

## MODULE- 1

### ELECTROCHEMISTRY AND ENERGY SYSTEM

#### Electrochemistry and energy storage systems:

Electrochemistry: Introduction, EMF of cell, Free Energy, Single electrode potential-Derivation of Nernst equation, Numerical problems based on Nernst Equation.

Reference Electrodes: Introduction, construction, working and applications of calomel electrode, ion selective electrodes: Introduction, construction, working and applications of Glass electrode, determination of pH using Glass electrode.

**Energy storage Systems:** Introduction, Classification of batteries (primary, secondary and reserved batteries). Construction, working and applications of Li-ion batteries. Advantages of Li-ion battery as an electrochemical energy system for electric vehicles. Recycling of Lithium-ion batteries, Introduction, brief discussion on direct recycling method, Sodium-ion battery-Introduction.

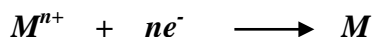
#### Introduction:

An important aspect of electrochemistry is the inter conversion of electrical energy and chemical energy that takes place through oxidation-reduction (redox) reaction. Redox reaction forms a basis of electrochemical cell.

In oxidation reaction, a species loses one or more electrons resulting in increase in oxidation number.



In reduction reaction, a species gains one or more electrons resulting in decrease in oxidation number.



**Definition of Electrochemistry:** It is a branch of chemistry which deals with the study of transformation of chemical energy into electrical energy and vice versa”.

**Electrochemical cells:** “An electrochemical cell is a device which converts chemical energy into electrical energy or electrical energy into chemical energy”

#### Types of electrochemical cells:

1. **Galvanic cells**- Devices which convert chemical energy into electrical energy through electrochemical reaction.

Example- Dry cell, Lead-acid cell, Ni-Cd cell etc.

2. **Electrolytic cells**- Devices which convert electrical energy into chemical energy.

### **Free energy :**

Gibbs free energy is the part of total energy of a system which is available to do useful work.  $G = H - T S$ .

Where, H = Enthalpy

T = Temperature

S = Entropy

**Cell potential (EMF of a cell):** It is the potential difference between the two electrodes of a galvanic cell which causes the flow of current from one to other.

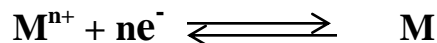
$$E_{\text{Cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

**Single electrode potential:** It is the potential developed at the junction of a metal and solution when a metal is in contact with its own ions due to loss or gain of electrons.

### **Nernst equation for single electrode potential:**

Nernst equation gives a relationship between single electrode potential and standard electrode potential through concentration of metal ions at a particular temperature.

Consider a reversible electrode reaction,



Equilibrium constant for the above reaction is,

$$K_c = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[M]}{[M^{n+}]} \dots\dots\dots (1)$$

According to thermodynamics, for a reversible process, equilibrium constant (K) is related to decrease in change in free energy ( $-\Delta G$ ) as, by Vant Hoff equation.

$$\Delta G = \Delta G^0 + RT \ln K_c \dots\dots\dots (2)$$

Where,  $\Delta G^0$  = Standard change in free energy

R = Universal gas constant

T = Temperature

Substituting 1 in 2 we have,

$$\Delta G = \Delta G^0 + RT \ln \frac{[M]}{[M^{n+}]} \dots\dots(3)$$

The decrease free energy (-ΔG) for any reversible process is equal to the maximum amount of work that can be obtained from a chemical cell reaction.

$$-\Delta G = W_{\max} \dots\dots\dots(4)$$

In case of a Galvanic cell,  $W_{\max}$  = Electrical energy supplied by the cell

$$= [(\text{difference in potential between two electrodes}) \times (\text{total charge flowing through the cell})]$$

If 'n' moles of electrons are flowing from anode to cathode, then the total quantity of charges flowing through the cell is 'n' Faradays (nF).

$$\therefore W_{\max} = E_{\text{cell}} \times nF = nFE \dots\dots\dots(5)$$

By comparing equation 4 and 5,

$$-\Delta G = nFE \dots\dots\dots(6) \text{ or } \Delta G = -nFE$$

Under standard conditions,

$$-\Delta G^0 = nFE^0 \quad (7) \text{ or } \Delta G^0 = -nFE$$

Substituting the values equation (6) and (7) in

$$\text{equation (3)} \quad -nFE = -nFE^0 + RT \ln K_c \quad (8)$$

Dividing throughout by -nF,

$$E = E^0 + \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]} \dots\dots\dots(9)$$

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

$$E = E^0 - \left\{ \frac{2.303RT}{nF} \log [M] - \frac{2.303RT}{nF} \log [M^{n+}] \right\} \dots\dots\dots(10)$$

***In case of metal-metal ion electrode, as 'M' is solid metal, [M] = 1***

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

(R is a gas constant =  $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ ; T= temperature in absolute scale  
(298K); F is Faraday =  $96,500 \text{ C mol}^{-1}$ )

$$E = E^0 + \frac{0.0591}{n} \log [M^{n+}] \quad \text{at 298 K}$$

**Nernst equation for emf of cells:**

**Where**  $E^0_{\text{cell}} = E^0_{\text{Cathode}} - E^0_{\text{Anode}}$

$$E_{\text{cell}} = E^0_{\text{cell}} + \frac{0.0591}{n} \log \frac{[\text{Species.at.Cathode}]}{[\text{Species.at.Anode}]}$$

## NUMERICALS

1. Calculate the Standard electrode potential of  $\text{Cu}^{+2}/\text{Cu}$  if its electrode at  $25^\circ\text{C}$  is 0.296V and  $[\text{Cu}^{+2}]$  is 0.015M

Solution:

Given,  $E = 0.296\text{V}$   $[M^{n+}] = 0.015\text{M}$   $n = 2$

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

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

$$0.296 = E^0_{\text{Cu}^{+2}/\text{Cu}} + \frac{0.0591}{2} \log[0.015]$$

$$0.296 = E^0_{\text{Cu}^{+2}/\text{Cu}} + 0.0295[-1.8239]$$

$$0.296 = E^0_{\text{Cu}^{+2}/\text{Cu}} - 0.0538$$

$$E^0_{\text{Cu}^{+2}/\text{Cu}} = 0.296 + 0.0538$$

$$E^0_{\text{Cu}^{+2}/\text{Cu}} = 0.3498\text{V}$$

2. Calculate the **Voltage** generated by the cell consisting of iron rod immersed in 1.0M  $\text{FeSO}_4$  manganese rod immersed in 0.1M solution of  $\text{MnSO}_4$  at  $25^\circ\text{C}$ . Given that  $E^0_{\text{Fe}^{+2}/\text{Fe}} = -0.44\text{V}$  and  $E^0_{\text{Mn}^{+2}/\text{Mn}} = -1.18\text{V}$ .

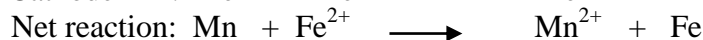
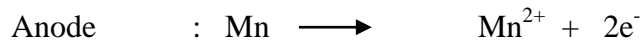
a) Write cell representation

b) Write cell reaction

Solution :

Cell representation :  $\text{Mn} | \text{Mn}^{2+}_{(0.1\text{M})} || \text{Fe}^{2+}_{(1\text{M})} | \text{Fe}$

Cell reaction :



$$E_{\text{cell}} = E^0_{\text{cell}} + \frac{0.0591}{n} \log \frac{[M^{n+} \text{ at cathode}]}{[M^{n+} \text{ at anode}]}$$

$$E^0_{\text{cell}} = E^0_{\text{Fe}^{+2}/\text{Fe}} - E^0_{\text{Mn}^{+2}/\text{Mn}}$$

$$= -0.44 - (-1.18)$$

$$E^0_{\text{cell}} = 0.74\text{V}$$

$$E_{\text{cell}} = 0.74 + \frac{0.0591}{2} \log \frac{[1.0]}{[0.1]}$$

$$= 0.74 + 0.0295 \log 10$$

$$E_{\text{cell}} = 0.74 + 0.0295 \times 1$$

$$E_{\text{cell}} = 0.7695\text{V}$$

3. Calculate the of  $\text{Zn}^{+2}/\text{Zn}$  at  $25^\circ\text{C}$  given that Standard electrode potential of Zn electrode is - 0.76V and  $[\text{Zn}^{+2}]$  is 0.1M

Solution :

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

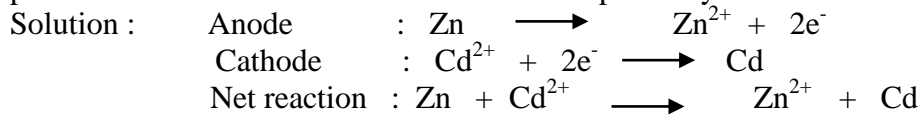
$$E_{\text{Zn}^{+2}/\text{Zn}} = E^0_{\text{Zn}^{+2}/\text{Zn}} + \frac{0.0591}{n} \log[\text{Zn}^{+2}]$$

$$= -0.76 + \frac{0.0591}{2} \log[0.1]$$

$$= -0.76 + 0.0295(-1)$$

$$E_{\text{Zn}^{2+}/\text{Zn}} = -0.7895 \text{ V}$$

4. Calculate the EMF of the cell,  $\text{Zn} | \text{ZnSO}_{4(1\text{M})} || \text{CdSO}_{4(1\text{M})} | \text{Cd}$  at 298K when the standard electrode potential of Zn is -0.76V and Cd is -0.40V respectively.



$$\begin{aligned} E_{\text{cell}}^0 &= E_{\text{Cd}^{2+}/\text{Cd}}^0 - E_{\text{Zn}^{2+}/\text{Zn}}^0 \\ &= -0.4 - (-0.76) \\ E_{\text{cell}}^0 &= 0.36\text{V} \end{aligned}$$

5. Calculate the Standard electrode potential of  $\text{Cu}^{2+}/\text{Cu}$  if its electrode at 28° C is 0.296V and  $[\text{Cu}^{2+}]$  is 0.03M

Solution :

$$\begin{aligned} E_{\text{Cu}^{2+}/\text{Cu}} &= E_{\text{Cu}^{2+}/\text{Cu}}^0 + \frac{2.303RT}{nf} \log[\text{Cu}^{2+}] \\ 0.296 &= E_{\text{Cu}^{2+}/\text{Cu}}^0 + \frac{2.303 \times 8.314 \times 301}{2 \times 96500} \log[0.03] \\ 0.296 &= E_{\text{Cu}^{2+}/\text{Cu}}^0 + 0.02986 [-1.5228] \\ 0.296 &= E_{\text{Cu}^{2+}/\text{Cu}}^0 - 0.04547 \\ E_{\text{Cu}^{2+}/\text{Cu}}^0 &= 0.296 + 0.04547 \\ E_{\text{Cu}^{2+}/\text{Cu}}^0 &= 0.3414\text{V} \end{aligned}$$

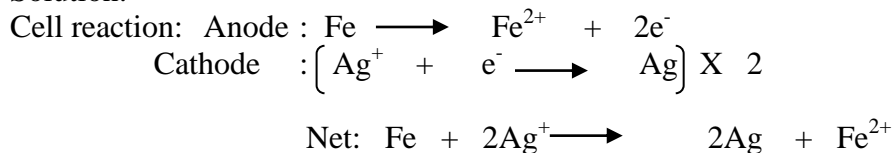
6. Calculate the  $E^0$  of  $\text{Ag}^+/\text{Ag}$  if its electrode at 27° C is 0.73V &  $[\text{Ag}^+] = 0.06\text{M}$

Solution :

$$\begin{aligned} E_{\text{Ag}^+/\text{Ag}} &= E_{\text{Ag}^+/\text{Ag}}^0 + \frac{2.303RT}{nf} \log[\text{Ag}^+] \\ 0.73 &= E_{\text{Ag}^+/\text{Ag}}^0 + \frac{2.303 \times 8.314 \times 300}{96500} \log[0.06] \\ 0.73 &= E_{\text{Ag}^+/\text{Ag}}^0 + 0.05952 [-1.2218] \\ 0.73 &= E_{\text{Ag}^+/\text{Ag}}^0 - 0.07272 \\ E_{\text{Ag}^+/\text{Ag}}^0 &= 0.73 + 0.07272 \\ E_{\text{Ag}^+/\text{Ag}}^0 &= 0.8027 \text{ V} \end{aligned}$$

7. Calculate the EMF of the cell,  $\text{Fe} | \text{FeSO}_{4(0.03)} || \text{AgCl}_{(0.1)} | \text{Ag}$  at 298K when the standard reduction potential of Fe and Ag are -0.44 and 0.80 volts respectively.

Solution:



$$\begin{aligned} E_{\text{cell}} &= E_{\text{cell}}^0 + \frac{0.0591}{n} \log \frac{[M^{n+} \text{ at cathode}]}{[M^{n+} \text{ at anode}]} \\ E_{\text{cell}}^0 &= E_{\text{Ag}^+/\text{Ag}}^0 - E_{\text{Fe}^{2+}/\text{Fe}}^0 \\ &= 0.8 - (-0.44) \\ E_{\text{cell}}^0 &= 1.24\text{V} \end{aligned}$$

$$\begin{aligned}
 E_{\text{cell}} &= 1.24 + \frac{0.0591}{2} \log \frac{[0.1]^2}{[0.03]} \\
 &= 1.24 + 0.0295 \log (0.333) \\
 E_{\text{cell}} &= 1.24 + 0.0295 \times (-0.4771) \\
 E_{\text{cell}} &= 1.24 + (-0.014) \\
 &= 1.226 \text{ V}
 \end{aligned}$$

### **Reference electrodes:**

*Reference electrodes are the electrodes whose potential is known and with reference to those, the electrode potential of any other electrode can be measured.*

There are 2 types of reference electrodes

- 1) Primary reference electrode
- 2) Secondary reference electrode

**Secondary reference electrodes:** *“The electrodes whose potential is measured with respect to SHE and then can be used as reference electrode for measuring potential of other electrodes” is called as secondary reference electrodes.*

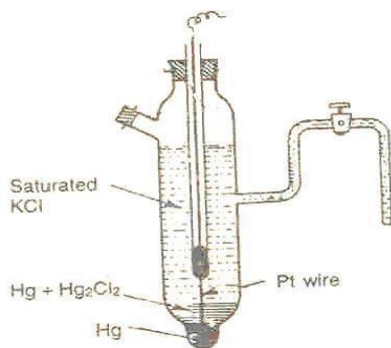
- Example
1. calomel electrode
  2. Ag-AgCl electrode

### **Calomel electrode:**

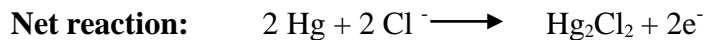
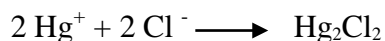
#### **Construction and working:**

1. Calomel electrode is a **Metal-metal salt electrode**
2. A Metal-metal salt electrode consists of Mercury, Mercurous Chloride and a solution of KCl.
3. Mercury is placed at the bottom of a glass tube.
4. A paste of Mercury and Mercurous Chloride (calomel) is placed above the Mercury. The space above the paste is filled with a KCl solution of known concentration.
5. A platinum wire is kept immersed into the mercury to obtain external electrical contact.
6. It is internally connected through salt bridge.

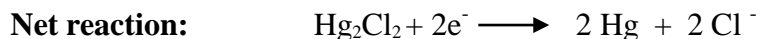
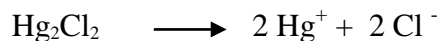
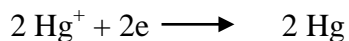
Calomel electrode can be represented as ,



The calomel electrode can acts as anode or cathode depending on the nature of the other electrode of the cell.



**When it is Cathode:-**



The net cell reversible electrode reaction is,



Nernst equation for calomel electrode is,

Electrode potential,  $E = E^0 + \frac{2.303RT}{nF} \log [\text{Cl}^-]^2$

$E = E^0 + \frac{2.303RT}{2F} 2\log [\text{Cl}^-]$  , Where n=2

$E = E^0 - 0.0591 \log [\text{Cl}^-]$  , at 298K



Therefore electrode potential of calomel electrode is depending upon the concentration of KCl. (The electrode potential decreases with increase in the concentration of chloride ions.

For 0.1N KCl  $E = 0.335V$

1N KCl  $E = 0.281V$

saturated KCl  $E = 0.242 V$ )

### **Applications:**

1. It is used as secondary reference electrode in the measurement of single electrode.
2. It is used as reference electrode in all potentiometer determinations.
3. It is used as external reference electrode in the pH measurement.

### **Ion selective electrode:**

“Ion selective electrode is one which selectively responds to a specific ion in a mixture and the potential developed at the electrode is a function of the concentration of that ion in the solution”

For egs. Glass electrode is sensitive to  $H^+$  ions .

### **Glass electrode (Glass pH electrode):**

It is more selective towards  $H^+$  ions in the solution containing mixture of ions and hence used in the measurement of concentration of  $H^+$  ions in the solution.

Glass electrode can be represented as ,

*$Ag / AgCl(s) / HCl(0.1M) / glass\ membrane$*

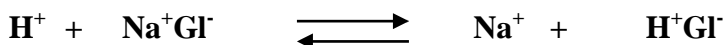
### **Construction:**

- A glass electrode consists of a long glass tube with glass membrane bulb at the bottom. Glass membrane bulb is made up of silicate corning glass with composition 22%  $Na_2O$ , 6%  $CaO$  and 72%  $SiO_2$ . The bulb is filled with 0.1M HCl.
- A silver-silver chloride electrode, which is used as an internal electrode is dipped in the solution provides an electrical contact. The bulb of the glass electrode is dipped into any solution containing hydrogen ions.
- If the hydrogen ion concentrations of the solution inside and outside the glass membrane are different then the potential develops across the glass membrane (**boundary potential**).

### Working:-

(An ion selective electrode generally consists of ion selective membrane in contact with an analyte solution on one side and an internal reference solution on the other side.)

- The Mechanism of potential development in ion selective electrodes is different from that of the other electrodes.
- Here the potential is a kind of **boundary potential** that develops across a membrane. Boundary potential is arisen across the membrane due to the movement of  $H^+$  ions with  $Na^+$  ions. **Boundary potential** established is also due to the below reaction:



$$E_b = E_2 - E_1 \dots \dots \dots (1)$$

$$E_b = (E_2^0 + \frac{0.0591}{n} \log C_2) - (E_1^0 + \frac{0.0591}{n} \log C_1) \dots \dots \dots (2)$$

Where  $C_2$  and  $C_1$  are the concentrations of analyte and internal standard solution (0.1M) respectively, and  $n=1$

Theoretically  $E_b = 0$ , when  $C_1 = C_2$

Here  $E_2^0 = E_1^0$

Thus

$$E_b = 0.0591 \log C_2 - 0.0591 \log 0.1 \dots \dots \dots (3)$$

Since  $C_1 = 0.1$  M, then

$$E_b = L + 0.0591 \log C_2$$

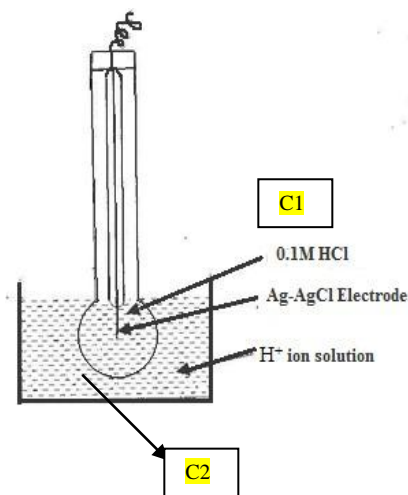
(Where  $L = -0.0591 \log C_1$ ).....(4)

$$E_b = L + 0.0591 \log [H^+] \quad \text{Since, } C_2 = [H^+] \dots \dots \dots (5)$$

$$E_b = L - 0.0591(-\log [H^+]) \dots \dots \dots (6)$$

$$E_b = L - 0.0591 \text{pH}$$

Since  $\text{pH} = -\log [H^+]$



**Overall potential of the glass electrode is the sum of 3 potentials,**

1. Boundary Potential ( $E_b$ )

2. Potential of Ag/AgCl ( $E_{Ag/AgCl}$ )

3. Asymmetric potential ( $E_{asymmetric}$ )

(Asymmetric potential is a small additional potential developed due to the curvature difference of glass membrane)

$$\text{i.e., } E_G = E_b + E_{Ag/AgCl} + E_{asymmetric} \dots \dots \dots (7)$$

$$= L - 0.0591\text{pH} + E_{Ag/AgCl} + E_{asymmetric} \dots \dots \dots (8)$$

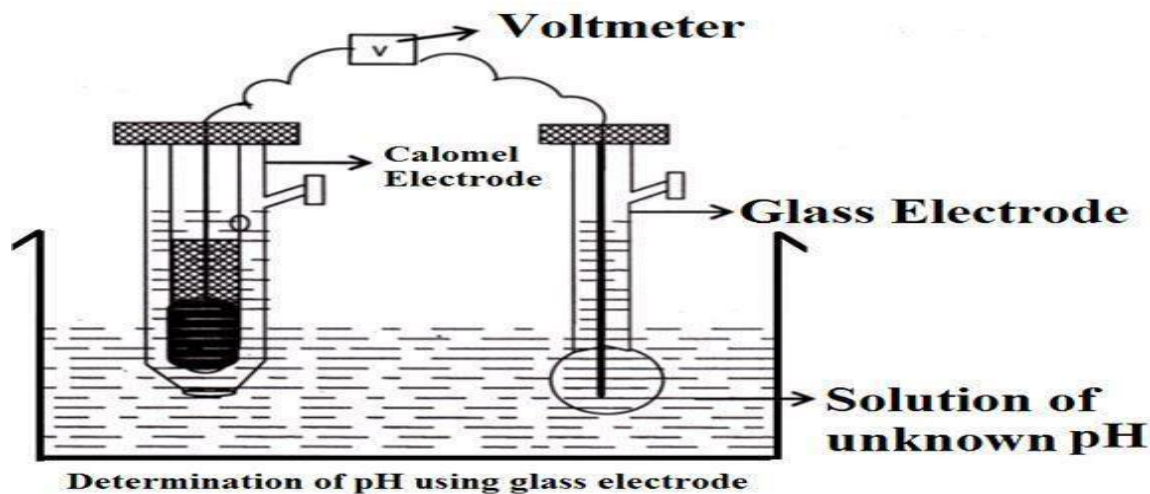
$$E_G = L^1 - 0.0591\text{pH.}$$

(Where  $L^1 = L + E_{Ag/AgCl} + E_{asymmetric}$  is constant for a

particular material.)

