

Module – 1

Electrochemistry and Battery Technology

Course Objectives:

To provide students with knowledge of engineering chemistry for building technical competence in industries, research and development in the field of Electrochemical and Battery technology.

Course Outcome:

On completion of this module, students will have knowledge in Electrochemical and concentration cells. Classical and Modern batteries and fuel cells.

Introduction:

Electrochemistry is the branch of chemistry, which deals with the interaction of matter and electrical energy i.e., producing electrical energy from chemical reaction (spontaneous process) or bringing out chemical reactions by applying electrical energy (non spontaneous process). A device used for producing an electrical current from a chemical reaction (redox reaction) is called an electrochemical cell. It gives the relationship between electrical, chemical phenomenon and the laws of interaction of this phenomenon. The laws of electrochemistry form the basis of electrolysis and electro synthesis.

Single electrode potential:

It is defined as the potential developed when an electrode is in contact with a solution of its own ions. It is denoted as **E**.

Standard Electrode potential:

It is defined as the potential developed when an electrode is in contact with a solution of 1M concentration, at 298 K and 1 atm pressure. It is denoted as **E°**.

Nernst equation:

Nernst derived an equation to establish relationship between electrode potential and concentration of metal ion.

Due to the power output from an electrochemical cell, the free energy decreases i.e.

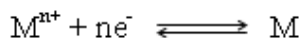
$$-\Delta G = nFE \quad (\text{or}) \quad \Delta G = -nFE$$

Under standard conditions the free energy ΔG is given by the equation

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

E° is a constant called standard electrode potential.

Consider a reduction reaction:



For spontaneous reaction, the change in the free energy depends on the concentration of reacting species.

$$\Delta G = \Delta G^\circ + RT \ln K_c$$

$$\text{Where } K_c = \frac{[\text{Products}]}{[\text{Reactants}]}$$

Substituting the value of K_c in above equation, we get

$$\Delta G = \Delta G^\circ + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$\Delta G = \Delta G^\circ + RT \ln \frac{[M]}{[M^{n+}]}$$

Substitute for ΔG and ΔG° in above equation

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

Under standard conditions $[M] = 1$

$$-nFE = -nFE^\circ + RT \ln \frac{1}{[M^{n+}]}$$

Dividing eq (5) by $-nF$ we get

$$E = E^\circ - \frac{RT \ln [1/M^{n+}]}{nF}$$

Converting \ln to \log we get

$$E = E^\circ - \frac{2.303RT \log [1/M^{n+}]}{nF}$$

Substituting for $R = 8.314$, $T = 298K$ and $F = 96500$ in eqn (6) we get

$$E = E^\circ - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]} \quad \text{or} \quad E = E^\circ + \frac{0.0591}{n} \log [M^{n+}]$$

In general Nernst equation is,

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[Product]}{[Reactant]}$$

Reference electrode

Reference electrode is that whose potentials is known and used for determination of potential of other electrodes.

Note: Types of reference electrodes:

Beyond syllabus:

Primary reference electrode:

Whose potential is fixed as zero at all temperature and pressure. Example: Standard hydrogen electrode (SHE).

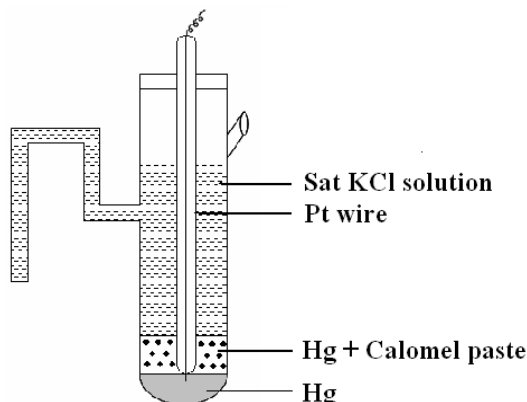
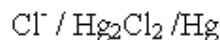
Secondary reference electrode:

Whose potential is known in connected with SHE. Secondary reference electrodes have several advantages over SHE. These electrodes are commonly used for determining the electrode potentials of other metals. The two commonly used secondary reference electrodes are *calomel electrode and silver-silver electrode*.

Calomel Electrode:

Construction:

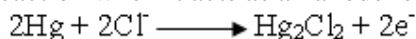
Calomel electrode consists of long glass tube with two side tubes. One at the top to fill sat KCl solution and the other side tube is connected to the salt bridge. Mercury is placed at the bottom which is covered with a layer of Hg and Hg₂Cl₂ (calomel) paste. The remaining portion is filled with saturated KCl solution. A platinum wire is dipped into the mercury and is used to provide external electrical contact. The calomel electrode is represented as,



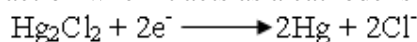
Working:

Calomel electrode behaves as anode or cathode depending upon the nature of other electrode.

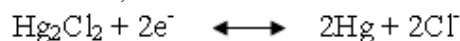
The half-cell reaction when it acts as an anode is



The half cell reaction when it acts as a cathode is



The electrode reaction is,



Applying Nernst equation,

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$E = E^\circ - \frac{0.0591}{n} \log \frac{[\text{Hg}]^2[\text{Cl}^-]^2}{[\text{Hg}_2\text{Cl}_2]}$$

$$E = E^\circ - \frac{0.0591}{2} \log [\text{Cl}^-]$$

The calomel electrode potential is depends on the concentration of chloride ions in KCl. If the concentration of chloride ions increases, the potential decreases and vice versa. (The potential of calomel is inversely proportional to the concentration of chloride ions)

The potential of calomel electrode is measured with respect to SHE and it depends on concentration of KCl solution used.

Conc. KCl	0.1N	1N	Saturated KCl
Potential (V)	0.334V	0.281V	0.242V

Applications:

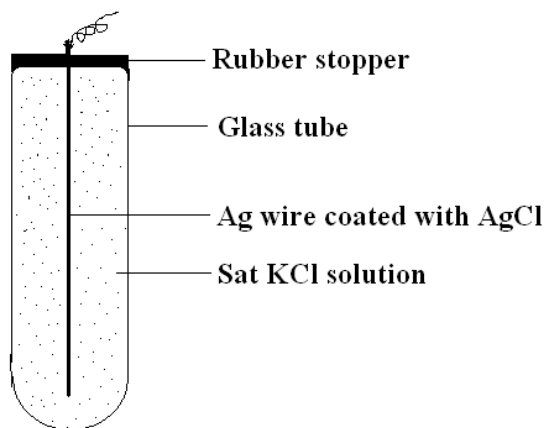
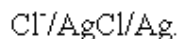
- Used to determine the potential of the other electrodes.

