respect to the solovent. The closure is the most important element of the autoclave.
- To prevent corroding of the internal cavity of the autoclave, prodective inserts are genrally used. These may have the same shape of the autoclave and fit in the internal cavity.
- Inserts may be made up of carbon free iron, glass or quarts, copper or Teflon depending on the temperature and material used.
- The process involves the use of a non-aqueous solvent under moderate to high pressure (typically between 1 atm and 10,000 atm) and temperature (typically between 100 °C and 1000 °C) that facilitates the interaction between reactants during synthesis
- High temperature and pressure facilitates the dissolution of the reactants and products are generally obtained in the nanocrystalline form. It is then washed and then dried.

Example-1:- Nano crystal of CdSe have been prepared by reacting cadmium stereate with selenium powder using toluene as solvent,tetrahydro phenolphthalein as reducing agent.

$$\text{Cadmium stereate} + \text{Selenium} \xrightarrow{\text{Toluene}} \text{CdSe}$$
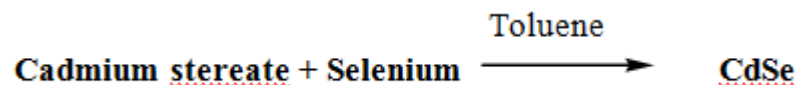
Example-2(eg-2):- Cadmium oxalate and chalcogens undergo reaction in presence of pyridine as solvent to produce cadmium nanoparticle.

$$\text{CdC}_2\text{O}_4 + \text{E} \xrightarrow{\text{Pyridine}} \text{CdE}$$
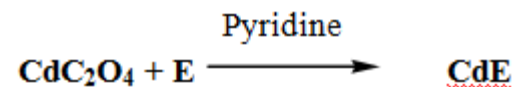
E = Chalcogenide(S,Se,Te)

Advantages:

- Relatively easy and cheap method.
- Products obtained are in crystalline form. So no purification required.
- Can be used for preparing nanomaterials of different morphology (powder, rod, wire, tube, single crystals and nanocrystals).
- Precise control over the size, shape distribution and crystallinity of nanoparticles by varying experimental conditions.
- Variety of organic solvents can be used as it helps the dispersion nanocrystallites and may stabilize some metastable phases.

Disadvantages:

- Inability to monitor crystals in the process of their growth.
- The need to expensive autoclave.
- Safety issues during the reaction process.

Applications

- Various kind of Nano structures canbe center sized of through solvothermal approaches including medal oxides carbonaceous Nano structures and etc.,
- This method can also be used produce zeolite ,nano wires, carbon nanotubes

iii. Sonochemical synthesis

- Sonochemistry is the research area in which molecules undergo chemical reaction due to the application of powerful ultrasound radiation (20 KHz–10 MHz).
- Application of ultrasound to chemical reactions and processes
- Ultrasound is the part of sonic spectrum (20KHz-10Mhz),can be divided into 3 regions

  1. Low frequency ,high power ultra sond (20-100KHz)
  2. High frequency ,medium power ultra sound (100KHz- 1MHz)
  3. High frequency ,low power ultra sound (1-10MHz)

- In this method, ultrasound wave is the driving force for the formation of various nanostructured materials.
- During sonication, microscopic bubbles are formed in the solution by a process known as cavitation and these bubbles grow and may implode.
- This cavity is called cavitation bubble and this process is called cavitation
- The implosion leads to the formation of large heat and pressure that speed up the reaction.

- During implosion, it forms extremely high temperatures as high as 5000^0K, and pressures upto 1800 atm and cooling rates can often exceed $\sim 10^{10}$K/s.
- This large amount of energy released can enhance the chemical reactivities and cause physical effects.
- In case of tellurium bundles of nanowhiskers, sonication leads to hot spots, which could cause local fluctuation in the solubility of tellurium an induce the seeding and growing t-Te.

Bubble forms → Bubble grows in successive cycles → Reaches unstable size → Undergoes violent collapse

5000 °C 2000 atm
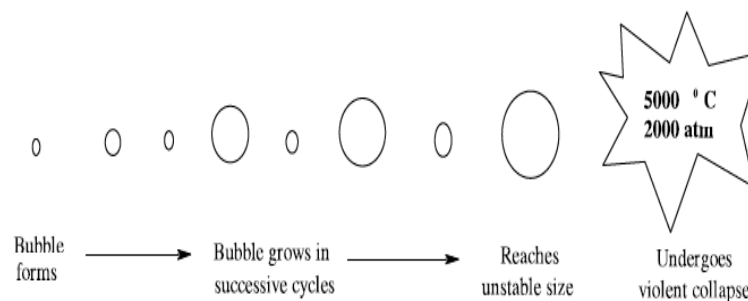
Cavitation bubble formation and collapse

Example-1

- Large-scale synthesis of bundles of t-Te nanowhiskers was carried out from metallic Te powder by sonication.
- In this synthesis, high-quality, uniform and crystalline nanowhisker bundles of t-Te were formed within 1 hour.
- Te powder along with KOH and water was stirred for form a dark purple solution.
- The unreacted Te powder was centrifuged and redispersed in water.

- The mixture was sonicated for 1 hour at 65-75^{0}C at different intervals of time

Example-2
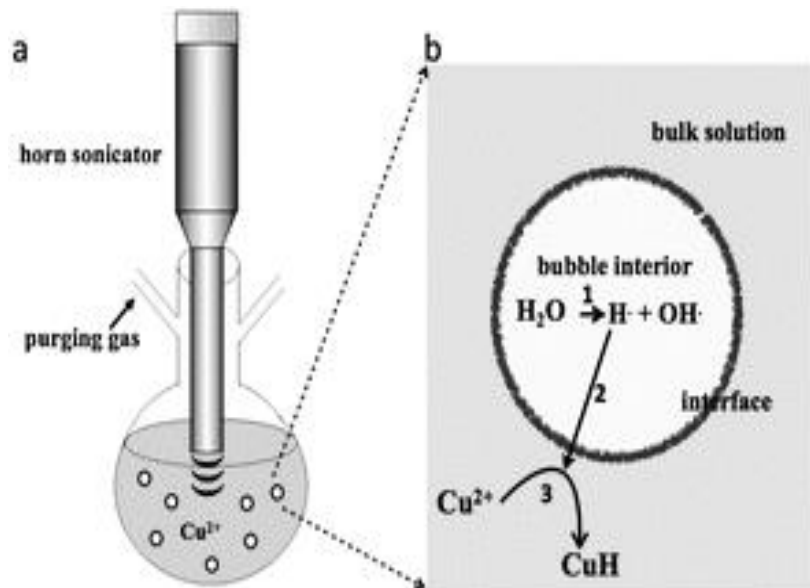
- The reduction reaction from Cu^{2+} to CuH is a chemical effect of the ultrasound irradiation.
- As mentioned earlier, the collapsing cavitation bubbles are known to break down the water matrix into hydrogen atoms (H) and hydroxyl radicals (OH) (eqn (1)).
- Furthermore, the hydrogen atoms can reduce Cu^{2+} to Cu^+ (eqn (2))
- In this synthesis, the solutions did not contain any stabilizing ligands for Cu^+. Therefore, Cu^+ ions are not stable and disproportionate into Cu^0 and Cu^{2+} (eqn (3)).

- Finally the Cu^0 atoms can combine with the hydrogen atoms to form the CuH products

$$H_2O \xrightarrow{ultrasound} H^{\bullet} + OH^{\bullet} \qquad (1)$$

$$Cu^{2+} + H^{\bullet} \rightarrow Cu^+ + H^+ \qquad (2)$$

$$2Cu^+ \rightarrow Cu^0 + Cu^{2+} \qquad (3)$$

$$Cu^0 + H^{\bullet} \rightarrow CuH \qquad (4)$$

Advantages
- Decrease of reaction time and increase of yield
- More uniform, smaller and pure crystals with minimal agglomerations are formed
- No chemical reducing agent is necessary for reaction
  - Possible switching of reaction pathway
  - Use of less or avoidance of phase transfer catalyst

Limitations
It produces only spherical metal nanoparticles

iv. PHOTOCHEMCAL SYNTHESIS
- In this method, metal nanoparticles are formed either by the direct photoreduction of a metal source or by the reduction of metal ions using photochemically generated intermediates such as excited molecules.radicals.
- It has been found that the reduction of metal salt precursors can also be done by radiolytic and photochemical methods.

- The main advantages of such a technique include the reduction of metal ions without using excess reducing agents.
- In this case, radiation is absorbed regardless of light-absorbing solutes and products. Also the rate of reduction reaction is known, since the number of reducing equivalents generated by radiation is well defined.
- Apart from this, photochemical synthesis does not require a specific and costly instrument
- Photochemical synthesis of nanoparticles is carried out by the light-induced decomposition of a metal complex or the reduction of a metal salt by photogenerated reducing agents such as solvated electrons.
- The former is called photolysis and the latter radiolysis.

Advantages:
- The convenience of use and the clean nature of the process,
- Controllable in situ generation of reducing agents,
- great versatility, and
- the possibility of nanoparticle synthesis in various medium including emulsions, surfactant micelles, polymer films, glasses, cells etc.

v. Chemical vapor deposition (CVD)
- Chemical Vapor Deposition is the formation of a non-volatile solid film on a substrate by the reaction of vapor phase chemicals (reactants) that contain the required constituents.
- The reactant gases are introduced into a reaction chamber and are decomposed and reacted at a heated surface to form the thin film.
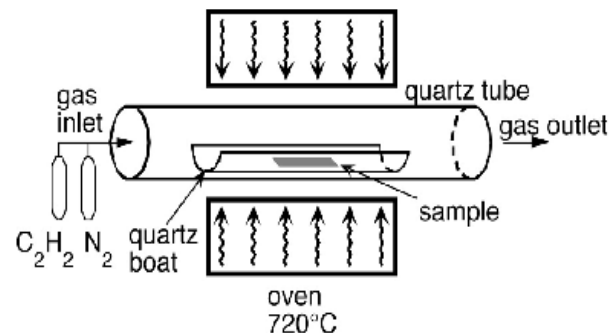
- CVD involves the formation of nanomaterials from the gas phase at elevated temperatures usually onto a solid substrate or catalyst.
- The process involves passing a hydro carbon vapor through a tubular reactor containing catalyst
- At temperature (600–1200 ºC) hydro- carbon decompose to carbon vapours, which condense on the cooler surface.
- The formed nanotubes diffuse to the growth sites.
- Desorption of products from the reacting surface.