The above equation for potential of glass electrode can be used to measure the pH of the solution.

### **Determination of pH using glass electrode:**



- For pH determination Glass electrode is immersed in the solution whose pH is to be determined and it is combined with a reference electrode such as a calomel electrode (saturated) through a salt bridge.
- The cell assembly is represented as,  $\text{Hg} | \text{Hg}_2\text{Cl}_2 | \text{KCl} || \text{Solution of unknown pH} | \text{glass} | 0.1\text{M HCl} | \text{Ag}^+ | \text{AgCl}$

### Step 1:

The emf of the above cell,  $E_{\text{cell}}$  is measured using an electronic **voltmeter** or **pH meter**.

- The emf of the cell is given by: |

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

$$E_{\text{cell}} = E_{\text{glass}} - E_{\text{cal}}$$

Since  $E_{\text{cal}}$ ,  $E_{\text{cell}}$  is known, so  $E_{\text{glass}}$  can be evaluated.

The potential of glass electrode  $E_G$  is given by,  $E_G = L' - 0.0591\text{pH}$

$$E_{\text{cell}} = E_G - E_{\text{cal}}$$

$$E_{\text{cell}} = L' - 0.0591\text{pH} - E_{\text{cal}}$$

$$\text{pH} = \frac{L' - E_{\text{cell}} - E_{\text{cal}}}{0.0591}$$

### Step 2:

$L'$  value is evaluated by dipping the glass electrode in a solution of known pH and measuring the emf of the cell formed when combined with a calomel.

$$E_{\text{Cell}} = E_G - E_{\text{cal}}$$

$$E_{\text{Cell}} = L' - 0.0591 \text{pH}_{(\text{Known})} - E_{\text{cal}}$$

$$L' = E_{\text{Cell}} + 0.0591\text{pH}_{(\text{known})} + E_{\text{cal}}$$

## UNIT- 2

### BATTERY TECHNOLOGY

**Galvanic cell:** Galvanic cell is a device for converting chemical energy into electrical energy through a spontaneous redox reaction.

**Battery:** It is a device consisting of two or more galvanic cells connected in series or parallel or both, which converts chemical energy into electrical energy through redox reaction.

**Principle components** of a battery are:

1. An anode where oxidation occurs.
2. A cathode where reduction occurs.
3. An electrolyte, which conducts ions.
4. A separator to separate anode and cathode compartments.

#### *Classification of the Battery:*

---

**1.Primary Batteries:** A battery which cannot be recharged(because the cell reactions are irreversible)

e.g. Zn-MnO<sub>2</sub>, Zn –Air , dry cell.

**2.Secondary Battery:** A battery which can be recharged(as the cell reactions are reversible) and also known as storage battery. e.g. Lead-acid battery, Li-ion battery

**3.Reserve battery:** In this battery, one of the components is stored separately and used whenever required. e.g. Mg-AgCl battery where battery is activated by the addition of water. It is used in missiles and military weapon system.

---

#### **Lithium-ion battery:**

##### **Construction:**

**Anode**-Lithium intercalated graphite.

**Cathode** – Lithium metal oxide such as (LiCoO<sub>2</sub>).

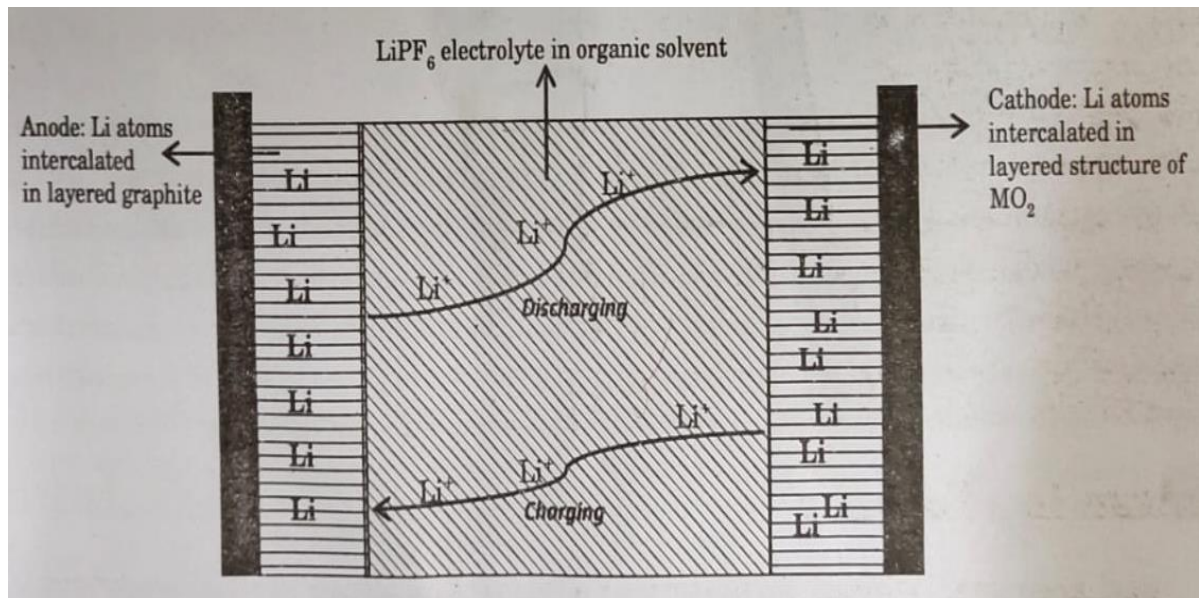
**Electrolyte** -A solution of lithium salt (LiPF<sub>6</sub>) in organic solvent.

**Separator**- non-woven polypropylene.

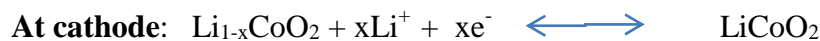
**Representation :**  $Li, C / LiPF_6, \text{ in organic solvent } / LiCoO_2$

- It is a rechargeable battery. In this battery lithium atoms occupy positions between graphite lattice layers.
- Lithium ions move between anode and cathode during discharging and charging process. Since both

anode and cathodes are intercalation materials lithium atoms insert and disinsert between layers.



### Working



**Applications:** Portable electronics, mobile phones, laptop, ipod etc.

### Advantages of Li-ion Battery as an electrochemical storage system for electric vehicles:

- **Eco-friendly:** They have relatively low levels of toxic heavy metals such as Cd, Pb, Hg etc compared to other types of batteries such as Lead-acid and Ni-Cd batteries.
- **Cell voltage :** Li-ion Battery has cell voltage of 3.7 V which is high compared to other batteries like Ni-MH(1.2 V)
- **Light weight and compact:** Electrodes commonly used in Lithium ion batteries, Lithium and carbon, are light weight on their own and this makes them light weight and compact compared to other batteries.
- **High energy density:** Li element has the ability to release and store large amounts of energy. This allows li-ion batteries to pack high energy in small size. Because of high energy efficiency Li- ion batteries last much longer between charges than other rechargeable batteries – a parameter which is

very important for electric car batteries. Performance at high temperatures is also good.

- **Low maintenance:** Ni-Cd or Ni-MH batteries have “memory effect” or “lazy battery effect” which causes them to hold less charge. They should be maintained by completely discharging or recharging them.  
Li-ion batteries don't suffer from memory effect and they give up their last bit of power.  
Hence maintenance is less.
- **Low self-discharge rate:** Self discharge rate of Li-ion batteries increases about 5% within first 24 hrs after charging and then tapers off to 1-2% per month.
- **More charge cycles:** Quality Li-ion batteries last about 1000 full charge cycles.

### **Recycling of Li-ion batteries**

Lithium-ion battery contains many precious metals like Cobalt, nickel, manganese, copper etc. All these materials can be recovered by recycling process. Recycling can be done by different methods like

- **Hydrometallurgical processing (Leaching method)**
- **Pyrometallurgical processing (Smelting method)**
- **Direct recycling process**

#### **Direct recycling process:**

- Direct recovery is a process of recovering useful components from spent lithium ion batteries.
- Dismantling of the battery components like plastic, copper, aluminium etc. immediate recovery of aluminium and copper is done.
- Crushing the anode and cathode with the electrolyte into small pieces.
- Dissolve these components using inorganic acids like concentrated sulphuric acid.
- Metals are separated by density separation or magnetic separation method.
- The separated metals can be used as electrode in Li-ion batteries.

### **Sodium ion battery**

It is similar to Li-ion Battery, but in this  $\text{Na}^+$  ions are the charge carriers. The largest advantage of sodium ion batteries is the high natural abundance and the lower cost of sodium compared with lithium.

**Anode:** Sodium absorbed on the surface of Hard carbon ( $\text{Na}_x\text{C}_6$ )

**Cathode:** Sodium transition metal oxide ( $\text{NaMO}_2$ ) where M= Fe, Ni, Mn, Co etc.

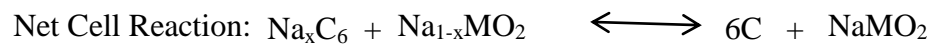
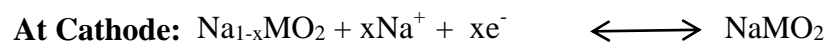
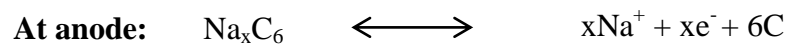
**Electrolyte:**  $\text{NaPF}_6$  in mixed organic carbonate solvents like ethylene carbonate, propylene carbonate, dimethyl carbonate etc.

**Separator:** Fine porous polymer film

**Representation:**  $\text{NaC}_6 \mid \text{NaPF}_6 \text{ dissolved in mixed organic solvents} \mid \text{NaMO}_2$

Cell Potential: 3.8V

**Working:** Cell reactions during discharge



**Applications:** it is used in electric vehicles and power too



## **MODULE- 2**

### **Corrosion and Metal finishing:**

#### **Corrosion and its control:**

Introduction, Electrochemical theory of corrosion, Factors affecting the rate of corrosion: ratio of anodic to cathodic areas, nature of corrosion product, nature of medium – pH, conductivity and temperature. Types of corrosion - Differential metal and differential aeration (pitting and water line). Corrosion control: Inorganic coating- Anodizing – Anodizing of aluminum, Cathodic protection - sacrificial anode and impressed current methods, Metal coatings – Galvanization. Corrosion Penetration Rate (CPR), numerical problems on CPR.

**Metal finishing:** Introduction, Technological importance. Electroplating: Introduction, Electroplating of chromium (hard and decorative). Electroless plating: Introduction, distinction between electroplating and electroless plating processes. Electroless plating of copper.

## **CORROSION AND ITS CONTROL**

**Definition of corrosion:** Corrosion is defined as the destruction of metals or alloys by the surrounding environment through chemical or electrochemical reactions.

**Example:** When iron is exposed to air in the presence of moisture, hydrated ferric oxide (rust) is formed.

**Electrochemical Theory Of Corrosion:** According to electrochemical theory, when a metal such as iron is exposed to corrosive environment, following changes occur.

A large number of tiny galvanic cells with anodic and cathodic regions are formed.

- Oxidation of metal takes place at the anodic region. e.g.  $\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$
- The  $\text{Fe}^{2+}$  ions dissolve, so corrosion takes place at the anodic region.
- The electrons travel through the conducting medium (moisture) from the anodic region to cathodic region.

### **Reactions:**

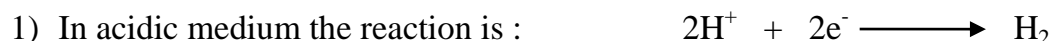
**Reaction at anodic region:** As mentioned above, oxidation of metal takes place at anode.



**Reactions at cathodic region:** At cathode, the reaction is either

a) Liberation of hydrogen or b) absorption of oxygen.

A) **Liberation of hydrogen** (In the Absence of Oxygen)



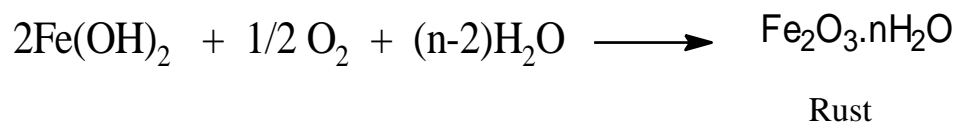
2) In neutral/alkaline medium, the reaction is:  $2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{H}_2 + 2\text{OH}^-$

B) **Absorption of oxygen** (In the Presence Of Oxygen)

3) In acidic medium, the reaction is :  $2\text{H}^+ + 2\text{e}^- + 1/2\text{O}_2 \longrightarrow \text{H}_2\text{O}$

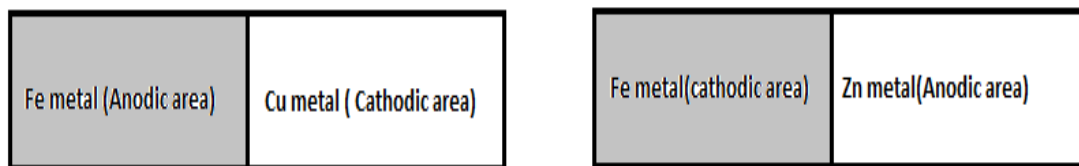
4) In neutral/alkaline medium, the reaction is :  $\text{H}_2\text{O} + 2\text{e}^- + 1/2\text{O}_2 \longrightarrow 2\text{OH}^-$

**Overall Reaction:**



**DIFFERENT TYPES OF CORROSION:**

1. **Differential metal corrosion:**

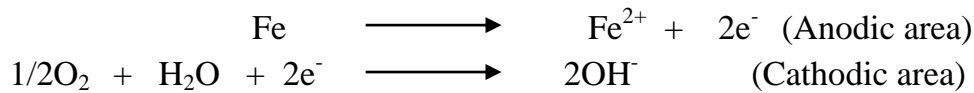


- This type of corrosion occurs when two **dissimilar metals** are in contact with each other and are exposed to a corrosive environment. The two metals differ in their electrode potentials. The metal with lower electrode potential acts as anode and the other metal with higher electrode potential acts as cathode.
- The anodic metal undergoes oxidation and gets corroded. A reduction reaction occurs at the cathodic metal. The cathodic metal does not undergo corrosion.

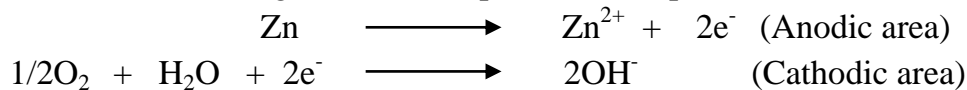
The general cell reactions may be represented as follows:

**Higher the potential difference** between the anodic and cathodic metals, **higher is the rate of corrosion.**

**Example:** When Fe(-0.44V) is in contact with Cu(0.34V), iron acts as anode and Cu acts as cathode because Fe has lower electrode potential compared to Cu. Therefore Fe undergoes corrosion.



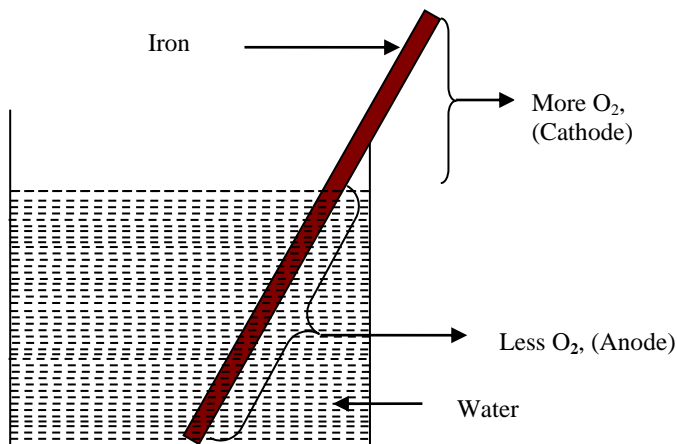
On the other hand, when iron (-0.44V) is in contact with Zn (-0.76V), iron acts as cathode because iron has higher electrode potential compared to Zn. Hence Zn undergoes corrosion.



Other examples:

1. Steel screws in copper sheet.
  2. Steel screws with copper washer.
  3. Bolt and nut made of different metals.
- 

## 2. Differential aeration corrosion:



- This type of corrosion occurs when two different parts of the **same metal** are exposed to **different oxygen concentrations**. (e.g. An iron rod partially dipped in water.)
- The part of the metal which is exposed to **less oxygen concentration acts as anode**. The part which is exposed to more oxygen concentration acts as cathode.
- The anodic region undergoes corrosion and the cathodic region is unaffected.

The reactions may be represented as follows:

**Cell reactions:**

At anode :  $M \longrightarrow M^{n+} + ne^-$  (Oxidation of metal M)

At cathode :  $H_2O + 1/2O_2 + 2e^- \longrightarrow 2OH^-$

**Other examples:**

1. Part of the nail inside the wall undergoes corrosion.
2. When a dirt particle sits on a metal bar, the part under the dirt undergoes corrosion.
3. Partially filled iron tank undergoes corrosion inside water.

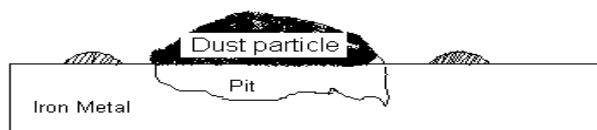
**Example for Differential aeration corrosion :**

- a) Pitting corrosion
- b) Waterline corrosion

a) **Pitting corrosion**: This is an example of differential aeration corrosion.

- When a small dust particle or water droplets gets deposited on a steel surface, the **region below the dust particle is exposed to less oxygen** compared to the remaining part.
- As a result, the region below the dust particle acts as anode undergoes corrosion and forms a pit. The remaining region of the metal acts as cathode and is unaffected.

The reactions may be represented as follows:

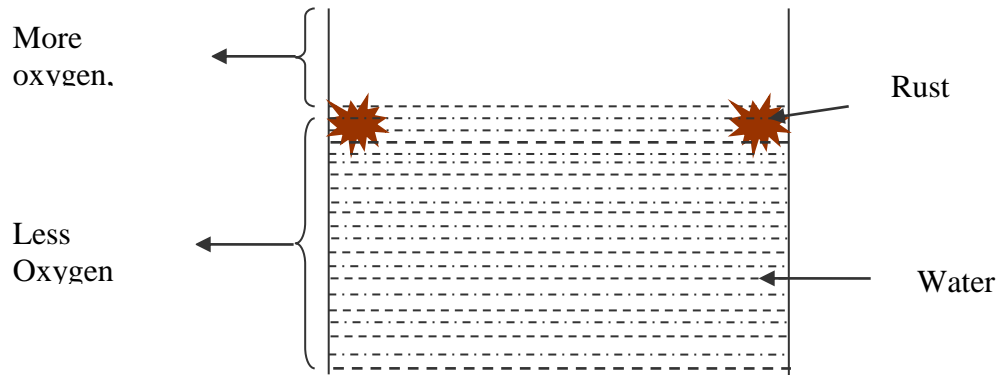
**Cell reactions:**

At anode :  $M \longrightarrow M^{n+} + ne^-$  (Oxidation of metal M)

At cathode :  $H_2O + 1/2O_2 + 2e^- \longrightarrow 2OH^-$

Formation of a small anodic area and a large cathodic area results in intense corrosion below the dust particle.

b) **Water line corrosion:** This is an example of differential aeration corrosion.

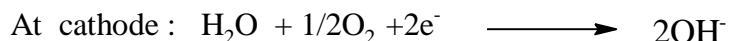
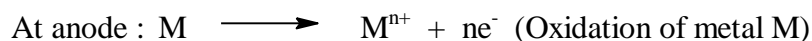


- When a steel tank is partially filled with water for a long time, the inner portion of the tank below the water line is exposed only to dissolved oxygen, whereas, the portion above the water line is exposed to more oxygen.
- Thus the portion below the water line acts as anode and undergoes corrosion. The upper portion acts as cathode and is unaffected.

A distinct brown line is formed just below the water line due to the deposition of rust.

The reactions may be represented as follows:

**Cell reactions:**



Other example: Ships which remain partially immersed in sea water for a long time undergo water line corrosion.

---

**FACTORS AFFECTING THE RATE OF CORROSION:**

1. **Nature of corrosion product:**

- If the corrosion product is insoluble, stable and non-porous, then it acts as a protective film which prevents further corrosion.
- The film acts as a barrier between metal surface and the corrosive environment.
- On the other hand, if the corrosion product is soluble, unstable and porous, then the corrosion process continues even after the formation of corrosion product.