- It is commonly used as reference electrode in all potentiometric determinations.
- Electrode potential is reproducible.

Silver - Silver Chloride Electrode:

Construction:

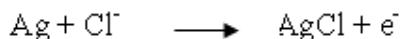
It consists of a long glass tube in which saturated KCl solution is filled. A silver wire is coated with AgCl by electrolytic process and placed inside the tube and which provides external electrical contact. The electrode is represented as,



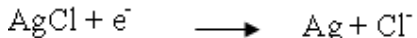
Working:

The electrode behaves as anode or cathode depending upon the nature of other electrode.

The half-cell reaction when it acts as an anode is



The half-cell reaction when it acts as a cathode is



The electrode reaction is



Applying Nernst equation to the above equation,

$$E_{cell}^{\circ} = \frac{0.0591}{n} \log \frac{(\text{product})}{(\text{reactant})}$$

$$E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{1} \log \frac{[\text{Ag}][\text{Cl}^-]}{[\text{AgCl}]}$$

$$E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{1} \log [\text{Cl}^-]$$

The Ag - AgCl electrode potential is depends on the concentration of chloride ions in KCl. If the concentration of chloride ions increases, the potential decreases and vice versa. (the potential of Ag - AgCl is inversely proportional to the concentration of chloride ions)

The potential of Ag - AgCl electrode is measured with respect to SHE and it depends on concentration of KCl solution used.

Conc. KCl	0.1N	1N	Saturated KCl
Potential (V)	0.29V	0.22V	0.199V

Applications:

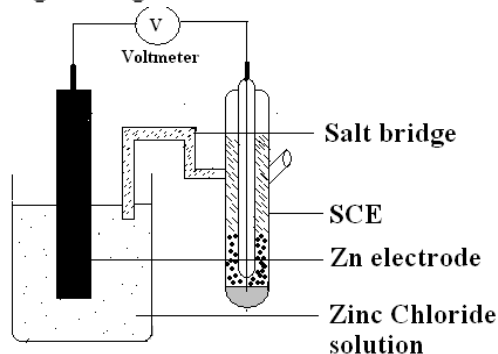
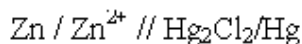
1. As a secondary reference electrode in ion selective electrodes.
2. In determining whether the potential distribution is uniform or not in ship hulls and old pipelines protected by cathodic protection.

Measurement of standard electrode potential using calomel electrode:

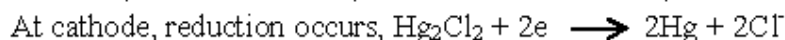
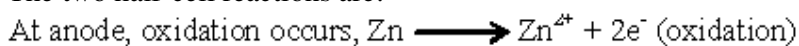
The electrode potential of unknown electrode is measured by connecting to a saturated calomel electrode through salt bridge. (The potential of saturated calomel electrode is fixed to 0.24V for sat KCl solution).

Ex: Zinc electrode coupled with saturated calomel electrode.

To measure the standard electrode potential of Zn, Zn electrode is dipped in Zinc chloride solution and coupled with saturated calomel electrode through voltmeter. Zinc electrode acts as anode and SCE acts as cathode. The emf of the cell is measured through voltmeter. Representation of the cell is



The two half-cell reactions are:



The standard electrode potential is calculated by substituting the potential values in the relation

$$\begin{aligned} E_{\text{cell}} &= E_{\text{SCE}} - E_{\text{Zn/Zn}^{2+}} \\ E_{\text{Zn/Zn}^{2+}} &= E_{\text{SCE}} - E_{\text{cell}} \\ &= 0.24 - 1.0 \\ E_{\text{Zn/Zn}^{2+}} &= -0.76\text{V} \end{aligned}$$

Ion-selective electrodes

The electrode, which responds to a specific ion in a mixture by ignoring other ion is known as ion selective electrode. It consists of a thin membrane in contact with ion solution.

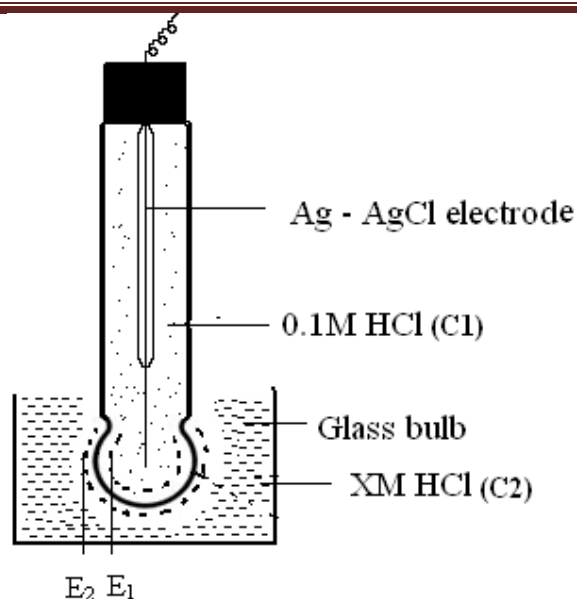
Glass Electrode:

This electrode works on the principle that when a thin, low resistivity glass membrane is in contact with a solution containing H^+ ions, a potential develops across the membrane and the solution. Potential developed depends on the concentration of hydrogen ions in the solution.

Cell representation: Ag / AgCl / HCl (0.1M) / Glass/ unknown solution

Construction:

It consist of a long glass tube with a thin walled glass bulb contains 0.1 M HCl [C_1]. Ag/AgCl electrode placed in to the solution to provide electrical contact. The glass electrode is dipped in unknown solution of concentration C_2 , the potential developed across the membrane by the exchange of ions with the composition of glass is known as the boundary potential E_b (E_1 & E_2). Even when $C_1=C_2$ a small potential is developed across the membrane is called as *asymmetric potential*.