The CVD method produces both single-wall and multi-wall nanotubes

Advantages:-
- Extremely high purity nanomaterials are produced.
- Can deposit which are hard to evoprate
- It can produce 1D nanomaterials

Dis advantages:-
- Expensive.
- Use of toxic gases causes a number of environmental problems

APPLICATIONS IN ELECTRONICS

- Nanomagnets are used as switches, transistors, in electrical circuits which lower power consumption.
- Silver nanoparticle ink was used to form the conductive lines needed in circuit boards.
- Combining gold nanoparticles with organic molecules to create a transistor known as NOMFET (Nanoparticle Organic Memory Filed –Effect Transistor).
- Nano wires are used to build transistors without p-n junctions.
- MOSFET (Metal Oxide Semi conductor Field Effect Transistor), performs both as switches and as amplifiers.
- Nanomaterials with less than 100nm in size are used in micropocesors in the electronic industry because smaller sizes allow faster processing times and also more processing power.
- The density of memory chips can be increased by nanomaterials.
- Integrated nanosensors are used for collecting , processing and communicating massive amounts of data with minimal size, weight and power consumption.

APPLICATIONS IN MEDICINE

- Nanotechnology has its applications in field of health and medicine called nanomedicine.
- Nanoparticles to deliver drugs, are engineered so that they are attracted to diseased cells, which allows direct treatment of those cells.
- Nanomedicine has the potential to enable early detection and prevention, and to essentially improve diagnosis, treatment and follow-up of diseases.
- Nanoparticles used to deliver vaccine and trigger a stronger immune response.
- Nanocapsules containing an enzyme, release insulin. When the glucose level rises the nanocapsules release hydrogen ions.
- Nanoparticle is used to defeat viruses. It delivers an enzyme that prevents the reproduction of viruses molecules in the patient's bloodstream.
- Gold nanorods are used for early detection of kidney damage.
- A sensor using nanotubes can detect a very low level of cancer cells, as low as 3-5 cancer cells in a one millilitre in 1ml of a blood sample.
- Gold coated nanoshells converts light into heat, enabling the destruction of tumours.
- Protein analysis can be done using nanomaterials.
- Nanotechnology is used to partially repair neurological damage.
- Nanotechnology can help to reproduce or to repair damaged tissue. This so called tissue engineering makes use of artificially stimulated cell. It might replace today's conventional treatments eg., transplantation of organs or artificial implants.
- The technology is also being used to develop sensors for cancer diagnostics.

UNIT –V
NANO MATERIALS
CONTENT BEYOND SYLLABUS

NANOTECHNOLOGY , ENERGY AND ENVIRONMENT

- The most advanced nanotechnology projects related to energy are as follows: storage, conversion, manufacturing improvements by reducing materials and process rates, energy saving by better thermal insulation and enhanced renewable energy sources.

- Using nanotechnology more clean and less expensive ways for energy production is desired. Nanotechnology has great contribution on renewal energies from solar technology, to nanocatalysis, fuel cells and hydrogen technology.

- Carbon nanotube fuel cells are being used to store hydrogen. These are the environmentally friendly form of energy. Researchers are trying to increase effectiveness of carbon nanotube at storing hydrogen. This has the potential to power cars.

- Nanotechnology can contribute to the further reduction of combustion engine pollutants by nanoporous filters, which can clean the exhaust mechanically, by catalytic converters based on nanoscale noble metal particles or by catalytic coating on cylinder walls and catalytic nanoparticles as additive for fuels.

- Nanotechnology can help in developingnew environmental safe and green technologies that can minimize the formation of undesirable by-products or effluents.

- Currently used light bulbs only convert approximately 5 percent of the electrical energy into light. Nanotechnological approaches like LEDs(light-emitting diodes) or QCAs (quantum-caged atoms) could lead to a strong reduction of energy consumption for illumination.

NANOTECHNOLOGY IN SPACE EXPLORATION

- Rocket scientist are actively researching new forms of space propulsion systems because today's rocket engines rely on chemical propulsion.

- Nanotechnology can make the structure of space planes much light thus can greatly improve their viability.

- Nanotechnology can improve the performance of laser sails. Using nanotechnology sails with 20nm thickness can be constructed making them light and more durable.

NANOELECTRONICS

- Using electrodes made from nanowires that would enable flat panel displays to be flexible as well as thinner than current flat panel displays.

- Using semiconductor nanowires to build transistors and integrated circuits.

- Transistors built in single atom thick graphene film to enable very high speed transistors.

- Researchers have developed an interesting method of forming PN junctions, a key component of transistors, in graphene. They patterned the p and n regions in the substrate. When the graphene film was applied to the substrate electrons were either added or taken from the graphene, depending upon the doping of the substrate. The researchers believe that this method reduces the disruption of the graphene lattice that can occur with other methods.

- Combining gold nanoparticles with organic molecules to create a transistor known as a NOMFET (Nanoparticle Organic Memory Field-Effect Transistor).
- Using carbon nanotubes to direct electrons to illuminate pixels, resulting in a lightweight, millimeter thick "nanoemmissive" display panel.
- Using quantum dots to replace the fluorescent dots used in current displays. Displays using quantum dots should be simpler to make than current displays as well as use less power.
- Making integrated circuits with features that can be measured in nanometers (nm), such as the process that allows the production of integrated circuits with 22 nm wide transistor gates.

- Using nanosized magnetic rings to make Magnetoresistive Random Access Memory (MRAM) which research has indicated may allow memory density of 400 GB per square inch.
- Researchers have developed lower power, higher density method using nanoscale magnets called magnetoelectric random access memory (MeRAM).
- Developing molecular-sized transistors which may allow us to shrink the width of transistor gates to approximately one nm which will significantly increase transistor density in integrated circuits.
- Using self-aligning nanostructures to manufacture nanoscale integrated circuits.
- Using nanowires to build transistors without p-n junctions.
- Using buckyballs to build dense, low power memory devices.

- Using magnetic quantum dots in spintronic semiconductor devices. Spintronic devices are expected to be significantly higher density and lower power consumption because they measure the spin of electronics to determine a 1 or 0, rather than measuring groups of electronics as done in current semiconductor devices.
- Using nanowires made of an alloy of iron and nickel to create dense memory devices. By applying a current magnetized sections along the length of the wire. As the magnetized sections move along the wire, the data is read by a stationary sensor. This method is called race track memory.
- Using silver nanowires embedded in a polymer to make conductive layers that can flex, without damaging the conductor.
- IMEC and Nantero are developing a memory chip that uses carbon nanotubes. This memory is labeled NRAM for Nanotube-Based Nonvolatile Random Access Memory and is intended to be used in place of high density Flash memory chips.
- Researcher have developed an organic nanoglue that forms a nanometer thick film between a computer chip and a heat sink. They report that using this nanoglue significantly increases the thermal conductance between the computer chip and the heat sink, which could help keep computer chips and other components cool.

UNIT –V
NANO MATERIALS
PART -A

1. What is Nano chemistry (or) Nanoscience?

Nano chemistry is defined as the study of phenomena and manipulation of materials at
atomic, molecular and macromolecular scales

2. What is Nano Technology?

The design ,characterization and application of structures,devices and systems by
controlled manipulation of materials at nano scales is known as Nano Technology

3. What are Nano particles?

Nano particles are particles, the size of which ranges from 1-50 nm.

4. Define nano wires.

Nano wires is a materials having an aspect ratio, length to width ratio greater than 20.

Nano wires are also referred to as quantum wires.

5. What are the characteristics of Nano wires?

- Nano wires are one dimensional material.
- Conductivity of a nano wire is less than that of the corresponding bulk materials.
- It exhibits distinct optical, chemical, thermal and electrical properties due to this large surface area.

6. What are nano rods?

Nano rod is a material having an aspect ratio in the range 1 to 20 with short dimension of
the materials being 10-100 nm.

7. What are nano clusters?

Nano clusters constitute an intermediate state of matter between molecules and bulk materials .these are fine aggregates of atoms or molecule.

8. What is magic number?

It is the number of atoms in the clusters of critical sizes with higher stability.

9. How are nanomaterials classified?

1.Zero-dimensional (0D) nanomaterials 2.One-dimensional (1D) nanomaterials.

3.Two-dimensional (2D) nanomaterials   4.Three-dimensional (3D) nanomaterials

10.Distinguish between bulk and nanoparticles

Nano particles	Bulk particles
1. Size is less than 100nm	Size is larger in micron size
2. Collection of few molecules	Collection thousands of molecules
3. Surface area is more	Surface area is less
4. Strength, hardness are more	Strength, hardness are less.

11. What are size dependent properties? Give examples.

On a nanometre scale, materials behave differently when compared to larger scales. Chemical and physical properties of a nanomaterial become size-dependent. Some of the major size dependent properties include

(i)   Thermal properties – melting temperature

(ii)   Optical properties – absorption and scattering of light

(iii)   Chemical properties – reactivity, catalysis

(iv)   Mechanical properties – mechanical strength

(v)   Electronic properties – conductance behaviour

(vi)   Magnetic properties – superparaagnetic effect.

12. What are the advantages of sonochemical method?

- Decrease of reaction time and increase of yield
- More uniform, smaller and pure crystals with minimal agglomerations are formed
- No chemical reducing agent is necessary for reaction
  - Possible switching of reaction pathway
  - Use of less or avoidance of phase transfer catalyst

13. State the advantages of electrodeposition

- It is relatively cheap and fast and allows complex shapes.
- It can be performed at low temperatures which will minimize inter diffusion of materials in the case of a multilayered thin film preparation.
- The film thickness can be controlled by monitoring the amount of charge delivered
- The composition and defect chemistry can be controlled by the magnitude of the applied potential, which can be used to deposit non-equilibrium phases.

14.List out the advantages of ball milling method of nanoparticle synthesis

- Few mg to several kgs of nanoparticle can be synthesized in a short time.
- This technique can be operated at large scale.
- It is useful in preparation of elemental and metal oxide nano crystals like Co, Cr, Al-Fe, Ag-Fe and Fe.
- Variety of intermetallic compounds of Ni and Al can be formed.

- Ball milling method is useful in producing new type building materials, fire – proof materials, glass ceramics, etc.

15. What are carbon Nanotubes?

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure.

Nanotubes have been constructed with length-to-diameter ratio of greater than 1,000,000.

These cylindrical carbon molecules have unusual properties and wide range of applications.

16. How is carbon Nanotubes classified?

Carbon nanotubes are classified into two types,

1. Single-walled nanotubes   2. Multi-walled nanotubes.

17. Mention some important applications of CNTs.

- It is used in storage devices.
- It is used as a catalyst.
- It is used as protective shield.
- As a good reinforcing element in composites.

18. List out the advantages and disadvantages of solvothermal process

Advantages

- Products obtained are in crystalline form.   So no purification required.
- Can be used for preparing nanomaterials of different morphology (powder, rod, wire,

tube, single crystals and nanocrystals).

- Precise control over the size, shape distribution and crystallinity of nanoparticles by

varying experimental conditions.

Disadvantages:

- Inability to monitor crystals in the process of their growth.

- The need to expensive autoclave.
- Safety issues during the reaction process.