Example: Aluminium, titanium and chromium form a protective film of metal oxide on the surface. Stainless steel forms a protective film of  $Cr_2O_3$  on the surface.

## 2. **Ratio of Anodic to cathodic areas:**

Smaller the anodic area and larger the cathodic area, more intense and faster is the corrosion. When cathodic area is large, demand for electrons for reduction reaction is high. To meet this demand oxidation reaction occurs more intensely at anodic area.

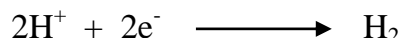
For example, a broken coating of tin on iron surface, results in intense corrosion at the broken region. Iron is anodic to tin. Exposed region of iron acts as anode with small area. Tin acts as cathode which has large area.

A broken coating of zinc on iron surface, results in less corrosion at the broken region. Iron is cathodic to zinc. Exposed region of iron acts as cathode with small area. Zinc acts as anode which has large area.

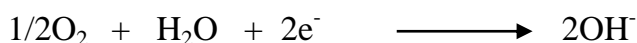
## 3. **p<sup>H</sup> of the medium:**

The rate of corrosion increases with decrease in pH.

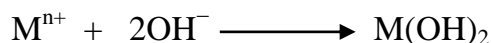
In acidic medium, rate of corrosion depends upon the rate of evolution of hydrogen at cathode area. When pH<4, rate of corrosion increases due to higher concentration of H<sup>+</sup> ions



If the pH is in between 4-10, the rate of corrosion depends upon the availability of O<sub>2</sub> on the cathodic area for reduction.



If pH>10, then the rate of corrosion is less (practically ceases) due to formation of insoluble metal hydroxide on the surface of metal.



## 4. **Temperature:**

Higher the temperature, higher is the rate of corrosion.

In general, the rate of a chemical reaction increases with increase in temperature. Corrosion is one such chemical reaction. Therefore, the rate of corrosion increases as the temperature increases.

Increase in temperature increases the **ionic conductivity** of the corrosive medium. This also contributes to the increase in corrosion rate.

## 5. Conductance of the medium:

Rate of corrosion increases with increase in conductance of the medium. As the conductance of the medium increases, ions can move easily through the medium.

Example: Metal immersed in sea water corrodes faster than metal immersed in river water

---

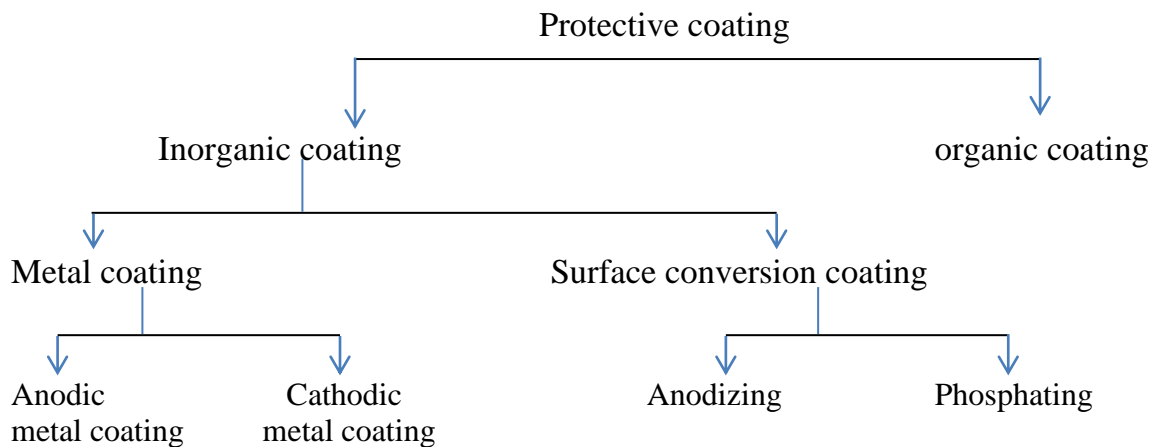
## CORROSION CONTROL

According to electrochemical theory, corrosion occurs due to oxidation and reduction reactions occurring at anodic and cathodic areas respectively. These two reactions are interdependent. Therefore by decreasing the rate of any one reaction or by preventing any one reaction, it is possible to decrease the rate of other reaction and hence rate of corrosion.

Following methods are commonly used to control corrosion

1. Protective coating
2. Cathodic protection
3. Anodic protection
4. Corrosion inhibitors
5. Design and selection of materials

1. **PROTECTIVE COATING:** Corrosion of metal mainly due to interaction of **metal surface** with **O<sub>2</sub> and moisture** in the atmosphere. Therefore, corrosion can be prevented by coating a protective layer over the surface of the metal.



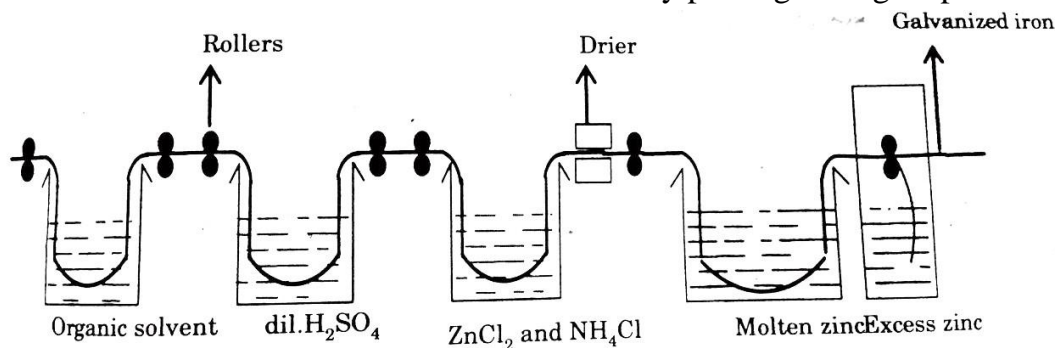
## INORGANIC COATING

**A) Metal coating:** “In this method, the corrosion of base metal is prevented by coating a layer of another metal over it”.

**1. Anodic metal coating:** Coating a layer of metal which is anodic to base metal. In this type of coating, rate of corrosion is less even if base metal is not completely covered. This is due to formation of large anodic and small cathodic area.

**Galvanizing:** Galvanizing is the process of coating zinc on iron by hot dipping method. It involves the following steps.

- The iron sheet is washed with organic solvents to remove organic matter on the surface.
- Then it is washed with dilute sulphuric acid to remove rust or oxide layer. This is called pickling
- The iron sheet is then treated with a mixture of aqueous solution of  $\text{ZnCl}_2 + \text{NH}_4\text{Cl}$ , which acts as a flux and dried. This helps the molten zinc to adhere strongly on the surface.
- The article is then dipped in a bath of molten zinc ( $450^\circ\text{C}$ ).
- The excess zinc on the surface is removed by passing through a pair of hot rollers.



### **Galvanizing**

**Application:** Galvanization of iron is carried out to produce roofing sheets, fencing wire, buckets, bolts, nuts, pipes etc.

**B) Surface area conversion:** In this method, outer surface of the base metal is converted into a protective coating through appropriate chemical modification.

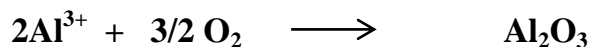
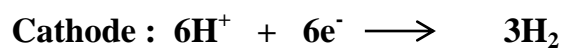
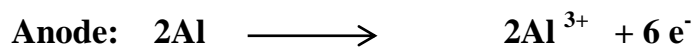
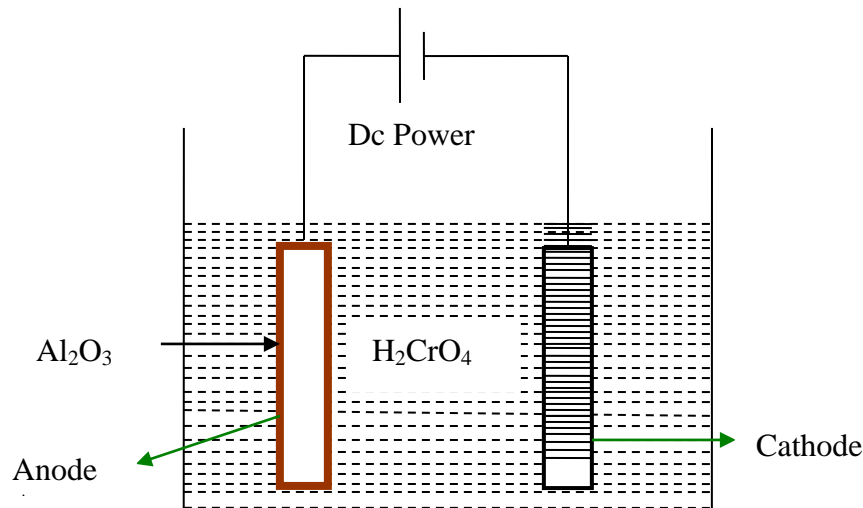
### **1. Anodizing**

Anodizing is the process of oxidation of outer layer of metal to its metal oxide by electrolysis. Oxide layer formed over the metal itself acts as a protective layer

**Anodizing of aluminum:** In this process Aluminum is cleaned, degreased polished and taken as anode in an electrolytic cell. It is immersed in an electrolyte consisting of 5-10% chromic acid.



Steel or copper is taken as cathode. Temperature of the bath is maintained at 35°C. A current density of 100 A /m<sup>2</sup> or more is applied which oxidizes outer layer of Al to Al<sub>2</sub>O<sub>3</sub> that gets deposited over the metal. This process is called anodizing of aluminium or anodic oxidation of aluminum.



**Applications:** anodized aluminium is used as an attractive highly durable, corrosion resistant material in roof, buildings, home appliances and computer parts.

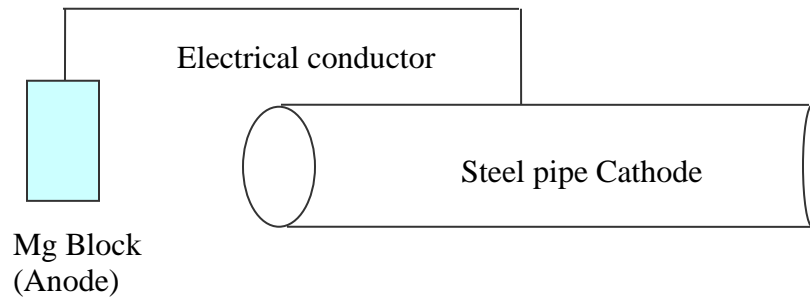
- **CATHODIC PROTECTION:-** In cathodic protection, electrons are supplied from the external source to prevent oxidation of metal at anodic area. Thus anodic area of metal is completely converted to cathodic area. Since cathodes do not undergo corrosion, the metal is protected against corrosion.

**The process where metal to be protected is made cathode, by supplying electrons from an external source is called as cathodic protection.**

**There are two methods of cathodic protection**

- Sacrificial anode method:
- Impressed current method

### Sacrificial anode method:



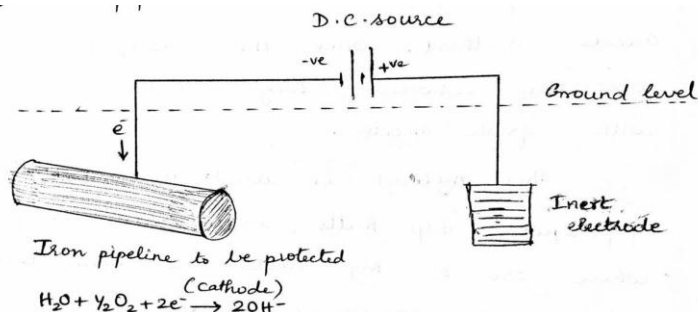
- In sacrificial anode method, the metal to be protected is connected to a more active metal.
- For example, when steel pipe is to be protected, it may be connected to a block of Mg or Zn. In such a situation, Mg or Zn act as anode and provide electrons to the steel pipe. Steel pipe acts as cathode and is unaffected. Here Mg or Zn which is anode undergoes sacrificial corrosion. When the sacrificial anode gets exhausted, it is replaced with new ones.

**Other examples:** Mg bars are fixed to the sides of ships to act as sacrificial anode.

Mg blocks are connected to buried pipe lines.

### Impressed current method (impressed voltage method)

- In impressed current method, the electrons are supplied from the source of direct current. The metal to be protected made negative by connecting to the negative terminal of an external d.c. power supply.
- The positive terminal is connected to an inert electrode such as graphite.
- Potential greater than potential of anodic reaction is applied in the reverse direction to prevent anodic reaction.
- Under these conditions, the metal acts as cathode and hence does not undergo corrosion. The inert electrode acts as anode and it also does not undergo corrosion because it is inert.



## **Corrosion Penetration Rate (CPR)**

The corrosion penetration rate (CPR) is defined in three ways:

- **The speed at which any metal in a specific environment deteriorates due to a chemical reaction in the metal when it is exposed to a corrosive environment.**
- The amount of corrosion loss per year in thickness.
- The speed at which corrosion spreads to the inner portions of a material.

The speed or rate of deterioration depends on the environmental conditions and the type and condition of the metal under study.

Corrosion penetration rate may also be known as corrosion rate.

The CPR is calculated as follows:

$$\text{CPR} = (K \times W) / (\rho \times A \times t)$$

where K = a constant

W = total weight lost

t = time taken for the loss of metal

A = the surface area of the exposed metal

$\rho$  = the metal density in g/cm<sup>3</sup>

The CPR is conveniently expressed in terms of either **mils per year** (mpy) or **millimeters per year** (mm/yr)

Where, 1 mil = 0.001 inch

	CPR in mpy	CPR mm/yr
K	534	87.6
W	(wt. loss) mg	mg
$\rho$	g/cm <sup>3</sup>	g/cm <sup>3</sup>
A	inch <sup>2</sup>	cm <sup>2</sup>
t	hrs	hrs

**Problems:**

1. A sheet of carbon steel one meter wide and three meters long has lost 40g to corrosion over the past six months. Convert that mass loss to a penetration rate of the steel in mm units and mpy units. What would be the corrosion rate? (Carbon steel density=7.8g/cc)

**To calculate CPR in mm/yr**

	Given	CPR mm/yr
K		87.6
W	40g	40X1000 mg
$\rho$	7.8 g/cm <sup>3</sup>	7.8 g/cm <sup>3</sup>
A	1mx3m=3m <sup>2</sup>	3x100x100 cm <sup>2</sup>
t	6 months	6x30x24 hrs

$$\text{CPR} = \frac{KW}{\rho X A X t}$$

$$\text{CPR} = \frac{87.6 \times 40 \times 1000 \text{mg}}{7.8 \text{ g/cm}^3 \times 3 \times 100 \times 100 \text{ cm}^2 \times 6 \times 30 \times 24}$$

$$\text{CPR} = 0.003466 \text{ mm/yr}$$

**To calculate CPR in mpy**

	Given	CPR in mpy
K		534
W	40g	40 x 1000 mg
$\rho$	7.8 g/cm <sup>3</sup>	7.8 g/cm <sup>3</sup>
A	1mx3m=3m <sup>2</sup>	3 x 1550 inch <sup>2</sup>
t	6 months	6 x 30 x 24 hrs

$$1 \text{ sq m} = 1550 \text{ sq inch}$$

$$\text{CPR} = \frac{KW}{\rho X A X t}$$

$$\text{CPR} = \frac{534 \times 40 \times 1000 \text{mg}}{7.8 \text{ g/cm}^3 \times 3 \times 1550 \text{ inch}^2 \times 6 \times 30 \times 24}$$

$$\text{CPR} = 0.1363 \text{ mpy}$$

2. A piece of corroded steel plate was found in a submerged ocean vessel, it was estimated that the original area was 10inch<sup>2</sup> and approximately 2.6 kg had corroded away during the submersion. Assuming a corrosionpenetration rate of 200mpy for this alloy in sea water, estimate the time in years, density of steel 7.9g/cc.

	Given	CPR in mpy
K		534
W	2.6kg	2.6 x 1000 x1000 mg
ρ	7.9 g/cm <sup>3</sup>	7.9 g/cm <sup>3</sup>
A	10 inch <sup>2</sup>	10 inch <sup>2</sup>
t	X	X hrs

CPR=
 $\frac{KW}{\rho XAXt}$

and

t=
 $\frac{KW}{\rho XAXcpr}$

$$t=\frac{534X2.6X10^6\;mg}{7.9g/cm^3X10in^2X200mpy}$$

$$t = 87873.41hrs$$

$t=\frac{87873.41}{365 * 4} = 10.03\;years$

## Module 2 (Unit II)

# METAL FINISHING

**Definition of metal finishing:** Metal finishing is the process of surface modification of a metal by deposition of a layer of metal or by converting the surface layer metal into its oxide film.

ELECTROPLATING and ELECTROLESS PLATING are two important techniques of metal finishing.

**Technological importance of metal finishing:** Metal finishing is carried out to obtain technologically important surface properties. These properties are:

1. A decorative appearance.
2. An improved corrosion resistance.
3. An improved heat resistance.
4. Improved surface hardness. (An improved resistance to wear and tear, Abrasion.)
5. Improved solder ability.
6. Good thermal conductivity, electrical conductivity.
7. Good optical reflectivity.

## ELECTROPLATING:

**Definition:** Electroplating is the process of electrolytic deposition of a metal on the surface of substrate; the substrate may be any metal, a polymer, a ceramic or a composite.

Or

Coating a layer of metal over the surface of material (metal, alloy, conducting polymer or any other conducting material) by applying an electric current is called as electroplating.

### **The main components of electroplating process are:**

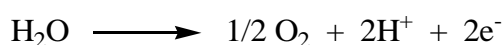
1. **Electroplating bath:** It contains a suitable salt solution of the metal being plated. It also contains other additives.
2. **Anode:** It may be a rod or pellets of the metal being plated. It may be an inert electrode. It should be electrically conducting.
3. **Cathode:** It is the article to be plated. It should have an electrically conducting surface.
4. **Inert vessel:** It may be a vessel made of rubber lined steel, plastic concrete or wood.
5. **D.C. power supply:** The positive terminal of the power supply is connected to the anode and the negative terminal is connected to the cathode.

### **Reactions at anode and cathode during electroplating:**

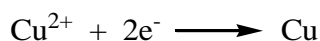
At anode oxidation takes place



When the anode used is an insoluble (inert) anode, oxygen evolution occurs at the anode:



At cathode, reduction occurs. The metal gets deposited on the cathode surface. For example:

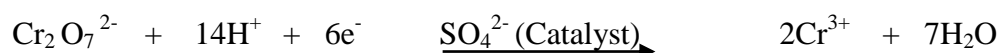


## ELECTROPLATING OF CHROMIUM

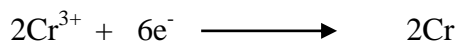
- The surface of the object is cleaned thoroughly. Oil and grease removed by organic solvent and then, treated with dilute  $\text{H}_2\text{SO}_4$  to remove oxide layer.
- Finally, the surface is washed with distilled water. Then, chromium plating is done under the following conditions.

	<b>Decorative Chromium Electroplating</b>	<b>Hard Chromium Electroplating</b>
<b>Plating bath composition</b>	Chromic acid ( $\text{H}_2\text{CrO}_4$ ) + $\text{H}_2\text{SO}_4$ in ratio 100 : 1	Chromic acid ( $\text{H}_2\text{CrO}_4$ ) + $\text{H}_2\text{SO}_4$ in ratio 100 : 1
<b>Operating temperature</b>	45-60 °C	45-60 °C
<b>Current density</b>	100 – 200 $\text{mA cm}^{-2}$	200-400 $\text{mA cm}^{-2}$
<b>Anode</b>	Insoluble anode: Pb-Sn alloy coated with $\text{PbO}_2$ .	Insoluble anode: Pb-Sn alloy coated with $\text{PbO}_2$
<b>Cathode</b>	Object to be plated	Object to be plated
<b>Anodic reaction</b>	Liberation of oxygen: $\text{H}_2\text{O} \longrightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$	Liberation of oxygen: $\text{H}_2\text{O} \longrightarrow \frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2\text{e}^-$
<b>Cathodic reaction</b>	$\text{Cr}^{3+} + 3\text{e}^- \longrightarrow \text{Cr}$	$\text{Cr}^{3+} + 3\text{e}^- \longrightarrow \text{Cr}$
<b>Applications</b>	1. Used in decorative coating in taps, handles, automobile bumpers, wheel rims 2. Used in corrosion resistant coating	1. Cutting edges of milling machine 2. Hand guns, aircraft landing parts.
<b>Thickness</b>	0.25- 0.75 micrometre	0.005-0.75 mm

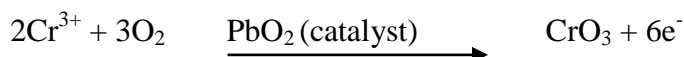
In chromic acid, chromium is present in 6+ oxidation state. It is first reduced to 3<sup>+</sup> state by a complex anodic reaction in the presence of sulphate ions.



The  $\text{Cr}^{3+}$  then gets reduced to Cr on the substrate surface.



For a good deposit, the  $\text{Cr}^{3+}$  concentration must be low. The  $\text{PbO}_2$  oxidizes  $\text{Cr}^{3+}$  to  $\text{Cr}^{6+}$ , thus reduce (control) the concentration of  $\text{Cr}^{3+}$ .