Working:

E₁ & E₂ is the potential developed at inner and outer membrane respectively
The boundary potential is,

$$E_b = E_2 - E_1$$

$$E_b = \frac{0.0591}{n} \log \frac{[C_2]}{[C_1]}$$

$$E = \frac{0.0591}{n} \log [C_2] + \frac{0.0591}{n} \log \left[\frac{1}{C_1} \right]$$

Where $\frac{0.0591}{n} \log [1/C_1] = L$ (constant)

$$E_b = L + \frac{0.0591}{n} \log [C_2]$$

Where n = 1

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

where C₂ = [H⁺] ions in outer membrane then,

$$E_b = L + 0.0591 \log [H^+]$$

$$E_b = L - 0.0591 \text{ pH} \quad (\text{pH} = -\log [H^+])$$

The glass electrode potential is ,

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

Substitute the value of E_b

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

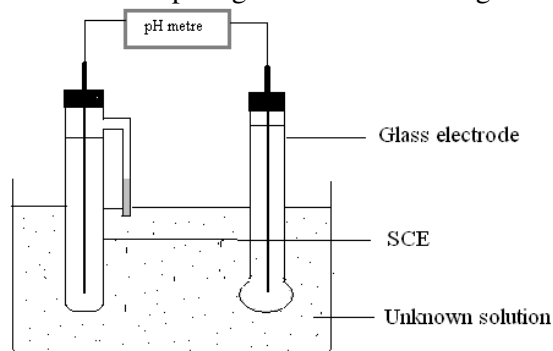
Where $L + E_{Ag/AgCl} + E_{asy} = L_1$ (constant)

$$E_G = L_1 - 0.0591\text{pH}$$

Determination of pH of a Solution using Glass Electrode

The potential of a glass electrode depends on the concentration of H^+ ions. Hence, pH of a solution can be determined by using glass electrode and calomel electrode assembly. The cell assembly is represented as

$Hg/Hg_2Cl_2/Cl^- // \text{solution of unknown pH} / \text{glass} / 0.1 \text{ M HCl} / AgCl / Ag$



The emf of a cell is determined by using voltmeter.

E_{cell} is the difference b/w glass electrode potential E_G and the calomel electrode potential E_{SCE}

$$E_{cell} = E_G - E_{SCE}$$

$$= L_1 - 0.0591\text{pH} - E_{SCE}$$

$$\text{pH} = \frac{L_1 - E_{SCE} - E_{cell}}{0.0591} \quad [K = L_1 - E_{SCE}]$$

$$\text{pH} = \frac{K - E_{cell}}{0.0591}$$

Electrolyte Concentration Cells :

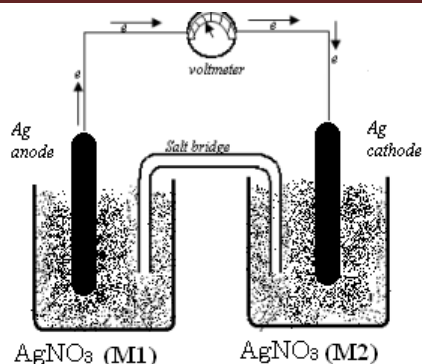
It is galvanic cell, which consists of two identical electrodes which are in contact with the same solution of electrolyte at different concentrations.

Example:

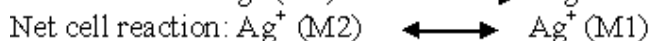
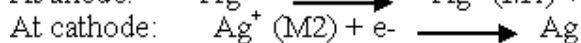
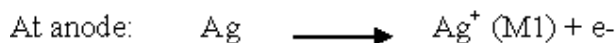
Consider two silver electrodes that are in contact with the $AgNO_3$ solution of different concentrations (M_1 and M_2) connected through voltmeter. The electrolytes are connected through salt bridge.

The cell representation $Ag / AgNO_3 (M_1) // AgNO_3 (M_2) / Ag$

Where M_1 and M_2 are the molar concentration of the Ag^+ ions in the two half-cells.



Electrode reaction:



The current produced in the cell due to migration of ions from higher concentration to lower concentration. This takes place until the concentration in the two Half -cells become equal ($M1=M2$) hence the production of current becomes zero.

Apply Nernst equation for the cell reaction,

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0591}{n} \log \frac{(\text{product})}{(\text{reactant})}$$

$$E_{\text{cell}} = E^{\circ}_C - E^{\circ}_A - \frac{0.0591}{n} \log \frac{(\text{M1})}{(\text{M2})}$$

E°_C & E°_A are of same metal so cancelled each other

$$E_{\text{cell}} = - \frac{0.0591}{n} \log \frac{(\text{M1})}{(\text{M2})} \quad (\text{or}) \quad E_{\text{cell}} = \frac{0.0591}{n} \log \frac{(\text{M2})}{(\text{M1})}$$

Battery Technology

Introduction

A battery is a portable energy source with three basic components-an anode (the negative part), an cathode (the positive part), and an electrolyte. As current is drawn from the battery, electrons start to flow from the anode through the electrolyte, to the cathode. A device enables the energy liberated in a chemical reaction to be converted directly into electricity. The term battery originally implied a group of cells in a series or parallel arrangement, but now it is either a single cell or group of cells. Examples: It ranges from small button cells used in electric watches, lead acid batteries used for starting, lighting and ignition in vehicles with internal combustion engines. The batteries are of great importance based on the ability of some electrochemical systems to store electrical energy supplied by the external source. Such batteries may be used for emergency power supplies, for driving electric vehicles, etc. For the commercial exploitation, it is important that a battery should provide a higher energy, power density along with long shelf life, low cost and compatible rechargeable units.

Classification of Batteries:

Batteries are classified as primary (non-rechargeable), secondary (rechargeable) and reserve (inactive until activated):

Primary battery:

The batteries, which produce electrical energy at the expense of free energy of active materials and produce energy only as long as active materials are present. These are not rechargeable batteries and are to be discarded after the use. These batteries are called as primary battery.

Example: Dry cell, Zn-MnO₂

Secondary battery:

The rechargeable batteries that produce electrical energy at the expense of free energy of active materials. These active materials are capable of restoring at respective electrodes on recharge and prepare for discharge once again. Such batteries are called secondary battery.

Example: Lead acid battery, NiMH battery, Ni-Cd battery

Reserve battery:

The high current batteries in which active materials are isolated from electrolyte due to their reactivity and are brought into contact whenever high potential is required for application are called reserve battery.

Example: Magnesium-water activated batteries, zinc-silver oxide batteries, etc.

Characteristics of a battery:

Cell potential / Voltage:

The cell potential or voltage of the battery is determined theoretically,

$$E_{\text{cell}} = (E_C - E_A) - \eta_A - \eta_C - iR_{\text{cell}}$$

Where E_C & E_A are reduction potential of cathode and anode, η_A & η_C are over potential at the anode and cathode and iR_{cell} is the internal resistance.

To attain the maximum cell potential or voltage from the battery, difference in the standard electrode potential must be high, the electrode reaction must be fast to minimize the over potential and internal resistance must be low.

Current:

“Is measure of the rate of flow of charges in a battery”.

To attain the maximum current from the battery, difference in the standard electrode potential must be high, the electrode reaction must be fast to minimize the over potential and internal resistance must be low.