PART-B

1. Distinguish between molecules, nanoparticles and bulk materials.
2. Discuss the solvothermal method of synthesis of nanomaterials.
3. Explain how nanomaterials are synthesized by the chemical vapour deposition.
4. Discuss the various size dependent properties of nanomaterials.
5. Explain how nanomaterials are synthesized by the electro deposition.
6. Give an account on sonochemical method of synthesis of nanomaterials.
7. Write short notes on photochemical synthesis of nanomaterials.
8. Write note on i.Nanowire ii.nanoclusters

CY19142- CHEMISTRY FOR ELECTRONICS ENGINEERING

LABORATORY MANUAL

2019 – 2020

RAJALAKSHMI ENGINEERING COLLEGE

NAME   : ——————————

BRANCH   : ——————————

DEPARTMENT OF HUMANITIES & SCIENCES–CHEMISTRY

RAJALAKSHMI ENGINEERING COLLEGE

THANDALAM-602 105

CONTENTS

Observations

Electrode system	Electrolyte concentration(M)	Observed cell potential (mV)	Ecalomel(mV)	Potential of electrode system(mV)

Calculations:

$E^0{}_{Cell} = E^0{}_R - E^0{}_L$

Standard Electrode Potential E^0 =

CONSTRUCTION AND DETERMINATION OF EMF OF SIMPLE ELECTROCHEMICAL CELLS AND CONCENTRATION CELLS

Exp.No.1   **Date:**

Aim:

   To determine the standard electrode potential of copper /zinc /silver electrode system.

Principle:

   The standard electrode potential of an electrode system can be determined by coupling with the reference electrodes such as calomel electrode. The influence of the concentration of the electrolyte on electrode potential can be studied by measuring the potential at different concentrations. The emf of concentration cell can be determined by constructing a cell with either zinc or copper electrodes immersed in different concentrations of the respective electrolytes.

Procedure:

   Prepare 100ml of .001N, .0005,.00025M of $ZnSO_4$/$AgNO_3$/$CuSO_4$ solution. Standardize the potentiometer using Weston-cadmium cell (E). Set up a galvanic cell by dipping Cu/Zn/Ag electrode in 0.1M $CuSO_4$/$ZnSO_4$/$AgNO_3$ solution respectively, kept in a beaker and the reference electrode (Calomel) through a salt bridge. Measure the emf of the cell using different concentrations of $CuSO_4$/$ZnSO_4$/$AgNO_3$ electrolytes.

Result:
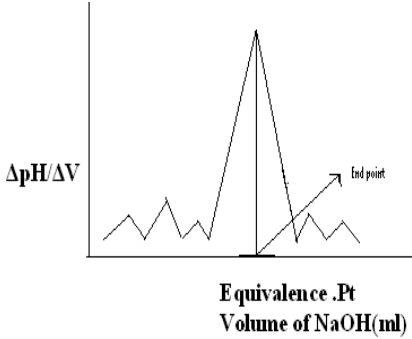
   Electrode potentials of the three systems under study are as follows:

   Electrode system:--------------------

   Electrolyte concentration: ----------------

   Potential (mv):------------------

SHORT PROCEDURE

CONTENTS	Estimation of Acid Std. NaOH Vs Acid	MODELGRAPH
Burette solution	Std. NaOH	
Pipette solution	20ml Acid	
Additional solution	30ml distilled water	
Electrode/Cell used	Ion selective electrode/pH electrode/combined electrode	
Instrument used	Digital pH meter	
End point	Sudden/rapid increase in pH value	

Std.NaOH Vs HCl

S.No	Volume of NaOH (ml)	pH	ΔpH	ΔV	ΔpH/ΔV

Volume of NaOH (V_1) = ----------- ml (from fair graph)

Strength of NaOH (N_1) = ----------- N

Volume of HCl (V_2) = 20 ml

Strength of HCl $(N_2) = (V_1 \times N_1) / V_2$

Strength of HCl   = ---------- N

Amount of HCl present   = Strength of HCl $\times$ Equivalent weight

in the given solution

                         = ----------- N$\times$36.5

7

ESTIMATION OF ACIDS BY PH METRY

Exp.No.2   **Date:**

Aim:

   To determine the strength and amount of given HCl by pH metry. A standard solution of
--------N NaOH is provided.

Principle:

   The pH of a solution is related to H^+ ions concentration by the following formula.

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

When NaOH is added slowly to HCl, H^+ ions get neutralized by OH^- ions. The pH
increases slowly.

$$H^+ + Cl^- + Na^+ + OH^- \longrightarrow Na^+ + Cl^- + H_2O$$
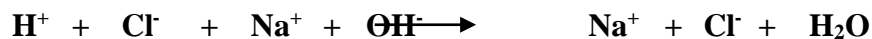
When all H^+ ions of HCl are neutralized at the end point, addition of NaOH causes high
increase in pH because of the excess OH^- ions.

Procedure :

   Fill the given Standard Sodium hydroxide solution in a clean burette. Transfer the given
solution of HCl carefully into a 100ml std.flask and make it up to the mark using distilled water.
Now pipette out 20 ml of the HCl solution into a clean beaker. Then dilute it to 50ml with
distilled water. Dip a glass electrode into the solution and connect to a pH meter.

   Now add NaOH gradually from the burette to HCl solution taken in the beaker. Note the
pH of the solution for each addition of NaOH. Continue the titration until at least 5 readings
after the endpoint. Plot a graph between $\Delta pH/\Delta V$ and the volume of Sodium hydroxide.

   Draw a graph as depicted in the diagram. The volume corresponding to the peak $\Delta pH/\Delta V$
is the sharp Equivalence Point and it is equal to the volume of NaOH exactly required for
neutralization of the strong acid.

RESULT

   Strength of the given HCl solution   =-----------N

   Amount of HCl present in the given solution   =---------g/l

CORROSION RATE WEIGHT LOSS METHOD

S.No.	Initial Weight (w$_1$ gm)	Final Weight (w$_2$ gm)	Weight loss (w$_1$-w$_2$)gm	Concentration of Hcl (N)	Time of exposure (hour)	Area (inch^2)

Calculation:

$$\text{Rate of Corrosion} = \frac{534 \ (w_1 - w_2)}{DAT} \ \text{Inch/Year}$$

w$_1$ = Initial Weight of the specimen

w$_2$ = Final Weight of the specimen

D = Density of the specimen for iron

T = Time of Exposure (hour)

A = Area of the specimen (inch) ^{2}

CORROSION EXPERIMENT (WEIGHT LOSS METHOD)

EXP.NO: 3   **DATE   :**

Aim:

　　　　To determine rate of corrosion of iron specimen in hydrochloric acid at room temperature by weight loss method.

Principle:

　　　　　Almost all metals undergo corrosion. Corrosion is an undesirable and slow process. The cost of replacement of materials and equipments lost through corrosion is estimated to be more than one lakh crore rupees per year. Thus corrosion is regarded as a cancer of metals that destroys economy and equipments. Generally metal surfaces are covered with impurities like rust and scales. These impurities at the time of coating ,will produce porous and discontinuous coating. In order to obtain an adherent, cohesive, smooth and uniform coating, the impurities must be completely removed by dipping them in an acid. This is known as acid cleaning or pickling. Pickling is generally employed to remove the scale by oxidation of metal.

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

　　　　Dilute hydrochloric acid is used as pickling solution. By dipping the metal plate in the acid, the metal ions along with rust get dissolved. Such dissolution is called corrosion. It is observed that as the time of dipping in acid increases and the acid concentration increase, the rate of corrosion also increase.

Materials required:

　　　　Iron pieces, Electronic Balances, Sand paper, Filter paper, Stop watch, Hydrochloric acid

Procedure:

Mild steel specimens of known dimensions are taken and are washed thoroughly with distilled water and are air dried. The initial weight of the specimen is noted(w_1 gm). Different concentrations (1N, 2N, 3N, 4N) of hydrochloric acid solutions prepared. They are known as pickling solutions. The mild steel specimens are dipped in 100ml of various hydrochloric acid solutions for about 30 minutes. After that they are taken out and thoroughly with distilled water and are air dried. Again the specimens are weighed. The final weight of the specimen is noted (w_2 gm). From the Weight loss (w_1-w_2) gm,the rate of corrosion can be calculated .

Result:

Rate of Corrosion   =....................Inch/Year

SHORT PROCEDURE

CONTENTS	Estimation of SA and WA Std. NaOH Vs SA+WA	MODELGRAPH
Burette solution	Std. NaOH	
Pipette solution	20ml acid mixture (SA+WA)	
Additional solution	30ml distilled water	
Electrode/Cell used	Conductivity cell	
Instrument used	Digital Conductivity meter	
End point	1. Decrease to increase of conductance 2. slow to rapid increase of conductance	

Std. NaOH Vs (SA + WA)

S.No.	Volume of NaOH added (ml)	Observed conductance (10^{-3} mho or m mho)

(i) Calculation of strength of Strong Acid

Volume of NaOH $\qquad (V_1) =$ --------- (a)ml (from graph)

Strength of NaOH $\qquad (N_1) =$ --------- N

Volume of HCl $\qquad (V_2) = 20$ ml

Strength of HCl $\qquad (N_2) =$ -------- ?

$$N_2 = (V_1 \times N_1) / V_2$$

Strength of HCl $\qquad\qquad =$ ---------- N

Amount of HCl present in the solution = Strength of HCl×36.5(eq.wt of HCl)

$$= \text{----------} \text{ g/l.}$$

CONDUCTOMETRIC TITRATION OF MIXTURE OF ACIDS

Exp. No.4   **Date:**

Aim:

        To determine the strength and amounts of strong acid (SA) and weak acid (WA) present in the given acid mixture. A Standard solution of NaOH of strength ….. N is provided.

Principle:

        Solution of electrolytes conducts electricity due to the presence of ions. Since Specific conductance of a solution is proportional to the concentration of ions in it, conductance of the solution is measured continuously during the titration, to find the end point.

$$HCl \;+\; NaOH \longrightarrow NaCl \;+\; H_2O \quad \text{(I neutralization)}$$

$$CH_3COOH \;+\; NaOH \longrightarrow CH_3COONa \;+\; H_2O \quad \text{(II neutralization)}$$

For example , when a mixture of HCl and CH_3COOH is titrated with NaOH the fast moving hydrogen ions are progressively replaced by slow moving sodium ions to form salt and water. As a result, conductance of the solution decreases. This decrease will take place until the HCl neutralisation point is reached.

        Further addition of alkali results in formation of sodium acetate. Since sodium acetate is a stronger electrolyte than acetic acid, conductance slowly increases until all acetic acid is completely neutralized(II-Neutralisation). Furthermore addition of alkali increases the conductance sharply due to the addition of fast moving OH^- ions.

Procedure:

        Fill up the burette with NaOH solution up to zero mark. Make up the given unknown solution (mixture of a weak & a strong acid) to 100ml in a standard flask with distilled water. Pipette out exactly 20ml of the made up solution into a clean 100ml beaker and dilute it to 50ml using distilled water. Introduce a conductivity cell into the solution and connect the terminals to a conductivity meter.