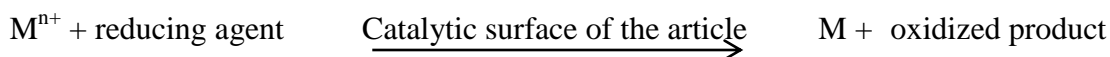


In chromium plating we do not use chromium metal as anode due to the following reasons.

- If chromium dissolves at anode, there will be a high concentration of  $\text{Cr}^{3+}$  in solution. In such cases, a black, (bad, burnt) deposit is obtained.
- In acidic solutions, chromium may undergo passivation.

## Electroless plating

“Controlled deposition of a layer of metal from its salt solution on a catalytically active surface of the material using a suitable reducing agent without using electrical energy” is called electroless plating.



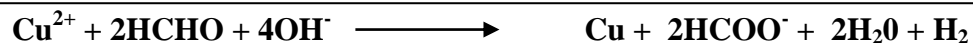
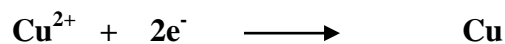
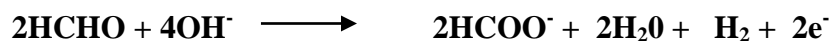
### Electroless plating of Copper:

#### **Pretreatment and activation of the surface:**

- ❖ Article to be plated is degreased by organic solvent and etched by dil.  $H_2SO_4$ .
- ❖ Metals like Fe, Co, Ni etc do not need further treatment.
- ❖ Non-metallic materials (e.g. glass, plastics, printed circuit boards, PCB) are activated by first dipping in  $SnCl_2$  and  $HCl$  solution, followed by dipping in  $PdCl_2$  solution and dried.

Plating bath solution	Copper sulphate
Reducing agent	Formaldehyde
Complexing agent	EDTA
Buffer	Sodium hydroxide and Rochelle salt
pH	11
Temperature	$25^{\circ}C$

#### Reactions:



**Applications:** Mainly used in printed circuit boards (PCB).

#### **Advantages of electroless plating:**

1. Electrical equipment is not required.
2. Semiconductors and insulators can also be plated.
3. Electroless plating baths have better throwing power.
4. Electroless coatings are harder than the electrodeposited coatings

#### **Distinction between electroplating and electroless plating:**

	<b>Electroplating</b>	<b>Electroless plating</b>
1	Requires electrical power source	Does not require electrical power source
2	Oxidation takes place at anode and reduction at cathode.	Both oxidation and reduction takes place at catalytically activated surface
3	Applicable only to conductors	Applicable for conductors, semiconductors and insulators
4	Not economical	Most economical
5	Give less uniform deposit on irregular shaped articles	Give more uniform coating on irregular shaped articles (due to better throwing power)
6	Holes cannot be plated	Holes can be plated
7	Does not require reducing agent	Requires reducing agent



## MODULE- 3

### Engineering Materials

**Polymers:** Introduction, Synthesis and applications of Polyurethanes. Polymer composites- Introduction, synthesis, properties & applications of Kevlar Fibre,

**Conducting Polymers:** Introduction, Synthesis & Mechanism of conduction in polyaniline and factors influencing conductivity of organic polymers.

**Biodegradable polymers:** Introduction and their requirements. Synthesis, properties and applications of Poly lactic acid.

**Nanomaterials:** Introduction, size dependent properties (Surface area, Electrical, Optical and Catalytic properties). Synthesis of nanomaterials: Top down and bottom up approaches, Synthesis by Sol-gel, and precipitation method, Nanoscale materials: Fullerenes, Carbon nanotubes and graphemes –Introduction, properties and applications.

## Engineering Materials

### Polymer:

A polymer is a compound of high molecular weight made by the combination of large number of small repeating chemical units called as monomers.

Example: Polypropylene, Polystyrene.

**Monomers:** These are simple molecules, which combine with each other to form polymers. Monomers are also called as building blocks of polymers.

**Polymerisation:** The process of linking up of monomers to form polymers with or without the elimination of by-products.

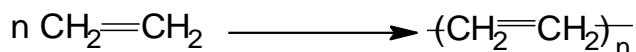
**Degree of polymerisation:** The total no. of monomers present in a single chain of polymer is called as degree of polymerisation. Where  $D_p = M_w/M_o$ .

### Types of polymerisation:

#### 1. Addition (chain-growth) Polymerisation:

The process in which a polymer is obtained from simple addition reaction of monomers without eliminating any simple molecule is called as addition polymerisation.

Example: polyethylene obtained by addition reaction of ethylene monomers.



#### 2. Condensation (step-growth) polymerisation:

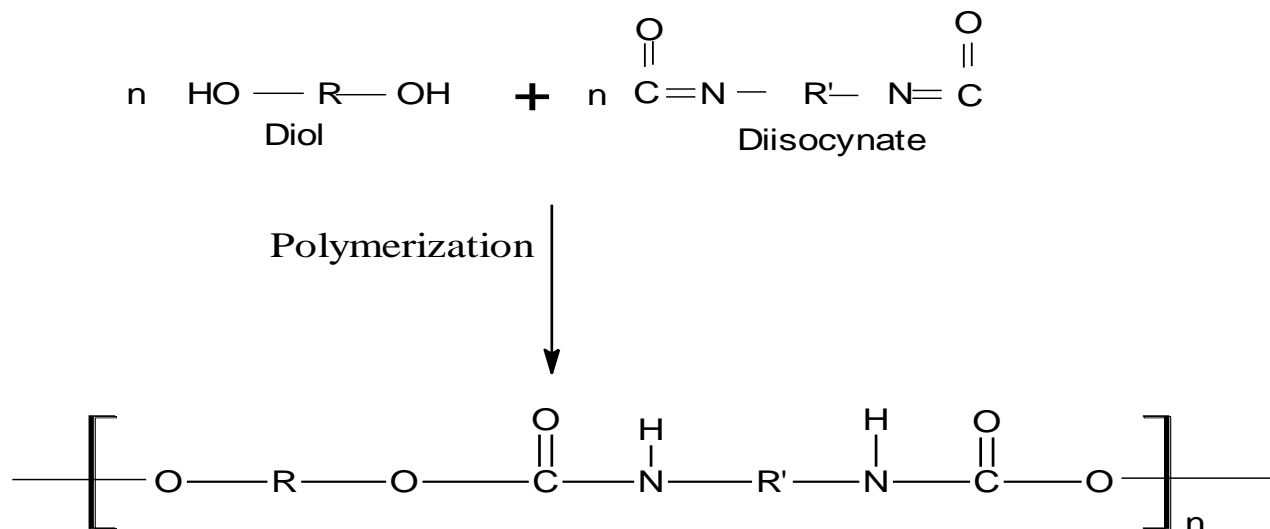
The process in which a polymer is obtained by condensation reaction of monomers with the elimination of small molecules like water,  $\text{CO}_2$  etc. Since the reaction occurs in steps and the polymer chain grows in each step it is called as step growth polymerisation.

Example: Nylon 6,6 is obtained by the condensation polymerisation of hexamethylenediamine and adipic acid.

## 1. POLYURETHANES:

### Synthesis:

**Polyurethanes** contains **–NHCOO–** group and are formed by the reaction between **di-isocyanate** and **diol**.



### Properties:

- Polyurethanes are highly flexible.
- High tensile strength.
- They are electrical insulator.
- Excellent resistance to abrasion and solvents.

**Applications:** Polyurethane is used

- As floor coating for gymnasium and dance floors.
- In lightweight garments and swim suits because of its stretching property.
- In making gaskets, seals, tyres and industrial wheels.
- As cushions in computer chairs, automobile seats and furniture.

### Polymer composites:

- A composite is a multiphase material made by the combination of two or more materials that exhibit specific properties. If any one of these material is polymer then it is known as polymer composite.
- Many composite materials made up of only two phases, matrix and dispersed phase (fiber in fiber composite).

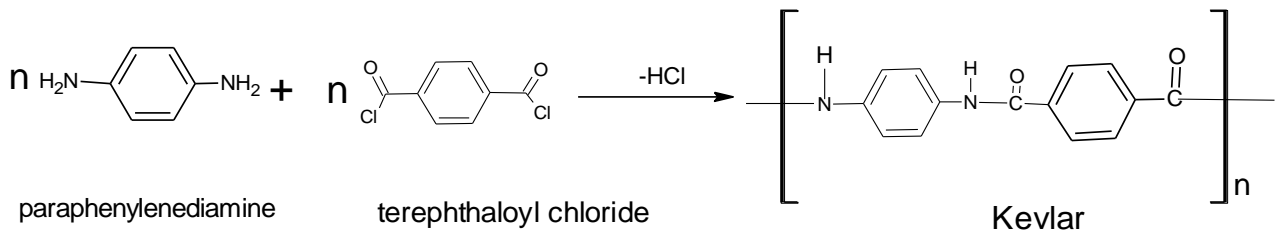
**Fiber Reinforced Composites:** These are the composite materials obtained by the combination of matrix and fiber.

Matrix is usually-polyester, polyurethane, epoxy resin.

Fibers are usually-thin glass sheet, Kevlar fibre

### KEVLAR FIBRE:

- ❖ It is an aromatic polyamide (-CONH<sub>2</sub> Group) with the name poly (para phenylene terephthamide).
- ❖ It is prepared by the condensation reaction of para-phenylenediamine and terephthaloyl chloride.



#### Properties:

1. It has very light weight.
2. It has high strength and stiffness.
3. It has very good abrasion and corrosion resistance.

#### Applications:

- ❖ Used in the aircraft panels and Race cars.
- ❖ Used in bullet proof vests.
- ❖ Used in puncture resistant bicycle tyres.

### Conducting polymers:

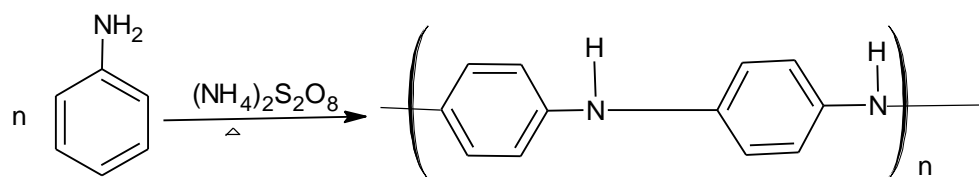
**Organic polymers having electrical conductivity in the order of a conductor are called as conducting polymers.** They are also called as synthetic metals. Conducting polymers are generally produced by doping an oxidizing or a reducing agent into an organic polymer with conjugated backbone consisting of pi-electron system.

Examples: Conjugated polymers such as polypyrrole, polythiophene, polyaniline,

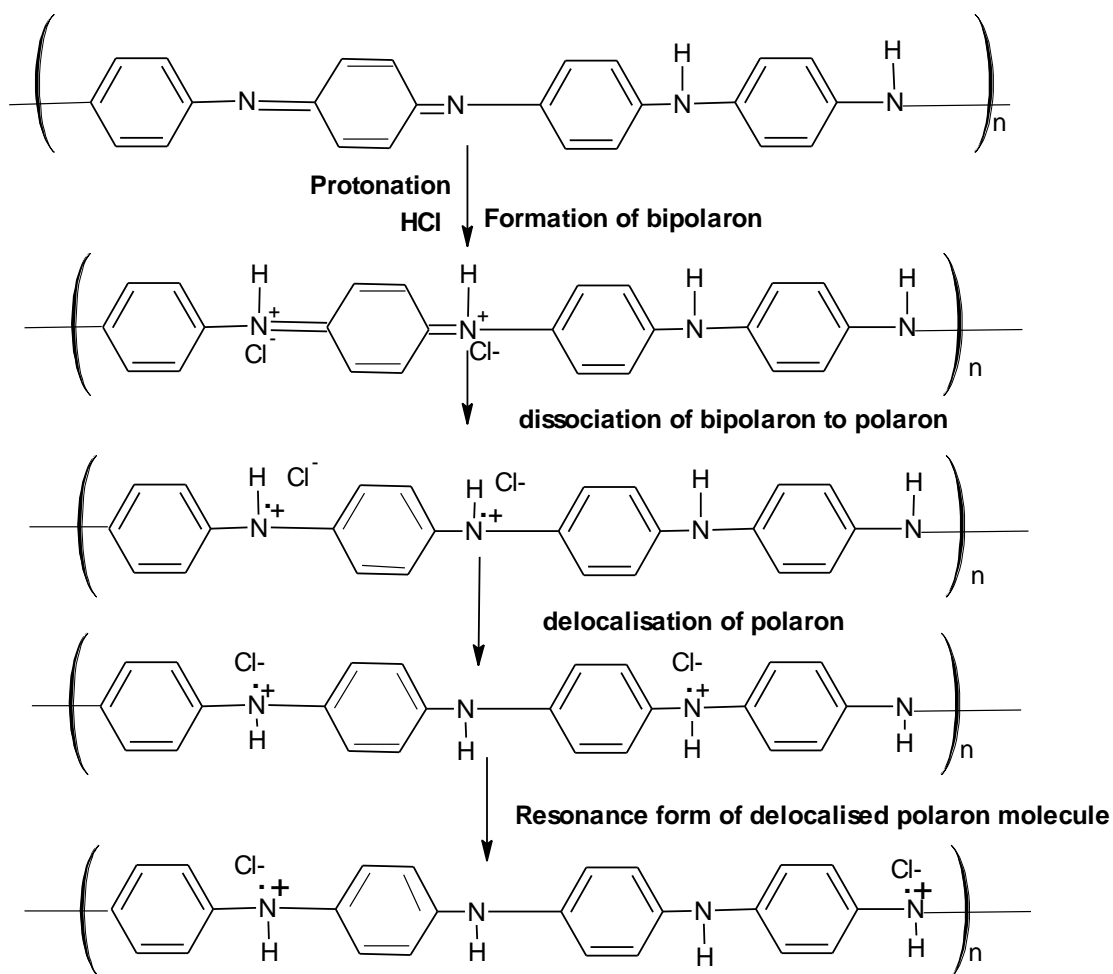
#### Mechanism of conduction in Polyaniline:

Polyaniline is obtained by the polymerisation of aniline dissolved in 1M HCl at 3-4<sup>0</sup>C in presence of ammonium persulphate as an initiator.

### General Reaction:



### Mechanism:



### Applications:

1. One of the important applications of conducting aniline is its use as an electrode material for **rechargeable batteries**.
2. Polyaniline has also attracted considerable attention as an electrochemical transducer for **biosensors** which are used in clinical technology.
3. Polyaniline shows **electrochromic properties** which can be used to produce **smart windows** that absorb sunlight and control solar energy.

### Factors influencing conductivity of Organic Polymer

- Density of charge carriers (number of charges per unit volume)

- Mobility of charge carriers.
- The polymer chain should contain conjugation(alternate sigma and double bond)
- Presence of aromatic rings in the chain with continuous resonance enhances conductivity.
- Polymer should have linear chains
- Reaction temperature
- Nature and concentration of the dopant.

## Biodegradable polymers

These are a special class of polymer that breaks down after its intended purpose by bacterial decomposition process to result in natural by-products such as gases (CO<sub>2</sub>, N<sub>2</sub>), water, biomass, and inorganic salts.

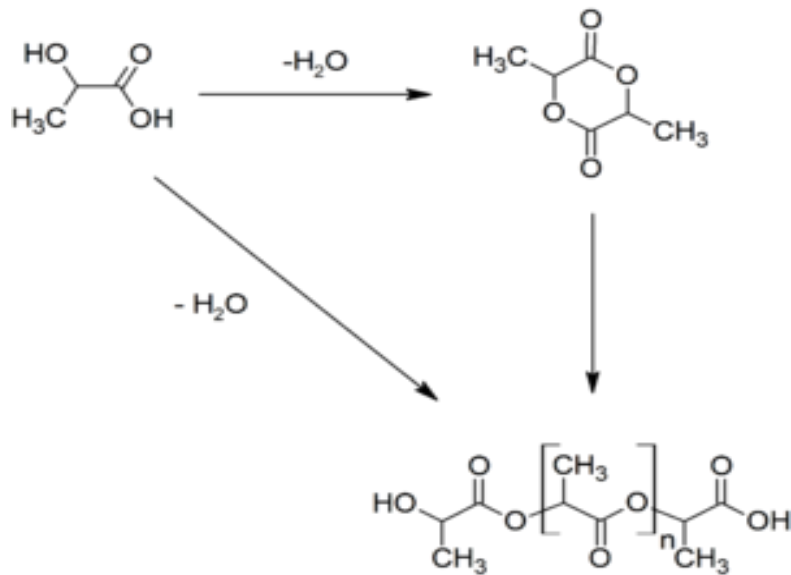
These polymers are found both naturally and synthetically made, and largely consist of ester, amide, and ether functional groups. Their properties and breakdown mechanism are determined by their exact structure. These polymers are often synthesized by condensation reactions, ring opening polymerization. There are vast examples and applications of biodegradable polymers.

Bio-based packaging materials have been introduced as a green alternative in the past decades, among which, **edible films** have gained more attention due to their environmentally-friendly characteristics, vast variety and availability, non-toxicity, and low cost.

### Polylactic acid

It also known as poly(lactic acid) or polylactide (abbreviation PLA) is a thermoplastic polyester with backbone formula  $(C_3H_4O_2)_n$ , formally, obtained by condensation of lactic acid  $C(CH_3)(OH)HCOOH$  with loss of water. It can also be prepared by ring-opening polymerization of lactide  $[C(CH_3)HC(=O)O-]_2$ , the cyclic dimer of the basic repeating unit.

PLA has become a popular material due to it being economically produced from renewable resources. But it's widespread application has been hindered by numerous physical and processing shortcomings. PLA is the most widely used plastic filament material in 3D printing.



### Properties

- PLA polymers range from amorphous glassy polymer to semi-crystalline and highly crystalline polymer
- Heat-resistant PLA can withstand temperatures of 110 °C.
- The high surface energy of PLA results in good printability, making it widely used in 3D printing
- PLA is soluble in a range of organic solvents

### Applications of bio degradable polymer(PLA)

Biodegradable polymers have been used with diverse applications such as:

- surgical sutures
- wound dressings
- tissue regeneration
- enzyme immobilization
- controlled drug delivery and gene delivery
- tissue engineering scaffold
- cryopreservation
- nanotechnology, medical implants and devices
- prosthetics

- augmentation
- cosmetics
- sanitation products
- coatings
- adhesives

## MODULE-4

**Green Chemistry:** Introduction, definition, Major environmental pollutants - Oxides Nitrogen, Sulphur and Carbon (Mention the impact of these pollutants on environment), Basic principles of green chemistry -brief discussion on 12 principles of green chemistry).

Various green chemical approaches – Microwave synthesis, Bio catalysed reaction (only explanation with examples), Solvent-free reactions- advantages and conditions. Synthesis of typical organic compounds by conventional and green route; i) Adipic acid – Conventional synthesis from Benzene, Green synthesis from glucose. ii) Paracetamol- Conventional and Green synthesis from Phenol Industrial applications of Green Chemistry

Green fuel: Hydrogen-production (Photo electrocatalytic and photo catalytic water splitting) and applications in hydrogen fuel cells. Construction, working and applications of Methanol-Oxygen fuel cell ( $\text{H}_2\text{SO}_4$  as electrolyte). Solar Energy: Introduction, construction, working and applications of photovoltaic cell.

### **Introduction**

Green chemistry, also called sustainable chemistry, an approach in chemistry that attempt to prevent or reduce pollution at its source by minimizing or eliminating the hazards of chemical feed stocks, reagents, solvents, and products. GC tries to improve the yield or efficiency of chemical products by modifying how chemicals are designed, manufactured and used.

**Definition:** GC is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use, and ultimate disposal. Green chemistry is also known as sustainable chemistry.

### **Environmental Pollutants:**

**AIR POLLUTANTS:** Substance present in the air (solid, liquid, or gaseous) in significant concentration to be injurious to living organisms or property or environment or intervene with the enjoyment of life.

Air pollutants are classified as: PRIMARY AIR POLLUTANTS

: SECONDARY AIR POLLUTANTS

**PRIMARY AIR POLLUTANTS:** Pollutants that are directly emitted into the atmosphere through natural or human activity.

**Important primary air pollutants are;**

1. Carbon monoxide
2. Oxides of nitrogen
3. Oxides of sulphur
4. Hydrocarbons
5. Particulate matter

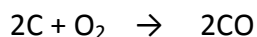


## **CARBON MONOXIDE: (CO)**

It is estimated that about 290 million tonnes of carbon monoxide is discharged into the atmosphere annually. It is **colourless, odourless, non-corrosive and toxic** in nature

### **Sources:**

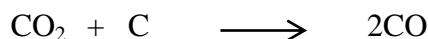
1. Carbon monoxide is released by the partial combustion of fuel in automobiles, industries & oil-refineries



2. Dissociation of CO<sub>2</sub> at very high temperature gives



3. Reaction between CO<sub>2</sub> and carbonaceous material at high temperature



### **III effects:**

1. When air contaminated with CO is inhaled, CO binds to haemoglobin to form carboxy-haemoglobin, which is about 300 times more stable than the oxygen-haemoglobin complex. This results in **headache, weak eyesight, nervousness & cardiovascular disorder**



2. High CO concentration can affect **leaf drop, leaf curling, reduction of leaf size & chlorophyll with premature aging.**

### **Control:**

1. CO can be controlled by passing flue gases through a catalytic converter containing Pt/Ru catalyst, which converts the toxic gas to non-toxic CO<sub>2</sub>
- $$2CO + O_2 \xrightarrow{Pt/Ru} 2CO_2$$
2. Modification of internal combustion engines
  3. Development of substitute fuels for gasoline which will yield low concentration of pollutants upon combustion.
  4. Development of pollution free power sources such as fuel cells to replace the internal combustion engine.