Capacity:

“The total amount of charge stored in a battery in Ampere hours.”

The theoretical capacity may be calculated using faradays relation, $C = WnF/M$, where W and M is weight and mass of the active material respectively and n is the number of moles of the electro active material.

Electricity storage density:

“Amount of electrical energy stored per unit weight of the battery.”

Energy efficiency:

The ratio of output energy to the input energy. Higher the efficiency, very good is the battery.

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

Cycle life:

“The total number of discharge and recharge cycles that are possible before the failure of the battery”. It is applicable only to secondary battery, higher the cycle life, better is the battery.

Shelf-life:

“The duration of storage of a battery without self discharge is known as shelf life of a battery”. It referred to storage duration of battery. If shelf life is high, better is the battery.

Zinc-air battery

Reactive species at anode: Granulated Zn

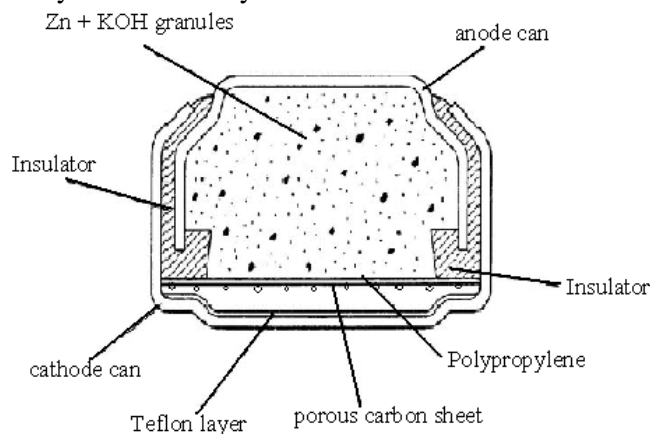
Reactive species at cathode: pure oxygen from air

Electrolyte: KOH

Separator: polypropylene

Voltage: 1.45V

The **zinc-air**, electrochemical system can formally defined as **zinc/potassium hydroxide/oxygen** battery but commonly known as “zinc-air” cell.



Construction:

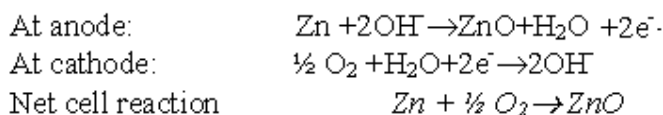
It consists of nickel-plated steel cans acting as anode and cathode..

1. The anodic can contain the zinc powder and electrolyte in the form of granules with a gelling agent.
2. The cathode active material is carbon sheet impregnated with MnO₂ (to increase the conductivity of cathode) with multiple air holes punched at the bottom to provide air access to the cathode. The sheet is laminated with Teflon layer (to diffuse the oxygen faster to cathode side) on one side.
3. The anodic and cathodic compartments are separated by polypropylene
4. The alkaline electrolyte is potassium hydroxide.
5. The output voltage is 1.45 Volts.

Working:

When the battery discharge, the following reactions takes place at respective electrodes.

Reactions:



Application:

- Used in hearing aids,

- In telecommunication devices such as pagers and wireless headsets
- In medical devices such as patient monitors, recorders, nerve & muscle stimulators and drug infusion pumps.

Nickel-metal hydride battery (Ni-MH)

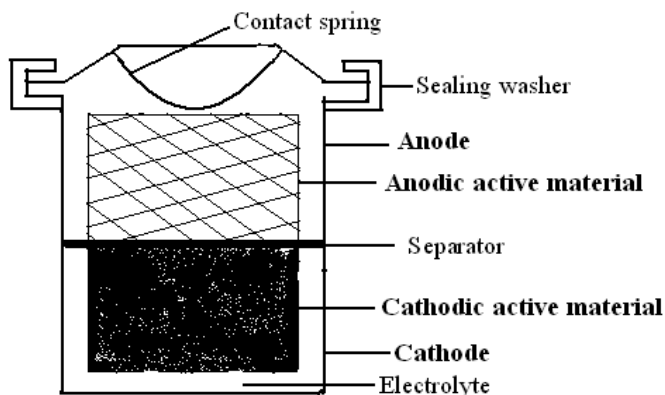
Anodic active material: MH

Cathodic active material: NiO (OH)

Electrolyte: 6M KOH

Separator: polypropylene

Voltage: 1.35V



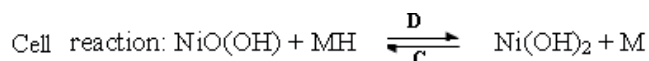
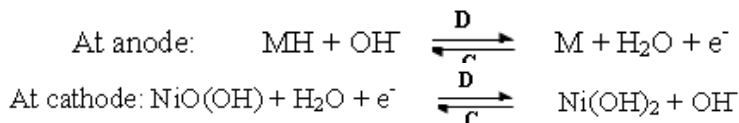
Construction:

1. In a Ni-MH cell, a hydrogen in the form of metal hydride (VH₂) acts as anodic active material and nickel oxy hydroxide as cathodic active material.
2. Both the anodic and cathodic compartments are made of Nickel grids and filled with its respective active materials.
3. The electrolyte used is potassium hydroxide solution.
4. Polypropylene used as a separator that separates the two electrodes and behaves as a medium for absorbing the electrolyte.
5. The output voltage is 1.35V.

Working:

When battery is discharging/charging, the following reactions takes place at respective electrodes.

Reactions:



Applications:

- Used in Cellular phones and laptops
- In Emergency lights and Power tools
- In electric vehicles

Lithium battery:

Lithium is the lightest of metals and it can float on water. The electrochemical properties of lithium are excellent and it is a highly reactive material. These properties give Lithium the potential to achieve very high energy and power densities in high-density battery applications such as automotive and standby power. Lithium batteries are primary batteries in which lithium metal (or) lithium compound acts as a Anode. A lithium cell can produce voltage from 1.5 V to about 3 V based on the types of materials used.

There are two types of lithium-based batteries available.

1. Lithium batteries
2. Lithium-ion batteries

In lithium batteries, a pure lithium metallic element is used as anode. These types of batteries are not rechargeable.

In lithium-ion batteries, lithium compounds are used as anode. These batteries are known as re-chargeable batteries. Therefore, Lithium ion batteries are considered as best than pure Lithium based batteries.

By comparison, lithium-ion batteries are rechargeable batteries in which lithium ions move between the anode and the cathode, using an intercalated lithium compound as the electrode material instead of the metallic lithium used in lithium batteries.