(ii) Calculation of strength of Weak Acid

Volume of NaOH (V_1) = ---------(b-a)ml (from graph)

Strength of NaOH (N_1) = -------- N

Volume of CH_3COOH (V_2) = 20 ml

Strength of CH_3COOH (N_2) = -------- ?

$$N_2 = (V_1 \times N_1) / V_2$$

Strength of CH_3COOH = ---------- N

Amount of CH_3COOH present in the solution =

Strength of $CH_3COOH \times 60$ (eq.wt of CH_3COOH)

= --------- g/l.

Add NaOH from the burette to the Acid mixture in the beaker in terms of 0.5ml increments. Stir the solution using a glass rod, and observe the conductance values for every addition. Continue the titration after the endpoint, for a minimum of 3ml of the burette solution. The conductance values decrease initially, then gradually increase and finally show a steep increase. The titration hence shows two endpoints (ie) I neutralization for (strong acid) & II neutralization for (weak acid). Calculate the strength and amount of the acids using the endpoints obtained from the graph.

Result:

    (i) The strength of acids present in the given unknown solution are

    a) Strong acid =---------- N   b) Weak acid = ---------- N

    (ii) The amount of Strong acid present in the given solution = -----------g/l

    (iii) The amount of Weak acid present in the given solution = -----------g/l

Determination of Potential:

S.No	Volume of Potassium dichromate added (mL)	Potential, E(mV)	ΔE	ΔE/ΔV

Model graph

ESTIMATION OF EXTENT OF CORROSION OF IRON PIECES BY POTENTIOMETRY

Exp. No.5   **Date:**

Aim:

      To estimate the amount of extent of corrosion by estimating the ferrous ions present in the whole of the given solution by potentiometric titration using standard decinormal potassium dichromate.

Principle:

      In potentiometric titration the potentials are measured when the titration is in progress. One electrode must maintain a constant potential but not necessarily a known potential (Reference electrode). The other electrode must serve as an indicator of the changes in ion concentration and must respond rapidly (indicator electrode). The solution must be stirred during the titration inorder to have uniform distribution. The equivalence point will be revealed by a sudden change in potential in the plot of EMF readings against volume of the titrating solution. For a reversible oxidation – reduction system,

$$\textbf{Oxidised form + ne}^{-} \rightarrow \textbf{Reduced form}$$

      This leads to the drastic increase in the potential. The subsequent addition of the Cr^{6+} ions to the solution merely increases the ratio of ($[Cr^{6+}]/[Cr^{3+}]$) where the change is slow. The abrupt change of the potential in the neighborhood of the equivalence point is dependent upon the standard potentials of the two oxidation – reduction systems that are involved and therefore upon the equilibrium constant of the reaction.

Procedure:

Pipette Solution:

      Iron pieces are taken and washed thoroughly and immersed in conc. sulphuric acid overnight. This is then made upto 200 mL.

Calculations

Volume of standard dichromate (V1) =----- (from graph)

Normality of standard dichromate (N1) = 0.1 N

Volume of ferrous solution (V2) = 20 mL

Normality of ferrous solution (N2) =

$$V1N1 = V2N2$$

$$N_2 = \frac{V1N1}{V2}$$

Amount of ferrous iron present in 100 mL of the given solution = Eq.wt X Normality

$$= 55.85 \ X \ N_2$$

The amount of ferrous ion present in the given solution is --------- g

Estimation of ferrous ions present by potentiometric titration:

The given solution obtained by immersing the iron pieces in the solution leading to corrosion is made upto 100 mL in a standard measuring flask. The burette is filled with standard potassium dichromate solution. 20 mL of the made up solution containing the Fe2+ ions is pipetted out into a clean beaker. Equal volume of dilute sulphuric acid is added to this solution.

Potentiometer is calibrated. The platinum and calomel electrodes are connected to the potentiometer terminals. They are dipped in the beaker containing ferrous ions solution. The potentiometer reading is noted. The dichromate solution is added in 1 mL portions. After each addition the solution is stirred and the EMF is noted. After a particular addition a sharp change in EMF is noted. The titration is continued for 10 more readings after the sharp change in EMF is noted. From the graph the value of $\Delta E/\Delta V$ is found.

Plotting the graph:

A differential graph is plotted with $\Delta E/\Delta V$ in y-axis and the volume of dichromate (mL) in x-axis. The volume of potassium dichromate corresponding to the peak of the curve is noted as the end point of titration from the titre value. From this the normality and amount of ferrous iron present in the given solution is calculated Equivalent weight of Ferrous = 55.85

RESULT

The amount of ferrous ion present in the given solution is --------- g

Determination of absorbance:

S.No	Concentration of Fe2+ ions (ppm)	Absorbance

Model graph
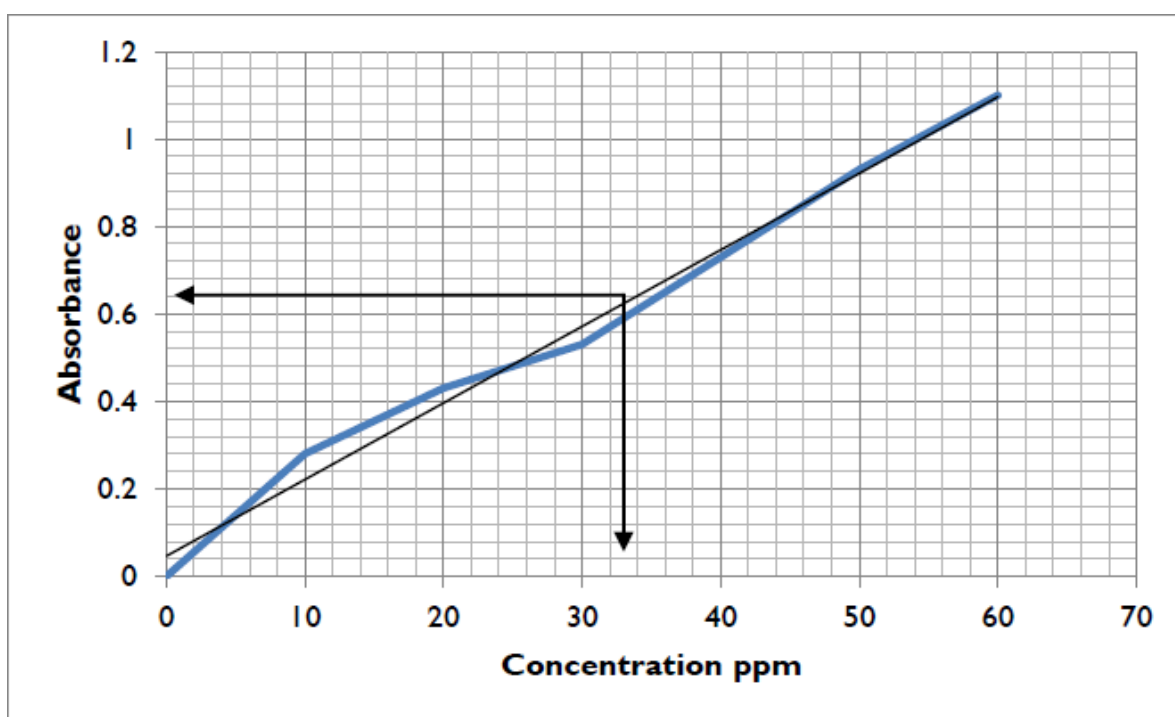
ESTIMATION OF COPPER / FERROUS IONS BY SPECTROPHOTOMETRY

Exp. No.6   **Date:**

Aim:

       To determine the amount of iron dissolved in the given sample by spectrophotometry

Principle:

       In spectrophotometry absorption of light radiation in visible region (400-700 nm) is measured. Thus in spectrophotometer, the percentage transmittance / absorption of light radiation is detected when light of certain intensity and frequency range is passed through the sample. It compares the intensity of transmitted light with that of the incident radiation.

       When a monochromatic light passes through a homogeneous coloured solution, a portion of incident light is reflected (Ir), and a portion of light is absorbed (Ia) and the remaining is transmitted (It)

$$Io = Ir + Ia + It$$

Where Io = Intensity of the beam of monochromatic light.

       Ir = Intensity of the reflected light.

       Ia = Intensity of the absorbed light.

       It = Intensity of the transmitted light.

Ir is usually eliminated. Thus the transmittance (T) of a solution is given by

$$T = \log \frac{I_t}{I_0}$$

Absorbance (A) or optical density (OD) is defined as

$$A = \log \frac{I_0}{I_t}$$

From the Lambert-Beers law

$$A = \varepsilon \, C \, t$$

Where ε is a molar extinction coefficient

         C is concentration (in g/l) of the absorbing medium

         t is thickness (in cm) of the absorbing medium.

If same sample cell (i.e. t is constant) is used for measurement of absorbance of solution having different concentrations then the extent of absorbance (A) is directly proportional to concentration (C) of the absorbing medium.

For the determination of the concentration of a substance, select the wavelength of maximum absorption for the compound. Construct a calibration curve by measuring the absorbance of four or five concentrations of the substance at the selected wavelength. Plot the graph with absorbance against concentration. If the compound obeys Beer's law a linear calibration curve passing through the origin will be obtained. If the optical density of the unknown solution is measured, the concentration can be obtained from the calibration curve.

Procedure:

Preparation of Ferrous ammonium sulphate (standard solution):

From stock solution given 1 mL, 2 mL, 3 mL, 4 mL, 5 mL, 6 mL is pipetted out in different 100 mL standard measuring flasks. 1-2 drops of 0.1 N potassium permanganate (until a slight pink colour is seen) and the 2-4 mL of 20% potassium thiocyanate (KCNS) is added and made upto 100 mL.

Preparation of unknown solution:

50 mL of the given sample is taken in 100 mL standard measuring flask. This is acidified with 1:1 HCl, and one drop of 0.1N Potassium permanganate and 2-4 drops of 20% potassium thiocyanate (KCNS) are added. It is made upto 100 mL (i.e. if the value is out of range it is diluted).The spectrophotometer is switched on and is allowed to warm up for ten minutes. The monochromator is adjusted for wavelength 480 nm. The blank sample is kept in the cell and light transmission is adjusted to 100 (or absorbance to zero). The standard solutions of known concentrations that are already prepared are kept in the sample holder one by one and the corresponding absorbance is noted. Similarly the OD/absorbance is noted for unknown solution.

Plotting the graph:

Using the absorbance value of different standard solutions, the calibration curve is drawn with concentration of ions in X-axis and absorbance in Y-axis. Using the calibration curve, with the measured absorbance of the unknown solution concentration of the given sample is found.