## **OXIDES OF NITROGEN (NO<sub>x</sub>): NO, NO<sub>2</sub>, & N<sub>2</sub>O are the common oxides of nitrogen**

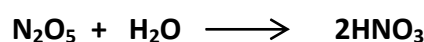
### **Sources:**

1. N<sub>2</sub> & O<sub>2</sub> are the main constituents of air these gases don't react with each other at a normal temperature, **when lightning strikes**, they combine to form oxides of nitrogen.
  2. When fossil fuel is burnt, nitrogen & oxygen combine to yield NO & NO<sub>2</sub>
- $$N_2(g) + O_2(g) \rightarrow 2NO(g)$$
- $$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$
3. Nitrogen fixation, bacterial decay of nitrogenous compounds leads to the release of oxides of

nitrogen in to the atmosphere.

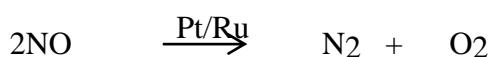
### III effect:

1. Higher levels of NO<sub>2</sub> can cause damage to the human respiratory tract, respiratory infections & Asthma.
2. It is unpleasant in odour and leads to irritation of eyes and even lung's congestion.
3. Long- term exposure to high levels of nitrogen di oxygen can cause chronic disease.
4. Formation of photochemical smog, which limits in visibility of road.
5. Causes acid rain – NO<sub>2</sub> reacts with H<sub>2</sub>O and O<sub>2</sub> to form HNO<sub>3</sub>. N<sub>2</sub>O<sub>5</sub> forms acid upon reaction with water



### Control:

1. **Oxides of nitrogen & carbon monoxide** can be controlled by passing these gases through a catalyst converter containing **Pt-Rh** catalyst ,which coverts these toxic gases to non-toxic nitrogen and carbon dioxide.



2. Treatment of flue gas by injecting into NH<sub>3</sub>, powdered limestone or aluminum dioxide.

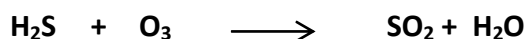
## OXIDES OF SULPHUR: (SO<sub>2</sub> and SO<sub>3</sub>)

### Source:

1. Oxides of sulphur are produced when sulphur containing fossil fuel is burnt.
2. Petroleum industries, oil refineries, sulphuric acid plants and nuclear power plants leads to sulphur dioxide and these further reacts with oxygen to give sulphur trioxide



3. Decay of animal or plants release H<sub>2</sub>S gas.
4. Thermal decomposition of H<sub>2</sub>S gas and atmospheric ozone.



5. Sulphide ore roasting plants leads to release of sulphur oxides.

### III effects:

1. Cardiac , respiratory and pulmonary disease
2. Eye irritation , throat troubles
3. Acid rain : SO<sub>3</sub> and SO<sub>2</sub> formed in atmosphere can combine with water vapour forming H<sub>2</sub>SO<sub>4</sub>

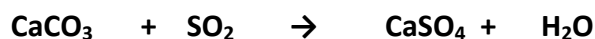
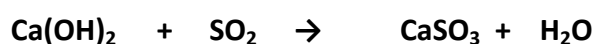


This causes Corrosion of metals, death of aquatic animals and effects the vegetation and fertility of the soil. It also reacts with marble leaving behind pitted and discolored surface.

4. Damages plant cells/membranes & chlorophyll metabolism; leading to reduction of growth.

#### Control:

1. Large amount of sulphur is removed by crushing & washing the coal before combustion.
2. Desulphurization method: The combustion of coal produces large amount of SO<sub>2</sub>, these flue gases are passed through slurry of lime or limestone. It converts SO<sub>2</sub> into CaSO<sub>3</sub>/CaSO<sub>4</sub>.



### Principles Of Green Chemistry:

1. **Prevent waste:** It is better to prevent waste than to treat or clean up waste after it has been created.
2. **Maximize atom economy:** Synthetic methods should be such that all the materials used in the process are converted into the final product.
3. **Design less hazardous chemical syntheses:** Synthetic methods should be designed to use and generate less toxic chemicals.
4. **Design safer chemicals and products:** Chemical products should be designed to affect their desired function while minimising their toxicity.
5. **Use safer solvents and reaction conditions:** The use of auxiliary substances (solvents, separation agents, etc,) should be made unnecessary whenever possible and innocuous when used.
6. **Increase energy efficiency:** Energy requirements should be recognized and synthetic methods should be conducted at ambient temperature and pressure.
7. **Use renewable feedstocks:** The raw material or feedstock should be renewable rather than depleting.
8. **Avoid chemical derivatives:** Unnecessary derivatization (blocking group/protection, and temporary modification of physical/chemical processes) should be avoided whenever possible.
9. **Use catalysts, not stoichiometric reagents:** Catalytic reagents are superior to stoichiometric reagents.
10. **Design chemicals and products to degrade after use:** At the end of their function chemical products should not persist in the environment and break down into harmless degradation products.
11. **Analyse in real time to prevent pollution:** Analytical methodologies for real-time, in-process monitoring should be developed to control and prevent formation of hazardous substances.
12. **Minimize the potential for accidents:** Substances used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

## Various Green Chemical Approaches:

### 1. Microwave synthesis

**Definition:** Microwave chemistry is the science of applying microwave radiation to chemical reactions. It involves selective absorption of electromagnetic waves by polar molecules or conducting ions in a solid.

Microwaves act as high frequency electric fields, and will heat up materials containing electric charges (such as polar molecules). Polar molecules (i.e. with permanent dipole moment) get heated up as their component molecules are forced to rotate as the field oscillates and lose energy in collisions. As microwaves are non-ionizing, they do not alter the molecular structure of the compounds being heated – it provides only thermal activation.

Conventional methods of organic synthesis usually need longer heating time, elaborate and tedious apparatus setup, resulting in higher cost of production. Excessive use of the solvents or reagents can also lead to environmental pollution.

#### Advantages of microwave synthesis over conventional methods

Microwave-assisted synthesis provides clean synthesis with the advantage of

- Uniform heating
- enhanced reaction rates,
- reduce reaction times,
- Higher yields,
- Purity in final product,
- Greater selectivity,
- Low operating cost: economic for the synthesis of a large number of organic molecules,
- Reduction in unwanted side reactions

#### Comparison of reaction times using microwave versus conventional heating

Compound synthesized	Reaction time	
:	Microwave	Conventional
Methyl benzoate	5 minutes	8 hours
4-nitrobenzyl ester	2 minutes	1.5 hours

### 2. Bio catalysed reactions: They involve metabolic transformation of chemicals to produce new product.

**Definition:** Biocatalysis is defined as the use of natural substances that include enzymes from biological sources or whole cells to speed up chemical reactions. Enzymes are very efficient biocatalysts. They are renewable, non-hazardous and are biodegradable.

Bio-catalysis avoids the use and contamination of products by metals such as palladium, platinum, and rhodium. Reactions are performed in an environmentally compatible solvent (water) at moderate

pH and temperature and thereby efficiency of the process is high and the environmental impact is reduced.

Examples for biocatalysis include

- Yeast-mediated transformations of sugars into alcohols, acids or gases.
  - Hydrolysis of starch into sugar by the enzyme amylase.
- 

### **Solvent Free Reactions (Dry Media Reaction)**

Solid state reaction follows the fifth principle of green chemistry which avoids using solvents and the chemical reactions mostly occur at room temperature which leads to energy efficiency.

**Definition: Solid-state reaction or solvent less reaction is a chemical reaction which takes place in the absence of a solvent.**

Large number of reactions occurs in solid state without solvent. Such reactions occur more efficiently and more selectively compared to reactions carried out in solvents.

A solvent-free or solid-state reaction may be carried out using the reactants alone or incorporating them in clays, zeolites, silica, alumina or other matrices (to achieve high degree of stereoselectivity in the products and to reduce by-products) and then heated by thermal process or irradiation with UV, microwave, ultrasonic or IR to bring about the reaction.

#### **Advantages:**

- Easy to handle,
- Reduce pollution,
- Comparatively cheaper to operate,
- Environmental friendly

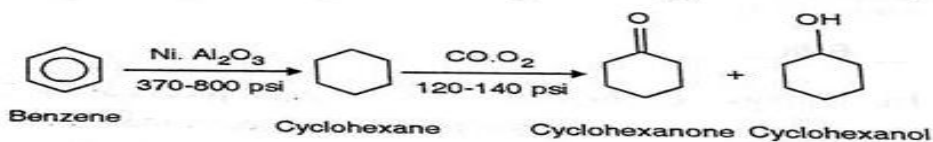
### **Adipic acid**

Adipic acid or hexanedioic acid is the organic compound with the formula  $(\text{CH}_2)_4(\text{COOH})_2$ . It is one of the most important dicarboxylic acid. About 60% of the adipic acid produced is used as monomer for the production of nylon.

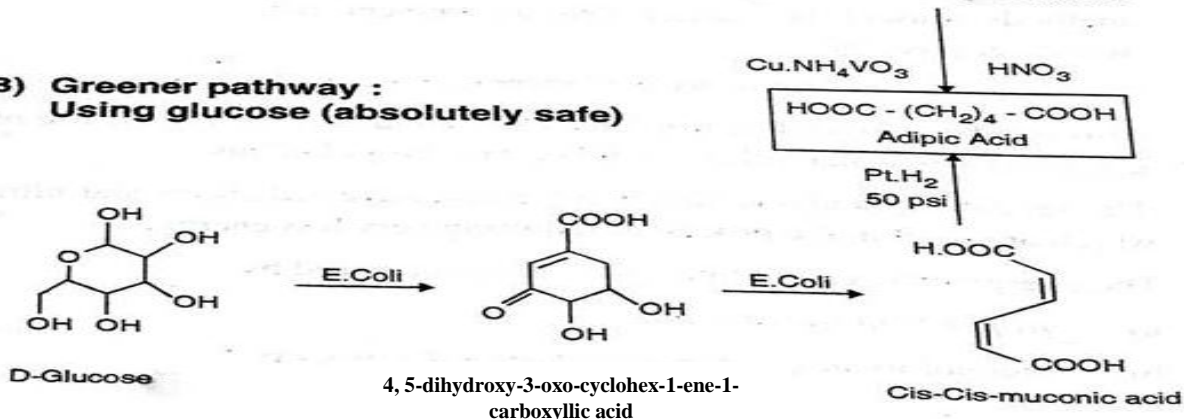
### **Conventional and Greener method for the synthesis of adipic acid**

**Synthesis of Adipic Acid:** New synthetic pathways have been reported for manufacture of adipic acid using glucose as starting material in place of traditionally used benzene. Traditional pathway requires high pressure and temperature greener pathway requires less temperature and pressure. The proposed green process is environmentally friendly and pure adipic acid is produced in high yield (70% to 79%).

**(A) Traditional pathway : Using Benzene (Carcinogenic solvent)**



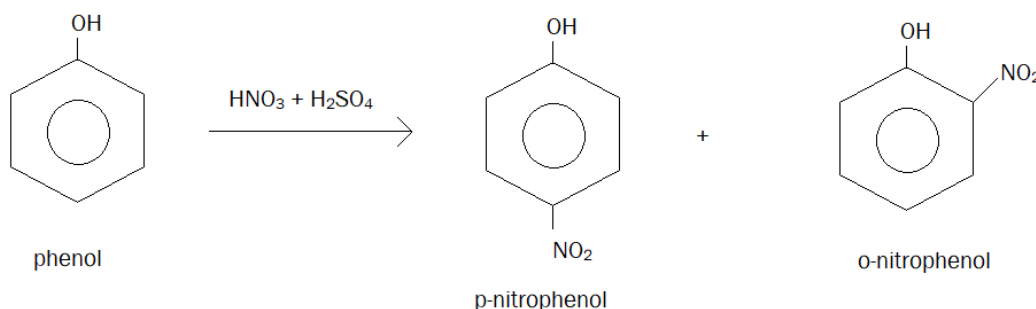
**(B) Greener pathway : Using glucose (absolutely safe)**



**Synthesis of Paracetamol (Acetaminophen)**

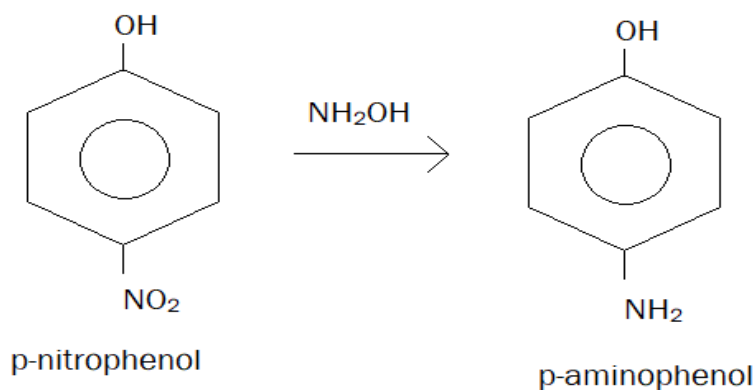
**Traditional method for the production of paracetamol:**

**Step 1:** Nitration reaction of phenol using nitrating mixture ( $\text{H}_2\text{SO}_4 + \text{HNO}_3$ ), to form p-nitrophenol and o-nitrophenol.

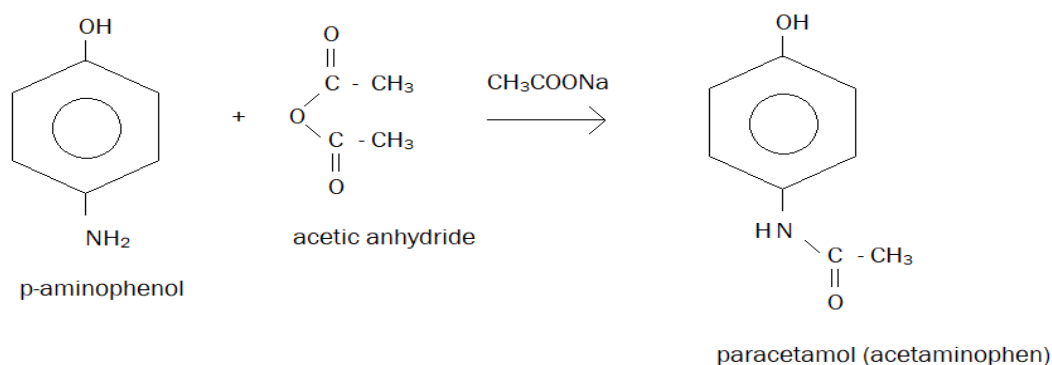


p-nitrophenol can be separated from o-nitrophenol by chromatographic methods and only p-nitrophenol is further used for the synthesis of paracetamol.

**Step 2:** p-nitrophenol is reduced to p-aminophenol using reducing agents such as hydroxylamine ( $\text{NH}_2\text{OH}$ )



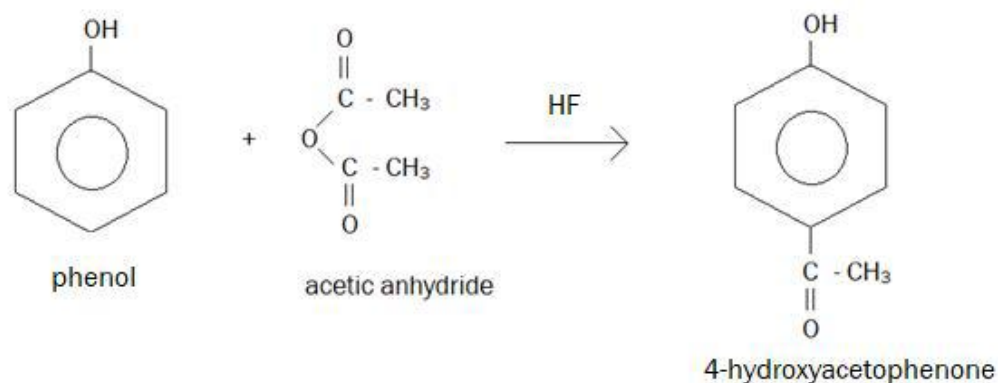
**Step 3:** Reaction of p-aminophenol with acetic anhydride in presence of sodium acetate ( $\text{CH}_3\text{COONa}$ ) results in the formation of paracetamol.



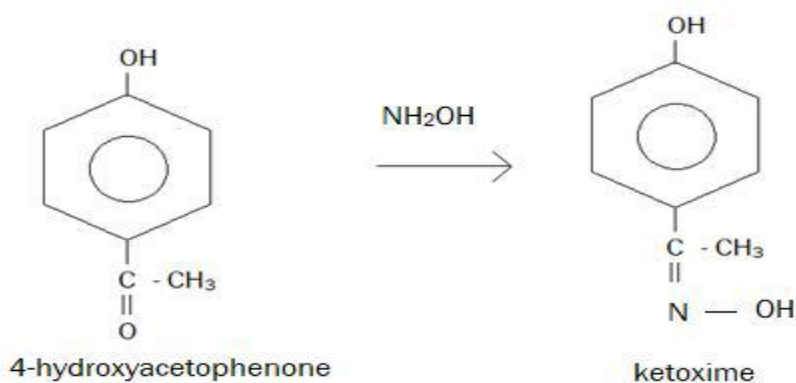
The % atom economy calculated for this synthesis is  $\approx 36\%$

### Green Synthesis of Paracetamol from Phenol

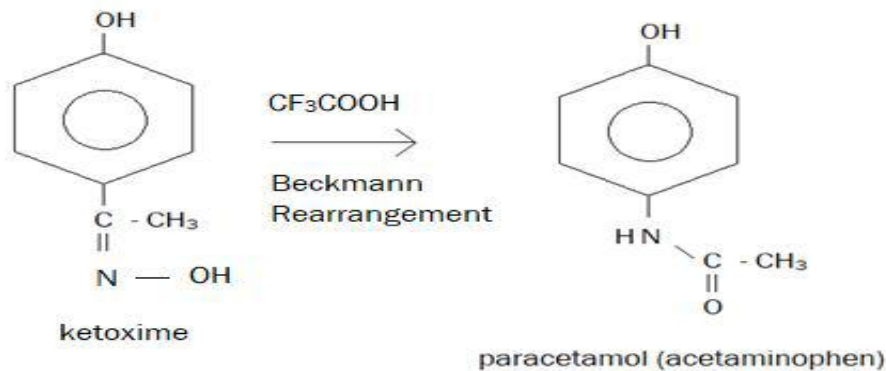
**Step 1:** Phenol reacts with acetic anhydride in the presence of strong acid like HF to undergo acylation reaction to produce 4-hydroxyacetophenone



**Step 2:** Reaction of aldehydes and ketones with hydroxylamine ( $\text{NH}_2\text{OH}$ ) gives oximes. 4-hydroxyacetophenone reacts with hydroxylamine to give corresponding ketoxime.



**Step 3:** Oximes in acidic medium (trifluoroacetic acid,  $\text{CF}_3\text{COOH}$ ) undergoes Beckmann rearrangement to produce substitute amides. Beckmann rearrangement of the above ketoxime gives paracetamol.



The % atom economy calculated for this green synthesis  $\approx 58\%$

## Green Chemistry Applications in Industries:

Chemical industry involves major chemicals, reagents, solvents, catalysts and almost all types of organic reactions for synthesis of active pharmaceutical substances. Therefore, many chemicals and chemical processes involved are hazardous, toxic and may show adverse effects on human health and environment.

The goal of green chemistry is to eliminate pollution at the source, to enhance efficiency, to save resources and energy, and to achieve sustainable development of chemistry and the chemical industry. Green technologies can be applied to pharmaceutical industry, polymer industry, food & flavour industry textile and tannery Industry and so on. Various applications include,

- Higher yields for chemical reactions, consuming smaller amounts of raw materials to obtain the same amount of product
- Fewer synthetic steps to allow faster manufacturing of products thereby increasing plant capacity, and saving energy and water
- Reduced waste, eliminating hazardous waste disposal, and end-of-the-pipe treatments
- Better performance so that less product is needed to achieve the same function
- Reduced use of petroleum products, slowing their depletion and avoiding their hazards and price fluctuations
- Increased consumer sales by earning and displaying a safer-product label.

## Green fuel

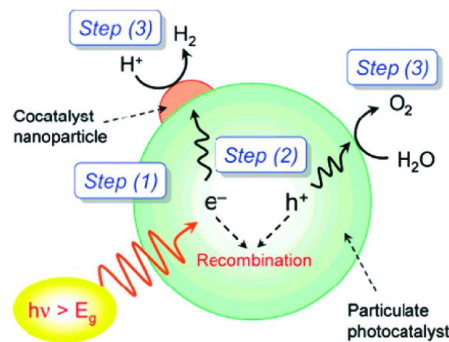
Hydrogen fuel production has gained increased attention as public understanding of global warming has grown. Methods such as **Photo catalytic water**, **Photo electro catalytic water splitting** are being investigated to **produce hydrogen**, a clean-burning fuel. Water splitting holds particular promise since it utilizes water, **an inexpensive renewable** resource.