LiMnO₂ battery

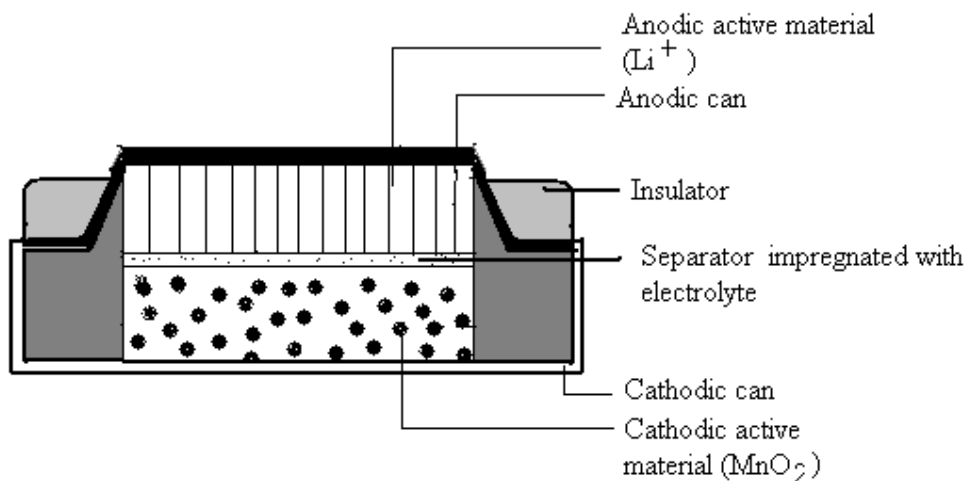
Anodic active material: Lithium

Cathodic active material: MnO₂

Electrolyte: Lithium halide (LiCl, LiBr, LiClO₄ and LiAlCl₄)

Separator: polypropylene

Voltage: 3.0



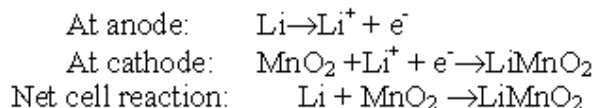
Construction:

1. Lithium Manganese Dioxide cell, is a primary battery. Anodic active material is Lithium metal (in the form of disc) and cathode is manganese dioxide (in the form of a pellet).
2. The electrolyte is lithium halide dissolved in organic solvent.
3. Separator is polypropylene impregnated with the electrolyte. It provides an electrical contact between the two electrodes.
4. The output voltage is 3.0V.

Working:

When battery is discharging, the following reactions take place at respective electrodes.

Reactions:



Application:

- Outdoor use (requiring a low temperature range)
- In high-discharge devices, which include digital cameras, electric watches, hearing aids, walkie-talkies, portable televisions, handheld video games, etc

Lithium-ion battery:

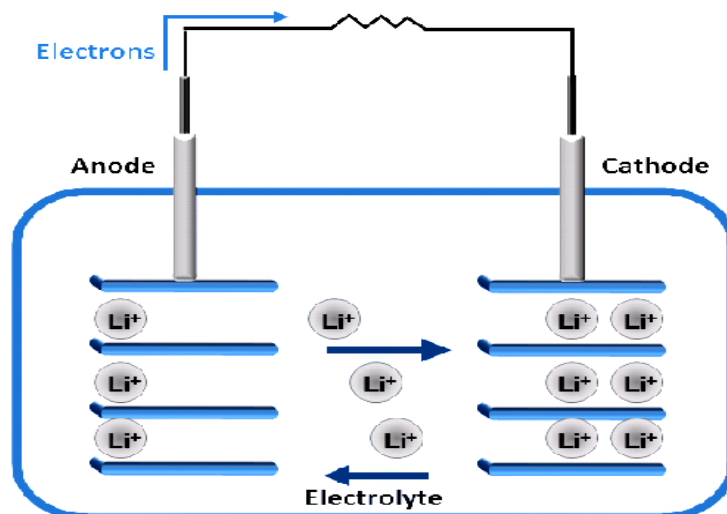
Anodic active material: Li^+ / graphite

Cathodic active material: LiCoO_2

Electrolyte: Lithium salt

Separator: polypropylene

Voltage: 3.6V



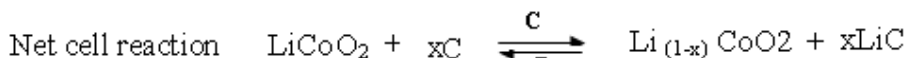
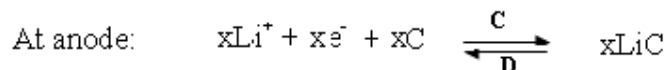
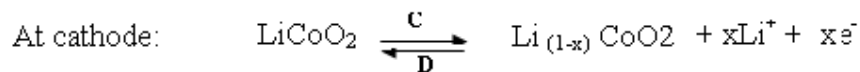
Construction:

1. In lithium-ion battery (Li-ion battery or LIB), the lithium ions (electrons) move from the negative electrode (anode) to the positive electrode (cathode) during discharge and back when charging.
2. Anode is made of carbon material with a high energy density and large doping capacity of lithium ion. Cathodes are metal oxide material containing lithium with capable of dedoping lithium ion during charging and undergo lithium doping during discharging.
3. Electrolyte is made of lithium salts in an organic solvent (LiPF_6 , LiBF_4 or LiClO_4 in an organic solvent, such as ether,). Lithium ion migrates between the two electrolytes via an organic solvent.
4. Separator used is polypropylene.
5. The output voltage of this battery is 3.6V.

Working:

During charging lithium ion in cathodic side (positive electrode) is migrated and move towards anodic side (negative electrode) and during charging lithium ions move from anode to cathode.

Reactions:



Application:

- The Li-ion batteries are used in mobile phones, cameras, calculators, LCD TVs, pagers, to operate laptop computers and aerospace application

FUEL CELLS

Fuel cell is a device, which converts chemical energy of the fuel, and oxidant into electrical energy. Electrical energy is obtained by the combustion of fuels in these galvanic cells. Here, the fuels are supplied from outside and do not form integral part of the cell. These do not store energy. Electrical energy can be obtained continuously as long as the fuels are supplied and the products are removed simultaneously. In these aspects, fuel cells differ from conventional electrochemical cells.

“Fuel cells are galvanic cells which converts chemical energy of the fuels into electrical energy through catalyzed redox reactions with elimination of minimum harmful biproducts”.

Fuel is represented as

Fuel / electrode / electrolyte / electrode / oxidant

At anode, fuel undergoes oxidation, when battery discharge potential, the following reactions takes place at respective electrodes.