Result:

The amount of iron present in the given solution =---- ppm (Obtained From the Graph)

Short procedure:

CONTENTS	TITRATION I Standardisation of $Na_2S_2O_3$ Std. $K_2Cr_2O_7$ Vs $Na_2S_2O_3$	TITRATION II Estimation of DO Std. $Na_2S_2O_3$ Vs Water Sample
Burette solution	$Na_2S_2O_3$	Std. $Na_2S_2O_3$
Pipette solution	20 ml Std. $K_2Cr_2O_7$	20ml of treated water sample*
Additional solution	1 Test tube of 2N H_2SO_4 + 10 ml of 10% KI	-------
Indicator	Starch	Starch
End point	Disappearance of blue colour	Disappearance of blue Colour

*200ml of sample water + 2ml of $MnSO_4$ + 2ml of alkaline KI- Shaken for 5 min. A brown gelatinous precipitate will be formed. Dissolve it with minimum amount of con. Sulphuric acid to get a clear yellowish solution.

TITRATION I

Standardisation of Sodium Thio Sulphate:

Std. $K_2Cr_2O_7$ Vs $Na_2S_2O_3$ **Indicator: Starch**

S.No.	Volume of std. $K_2Cr_2O_7$ (ml)	Burette Reading (ml)		Volume of $Na_2S_2O_3$ (ml)	Concordant value (ml)
		Initial	Final		

Volume of potassium dichromate (V_1) = 20 ml

Strength of potassium dichromate (N_1) = ------- N

Volume of sodium thio sulphate (V_2) = ------- ml

Strength of sodium thio sulphate (N_2) = ------ ?

$$N_2 = V_1N_1/V_2$$

$$N_2 = 20\ ml \times \text{-------} / \text{-------}$$

Strength of sodium thio sulphate (N_2) = ------ N

23

DETERMINATION OF DISSOLVED OXYGEN IN WATER SAMPLE
(WINKLER'S METHOD)

Exp. No.7   **Date:**

Aim:

To determine the amount of dissolved oxygen (DO) in the given water sample by Winkler's method. A standard solution of potassium dichromate of strength -------N is provided.

Principle:

There are two methods, widely used to determine DO. They are,

      (a) Winkler's method by iodometry

      (b) Electrometric method using a membrane electrode

winkler's method:

DO in water reacts with Mn^{2+} ions in alkaline medium to form a brown colour basic manganic oxide.

$$MnSO_4 + 2\,KOH \longrightarrow Mn(OH)_2 + K_2SO_4$$

$$2Mn\,(OH)_2^- + O_2 \longrightarrow 2\,MnO(OH)_2 \downarrow (\text{brown precipitate})$$

Manganic oxyhydroxide

This brown precipitate dissolves in con. H_2SO_4 and liberates iodine with KI. The Iodine liberated is equivalent to the initial amount of DO present in the given water sample.

$$MnO(OH)_2 + H_2SO_4 \longrightarrow MnSO_4 + 2H_2O + [\,O\,]\ (\text{Nascent oxygen})$$

$$2\,KI + H_2SO_4 + [\,O\,] \longrightarrow K_2SO_4 + H_2O + I_2\ (\text{Liberated Iodine})$$

The liberated iodine is estimated by titration with sodium thiosulphate.

$$I_2 + Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2\,NaI$$

[Note: Starch + I_2 $\longrightarrow$ Blue coloured complex]
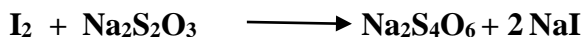
The stoichiometric expression relating DO and sodium thiosulphate is

1 ml of 0.0125N $Na_2S_2O_3$ $\equiv$ 0.1 mg DO

Sodium thiosulphate (being a secondary standard) is standardised iodometrically using standard $K_2Cr_2O_7.$

Iodometry:(oxidant + excess I^-) $\equiv$ I_2 (liberated)   Vs $S_2O_3^{2-}$

The net reaction is

$Cr_2O_7^{2-}$ + 14H^+ + 6I^- $\longrightarrow$ 2Cr^{3+} + 7H_2O + 3I_2
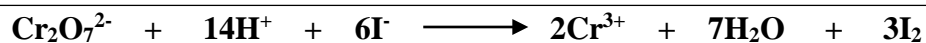
TITRATION II

Estimation of DO:

Std. $Na_2S_2O_3$ Vs Treated water sample   **Indicator :Starch**

S.No.	Volume of water sample (ml)	Burette Reading (ml)		Volume of std. thio (V_2) ml	Concordant value (ml)
		Initial	Final		

Volume of sodium thio sulphate (V_1) = -------- ml

Strength of sodium thio sulphate (N_1) = ------- (from the titration I)

Volume of DO water sample (V_2) = 20 ml

Strength of DO water sample (N_2) = -------- ?

According to the law of volumetric analysis

$$V_1N_1 = V_2N_2$$

$$N_2 = V_1N_1/V_2$$

$$=----------N$$

Amount of DO   = Strength of DO in water sample $\times$ 8 g/l

=------------ g/l

Amount of DO   = ----------- $\times$ 1000 ppm (or) mg/l

=----------- ppm (or) mg/l

In iodometric titrations, a slight excess of KI is added to ensure the completion of the oxidation. Starch is added as an indicator which forms an intense blue coloured weak adsorption complex with iodine liberated in low concentrations. The complex gets readily broken when thio sulphate is added and hence a sharp colour change that is disappearance of blue colour occurs at the end-point.

PROCEDURE

TITRATION I

Standardisation of Sodium Thio Sulphate:

Pipette out 20ml of std. $K_2Cr_2O_7$ solution into a clean conical flask. Add 10ml of 10% KI solution and 20ml of dil.sulphuric acid. Titrate the liberated iodine against sodium thio sulphate in the burette. When the solution turns yellow (pale) colour, add 2 to 3 drops of freshly prepared starch indicator so that the solution assumes intense blue colour. Continue the addition of sodium thio sulphate till the blue colour disappears leaving behind a pale green colour (due to the presence of Cr^{3+} ions). Repeat the titration to get a concordant value.

ESTIMATION OF DO (WINKLERS METHOD):

Fill the given water sample in a reagent bottle up to the rim and stopper it. This is done in order to exclude any air column present in the closed bottle that may increase the actual DO leading to an error. Remove the stopper and add 2 ml of alkaline manganous sulphate and 2ml of 10% alkaline KI. In this process, some sample may overflow. The overflow may also occur when the stopper is inserted after the addition of each reagent. Mix well the contents in the bottle by turning it several times up and down till the formation of a brown coloured basic manganic oxide precipitate. Dissolve it by adding concentrated sulphuric acid to form a clear yellow solution. Pipette out 20 ml of the clear solution into a clean conical flask and add few drops of starch solution. Titrate the resultant blue coloured solution against the standardised sodium thiosulphate. The disappearance of blue colour is the end point. Repeat the titration for duplicate.

RESULT

The amount of DO present in the given water sample = -----------mg/l (or) ppm.

Short Procedure:

CONTENTS	TITRATION I Standardisation of EDTA (EDTA Vs Std. hard water)	TITRATION II Determination of total hardness (Std. EDTA Vs sample hard water)	TITRATION III Determination of permanent hardness (Std. EDTA Vs Boiled hard water)
Burette solution	EDTA solution	Std. EDTA solution	Std. EDTA solution
Pipette solution	20ml Standard hard Water	20ml Sample hard water	20ml Boiled hard water
Additional solution	5ml ammonia buffer	5ml ammonia buffer	5ml ammonia buffer
Indicator	4-5 drops EBT	4-5 drops EBT	4-5 drops EBT
End point	Wine red to steel blue colour	Wine red to steel blue colour	Wine red to steel blue colour

TITRATION I

STANDARDISATION OF EDTA:

Std. hard water Vs EDTA   **Indicator: EBT**

S.No.	Volume of Std. hard water (ml)	Burette Reading (ml)		Volume of EDTA (V_1) ml	Concordant value (ml)
		Initial	Final		

 Calculation:

Standardisation of EDTA

Volume of Std. hard water (V_1)   = 20 ml

Strength of Std. hard water (N_1)   = ------ N

Volume of   EDTA   (V_2)   = ------- ml

Strength of EDTA   (N_2)   = ------- ? N

$\qquad\qquad\qquad\qquad\qquad\qquad\quad = (20 \times N_1)/ V_2$

$\qquad\qquad\qquad\qquad\qquad\qquad\quad$ = ------ N

Strength of EDTA   = ------ N

ESTIMATION OF HARDNESS OF WATER BY EDTA METHOD

Exp. No. 8   **Date:**

Aim:

To estimate the amount of total, temporary and permanent hardness in the given sample of hard water. A standard hard water of………N is provided.

Principle:

The estimation is based on complexometric titration. The total hardness of water is estimated by titrating it against EDTA using EBT indicator.

$$EBT + M^{n+} \xrightarrow{pH = 9\text{-}10} [EBT\text{-}M]$$

Unstable complex (Wine red colour)

$$[EBT\text{-}M] + EDTA \xrightarrow{pH = 9\text{-}10} [EDTA\text{-}M] + EBT$$

Stable complex   **Steel blue colour**
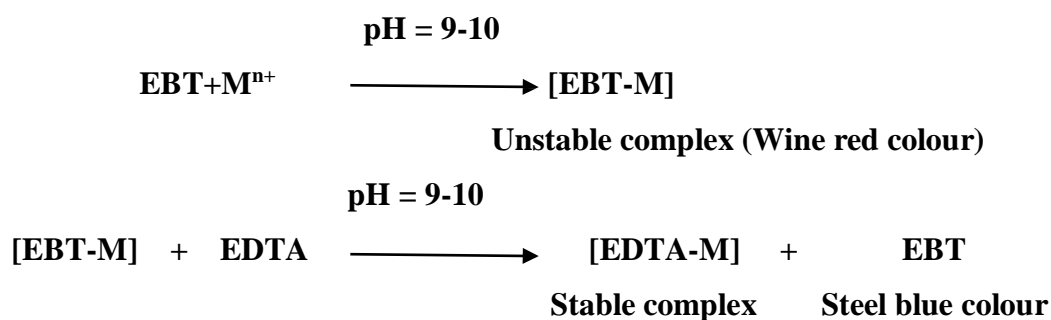
EBT indicator forms wine red coloured complex with hardness causing metal ions present in water. On addition of EDTA, metal ions preferably form complexes with EDTA and steel blue EBT indicator is set free. Therefore change of colour from wine red to steel blue denotes the end point.

Temporary hardness is removed by boiling the water.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 \downarrow + CO_2 \uparrow + H_2O$$

$$Mg(HCO_3)_2 \longrightarrow Mg(OH)_2 \downarrow + 2CO_2 \uparrow$$
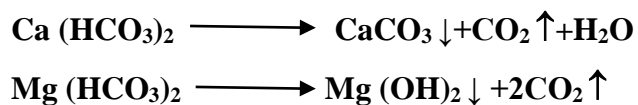
The precipitate is filtered and the remaining permanent hardness is estimated using EDTA.