## Photo catalytic water splitting

Splitting of water to get hydrogen by using a photo catalyst and by using solar energy is called **Photo catalytic water splitting**. This process can be more efficient if the photo catalyst is directly suspended in water. So that the reaction takes place in one step.

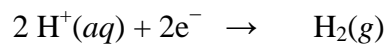
### Working of Photo catalytic water splitting



The light energy excite an electron( $e^-$ ) in the catalyst and results in the production of hole ( $h^+$ ).The produced hole ( $h^+$ ) will react with the neighbouring water molecule to form hydrogen ions ( $H^+$ ).



The  $H^+$  ions combine to produce hydrogen at the surface of co catalyst using the electrons.



The produced hydrogen can be used as fuel in  $H_2$  fuel cell. Photocatalyst and cocatalyst are directly kept in contact with water. There is a possibility of recombination of electron and hole resulting in decrease of efficiency. It is one of the drawbacks of Photo catalytic water splitting. But still it is used to produce hydrogen.

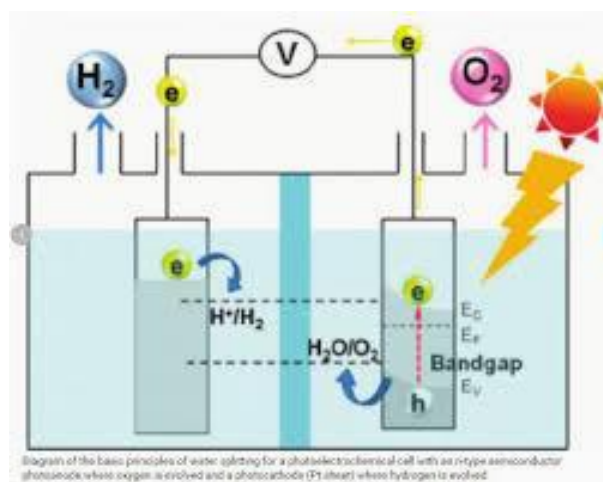
## **Photo electro catalytic water splitting**

Photo electro catalytic (PEC) water splitting is the artificial photosynthesis approaches for hydrogen fuel production. The reaction takes place at the electrode or electrolyte interface

### **It involves**

- Photo generated carriers on the surface( $e^-$  and  $h^+$ )
- Reactants adsorbed on the surface or in the electrolyte.

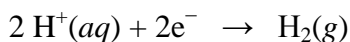
## Working of Photo electro catalytic water splitting



The light energy excites an electron ( $e^-$ ) from the semiconducting material (electrode). Thus produced hole ( $h^+$ ) will react with the neighbouring water molecule to produce hydrogen ions ( $H^+$ ).



The  $H^+$  ions formed will bond with each other and with two electrons ( $2e^-$ ) to form  $H_2(g)$ .



- Hydrogen will appear at the cathode, and oxygen will appear at the anode. Hydrogen gas released in this way can be used as hydrogen fuel, or remixed with the oxygen to create oxyhydrogen gas, which is used in welding and other applications.

### **Applications:**

#### **Hydrogen –Oxygen Fuel Cell ( $H_2$ - $O_2$ Fuel cell)**

##### **Construction:**

Anode & Cathode	– Made up of graphite impregnated with Pt/Ru electrocatalysts
Fuel	– Hydrogen
Oxidant	– $O_2$
Electrolyte	– KOH)
Separator	– Sulphonic acid polymer membrane.
Operating temperature	– $75^{\circ}C$
Uses	- space vehicles, submarines, automobiles, military power systems.

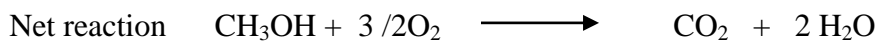
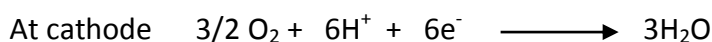
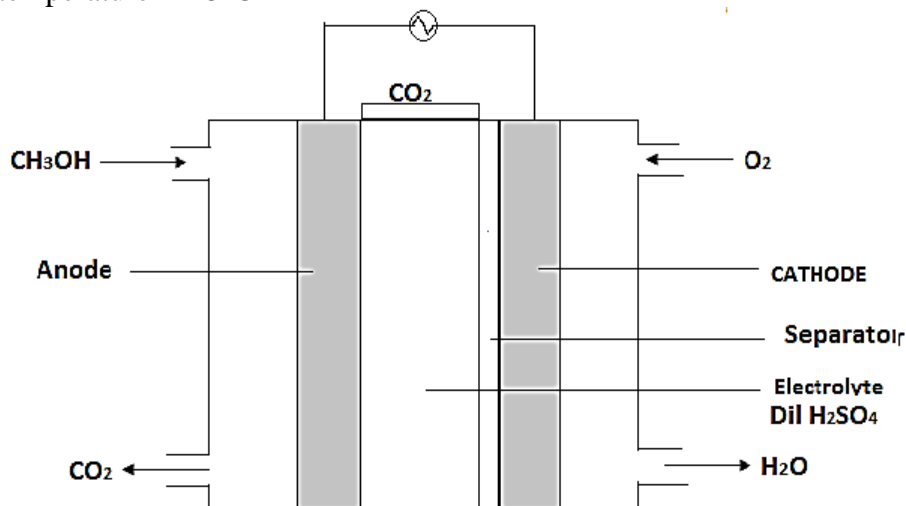
Hydrogen –Oxygen Fuel Cell is a simplest type of fuel cell in which hydrogen gas is used as a fuel and oxygen as oxidant. In this cell, both the electrodes are made up of porous graphite impregnated with an electrocatalyst. The electro-catalyst is an alloy of Pt- Ru-Co or Pt-Ru-Ni. The

electrolyte is an aqueous solution of KOH. The hydrogen gas fuel is continuously supplied at the anode and oxygen is supplied at the cathode. The overall cell reaction is electrochemical combustion of hydrogen producing water as the product. It is used in space vehicles, submarines, automobiles, military power systems.

## **Methanol – Oxygen fuel cell**

### **Construction:**

Anode & Cathode – Made up of porous nickel sheets impregnated with Pt/Ru electrocatalysts  
 Fuel – Methanol  
 Oxidant – O<sub>2</sub>  
 Electrolyte – Sulphuric acid(dilute)  
 Separator – Sulphonic acid polymer membrane.  
 Operating temperature – 25<sup>0</sup>C



A membrane is inserted adjacent to the cathode on the electrolyte side to minimize the diffusion of methanol into the cathode and thereby prevents the oxidation of methanol at cathode. Methanol – H<sub>2</sub>SO<sub>4</sub> mixture is circulated through the anode chamber. Pure oxygen is passed through the cathode chamber.

**The advantage of acid electrolyte is that the CO<sub>2</sub>, a product of the reaction, can be easily removed.**

**Uses:** It is used in large-scale power production.

Military applications.

# Solar Energy

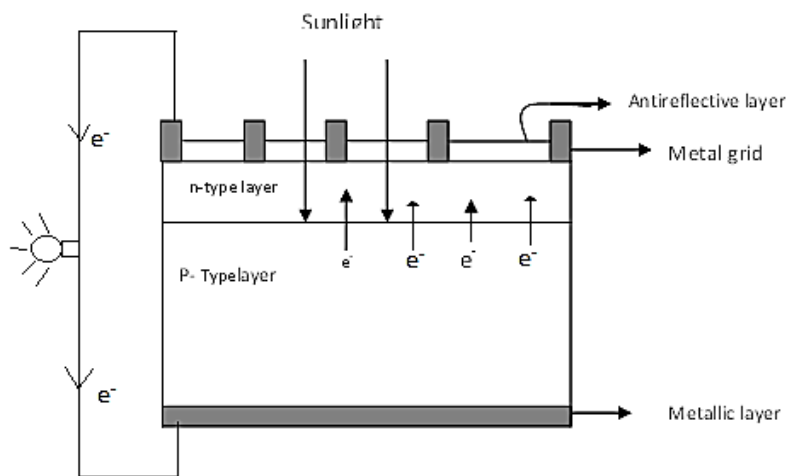
Solar power is the conversion of sunlight into electricity, either directly (example: PV cells, solar heaters), or indirectly (example: fossil fuel, ocean thermal energy)

## Photovoltaic Cells:

**Photovoltaic cells are semiconductor device which convert solar energy into electrical energy.**  
(Photovoltaic cell is based on the principle of photoelectric effect).

### Construction of Photovoltaic Cell:

- A typical silicon **PV cell** is composed of a n-type silicon on top of p-type silicon.
- Hence a p-n junction is formed between the two.
- A **metallic grid** forms one of the electrical contacts of the PV cell, over n-type semiconductor and coated with an **antireflective layer** ( $\text{TiO}_2$ ) between the grid lines increase the amount of light transmitted to the semiconductor (prevent reflection of solar radiation).
- The other electrical contact is formed by a **layer of noble metal** (like silver) on the back of p-type semiconductor



### Working of PV cell :

Electromagnetic radiation consists of particles called **photons**. The photons carry a certain amount of energy given by the Planck quantum equation,

Planck relation:

$$E = h\nu = \frac{hc}{\lambda}$$

where:

E = energy  
h = Plank constant  
 $\nu$  = frequency  
c = speed of light  
 $\lambda$  = wavelength

- When electromagnetic radiation (sunlight) is incident to the plane of solar cell, the photons are absorbed (which possess energy sufficient to overcome the barrier potential). That results in drifting of electrons. Thus electron-hole pairs are generated. The drifted electron will move from p- type semiconductor towards n-type through p-n junction to recombine with holes).
- Since p-n junction allows only one way movement of electrons, these electrons must flow through the external circuit to **recombine with holes**. This movement of electrons through the external circuit generates an electric current.

## Applications of Photovoltaic Cells

The photovoltaic systems can be used to supply electricity for:

- telecommunication repeater stations
- water pumps
- navigational aids
- laptop computers
- cottages and remote residences
- parks in remote regions
- supplying occasional power

### Advantages:

- Fuel source is vast and essentially infinite(renewable)
- No emissions, no combustion or radioactive residues for disposal.
- Environment friendly.
- Low operating cost (no fuel).
- No moving parts and so no wear and tear.
- They do not corrode
- They operate at ambient temperature.
- Can be integrated into new or existing building structures.
- High public acceptance and excellent record.

**Disadvantages:**

- High installation cost.
- It works only in presence of sunlight.
- 
- Efficiency of solar cells depends on the seasonal variations, latitude and climate.
- Space required to generate unit power output is relatively more.
- Poor reliability of auxiliary elements including storage.
- Dust often accumulates on the panel thus reducing its efficiency.

## **MODULE – 5**

### **Water Chemistry, chemical analysis and Instrumental methods of analysis**

#### **Water chemistry:**

Introduction, sources and impurities in water, Potable water; meaning and specifications (as per WHO standards), Hardness of water, types, determination of hardness using EDTA titration, numerical problems on hardness of water. Definition of Biological oxygen demand (BOD) and Chemical Oxygen Demand (COD), determination of COD of waste water sample and Numerical problems on COD.

#### **Methods of Chemical Analysis:**

Volumetric Analysis: Introduction, principles of titrimetric analysis, requirement of titrimetric analysis, primary and secondary standards. Requirement of a primary standard solution, units of standard solutions- Definition of normality, molarity, molality, mole fraction, ppm.

#### **Instrumental methods of analysis:**

Introduction, Theory, Instrumentation and applications of Colorimetry, Flame Photometry, Potentiometry, Conductometry (Strong acid with strong base, weak acid with a strong base, mixture of strong acid and a weak acid with a strong base)

## **WATER CHEMISTRY**

Water is nature's most wonderful, abundant and useful compound. Water is not only essential for the lives of animals and plants but also occupies a unique position in industries.

**Sources of Water:** The sources of water classified as:

**Rain water:** Purest form of water is rain water. It may contain many impurities like dissolved gases and suspended solid (particulates) during downstream.

**River water:** Contains dissolved minerals of soil such as chlorides, sulphates, bicarbonates of sodium, calcium, Mg, Fe etc. It is also contains the organic matter, small particles of soil and sand in suspension.

**Lake water:** It contains less dissolved minerals but high quantity of organic matters.

**Sea water:** It is the most impure form of natural water. It contains dissolved salts such as NaCl, sulphates of sodium, bicarbonates of K, Mg & Ca, and bromides of K & Mg.

**Underground water:** Clear in appearance but contains many dissolved salts and organic matter.

### **Types of impurities in water:**

**Dissolved gasses:** The water mainly contains carbon dioxide and oxygen. If water contains ammonia, hydrogen sulphides and oxides of sulphur it gives bad smell and taste to water. Dissolved gases can be removed by degasification.

**Dissolved mineral salts:** These are the soluble impurities in water which includes carbonates, bicarbonates, chlorides and sulphides of calcium and magnesium. Oxides of iron, lead etc.

**Suspended impurities:** These are insoluble impurities, which can be removed by filtration or settling.

There are of two types:

Clay, silica, oxides of iron are inorganic impurities.

Wood and disintegrated part of dead animals are organic impurities.

Organic matter: It includes vegetable and animal matters i.e., decayed plants and animals.

**Biological impurities:** These consist mainly bacteria and other microorganisms (algae and fungi) which are responsible for water borne diseases. These can be removed by chlorination.

**Colloidal impurities:** They consist of proteins, amino acids, ferric hydroxides, clay etc. They are removed by adding coagulants followed by filtration.

### **Potable water**

Potable comes from the Latin word **potare**, meaning "**to drink**". It comes from natural sources and is treated for microorganisms, bacteria, toxic chemicals, viruses and faecal matter.

Potable water is defined as **water that is suitable for human consumption** (i.e., water that can be used for drinking or cooking). Water can be made potable by boiling. Boiling is the surest method to kill disease-causing organisms, including viruses, bacteria, and parasites.

The permissible limits of impurities for domestic water as prescribed by the World Health Organisation (WHO) are given in the following table:

Parameters	WHO Standard
pH	6.5-9.2
BOD	6 mg/L
COD	10 mg/L
TSS	5 mg/L
TDS	500 mg/L
Sulphate	200 mg/L
Chloride	500 mg/L
Nitrate	45 mg/L
Lead	0.01 mg/L
Total hardness	600 mg/L

### **Hardness of water**

Hardness is caused by the divalent metal ions of calcium and magnesium. It arises largely due to contact of water with soil and limestone.

- Hard water is unsuitable for washing purposes as it consumes large quantity of soap.
- It produces scales in hot-water pipes, heaters and boilers. The scales result in an increase in consumption of fuel and decrease in the life of boiler.

There are mainly two types of hardness.

1. **Temporary hardness (carbonate hardness)**
2. **Permanent hardness**



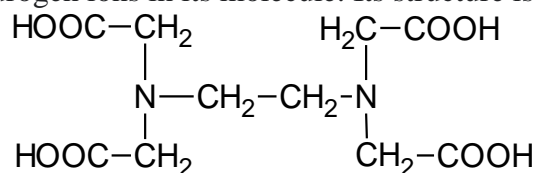
**Temporary hardness** is due to the presence of bicarbonates and carbonates of calcium and magnesium and can be removed by physical treatment such as boiling.

**Permanent hardness** is due to the presence of chlorides and sulphates of calcium and magnesium. It can be removed by chemical treatment.

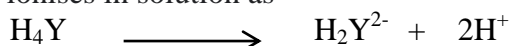
Hardness of water sample can be determined by using standard EDTA solution and it is expressed in parts per million (ppm) of  $\text{CaCO}_3$ .

#### Determination of hardness using EDTA

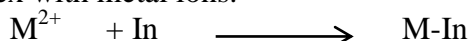
**EDTA** is a hexadentate ligand and forms complexes with  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions. It is commonly represented as  $\text{H}_4\text{Y}$ , has two replaceable hydrogen ions in its molecule. Its structure is,



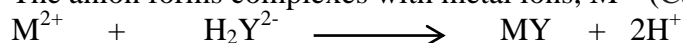
EDTA ionises in solution as



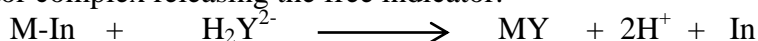
Total hardness is determined by titrating a known volume of water sample against standard EDTA solution at pH10 using Eriochrome Black- T indicator. Eriochrome Black –T indicator forms a wine-red complex with metal ions.



The anion forms complexes with metal ions,  $\text{M}^{2+}$  ( $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ )



On adding EDTA, it forms a complex first with free metal ions and near the equivalence point with metal-indicator complex releasing the free indicator.



The color of the free indicator is blue. Hence, a colour change from wine red to blue is seen at the equivalence point. Since  $\text{H}^+$  ions are released buffer ( $\text{NH}_3\text{-NH}_4\text{Cl}$ ) is used to maintain pH of 10.

To determine the temporary hardness, another portion of the same water sample is boiled whereby the soluble bicarbonates are converted to insoluble carbonates. The precipitate of calcium carbonate is allowed to settle and then filtered. The filtrate is titrated against EDTA which gives the permanent hardness. The difference between the total hardness and the permanent hardness gives the temporary hardness.

#### **Numericals:**

100ml of a sample of water required 18ml of 0.01M EDTA for titration using Eriochrome black-T indicator. In another experiment, 100ml of the same sample of water was gently boiled and the precipitate was removed by filtration. The filtrate required 9.0ml of 0.01M EDTA using Eriochrome black-T indicator. Calculate (i) the total hardness and (ii) carbonate hardness.

(i) *Total hardness*

$$\begin{aligned} 1000\text{ml of 1M EDTA} &= 100\text{g of CaCO}_3 \\ 1\text{ml of 1M EDTA} &= \frac{100}{1000} \text{ g of CaCO}_3 \\ 18\text{ml of 0.01M EDTA} &= \frac{100 \times 18 \times 0.01}{1000} \text{ g of CaCO}_3 \\ &= 0.018\text{g of CaCO}_3 \\ 100\text{ml of the water sample contains } &0.018\text{g of CaCO}_3 \\ 10^6 \text{ ml of the water sample contains } &180\text{ppm of CaCO}_3 \end{aligned}$$

**Total hardness of the water sample = 180ppm of  $\text{CaCO}_3$**

(ii) *Permanent hardness*

$$1000\text{ml of 1M EDTA} = 100\text{g of CaCO}_3$$

$$\begin{aligned}
 1\text{ml of } 1\text{M EDTA} &= \frac{100}{1000} \text{ g of CaCO}_3 \\
 9.0\text{ml of } 0.01\text{M EDTA} &= \frac{100 \times 9 \times 0.01}{1000} \text{ g of CaCO}_3 \\
 &= 0.009\text{g of CaCO}_3 \\
 100\text{ml of the water sample contains } &0.009\text{g of CaCO}_3 \\
 10^6 \text{ ml of the water sample contains } &= 0.009 \times 10^6 \text{ ppm of CaCO}_3 \\
 &= 90\text{ppm of CaCO}_3
 \end{aligned}$$

**Permanent hardness of the water sample = 90 ppm of CaCO<sub>3</sub>**

(iii) *Carbonate hardness*

**Carbonate hardness = 180-90 = 90ppm of CaCO<sub>3</sub>**

2. 50ml of a sample of water required 8.5ml of 0.01M EDTA for titration using Eriochrome black-T indicator. In another experiment, 50ml of the same sample of water was gently boiled and the precipitate was removed by filtration. The filtrate required 7.0ml of 0.01M EDTA using Eriochrome black-T indicator. Calculate (i) the total hardness and (ii) carbonate hardness.

(i) *Total hardness*

$$\begin{aligned}
 1000\text{ml of } 1\text{M EDTA} &= 100\text{g of CaCO}_3 \\
 1\text{ml of } 1\text{M EDTA} &= \frac{100}{1000} \text{ g of CaCO}_3 \\
 8.5\text{ml of } 0.01\text{M EDTA} &= \frac{100 \times 8.5 \times 0.01}{1000} \text{ g of CaCO}_3 \\
 &= 0.0085\text{g of CaCO}_3 \\
 50\text{ml of the water sample contains } &0.0085\text{g of CaCO}_3 \\
 10^6 \text{ ml of the water sample contains } &\frac{0.0085 \times 10^6}{50} \text{ ppm of CaCO}_3
 \end{aligned}$$

**Total hardness of the water sample = 170ppm of CaCO<sub>3</sub>**

(ii) *Permanent hardness*

$$\begin{aligned}
 1000\text{ml of } 1\text{M EDTA} &= 100\text{g of CaCO}_3 \\
 1\text{ml of } 1\text{M EDTA} &= \frac{100}{1000} \text{ g of CaCO}_3 \\
 7.0\text{ml of } 0.01\text{M EDTA} &= \frac{100 \times 7 \times 0.01}{1000} \text{ g of CaCO}_3 \\
 &= 0.007\text{g of CaCO}_3 \\
 50\text{ml of the water sample contains } &0.007\text{g of CaCO}_3 \\
 10^6 \text{ ml of the water sample contains } &= \frac{0.007 \times 10^6}{50} \text{ ppm of CaCO}_3 \\
 &= 140\text{ppm of CaCO}_3
 \end{aligned}$$

**Permanent hardness of the water sample = 140 ppm of CaCO<sub>3</sub>**

(i) *Carbonate hardness*

**Carbonate hardness = 170-140 = 30ppm of CaCO<sub>3</sub>**

## **BIOLOGICAL OXYGEN DEMAND:**

The amount of oxygen required for the oxidation of biologically oxidizable compounds (impurities) present in 1 litre of waste water over a period of five days at 20°C

- Dissolved oxygen in water is determined by Winklers method.
- DO<sub>1</sub> is the Dissolved Oxygen of the sample in mg/ml at the start of the experiment (1<sup>st</sup> day)
- DO<sub>2</sub> is the Dissolved Oxygen of the sample in mg/ml after 5 days.

$$\text{BOD} = [\text{DO}_1 - \text{DO}_2] \text{ mg of oxygen/liter}$$

## **CHEMICAL OXYGEN DEMAND:**

*It is the amount of oxygen in milligrams required to oxidize organic and inorganic compounds (impurities) present in 1 litre of waste water using a strong oxidizing agent like  $\text{K}_2\text{Cr}_2\text{O}_7$ .*

### **Procedure:**

- A known volume waste water (V ml), 1g mercuric sulphate and 1g silver sulphate are added to 250 ml conical flask, followed by the addition of a known amount potassium dichromate and sulphuric acid.
- The above mixture is refluxed for two hours and cooled.
- Titrate the mixture against standard FAS solution, till the colour changes from green to brown using Ferroin as an indicator.