At cathode, oxidant is reduced, oxidant + ne \longrightarrow reduced product

Limitation of Fuel cell

- Power output is moderate.
- Fuels are to be stored in tanks under very high pressure in tanks.
- The refueling and the starting time of fuel cell vehicles are longer and the driving range is shorter than in a “normal” car.
- It generates only DC and should be converted to AC.

Advantages of fuel cells:

- Do not pollute the atmosphere
- Electrical energy can be obtained continuously.
- Fuel cell provides high quality of DC power.
- Fuel cells have a higher efficiency than diesel or gas engines.

Difference between conventional cell and fuel cell

S. No	Conventional battery	Fuel cells
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1	Battery makes electricity from the energy it has stored inside the battery	Fuel cell makes its electricity from fuel in an external fuel tank
2	Battery may run dead	Fuel cell will make electricity as long as fuel is supplied
3	Store chemical energy	Do not store chemical energy
4	Reactants are not supplied and the products are not removed	Reactants are supplied continuously and the products are removed simultaneously
5	Construction cost is high	Construction cost is low
6	Life time is less	Life time is higher than battery
7	Battery produce electricity depends on concentration of the electrolyte	fuel cell will produce electricity as long as it has a fuel supply
8	Recharge of the cell is required.	Recharge of the fuel cell is not required.

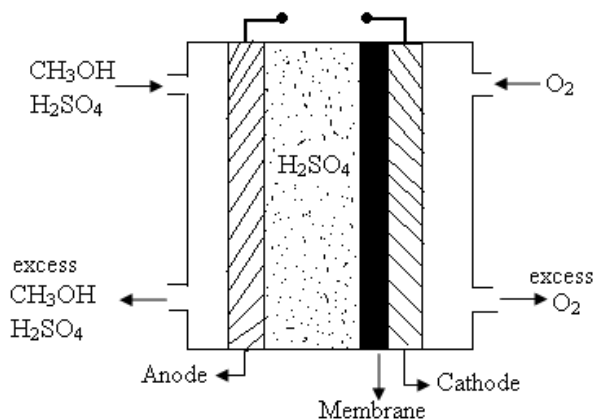
Methanol – oxygen fuel cell

Fuel: CH_3OH

Oxidant: Oxygen

Electrolyte: H_2SO_4

Voltage: 1.2V

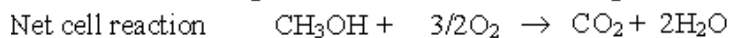
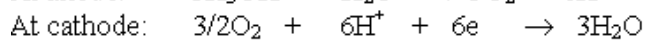
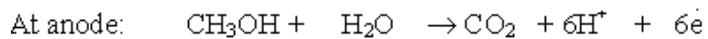


Construction:

1. It consists of anodic and cathodic compartments. Both the compartments contain platinum electrode.
2. Methanol containing H_2SO_4 is passed through anodic compartment. Oxygen is passed through cathodic compartment.
3. Electrolyte used is of sulphuric acid.
4. A membrane made of cellulose is provided which prevents the diffusion of methanol into the cathode.
5. The output voltage is 1.2V.

Working:

Reactions:



Application:

- Used in military applications
- Large-scale power productions.

Note:

1. *KOH is not used as electrolyte as it reacts with CO₂ and gets converted into carbonate. Thus, conductivity of the electrolyte decreases as well as the efficiency.*
2. *The advantage of acid electrolyte is that the CO₂, a product of the reaction can be easily removed.*

Module-2**Corrosion Science and Metal Finishing**

Corrosion: Introduction, Electrochemical theory of corrosion, Factors affecting the rate of corrosion: ratio of anodic to cathodic areas, nature of metal, 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: Anodizing – Anodizing of aluminium, Cathodic protection - sacrificial anode and impressed current methods, Metal coatings - Galvanization.

Metal finishing: Introduction, Technological importance. Electroplating: Introduction, principles governing electroplating-Polarization, decomposition potential and overvoltage. Electroplating of chromium (hard and decorative). Electroless plating: Introduction, electroless plating of nickel & copper, distinction between electroplating and electroless plating processes.

RBT Levels: L1 & L2)

Course outcome: Causes & effects of corrosion of metals and control of corrosion. Modification of surface properties of metals to develop resistance to corrosion, wear, tear, impact etc. by electroplating and electroless plating.

Corrosion Science**Introduction:**

The term corrosion is used to denote a change. A metal changes from its elementary state to the combined state when it comes in contact with liquid medium. This is actually due to the chemical interaction between the metal and the environment.

Definition: “*The spontaneous deterioration and consequent loss of a metal/alloy due to chemical/electrochemical attack by the environment*”.

Example: When iron metal is exposed to the moist environment, the metal forms a hydrated ferric oxide called rust which is relatively non-protective.

Most of the corrosion cases are electrochemical in nature taking place by an electrochemical attack on the metal in the presence of air and moisture (H₂O) called **wet corrosion**. The mechanism of the wet corrosion is explained on the basis of electrochemical theory of corrosion.

Electrochemical theory of corrosion:

According to this theory,

1. When a metal is in contact with moist air or when dissimilar metals are contact with each other in a solution, large numbers of galvanic cells are formed with the existence of anodic and cathodic area on the metal.
2. In this corrosion, oxidation of the metal and reduction of species present in solution takes place.
3. The anodic part of the metal undergo oxidation and suffers from corrosion, cathodic part undergo reduction and protected from corrosion.
4. The electrons are transferred through the metal from anode to cathode.
5. During corrosion the following reactions takes place.

At anode (oxidation reaction) : $M \rightarrow M^{n+} + ne^{-}$

The reaction at cathode (reduction reaction) depends on the nature of the environment:

If the medium is acidic,

In the presence of dissolved oxygen: $2H^{+} + \frac{1}{2}O_2 + 2e^{-} \rightarrow H_2O$

In the absence of dissolved oxygen: $2H^{+} + 2e^{-} \rightarrow H_2 \uparrow$

If the medium is alkaline/neutral,

In the presence of dissolved oxygen: $H_2O + \frac{1}{2}O_2 + 2e^{-} \rightarrow 2OH^{-}$

In the absence of dissolved oxygen: $2H_2O + 2e^{-} \rightarrow 2OH^{-} + H_2 \uparrow$

Example: Rusting of an Iron in the presence of moist air

Anodic reaction : $Fe \rightarrow Fe^{2+} + 2e^{-}$

Cathodic reaction : $H_2O + \frac{1}{2}O_2 + 2e^{-} \rightarrow 2OH^{-}$

Products of anode & cathode : $Fe^{2+} + 2OH^{-} \rightarrow Fe(OH)_2$

In the presence of oxygen : $2Fe(OH)_2 + \frac{1}{2}O_2 \rightarrow Fe_2O_3 \cdot 2H_2O$
(Rust)

Factors affecting the rate of corrosion

Nature of the metal:

- 1) Position of the metal/alloy in the galvanic series decides the rate of corrosion.
- 2) The metal top in the series is more anodic and undergoes corrosion faster than the metal below it.
- 3) The rate of corrosion depends upon the difference in the position of the metals in the galvanic series. Greater the difference faster is the corrosion at anode.