TITRATION II

DETERMINATION OF TOTAL HARDNESS

Std. EDTA   Vs Sample hard Water   **Indicator: EBT**

S.No.	Volume of sample hard water (ml)	Burette Reading (ml)		Volume of EDTA (V_2) ml	Concordant value (ml)
		Initial	Final		

Calculation:

Estimation of total hardness

Volume of   EDTA(V_1)   = --------- ml

Strength of EDTA (N_1)   = ----------N   (From the titration I)

Volume of Sample hard water (V_2)   =   20 ml

Strength of Sample hard water (N_2)   = -------- ?

$\qquad\qquad N_2 \qquad\qquad$ = $(V_1 \times N_1)/ 20$

Strength of Sample hard water   = --------- N.

Total hardness of the hard water sample   = Strength of the hard water sample

$\qquad\qquad\qquad\qquad$ ×Eq.wt. of $CaCO_3$

$\qquad\qquad\qquad\qquad$ = --------- × 50 g/l

Therefore, Total hardness   = --------- × 1000 ppm or mg/l

PROCEDURE

TITRATION I

STANDARDISATION OF EDTA

     Pipette out 20ml of standard hard water into a 250ml conical flask. Add 5ml of ammonia buffer solution and 4-5 drops of Eriochrome Black-T indicator. Fill the burette with EDTA solution. Titrate the conical flask solution against the EDTA. The change in colour from wine red to steel blue is the end point. Repeat the titration to get concordant values. Let the titre value be V_1 ml.

TITRATION II

DETERMINATION OF TOTAL HARDNESS

     Pipette out 20ml of the sample hard water into a clean conical flask. Add 5ml of ammonia buffer solution and 4 -5 drops of Eriochrome Black-T indicator. Titrate the wine red colour solution against the EDTA taken in the burette. The appearance of steel blue colour is the end point. Repeat the titration to get concordant values. Let the titre value be V_2 ml.

TITRATION III

DETERMINATION OF PERMANENT HARDNESS

     Take 100ml of hard water sample in a 250ml beaker and boil gently for about 20 minutes. Cool, filter it into a 100ml standard flask and make the volume up to the mark. Pipette out 20ml of boiled hard water into a clean conical flask. Add 5ml of ammonia buffer solution and 4 -5 drops of Eriochrome Black-T indicator. Titrate the wine red coloured solution against the EDTA taken in the burette. The appearance of steel blue colour is the end point. Repeat the titration to get concordant values. Let the titre value be V_3 ml.

The temporary hardness is calculated by subtracting permanent hardness from total hardness.

TITRATION III

DETERMINATION OF PERMANENT HARDNESS

Std. EDTA Vs Boiled hard water sample   **Indicator: EBT**

S.No.	Volume of boiled hard water (ml)	Burette Reading (ml)		Volume of EDTA (V_3) ml	Concordant value (ml)
		Initial	Final		

Calculation

Estimation of permanent hardness of the hard water

Volume of EDTA (V_1) = ------- ml

Strength of EDTA (N_1) = ------ N (From the titration I)

Volume of boiled hard water sample (V_2) = -------20 ml

Strength of boiled hard water sample (N_2) =   ?

$$N_2 = (V_1 \times N_1)/ 20$$

$$=   N$$

Strength of boiled hard water sample   = ------- N.

Permanent hardness = Strength of the boiled hard water sample $\times$ Eq.wt of $CaCO_3$

$$= ------ \times 50 \text{ g/l}$$

Therefore, Permanent hardness of the hard water sample

$$= ------ \times 1000 \text{ ppm or mg/l}$$

Calculation of temporary hardness

Temporary hardness of the given sample of water = Total hardness – Permanent hardness

$$= ------------ \text{ ppm}$$

RESULT

(i) Amount of total hardness present in the given sample water   = ------ ppm (or) mg/ l

(ii) Amount of permanent hardness present in the given sample water = -----ppm (or) mg/ l

(iii) Amount of temporary hardness present in the given sample water = ---- ppm (or) mg/ l

SHORT PROCEDURE

CONTENTS	TITRATION I **Standardisation of HCl (Std NaOH Vs HCl)**	TITRATION II **Estimation of alkalinity in water sample (Std HCl Vs water sample)**
Burette solution	HCl	Std. HCl
Pipette solution	Std. NaOH	Water sample
Indicator	Phenolphthalein	(i) Phenolphthalein (ii) Methyl orange
End point	Disappearance of pink colour	(i) Disappearance of pink colour (ii) Appearance of reddish orange colour

Strength of HCl   = ----------- N

Relationship between P&M	Nature of alkalinity	Amount of individual alkalinities	OH^-	HCO_3^-	CO_3^{2-}
P = M	only OH^-	$\dfrac{(P \text{ or } M) \times N \times 50}{20}$	xxx	0.0	0.0
2P = M	only CO_3^{2-}	$\dfrac{(2P \text{ or } M) \times N \times 50}{20}$	0.0	0.0	xxx
P =0, M≠0	only HCO_3^-	$\dfrac{M \times N \times 50}{20}$	0.0	xxx	0.0
2P > M	OH^- & CO_3^{2-}	$OH^- = \dfrac{(2P - M) \times N \times 50}{20}$ $CO_3^{2-} = \dfrac{2(M-P) \times N \times 50}{20}$	xxx	0.0	xxx
2P < M	HCO_3 & CO_3^{2-}	$HCO_3^- = \dfrac{(M-2P) \times N \times 50}{20}$ $CO_3^{2-} = \dfrac{(2P) \times N \times 50}{20}$	0.0	xxx	Xxx

ESTIMATION OF ALKALINITY BY INDICATOR METHOD

Exp. No.9 **Date:**

Aim:

To determine the types and amounts of alkalinity in the given water sample. A standard solution of NaOH of strength------ N is given.

Principle:

Alkalinity in water is due to the presence of soluble hydroxides, bicarbonates and carbonates. Alkalinity can be determined by

 i. Potentiometric titrations

 ii. pH metry

 iii. Titrimetry using different indicators

Determination of various types and amounts of alkalinity is easily carried out by t itration with standard HCl employing the indicators phenolphthalein and methyl orange independently or in succession.

The following reactions occur when different types of alkalinity are neutralized with acid.

OH^- + H^+ $\longrightarrow$ H_2O completed at pH 8.2-9.0--------------------------- **(1)**

CO_3^{2-} + H^+ $\longrightarrow$ HCO_3---**(2)**

HCO_3^- + H^+ $\longrightarrow$ (H_2CO_3) $\longrightarrow$ H_2O + $CO_2\uparrow$ completed at pH 4.2-5.5 --------- **(3)**

Neutralization (1) & (2) will be notified by phenolphthalein end-point while all the three will be accounted by methyl orange end-point. Bicarbonate in eqn.-3 may be due to the existence of soluble free bicarbonate salts or bicarbonate resulting from half neutralization of soluble carbonates (eqn.-2)

Various steps to be followed:

 a) A known volume of water sample is titrated against std. HCl using phenolphthalein indicator till the phenolphthalein end-point (P) and the titration is continued without break using methyl orange indicator till the methyl orange end-point (M).

TITRATION I

STANDARDISATION OF HCl

Std. NaOH Vs HCl   **Indicator: Phenolphthalein**

S.No.	Volume of NaOH (ml)	Burette Reading(ml)		Volume of HCl (ml)	Concordant value (ml)
		Initial	Final		

Volume of sodium hydroxide (V_1) = 20 ml

Strength of sodium hydroxide (N_1) =-------- N

Volume of HCl (V_2) =-------- ml

Strength of HCl (N_2) = --------- ?

$$N_2 = V_1N_1/V_2$$

$$= V_1 \times N_1 / 20$$

Strength of HCl (N_2) =-------- N

TITRATION – II ESTIMATION OF ALKALINITY IN WATER SAMPLE

Std. HCl Vs Water sample   **Indicators: 1. Phenolphthalein**

2. Methyl orange

S.No.	Volume of water sample (ml)	Burette Reading			Volume of HCl (ml)		Concordant Value (ml)	
		Initial	Final		P	M	P	M
			P	M				

Phenolphthalein end point   (P)   = ----------ml

Methyl orange end point   (M)   = ----------ml

b. From the magnitudes of the P & M, the nature of alkalinity can be arrived as follows:

(i) $P = M$ =>   **Presence of only OH$^-$**

(ii) $2P = M$ =>   **Presence of only CO$_3^{2-}$**

(iii) $P = 0, M \neq 0$ =>   **Presence of only HCO$_3^-$**

(iv) $2P > M$ =>   **Presence of OH$^-$ & CO$_3^{2-}$**

(v) $2P < M$ =>   **Presence of HCO$_3^-$ & CO$_3^{2-}$**

(Mixture of OH$^-$ & HCO$_3^-$ is not listed since they do not exist together and are considered equivalent to CO$_3^{2-}$).

TITRATION – I

PROCEDURE:

STANDARDISATION OF HCl:

Pipette out 20 ml of the given standard NaOH solution into a clean conical flask and add 2 drops of phenolphthalein indicator. Titrate the solution against the given HCl taken in the burette. End point is disappearance of pink colour. Note the titre value from the burette and repeat the titration to get concordant value.

TITRATION – II

ESTIMATION OF ALKALINITY IN WATER SAMPLE

Pipette out 20 ml of water sample into a clean conical flask. Add few drops of phenolphthalein indicator and titrate the solution against the standardized HCl taken in the burette. The end point is the disappearance of pink colour. Note the end point as P. Then add few drops of methyl orange indicator in to the same solution. The solution colour change to yellow. Continue the titration with same HCl solution without break (without refilling the burette) till the end point is reached. The end point is change of colour from yellow to reddish orange. Note the titre value as M. Repeat the experiment to get concordant value.

(i) Amount of OH⁻ in water sample:

Volume of HCl $\qquad$ $(V_1) = (2P-M)$ ml

Strength of HCl $\qquad$ (N_1) = ------- N

Volume of water sample $\qquad$ $(V_2) = 20$ ml

Strength of OH⁻ in water sample (N_2) = ------- ?

$$N_2 = (2P-M) \times \text{-------} N/20$$

Amount of OH⁻ in water sample $\quad = N_2 \times 50$ g/lit (50 is the eq.wt of $CaCO_3$)

$$= N_2 \times 50 \times 1000 \text{ mg/l.}$$

$$= \text{-------------- ppm.}$$

(ii) Amount of CO₃²⁻ in water sample:

Volume of HCl $\qquad$ $(V_1) = 2(M-P)$ ml

Strength of HCl $\qquad$ (N_1) = ------ N

Volume of water sample $\qquad$ $(V_2) = 20$ ml

Strength of CO_3^{2-} in water sample (N_2) = ------- ?

$$N_2 = 2(M-P) \times \text{------} N/20$$

Amount of CO_3^{2-} in water sample $\quad = N_2 \times 50$ g/l.

$$= N_2 \times 50 \times 1000 \text{ mg/l.}$$

$$= \text{---------- ppm.}$$

RESULT

The types of alkalinity present in the water sample = ------ & ------- ions.