**Blank:** The same procedure is repeated for Vml of distilled water

### **Observation and calculations:**

Normality of FAS solution =  $N_{\text{FAS}}$

Volume of FAS solution consumed for back titration = y ml  
Volume of FAS consumed for blank titration = x ml

1 ml of 1N FAS solution = 8 mg of oxygen

(x-y) ml of  $N_{\text{FAS}}$  solution =  $8 \cdot N_{\text{FAS}} \cdot (x-y)$  mg of oxygen

i.e., V ml of waste water sample =  $8 \cdot N_{\text{FAS}} \cdot (x-y)$  mg of oxygen

1000 ml of the waste water sample =  $\frac{8 \cdot N_{\text{FAS}} \cdot (x-y) \times 1000}{\text{Volume of water sample taken}}$  mg of oxygen

$$\text{COD of the waste water sample} = \frac{8 \cdot N_{\text{FAS}} \cdot (x-y) \times 1000}{\text{Volume of water sample taken}} \text{ mg of oxygen/litre}$$

(Volume of water sample taken can be 20, 25, 30 ml....)

**1) Define COD. Calculate COD of 25cc of effluent sample which requires 8.3cc of 0.001M  $K_2Cr_2O_7$  for its complete oxidation?**

Solution:  $N \times \text{Eq Wt} = M \times \text{Mol.wt}$

$$N_{K_2Cr_2O_7} = \frac{\text{molarity} \times \text{molecular weight}}{\text{Equivalent weight}} = \frac{0.001 \times 294}{49} = 0.006 N_{K_2Cr_2O_7}$$

$$1\text{ml } 1N \text{ FAS} = 1\text{ml } 1N \text{ } K_2Cr_2O_7$$

$$\text{COD} = \frac{8 \times N_{\text{FAS}} \times (x-y) \times 1000}{V}$$

$$= \frac{8 \times 8.3 \times 0.006 \times 1000}{25}$$

$$= 15.9 \text{ mg of } O_2/\text{ltr}$$

**2)  $20\text{cm}^3$  of sewage sample consumes  $30\text{cm}^3$  of 0.01N  $K_2Cr_2O_7$  for oxidation of impurities. Calculate the COD of the sample.**

Solution:  $1\text{ml } 1N \text{ FAS} = 1\text{ml } 1N \text{ } K_2Cr_2O_7$

$$\text{COD} = \frac{8 \times N_{\text{FAS}} \times (x-y) \times 1000}{V}$$

$$= \frac{8 \times 0.01 \times 30 \times 100}{20}$$

$$= 120 \text{ mg of oxygen/litre}$$

**3) 30cc of waste water was mixed with 25cc of  $K_2Cr_2O_7$ , acidified and refluxed. The unreacted  $K_2Cr_2O_7$  required 8.2cc of 0.2N FAS. In a blank titration 25cc of  $K_2Cr_2O_7$  acidified required 15.4cc of same FAS. Calculate COD of waste water sample.**

$$\text{COD} = \frac{8 \times N_{\text{FAS}} \times (X-Y) \times 1000}{V}$$

$$= \frac{8 \times 0.2 \times (15.4 - 8.2) \times 1000}{30}$$

$$= 384 \text{ mg of oxygen/litre}$$

**4) Define COD. Calculate COD of effluent sample when  $25\text{cm}^3$  of the effluent sample requires  $8.5\text{cm}^3$  of 0.001N  $K_2Cr_2O_7$  for complete oxidation.**

Solution:  $1\text{ml } 1N \text{ FAS} = 1\text{ml } 1N \text{ } K_2Cr_2O_7$

$$\begin{aligned}
 \text{COD} &= \frac{8 \times N_{\text{FAS}} \times (x-y) \times 1000}{V} \\
 &= \frac{8 \times 0.001 \times 8.5 \times 1000}{25} \\
 &= 2.72 \text{ mg of oxygen/litre}
 \end{aligned}$$

**5) Calculate COD of effluent sample when 25ml of effluent requires of 8.9 ml of 0.002M  $\text{K}_2\text{Cr}_2\text{O}_7$  for complete oxidation.**

Solution:  $N \times \text{Eq Wt} = M \times \text{Mol. Wt}$

$$\begin{aligned}
 N_{\text{K}_2\text{Cr}_2\text{O}_7} &= \frac{\text{molarity} \times \text{molecular weight}}{\text{Equivalent weight}} \\
 &= \frac{0.002 \times 294}{49} \\
 &= 0.012 N_{\text{K}_2\text{Cr}_2\text{O}_7}
 \end{aligned}$$

1ml 1N FAS = 1ml 1N  $\text{K}_2\text{Cr}_2\text{O}_7$

$$\begin{aligned}
 \text{COD} &= \frac{8 \times N_{\text{FAS}} \times (x-y) \times 1000}{V} \\
 &= \frac{8 \times 0.012 \times 8.9 \times 1000}{25} \\
 &= 34.176 \text{ mg of oxygen/litre}
 \end{aligned}$$

**6) In a COD experiment 28.1ml and 14ml of 0.05M FAS solution were required for blank and sample titration respectively. The volume of test sample used was 25ml. Calculate the COD of the sample.**

$$N_{\text{FAS}} = M_{\text{FAS}}$$

$$\begin{aligned}
 \text{COD} &= \frac{8 \times N_{\text{FAS}} \times (X-Y) \times 1000}{V} \\
 &= \frac{8 \times 0.05 \times (28.1-14) \times 1000}{25} \\
 &= 225.6 \text{ mg of oxygen/liter}
 \end{aligned}$$

**7) 20ml of sample of COD analysis was reacted with 10ml of 0.25N  $\text{K}_2\text{Cr}_2\text{O}_7$  and the unreacted dichromate required 6.5ml of 0.10N Ferrous ammonium sulphate. 10ml of same  $\text{K}_2\text{Cr}_2\text{O}_7$  and 20ml of distilled water under the same conditions as the sample required 26.0ml of 0.10N FAS. What is the COD of the sample?**

$$\begin{aligned}
 \text{COD} &= \frac{8 \times N_{\text{FAS}} \times (x-y) \times 1000}{V} \\
 &= \frac{8 \times 0.1 \times (26-6.5) \times 1000}{20} \\
 &= 780 \text{ mg of oxygen/litre}
 \end{aligned}$$

## **Volumetric analysis**

- It is a quantitative analytical method which is widely used.
- It involves measurement of the volume of a solution whose concentration is known and can be used to determine the concentration of the analyte.
- Another name for volumetric analysis is titrimetric analysis

### **Principles of Titrimetric Analysis**

- Reagent called titrant or standard solution is added by means of a burette to the sample to be analysed called the titrand (analyte).
- Indicator is added to the analyte at the beginning of the titration.
- Towards the endpoint of the titration colour of the indicator changes.

### **Requirements of titrimetric analysis**

- A device to measure the mass or volume of sample (e.g., pipette, graduated cylinder, volumetric flask, analytical balance etc).
- A device to measure the volume of the titrant added (i.e., burette).
- The titrant should be a standard solution (known concentration) which reacts with the analyte.
- The reaction should proceed to a stable and well defined equivalence point.
- The titrant's and sample's volume must be accurately known.
- The reaction must proceed with a definite chemistry without any complicating side reactions.
- The reaction should be nearly complete at the equivalence point.
- The reaction rate should be fast enough to be practical.
- An indicator by which the endpoint can be determined.

### **Primary and Secondary Standards**

A primary standard is a chemical or reagent used to prepare standard solutions. e.g.  $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$  etc. It has certain properties such as

- (a) It is extremely pure,
- (b) Highly stable
- (c) It is anhydrous
- (d) It is less hygroscopic
- (e) Has very high molecular weight
- (f) Can be weighed easily
- (g) Should be ready to use and available
- (h) Should be preferably non toxic
- (i) Should not be expensive

## **Requirements of a primary standard solution**

- Have long term stability in solvent.
- React rapidly with the analyte.
- React completely with analyte.
- Be selective to the analyte.

## **Secondary Standards**

Secondary standards are used in the laboratory for specific analysis and their concentration varies with time. When kept open, they easily react with the components of air ( $O_2$ ,  $CO_2$  etc.), e.g.  $HCl$ ,  $H_2SO_4$ ,  $NaOH$ ,  $KOH$ ,  $KMnO_4$ , etc. They are generally standardized against a primary standard.

- Secondary standard solutions are not very pure.
- Secondary standards are reactive than primary standards.
- Secondary standards are somewhat hygroscopic.
- Secondary standard solutions are used for specific analytical experiments.

## **Units of standard solutions:**

- Normality
- Molarity
- Molality
- Mole-fraction
- Ppm

**Solution:** is a homogeneous mixture of solute and solvent whose proportion varies within certain limits.

**Solute:** is the substance present in smaller quantities in a solution.

**Solvent:** is the substance present in larger quantities in a solution.

## **Normality (N)**

Normality is defined as the number of gram equivalents of solute present in 1000 ml of solution. Normality is represented by the symbol 'N'.

### **Normal solution (Normality – 1N)**

A normal solution contains one-gram equivalent of solute present in one litre of solution.

### **Decinormal Solution (Normality = 0.1N)**

A decinormal solution contains one tenth of a gram equivalent of solute in one litre of solution.

### Formula

$$\text{Normality (N)} = \frac{\text{Mass of solute X 1000}}{\text{Equivalent mass of solute X volume of solution}}$$

### **Molarity (M)**

Molarity is the number of moles of solute present in 1000 ml or one litre of the solution. It is represented by the symbol 'M'.

#### Molar solution (Molarity =1M)

A Molar solution contains one mole of solute in one litre (1000 ml) of the solution.

### Formula

$$\text{Molarity, M} = \frac{\text{Mass of the solute X 1000}}{\text{Molecular mass of the solute X Volume of the solution}}$$

Or

$$\text{Molarity} \times \text{Molecular mass} = \text{Mass of solute present in 1000ml of solution.}$$

### **MOLALITY (m)**

Molality is defined as the number of moles of solute in a solution corresponding to 1000g (1Kg) of the solvent. It is represented by the symbol 'm'. The SI unit for *molality* is mol/kg.

#### Molal solution (Molality =1m)

A Molal solution contains one mole of solute in one Kg of solvent.

### Formula

$$\text{Molality} \times \text{Molecular mass} = \text{Mass of solute in 1000g of solvent}$$

$$\text{Molality, m} = \frac{\text{Mass of solute x 1000}}{\text{Molecular mass of solute x Mass of solvent}}$$



## **Mole-fraction of solvent ( $x_1$ )**

Mole-fraction of solvent is the ratio of number of moles of solvent to the total number of moles present in the solution. Let the no. of moles of solvent be denoted as  $n_1$  and the no. of moles of the solute as  $n_2$ .

$$\begin{aligned}\text{Mole-fraction of solvent} &= \frac{\text{Number of moles of solvent (}n_1\text{)}}{\text{Total number of moles present in solution (}n_1+n_2\text{)}} \\ &= \frac{n_1}{n_1 + n_2}\end{aligned}$$

## **Mole-fraction of solute ( $x_2$ )**

Mole-fraction of the solute is the ratio of number of moles of solute to the total number of moles present in the solution.

$$\begin{aligned}\text{Mole-fraction of solute} &= \frac{\text{Number of moles of solute}}{\text{Total number of moles present in solution}} \\ &= \frac{n_2}{n_1 + n_2}\end{aligned}$$

(Total number of moles present in the solution = number of moles of solute + number of moles of solvent)

***In any solution, the sum of mole-fraction of solute and solvent is equal to one***

***i.e.  $x_1 + x_2 = 1$ .***

*Mass in gram*

***Note: Number of moles =  $\frac{\text{Mass in gram}}{\text{Molecular Mass}}$***

## **Parts per million (ppm)**

It is a way of expressing very dilute concentrations of substances. Just as percentage means out of hundred, so parts per million or ppm means out of a million. Usually describes the concentration of something in water or soil.

One ppm is equivalent to 1 milligram of a substance per liter of water (mg/l)

or 1 milligram of a substance per kilogram of soil (mg/kg).

$$\text{ppm} = \frac{\text{number of parts of the component} \times 10^6}{\text{total no. of parts of all components}}$$

$$\text{ppm} = \frac{\text{mass of the solute} \times 10^6}{\text{mass of the solution}}$$

One ppm denotes one part in 1,000,000 parts i.e., one part in  $10^6$ .

Similarly **parts-per-billion** denote one part in billion (one part in  $10^9$ )

## **INSTRUMENTAL METHOD OF ANALYSIS**

Analytical chemistry is the study of separation, identification and quantification of the chemical component of materials.

Qualitative analysis: Used to determine, the identity of chemical species in the sample.

Quantitative analysis: Used to determine amount or concentration of chemical species in the sample.

Analytical method can be divided into **Classical method** and **Instrumental method**.

Instrumental methods are further classified into **Classical instrument method** and **Advanced instrument method**.

Classical instrument method: In this method, the analyte sample is estimated by carrying chemical reaction between analyte and reagent. Some of techniques involved are:

- a. Colorimetry
- b. Flame photometry
- c. Atomic absorption spectroscopy
- d. Potentiometry
- e. Conductometry.

### **COLORIMETRY**

Colorimetry is used to determine the concentration of compounds in a solution. This method is used for solution which are themselves coloured or which gives colour with a suitable reagent. The intensity of colour is directly proportional to concentration of the solution.

**Theory** : This method is based on **Beer-Lamberts law**.

According to **Beer-Lamberts law**, when a monochromatic light is passed through a solution, part of light is absorbed by solution. The extent of absorption depends on the concentration of the solution and path length of the light through the solution.

$$A = \epsilon \cdot c \cdot t$$

Where, A = Absorbance

$\epsilon$  = molar extinction coefficient,

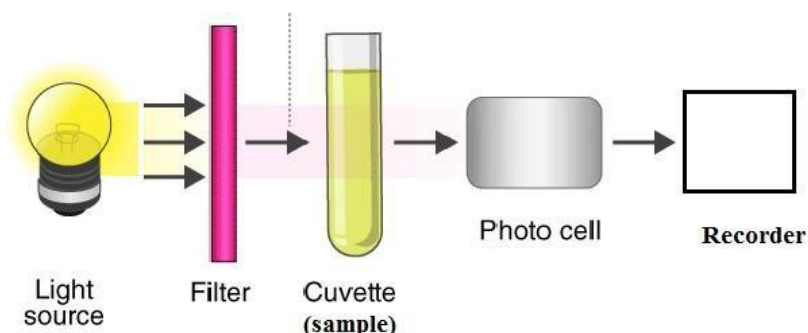
c = concentration of the solution;

t = path length & is constant for a given substance at a given wavelength.

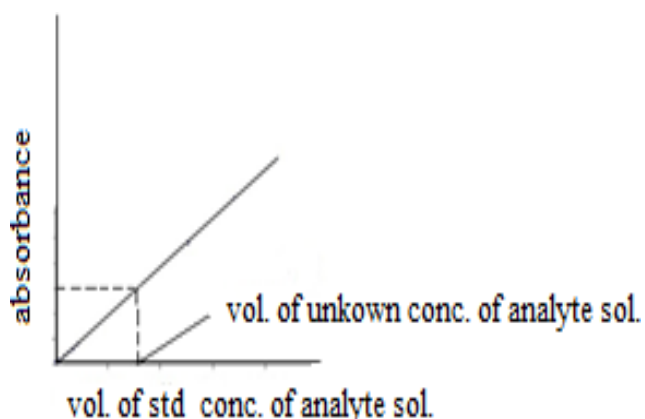
If t, is kept constant, then, A directly proportional C. Hence a plot of absorbance against concentration gives a straight line.

**INSTRUMENTATION:** Calorimeter are made of following components

- Light source.
  - A filter which provides desired wavelength range.
  - A sample cell.
  - A photocell detector.
  - Recorder.
- First, a blank solution is taken in the sample cell and monochromatic light of suitable wavelength is allowed to fall. Its absorbance is adjusted to zero.



- Then the different analyte solutions of known concentration are placed in sample cell one by one and its absorbance is noted.
- The absorbance for analyte solution of unknown concentration is noted.
- A plot of absorbance versus standard concentrations of analyte is used to find unknown concentration of analyte in the sample.



## Application:

- Determination of the composition of colored complex
- Used in soil testing for analysis of soil and plant nutrients.
- Used in food testing laboratories to check concentration of chemical parameters.
- Used in clinical laboratories for analysis of biomolecules such as glucose, urea.

## FLAME PHOTOMETRY

The process of measurement of **emission of radiation**, when the analyte sample is introduced into the flame is called flame photometry.

## THEORY:

The intensity of the emitted radiation is related to the concentration of ions, by an expression similar to Beer's relation,

$$E = k\alpha c,$$

Where, E = emitted radiation.

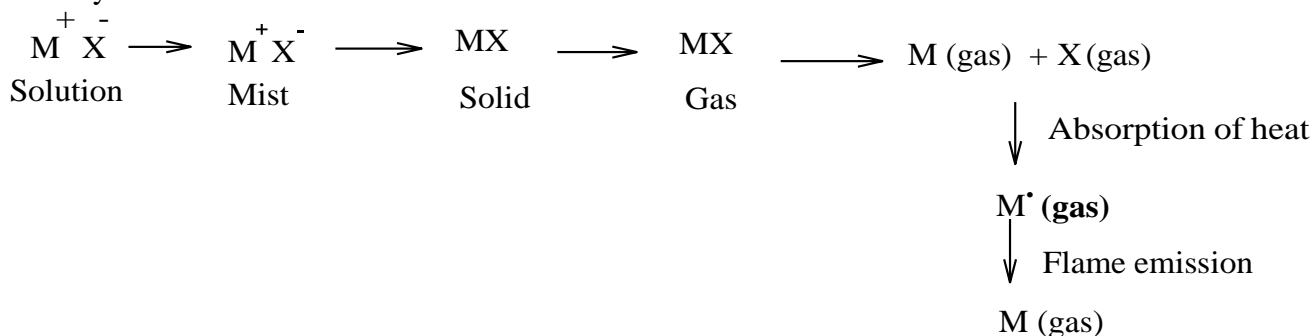
k = constant.

$\alpha$  = efficiency of atomic excitation.

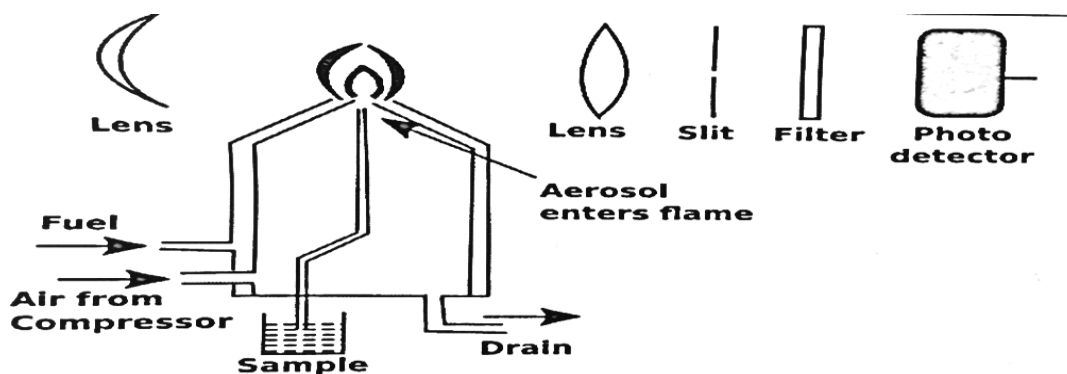
c = concentration of the solution.

- When the solution of metallic salt, in the form of small droplets is subjected to flame, series of changes takes place.
  - a) First, solvent evaporates leaving behind salt.
  - b) Salt then gets vaporized to vapors.
  - c) Vapors dissociates into gaseous atoms.
- Gaseous metallic atoms absorb the heat energy from the flame and gets excited to higher energy level.
- The excited atoms are not stable, and they return to ground state by emitting radiation in the form of light.
- The intensity of light radiation emitted is measured by a flame photometer.
- Emitted radiation measured directly proportional to the concentration of metal ions in the solution.

The sequence of changes taking place at the flame, when metal salt solutions are aspirated may be summarized as follows.