Nature of the corrosion product:

- 1) In a moist atmosphere almost all metals get covered with a thin surface film of metal oxide as the corrosion product.
- 2) If the corrosion product is nonporous protective in nature prevents the further corrosion. The layer acts as a barrier between the fresh metal surface and corrosive environment.
- 3) If the corrosion product is porous, it continues the corrosion processes.

pH of the medium:

- 1) The rate of corrosion increases with decrease in pH of the medium.
- 2) Acidic media are generally more corrosive than alkaline/neutral media. This is due to evolution of hydrogen at cathode.
- 3) When the $pH < 4$, the rate of corrosion increases due to higher concentration of H^{+} ions. When $pH > 10$, the rate of corrosion decrease due to formation of insoluble metal hydroxides on the surface of metal.

Temperature:

- 1) Generally rate of corrosion increases with increase in temperature.
- 2) As the temperature increases conductance of the ions in the medium increases which reduces the polarization. Therefore the rate of corrosion increases.
- 3) A passive metal become active at high temperature and increases the rate of corrosion.

Area effect:

- 1) The rate of corrosion (x) is directly proportional to the ratio of area of cathode to the area of anode. i.e., $x = \text{area of cathode} / \text{area of anode}$
- 2) Higher the value of x , greater is the rate of corrosion.
- 3) When anode is small and cathode is large, all the electrons liberated at anode and are consumed at the cathode. Therefore the rate of anodic reaction is greater and increases the extent of corrosion.

Conductivity:

- 1) The rate of corrosion increases with increase in the conductance of the medium.
- 2) As the conductance of the medium increases, ions can move easily through the medium.
- 3) This decreases the polarization potential and due to this rate of corrosion increases.

Types of corrosion: Corrosion can be classified into 3 types as follows

- 1) Differential metal corrosion (Galvanic corrosion)
- 2) Differential aeration corrosion
- 3) Stress corrosion

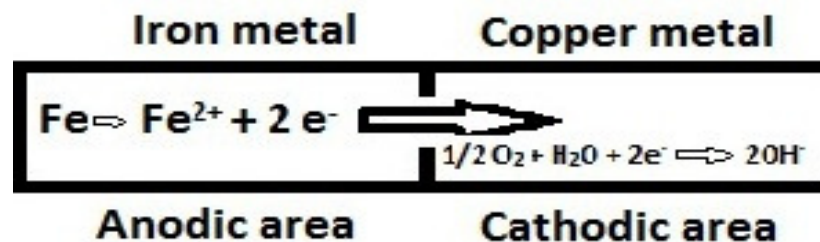
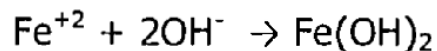
Differential metal corrosion (Galvanic corrosion)

- 1) When two dissimilar metals are in direct contact with one another and exposed to a corrosive medium, the metal with lower electrode potential becomes anode and suffers from corrosion, whereas the metal with higher electrode potential becomes cathode and protected from corrosion. This type of corrosion is known as differential metal corrosion or galvanic corrosion.
- 2) The rate of corrosion depends mainly on the difference in the position of the two metals in galvanic series.
- 3) Higher the difference, faster is the rate of corrosion.

Example: Electrode potential of iron (-0.44 V) is less than that of copper (0.34 V). Therefore when iron is in contact with copper, iron becomes anodic and undergoes corrosion, whereas copper becomes cathodic and protected from the corrosion.

At anode: $\text{Fe} \rightarrow \text{Fe}^{+2} + 2\text{e}^-$

At cathode: $\text{H}_2\text{O} + \frac{1}{2} \text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^-$

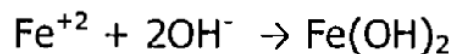
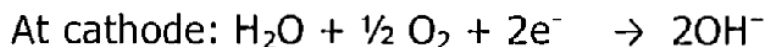
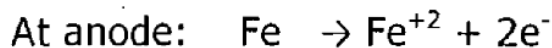
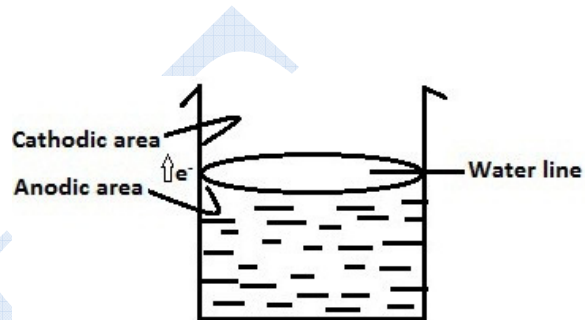


Differential aeration corrosion

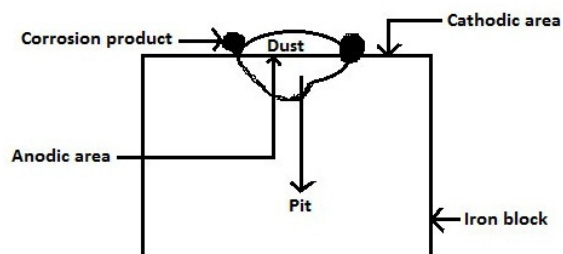
- 1) When a metal is exposed to different concentration of air (O_2), part of the metal exposed to lower concentration of O_2 becomes anodic and undergoes corrosion.
- 2) Other part of the metal exposed to higher concentration of O_2 becomes cathodic and protected from the corrosion.
- 3) The difference in O_2 concentration produces a potential difference and causes corrosion. This type of corrosion is called differential aeration corrosion.

Example: 1 Water line corrosion

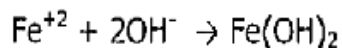
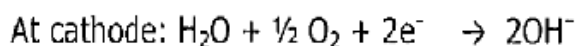
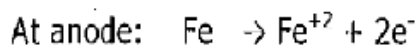
- 1) It is observed in steel or iron water tank partially filled with water. Part of the tank just below water level is exposed to lower concentration of O_2 becomes anodic and undergoes corrosion.
- 2) Part of the tank above the water line which is exposed to higher concentration of O_2 becomes cathodic and protected from the corrosion.
- 3) More corrosion is observed just below the water line; hence this type is called water line corrosion.