The individual amount of alkalinity present in the water sample = ------- ppm (or) mg/l &

= ------- ppm (or) mg/l

SHORT PROCEDURE

CONTENTS	TITRATION I Standardization of Silver Nitrate	TITRATION II Estimation of chloride
	Std. NaCl Vs AgNO₃	Std. AgNO₃ Vs Water Sample
Burette solution	AgNO₃	Std. AgNO₃
Pipette solution	20 ml Std. NaCl	20 ml Water sample
Indicator	1 ml of 2% K₂CrO₄	1 ml of 2% K₂CrO₄
End point	Appearance of reddish brown colour	Appearance of reddish brown colour

TITRATION I

STANDARDISATION OF AgNO₃

Std. NaCl Vs AgNO₃   **Indicator: Potassium chromate**

S.No.	Volume of NaCl (ml)	Burette Reading (ml)		Volume of AgNO₃ (ml)	Concordant Value (ml)
		Initial	Final		

Volume of sodium chloride (V_1) = 20 ml

Strength of sodium chloride (N_1) = ------ N

Volume of silver nitrate (V_2) = ------ ml

Strength of silver nitrate (N_2) = ------- ?

$$N_2 = V_1N_1/V_2$$

$$N_2 = 20 \text{ ml} \times \text{-------- /--------}$$

Strength of silver nitrate (N_2) =-------- N

ESTIMATION OF CHLORIDE CONTENT ION BY ARGENTOMETRIC METHOD

**Exp. No.10**   **Date:**

Aim:

To estimate the amount of chloride present in the given water sample, being supplied with a standard solution of sodium chloride of strength-------- N.

Principle:

Generally water contains chloride ions in the form of $NaCl$, KCl, $CaCl_2$, and $MgCl_2$. The concentration of chloride ions more than 250 ppm is not desirable for drinking purpose. The total chloride ions can be determined by Argentometric method (Mohr's Method).

In this method Cl^- solution is directly titrated against $AgNO_3$ using potassium chromate (K_2CrO_4) as indicator

$$AgNO_3 \ + \ \ Cl^- \longrightarrow \ \ \ AgCl\downarrow \ \ \ + \ \ NO_3^-$$
$$\textbf{(In water)} \qquad\qquad \textbf{(White ppt)}$$
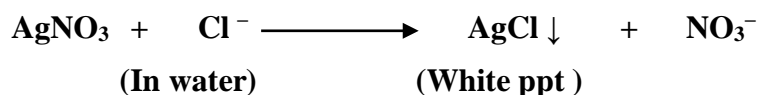
At the end point when all the Cl^- ions are removed. The yellow colour of chromate changes to reddish brown due to the following reaction.

$$2AgNO_3 \ \ + K_2CrO_4 \longrightarrow \ \ Ag_2CrO_4 \ \ \ +2KNO_3$$
$$\textbf{(Yellow)} \qquad\qquad \textbf{(Reddish brown)}$$
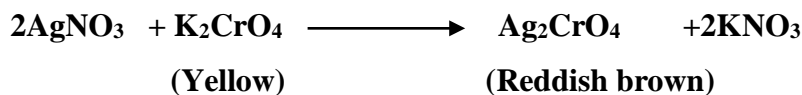
PROCEDURE
TITRATION I
STANDARDIZATION OF AgNO₃

Wash the burette with distilled water and rinse with small amount of $AgNO_3$ solution. Fill the burette with same solution up to the zero mark without any air bubbles. Wash the pipette with distilled water and rinse with a small amount of standard NaCl solution. Pipette out 20 ml of the solution in to a clean conical flask. Add 1ml of 2% K_2CrO_4 indicator solution and titrate against $AgNO_3$ taken in the burette. The end point is the change of colour from yellow to reddish brown. Repeat the titration to get concordant value.

TITRATION II

ESTIMATION OF CHLORIDE IN WATER SAMPLE

Std. AgNO₃   Vs Water Sample   **Indicator: Potassium Chromate**

S.No.	Volume of water sample (ml)	Burette Reading (ml)		Volume of AgNO₃ (ml)	Concordant Value (ml)
		Initial	Final		

Volume of silver nitrate (V_1) = -------- ml

Strength of silver nitrate (N_1) = --------N

Volume water sample (V_2) = 20 ml

Strength of Chloride ions (in water) (N_2) = ------ N

$$N_2 = \frac{V_1 \times N_1}{V_2}$$

Strength of Chloride ions (in water) (N_2) = ------- N

Calculation of amount of Chloride ions

Amount of chloride ions present in 1 litre of water sample

= Equivalent weight of Chloride ion (35.45) × Strength of chloride ions in water

= 35.45 × ------------------ g

= ------------ g

Amount of Chloride ions present in 1 litre of the water sample

= --------------- g × 1000ppm

= ------------ mg / l or ppm

TITRATION II

ESTIMATION OF CHLORIDE ION

Pipette out 20 ml of the given water sample in to a clean conical flask and add 1 ml of 2% K_2CrO_4 indicator solution. Then titrate the solution against standardized $AgNO_3$ solution taken in the burette. The end point is the change of colour from yellow to reddish brown. Repeat the titration to get concordant value.

RESULT

Amount of chloride ions present in the given water sample   =--------- ppm

Calculation:

Solvent used $= $ Water

K of the polymer solvent system $= $ ------

a of the polymer-solvent system $= $ ------

Volume of liquid taken for finding the flow time $= $ 10ml

Flow time of the solvent (t_0) $= $ ------ sec

S.No.	Conc. g/dl or (%)	Flow time (t)sec	$\eta_r = t / t_0$	$\eta_{sp} = \eta_r - 1$	η_{sp} / C

S.No.	Polymer	Solvent	K x 10^{-5}	a
1	Polyvinyl alcohol	Water	45.3	0.64
2	Polyvinyl pyrrolidone	Water	39.3	0.59
3	Polystyrene (atactic)	Benzene	11.5	0.73
4	Polystyrene (isotactic)	Benzene	10.6	0.735

DETERMINATION OF MOLECULAR WEIGHT OF A POLYMER BY VISCOMETRY METHOD.

Exp. No.11   **Date:**

Aim:

> To determine the molecular weight (M) of a polymer by viscometry method.

Principle:

Viscosity average method is based on the flow behavior of polymer solutions. According to Mark – Hawnik equation, the intrinsic viscosity of a polymer is given as

$$[\eta]_{int} = KM^a$$

Where,

> M = molecular weight of the polymer
>
> K & a are constants for a particular polymer – solvent system
>
> $[\eta]_{int}$ = Intrinsic viscosity = $[\eta_{sp}/C]_{C=0}$ = $[\eta_r/C]_{C=0}$
>
> η_{sp} = specific viscosity = $\eta_r - 1$
>
> η_r = relative viscosity = η/η_0 = t / t_0

Since accurate measurement of absolute viscosity is a difficult task, relative viscosity is taken into account for finding the molecular weight.

> η = Viscosity of the polymer solution
>
> η_0 =   Viscosity of the pure solvent
>
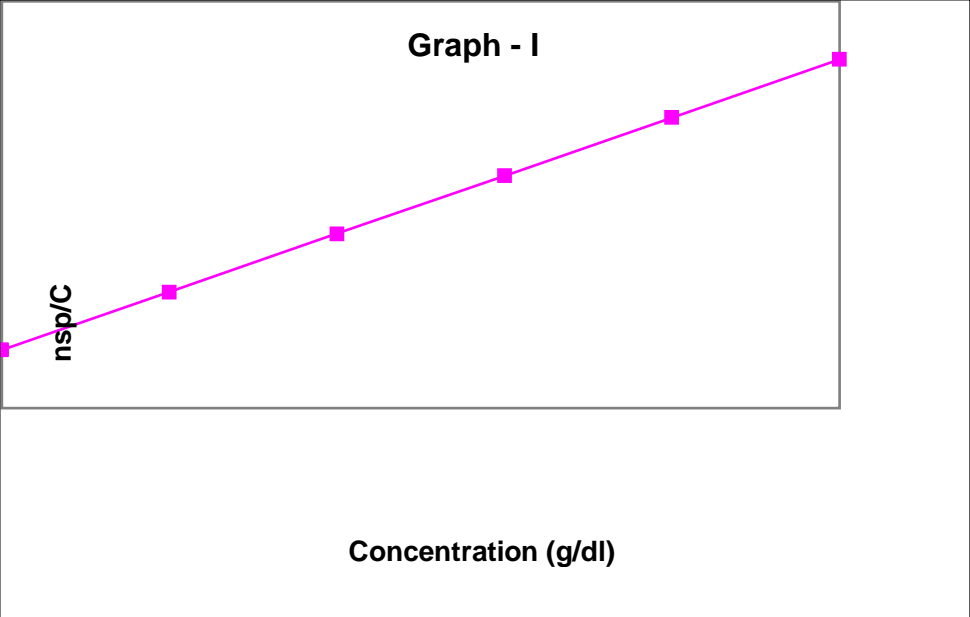> t   = flow time of the polymer solution
>
> t_0 = flow time of the pure solvent

> The flow time of the polymer solution (t) and that of the pure solvent (t_0) are found experimentally and substituted to get η_{sp}, η_r and $[\eta]_{int}$.

Knowing K & a, molecular weight of the polymer solution is calculated.

DP = M / m (M= mol.wt of polymer, m = mol. wt of monomer)

Graph - I

nsp/C

Concentration (g/dl)

PROCEDURE:

Accurately take 1g weight of polyvinyl alcohol, dissolve it in water and make up to 100ml (1dl) in a standard flask. From the solution, Prepare the polymer solutions of concentration 0.1g/dl,0.2g/dl,0.3g/dl,0.4g/dl and 0.5g/dl using the relation $V_1N_1 = V_2N_2$

[E.g. for preparing 100ml of 0.2g/dl from 1g/dl solution x ml polymer is made up to 100ml with water where x is caculated using the relation, x ml $\times$ 1 g / dl = 0.2 g / dl $\times$ 100ml]

$$[\eta] = KM^a$$

$$M^a = [\eta]/K$$

$$a \log M = \log[\eta] - \log K$$

$$logM = \frac{\log[\eta] - logK}{a}$$

$$M = antilog \quad \{\underline{\log [\eta] - \log K}\}$$
$$a$$

Rinse the Ostwald viscometer with water, and then fill with 10ml of distilled water. Using a rubber bulb, suck the water in the viscometer to the upper bulb. Allow the water to flow from the upper mark till the lower mark in the viscometer. Using a stop clock measure the time taken for water to flow from the upper mark to the lower mark and note the value as t_0 sec.

Drain the water from the viscometer completely and take 10ml of the polymer solution of 0.1g/dl concentration in it. Note the flow time of the polymer solution as t sec. Repeat the procedure with the other solutions of the polymer.