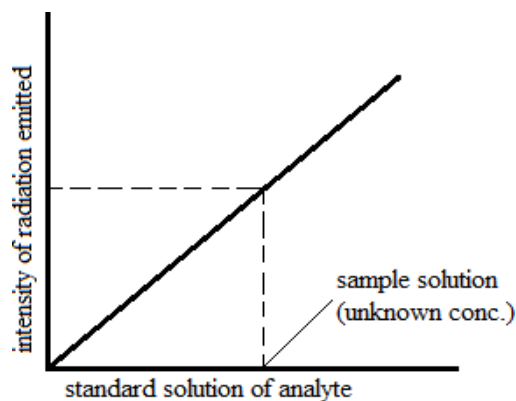
## INSTRUMENTATION:



- i) By the pressure regulator air is passed into atomizer.
- ii) Sample is drawn into the atomizer through the capillary tube, and then sample solution mixes with air as fine **mist**.
- iii) The mist passes into the flame of burner and burns.
- iv) The radiation emitted pass through a lens, then into a filter and finally into a detector.
- v) The detector displays the emission intensity.

Then the calibration curve is obtained by plotting the emission intensity against the concentration of the standard solutions.

From the calibration curve, the concentration of the sample solution can be determined.



### Applications:

1. For qualitative determination of cations like Na, K, Ca, Ba, Cu. Since these easily get excited to higher energy level at low temperature.
2. For quantitative analysis to determine the concentration of group IA and IIA elements. For example,
3. Concentration of calcium in hard water.
4. Concentration of Sodium, potassium in Urine
5. Concentration of calcium and other elements in bio-glass and ceramic materials.

## **POTENTIOMETRY**

It deals with a estimation of chemical substances in the solution by measuring the potential value.

### **THEORY:**

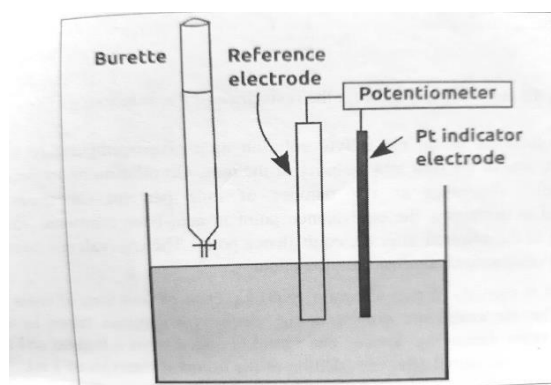
In potentiometry the amount of substance (metal ion) in the solution is estimated by measuring the EMF between 2 electrodes that are dipped in the solution.

The relation between electrode potential and metal ion concentration is given by theNernst equation.

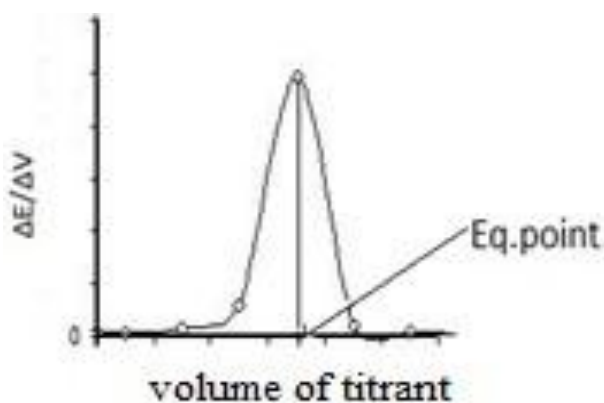
$$E = E^0 + \frac{0.0591}{n} \log [M^{n+}]$$

It can be seen from the equation that the potential of an electrode E depends upon the concentration of the ion  $M^{n+}$

### **Instrumentation:**



- Potentiometer consists of 2 electrodes i.e a reference electrode and an indicator electrode which are connected to a device (potentiometer) for measuring the potential.
- The indicator electrode responds rapidly to the changes in the potential due to the concentration changes of the analyte.
- A known volume of the analyte is taken in a beaker and its potential is measured by connecting the assembly to a potentiometer.
- The titrant is added in increments of 0.5ml and the potential is measured each time.
- Near the equivalence point there is sharp increase in the potential. The end point is determined by plotting change in potential against the volume of titrant.



### Applications:

- It finds applications in oxidation reduction titrations to estimate the concentration of analyte in the sample solution.

In redox titration the indicator electrode such as platinum and the reference electrode, generally a saturated calomel electrode is used. The potential of the electrode depends on the concentration of the substance being oxidized or reduced.

$$E_{\text{cell}} = E_{\text{cell}}^0 + \frac{0.0591}{n} \frac{[\text{Oxidised}]}{[\text{Reduced}]}$$

- Used in precipitation titrations, which involves insoluble salt metals. (For example titration of silver ion with a halide ion. Silver electrode is used as indicator electrode)
- Used in complexometric titrations.
- Used to titrate non-aqueous solvents

## **CONDUCTOMETRIC TITRATION**

Determination of quantity of material present in the solution by measuring its electrical conductivity.

### **THEORY:**

Conductivity is a measure of ability of a solution to carry an electric current. Electrolyte solution conducts current by the migration of ions under the influence of an electric field. This obeys Ohm's law,

$$E = IR$$

where, E = Applied potential, I = Current, R = Resistance

Conductance is a reciprocal of resistance, i.e.  $C = \frac{1}{R}$

Resistance depends on length and cross sectional area of the conductor (resistance is directly proportional to the length of conductor and inversely proportional to the cross sectional area of the conductor)

$$\text{i.e. } R = s \cdot \frac{l}{a}$$

where, s = specific resistance,

l = length of the conductor

a = area of cross section of the conductor

$$C = \frac{1}{s} \cdot \frac{a}{l}$$

$K = \frac{1}{s}$ , where K = specific conductance

$$C = K \cdot \frac{a}{l}$$

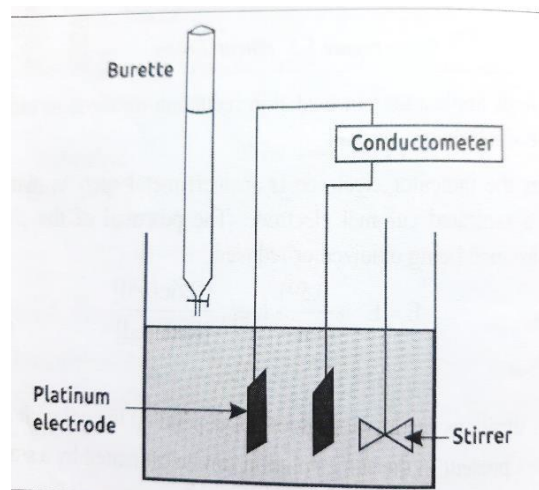
### **INSTRUMENTATION:**

1. Conductivity cell: Two Pt electrodes of area  $1\text{cm}^2$  and at 1cm apart
2. Conductivity meter: To display the reading during titration.
3. Magnetic stirrer: To maintain uniform concentration.

Analyte solution is taken in the beaker, and a magnetic stirrer is placed. Conductivity cell is dipped in the solution which is connected to the conductometer. Initial reading is noted. The titrating reagent (known ml) is added and conductance is measured after stirring. The addition of titrating agent is continued until at least 5 readings beyond the equivalence point.

A graph of conductance vs volume of titrant is plotted. And the equivalence point is noted.

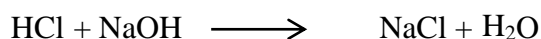




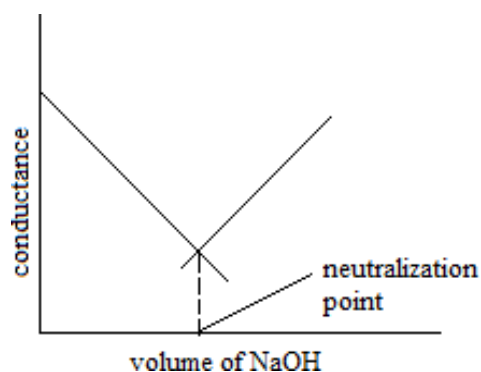
**Applications:** Used in estimation of acid or base present in the sample solution like,

1. **Conductometric titration: Strong acid v/s strong base (HCl v/s NaOH)**

If the strong acid like HCl is titrated against a strong base such as NaOH, the conductance first decreases due to replacement of fast moving  $\text{H}^+$  ions by slow moving  $\text{Na}^+$  ions.

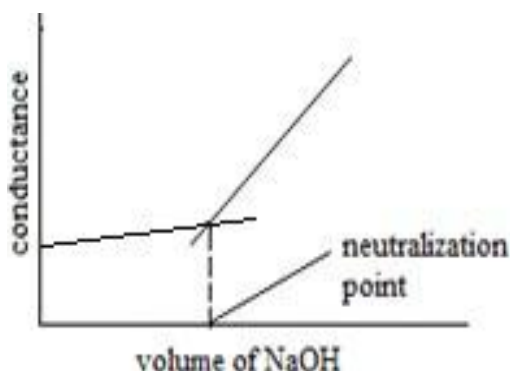


After the neutralization point, conductivity rapidly rises with further addition of NaOH because of continuous addition of fast moving  $\text{OH}^-$  ions. A plot of conductance against the volume of base added is shown in the figure. The point of intersection of two curves gives the neutralization point.

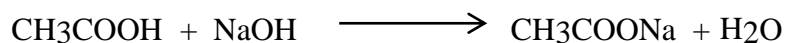
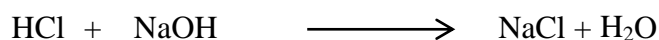


## 2. Weak acid v/s Strong base ( $\text{CH}_3\text{COOH}$ v/s $\text{NaOH}$ )

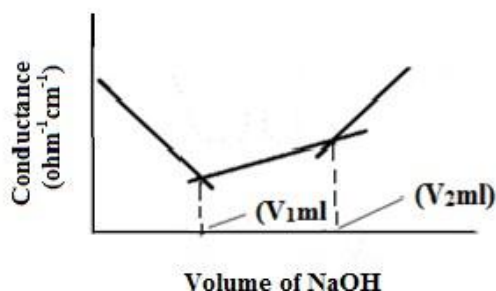
The conductance of the acid will be initially low since acetic acid is a weak electrolyte. When  $\text{NaOH}$  is added to the acid, the salt formed is highly ionized (ions are more) and the conductance increases. On complete neutralization of the acid, further addition of base leads to an increase in the number of mobile  $\text{OH}^-$  ions. Hence the conductance increases sharply.



## 3. Mixture of strong acid and weak acid v/s strong base ( $\text{HCl}$ , $\text{CH}_3\text{COOH}$ v/s $\text{NaOH}$ )



Before the addition of alkali, the acid ( $\text{HCl}$ ) solution exhibits high conductance due to fast moving  $\text{H}^+$  ions. When  $\text{NaOH}$  is added to  $\text{HCl}$  solution, the fast moving  $\text{H}^+$  ions are replaced by slow moving  $\text{Na}^+$  ions. Hence the conductance decreases initially till the first neutralization point ( $V_1$ ). Further addition of alkali leads to a gradual increase in conductance, because the poorly conducting acid (acetic acid) is gradually converted to highly conducting salt ( $\text{CH}_3\text{COONa}$ ). After complete neutralization of weak acid ( $V_2$ ) conductance sharply increases due to fast moving  $\text{OH}^-$  ions.



### Other applications:

1. Displacement titration ( salt of weak acid titrated against strong acid )
2. Precipitation titration ( silver nitrate against sodium chloride )
3. Complexation titrations ( EDTA vs metal ion)

## NANOMATERIALS

- In chemistry, **nano material** refers to a material with at least one of its dimension (length, width or breadth) in nano scale.i.e  $10^{-9}$ m. And the size varies from 1-100nm. A nanometer is one billionth of a meter- approximately 100,000 times smaller than the diameter of a human hair.
- Nanomaterials are of interest because at this scale optical, magnetic, electrical, and other properties will change. These emergent properties have the potential for great impacts in electronics, medicine, and other fields.

## SIZE DEPENDENT PROPERTIES OF NANOMATERIALS

### 1. Surface area

- Some properties like **catalytic activity**, **gas adsorption** and **chemical reactivity** depend on the surface area of the material.
- When bulk material is subdivided into nanomaterial, the total volume of the material remains same, but the collective surface area is greatly increased. Due to increased surface area, the material becomes catalytically active or chemically reactive or gets good gas adsorption property.

Ex: **Bulk** Gold – Catalytically **inactive**,      **Nano** Gold – Catalytically **active**

### 2. Electrical properties

- In bulk material electronic bands are continuous, due to overlapping of orbitals of billions of atoms, the material acts as conductor.
- But, in nanosize materials, very few atoms or molecules will be present, so electronic bands become separate.
- Hence, some metals which are good conductors in bulk become semiconductors and insulators as their size is decreased to nano level.

### 3. Optical properties

- The separate electronic states of nanomaterials allow absorption and emission of light of specific wavelength. Hence they exhibit unique colors different from bulk materials.
- Nanoparticles of metals exhibit unique optical property called as **surface plasmon resonance**.
- When light hits the surface of metal particle, surface electrons start oscillating back and forth in a synchronized way in a small space; this is called as **Surface Plasmon Resonance**.
- Resonating electrons have a cross-sectional area very much higher than the nanoparticle.
- Depending on the frequency of oscillation, resonating electrons can capture radiation of different wavelength.
- Ex : **Bulk** Gold - Yellow colour  
Nano Gold - Red colour

### 4. Catalytic property

The catalytic property of material depends on particle size. If the size of the particle reduces from bulk to nanoscale, surface to volume ratio increases drastically, that leads to high catalytic activity of the same material.

Ex: **Bulk** Gold - Catalytically **inactive**, **Nano** Gold – Catalytically **active**

## SYNTHESIS OF NANO MATERIALS:

Nanomaterials deal with very fine structures: a nanometer is a billionth of a meter. There are many techniques available to synthesize nanomaterials which can be generally grouped as Top-Down and Bottom-Up approaches.

**1) The top down method:** bigger materials are broken down into small nano-size materials by means of various physical methods like laser ablation, electric arc method etc. There are few major drawbacks in top=down approach, mainly

- a) Expensive apparatus
- b) Crystallographic damage and internal stress in nano material
- c) Nanomaterial obtained is generally contaminated.

**2) The bottom up approach:** In bottom up approach desired nanomaterial is built from the bottom, i.e by orderly assemble of growth species like atom, ion or molecule. This method involves simple chemical reactions. Some advantages of bottom up approach are,

- a) The method is simple and economically viable.
- b) Nanostructures with less defects and high purity can be synthesized.

### 1. SOL-GEL PROCESS

- In sol-gel process, either **metal salt or alkoxide** is used as precursor (starting material).
- It is mainly used in the synthesis of uniform nanoparticles of **metal oxides**.

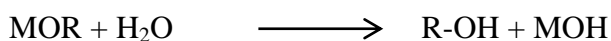
**Steps involved in synthesis:**

1. Preparation of Sol
2. Conversion of Sol to Gel.
3. Aging of Gel.
4. Drying of the Gel (evaporation)
5. Heating at high temperature (calcination)

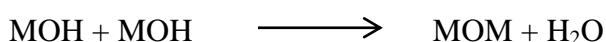
**Step 1: Sol** is prepared by dispersing precursors in a solvent. (Sol is a solid particle dispersed in a liquid medium.)

**Step 2:** Sol is further converted into a gel by hydrolysis and condensation of precursors.(adding acid or base as catalyst)

**Hydrolysis of alkoxides**



**Condensation of hydrolysed species** with each other (releases water)



**Step 3:** Aging (keeping for a known period of time) of colloid solutions takes place, i.e. colloids can increase their particle size and grows into a sol-gel.

**Step 4:** Then the gel is dried by evaporation (solvent get evaporated)

**Step 5:** Calcined (heating to high temperature) to produce nanoparticles.

*The particle size depends on concentration of precursor, rate of hydrolysis and condensation reactions and aging time. The nano particles obtained by this process have a size ranging from 1-100nm*

## PRECIPITATION METHOD

Precursor-Inorganic metal salt (usually nitrate, or acetate of metal) dissolved in water.

- Metal cations exist in the form of metal hydrate species, such as  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ ,  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ .
- To this addition of precipitating agent such as NaOH,  $\text{NH}_4\text{OH}$ , NaBr or  $\text{Na}_2\text{CO}_3$  results in change in pH and increase in ions concentration.
- The concentration of ions in the solution increases and reaches a critical level called as Super saturation.
- At super saturation, condensation of precursor happens and **nucleus** formation is initiated.
- Nucleus further grows into particles, which gets precipitated.
- The product obtained is filtered, washed with water, air dried and calcinated at higher temperature.
- If super saturation and rate of nucleation are slow then the precipitate with wide particle size is formed.
- If super saturation and rate of nucleation are rapid then nucleus formed will burst, so particles with small size formed.
- Thus nano particle of **desired size** can be obtained by controlling **super saturation and rate of nucleation**.

*Ex: ZnS nanoparticles are prepared precipitation process.*

To the hydrated Zinc acetate precursor solution, thioacetamide (TAA) precipitating agent is added to get ZnS nanoparticle.  $\text{Zn}^{2+} + \text{S}^{2-} \longrightarrow \text{ZnS}$

# NANOSCALE MATERIALS

## CARBON NANOTUBES:

- Carbon Nanotubes are new allotropes of carbon.
- **CNTs are cylindrical tubes with a central hollow core, formed by rolling up of a graphene sheet, its end are capped by a hemisphere of fullerene structure.** It is a one dimensional nano material with aspect ratio greater than 1000.
- These have one hundred times tensile strength of steel, thermal conductivity better than diamond, and electrical conductivity similar to copper.

### Types of CNTs

1. Single walled CNTs (SWCNTs): They are formed by rolling up of single graphene layer. It's diameter is 1.4nm and length can go up to few micrometres.
2. Multi walled CNTs (MWCNTs): They are formed by rolling up of 2 or more graphite layers. Its diameter varies from 30 to 50 nm and length can go up to few micrometres.

### Properties and Application

1. CNTs exhibit high electrical conductivity and thermal conductivity. They have low density and very high mechanical strength.

***Application-*** *Electrode material for Li-ion rechargeable batteries.*

*Metallic connection between components of integrated circuits.*

2. CNTs can emit electrons when subjected to high electric field and the process is called as Field emission.

***Application-Field emission X ray tubes.***

3. SWCNTs efficiently absorb radiation in the near infrared range (700-1100nm) and convert it into heat.

***Application-Cancer thermotherapy***

4. CNT is composed of  $sp^2$  C-C bond which are stronger than  $sp^3$  bond of diamond. Thus mechanical property of CNT is stronger than diamond.

***Application- Composite material with enhanced mechanical strength.***

## FULLERENES:

1. Fullerenes are class of molecules made of only carbon atoms having closed cage like structure.
2. Many number of fullerene molecules with different carbon atoms like  $C_{60}$ ,  $C_{70}$ ,  $C_{74}$ ,  $C_{78}$  etc., have been prepared.
3.  $C_{60}$  is the smallest, stable and abundant fullerene, obtained by usual preparation methods.
4.  $C_{60}$  has **spherical** shape and resembles a football and commonly known as bucky ball.
5. Fullerenes are made up of pentagons and hexagons. Pentagons gives curvature required to form closed structure.
6. All fullerenes contain **12 pentagons** and different numbers of hexagons.
7. Each fullerene has  **$2(10+M)$**  number of carbon atoms corresponding to 12 pentagons and M number of hexagons.

**M number of hexagons.**

### **Properties and Application.**

1. Single  $C_{60}$  molecule theoretically can take up maximum of 60 hydrogen atoms.

#### ***Application- Hydrogen storage material for fuel cells***

*Electrode material in secondary batteries. Ex- Nickel Metal Hydride battery.*

2. Each  $C_{60}$  molecule can absorb more than 100 photons in a nanosecond and transfer that energy (230V) to its vibrational energy.

***Application-Used as optical limiters. Optical limiters are used to protect materials from damage, by intense incident light radiation.***

3. A polymer composite of  $C_{60}$  molecule and polyvinylcarbazole exhibits very high photoconductivity.

#### ***Application- Used in Photocopying applications.***

4.  $C_{60}$  molecule readily accepts electron and forms " $C_{60}$  meta stable anion" and becomes catalytically active.

***Application : Catalyst in organic reactions such as hydrogenation-dehydrogenation reactions.***



### 3. GRAPHENES

- Graphene is a two dimensional crystalline allotrope of carbon consisting of a single layer of carbon atoms arranged in a hexagonal lattice.
- It is a semi-metal with a small overlap between the valence and the conduction bands.
- Its carbon atoms are densely packed in a regular hexagonal pattern.
- The atoms are about  $1.42 \text{ \AA}$  apart.
- Each carbon atom is bonded to three carbon atoms and is  $sp^2$  hybridized.

#### Properties:

1. Very high **electrical conductivity** (One of the most useful properties of graphene because of a zero-overlap semimetal).

*Applications: It is used in light-emitting diodes(LED), capacitors, field effect transistors(FETs)*

2. It is **the strongest material**. So composite materials of graphene enhance the mechanical property.

*Applications: Used in aerospace, building materials etc*

3. It is a material with the **highest surface-area to volume ratio**.

*Applications: It is used in batteries and super capacitors (as it store more energy and charge faster)*

4. Graphene **does not oxidize in air** or biological fluids.

*Applications: Used in biosensor (to detect chemical substance)*