Calculate η_{sp} / c from the values of t and t_0, and draw the graph taking η_{sp} / c Vs c. Extrapolate the straight line obtained to zero concentration. The intercept value is equal to $[\eta]_{int.}$ Calculate the molecular weight of the polymer (M) using the formula

$$[\eta]_{int} = KM^a \quad \text{(constant K and a are given in the table)}$$

RESULT

The molecular weight of the given polymer =

Heating:

S.No.	Time(min)	Temperature °C

Cooling:

S.No.	Time(min)	Temperature° C

DETERMINATION OF PHASE CHANGE TEMPERATURE OF A SOLID

Exp. No.12   **Date:**

Aim

To determine the transition temperature of a hydrated salt by thermometric method.

Principle:

The crystalline solids on heating lose their water of crystallization at a particular temperature to change into an anhydrous form or less hydrated form. This transition takes place at constant temperature and is accompanied by absorption or evolution of heat. The temperature at which such a transition takes place is called the transition temperature.

Procedure:

The given hydrated salt along with a few ml of a non-polar solvent such as paraffin liquid or toluene is placed in the inner tube of the transition temperature apparatus, fitted with a stirrer and thermometer. The bulb of the thermometer should be kept immersed in the sample. The inner tube is then placed inside the outer jacket and this arrangement is immersed into a water bath. The temperature of the bath is slowly raised by using a small flame. The rate of increase in temperature of the salt is kept uniform by slow and regular stirring. The temperature is recorded for every minute. The temperature increases gradually, remains constant for some time and again increases.

The transition temperature apparatus is taken out of the water bath. It is allowed to cool slowly with constant stirring. The temperature is recorded for every minute. At one point, the temperature will remain constant. Cooling is continued further for some more time.

A graph is plotted taking time in the x-axis ad temperature in the y-axis. Two curves will be obtained; one for heating and the other for cooling. The curve has an approximately horizontal portion. The temperature corresponding to the horizontal portion in the graph is noted. This gives the transition temperature of the given salt hydrate.

http://physicsexperiments.eu/
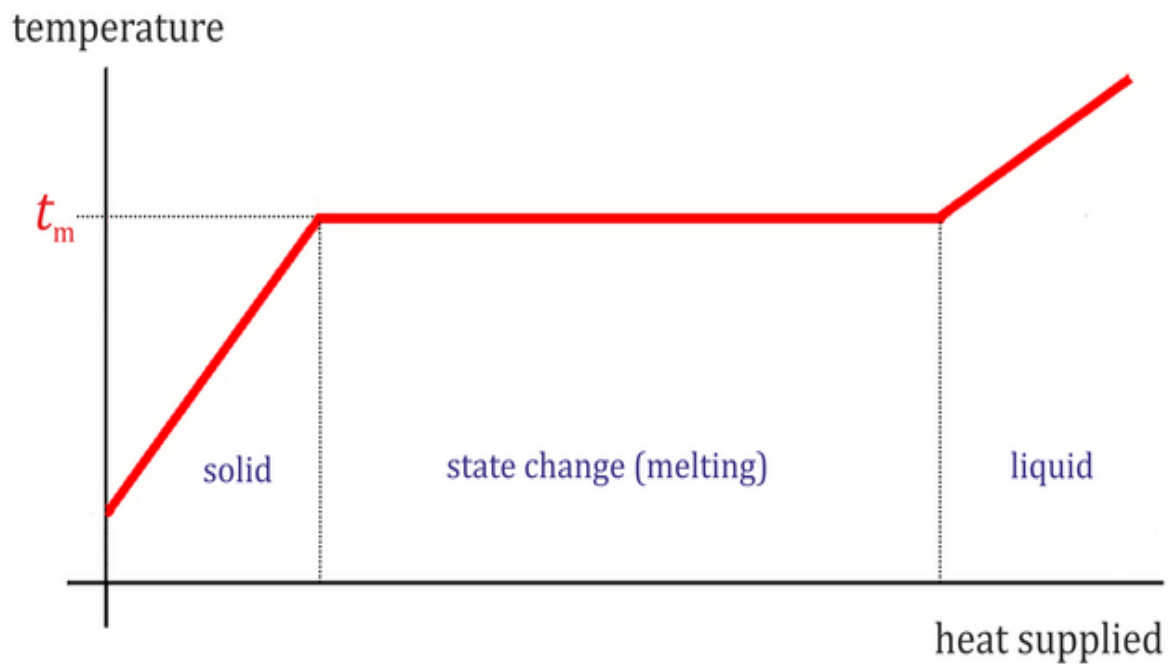
Equation	Transiton temperature (^{o}C)
$CH_3COONa.3H_2O \leftrightarrow CH_3COONa + 3H_2O$	58.3
$Na_2S_2O_3.5H_2O \leftrightarrow Na_2S_2O_2.2H_2O + 3H_2O$	48.2
$NaBr.2H_2O \leftrightarrow NaBr + 2H_2O$	50.8
$MnCl_2.4H_2O \leftrightarrow MnCl_2.2H_2O + 2H_2O$	58.5

Result:

        The transition temperature of the given salt hydrate =_____ºC

VIVA-VOCE – QUESTION BANK

Experiment: 1.construction and determination of emf of simple electrochemical cells and concentration cells

1. What is single electrode Potential?
2. What is standard electrode potential?
3. Define EMF
4. What is a concentration cell?
5. Give some examples for reference electrodes.

Experiment: 2 Estimation of acids by pH metry

1. Define pH
2. Give the principle of pH metry ?
3. Name the electrodes used in the determination of pH of a solution.
4. Which electrode act as anode and which acts as cathode? Why?
5. What is the effect of temperature on pH?
6. What is the effect of dilution on pH of an acid solution?
7. What is the pOH of pure water at 25°C
8. What is a combined electrode?
9. What is the significance of pH titration?
10. Brief the function of calomel electrode?
11. What are the pH of lime juice, blood and de-ionised water?

Experiment:3 Determination of corrosion rate on mild steel by weight loss method

1. What is weight loss method?
2. Define corrosion.
3. What are the types of corrosion?
4. What is the formula for Rate of Corrosion?
5. Explain about acid pickling
6. What is Rust. Give its formula?
7. Which is regarded as a cancer that destroys economy and equipments?
8. Define Pilling Bedworth Ratio.
9. What is galvanic corrosion?
10. What is Decarburization?

Experiment: 4 Estimation of mixture of acids by conductometry

1. Define the term conductivity.
2. Give the unit of conductance.
3. What is specific conductance?
4. Define Equivalent conductance and molar conductance.
5. List out the advantages of conductometric titrations.
6. Draw the rough graph obtained by plotting conductance Vs Vol of NaOH in the estimation of mixture of acids (SA+WA).
7. Which acid will be neutralised first when a mixture of HCl and acetic acid is titrated against NaOH?
8. Why the conductance decrease until the first neutralization point?
9. The second neutralization point conductance increases slowly and then shows steep rise. Explain

Experiment:5 Estimation of extent of corrosion of iron pieces by potentiometry

1. What is an electrochemical cell?
2. Define reduction potential
3. Mention the factors affecting electrode potential?
4. Give the formula to calculate EMF of a cell
5. Name the electrodes acting as cathode and anode in the experiment
6. What is redox titration?
7. Explain the redox reaction that takes place when $FeSO_4$ is titrated against $K_2Cr_2O_7$.
8. Platinum electrode is a oxidation – reduction electrode in the presence of Fe^{2+} and Fe^{3+} Why?
9. What is the reduction potential of calomel electrode?
10. Give the advantages of Potentiometric titrations.
11. What is calomel electrode?

Experiment: 6 Estimation of copper / ferrous ions by spectrophotometry

1. What is the principle of spectrophotometry?
2. How is the light from a monochromatic source gets distributed on falling upon a medium?
3. What is absorbance?
4. What is transmittance?
5. What is a spectrophotometer and spectrophotometry?
6. State Beer-Lamberts law?
7. What is the role of KCNS in the estimation of iron by spectrophotometry?
8. Why is the monochromator adjusted for $\lambda = 480nm$ during the estimation of iron?
9. Mention the working range of wave length of spectrophotometer?

Experiment: 7 Estimation of DO by winkler's method

1. What is the extent of oxygen dissolution in water at $30°C$?
2. What is the need of determining the amount of DO in water?
3. What is Winkler's reagent?
4. What are the reactions involved in DO estimation?
5. Why do we dissolve the precipitate formed in $Conc.H_2SO_4$?
6. What are the principle behind iodometry and iodimetry?
7. What is the name of the brown precipitate we get in the estimation?
8. How can we avoid dissolution of O_2 in water?
9. Why should we put stopper on the bottle used for DO estimation?
10. Explain the process of Winkler's method of estimation of DO

Experiment: 8 Determination of total, temporary and permanent hardness by EDTA method.

1. What is Hardness?
2. What are the two types of hardness?
3. Write the structure of EDTA.
4. Give the reaction between EBT and hardeness causing ions.
5. What is the pH range for complex stability in EDTA method?
6. What is the buffer used in the titration?
7. Give reason for the formation of red and blue colours in the titration.

8. What are the disadvantages of hardness?

9. What may be the range of hardness in a portable water sample?

10. What is the need of filtration during the experiment?

11. What are the units by which hardness is expressed?

12. What is the other name for Eriochrome black T?

13. Why is $CaCO_3$ used as reference in hardness calculations?

Experiment : 9 Estimation of alkalinity by indicator method

1. What is alkalinity?

2. What are the ions responsible for alkalinity in water?

3. What are the five possible alkalinities in water?

4. What are the indicators used in the titration?

5. What is the equivalent weight of $CaCO_3$.

6. What is the reaction of Phenolphthalein end point?

7. What is ppm?

8. Explain Lewis concept.

9. Expalin Bronsted – Lowry concept.

10. What is the colour of phenolphthalein in acidic and basic medium?

11. What is the colour of methyl orange in acidic and basic medium?

Experiment:10 Estimation of chloride by argentometric method

1. Explain the principle behind the argentometry?

2. Why do we get a blurred solution during the titration?

3. What type of medium is preferred for chloride estimation?

4. What is the colour change that infers the end point?

5. What is the relationship between ppm and g/ml?

6. What are the different sources of chloride in water?

Experiment: 11 Determination of molecular weight of a polymer by viscometry method.

1. What are polymers and monomers?

2. Define viscosity.

3. What is intrinsic viscosity? How is it related to molecular weight?

4. What are the values of 'K' and "a" for water-PVA system?

5. What is specific viscosity?

6. How is degree of polymerization found from molecular weight of a polymer?

7. What is name of the viscometer used in theis experiment?

Experiment: 12 Determination of phase change temperature of a solid

1. Define transition temperature.

2. What is a hydrated salt? Give example.

3. What do you mean by thermometric method?

4. How are cooling curves drawn?

5. Mention the transition temperature of any two hydrated salts.