**Example: 2 pitting corrosion**

1. Pitting corrosion is observed when dust particles get deposited over the metal surface.
2. The portion of the metal covered by dust which is less aerated becomes anodic and suffers from corrosion.
3. Thus, metal is lost below the surface of dust particle forming a deep and narrow pit.
4. The adjacent area of the metal which is exposed to higher concentration of O_2 becomes cathodic and protected from corrosion.



The reactions involved are as follows



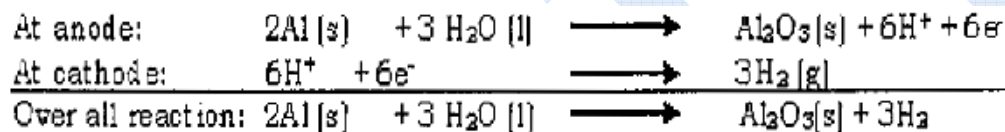
Corrosion control**Inorganic coatings (Chemical conversion coatings)**

These coatings are produced at the surface of the metal by chemical/electrochemical reactions.
Examples: Anodizing and Phosphating

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 protective layer.

Anode : Aluminium
Cathode : Steel or Copper
Electrolyte : 5-10% chromic acid
Temperature : 30-40 °C
Applied potential : 0-40 V

Aluminum is made as anode and copper or steel is used as cathode. The electrodes are immersed in an electrolyte consisting of 5-10% chromic acid. The temperature is maintained at 30-40 °C. Potential of 0-40 V is applied which oxidizes outer layer of Al to Al₂O₃ and that get deposited over the metal. The reactions involved are as follows



The anodized coatings are thicker than the natural oxide film and possess improved corrosion resistance as well as resistance to mechanical injury.

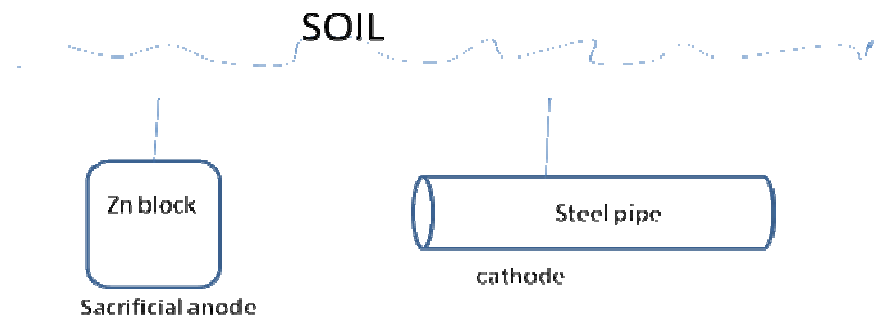
Cathodic Protection: The principle is to force the metal to be protected to behave as cathode. There are two types of cathodic protections namely,

- 1) Sacrificial anodic protection.
- 2) Impressed current cathodic protection.

Sacrificial anodic protection:

- 1) The metal to be protected is connected to a more anodic metal using a metallic wire.
- 2) The more active metal gets corroded while the parent structure is protected from corrosion.
- 3) The more active metal so employed is called sacrificial anode.
- 4) The sacrificial anodes to be replaced by fresh ones as and when it is required.
- 5) Commonly used sacrificial anodes are:
Mg, Zn, Al etc.

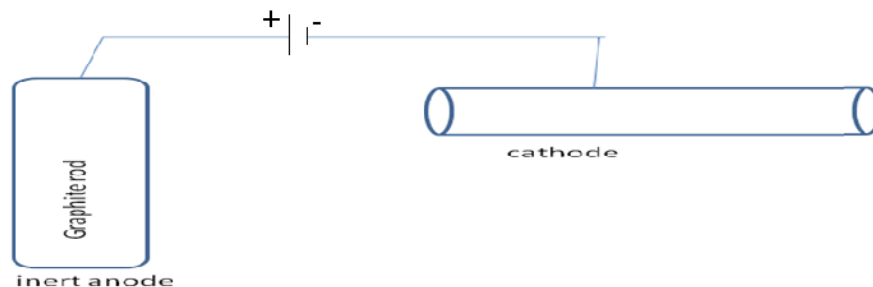
Example: steel pipe is protected by connecting it to a block of Zn. In such cases steel acts as a cathode and is unaffected or protected from corrosion and Zn act as



anode and undergoes sacrificial corrosion.

Impressed current protection:

- 1) In this method, electrons are supplied from a source of direct current.
- 2) Metal structure to be protected acts as cathode and connected to -ve terminal of battery.
- 3) The inert metal like graphite act as anode and connected to + ve terminal of battery.
- 4) When DC current is applied in a reverse direction to nullify the corrosion reaction.
- 5) Since anode is inert metal no reaction takes place at anode therefore the cathodic metal is protected from corrosion.

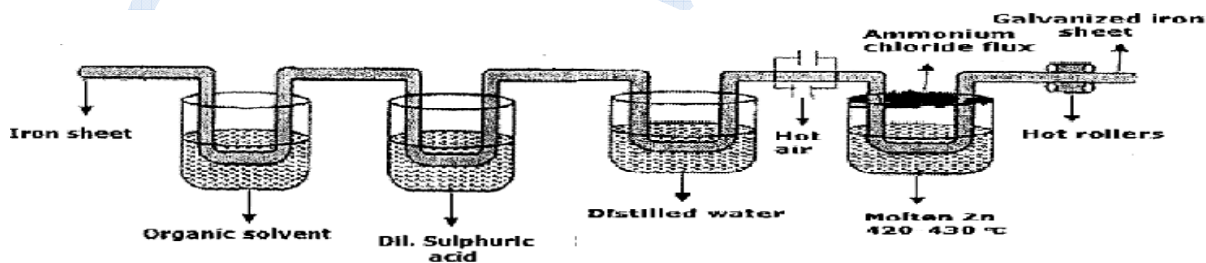


Impressed current protection

Metal coatings

Metal coatings can be applied on the base metal by hot dipping process. This method is used for producing a coating of low melting metals such as Zn, Al, Sn etc, on iron/steel metals which have relatively high melting point. Example: Galvanizing and Tinning

Galvanization: Coating of zinc on iron or steel by hot dipping process is called galvanizing. (M.P of Zn=419 °C) It is carried out as follows,



- 1) The iron sheet is subjected to pretreatment by degreasing with organic solvent.
- 2) The sheet is passed through dilute H_2SO_4 to remove any rust.
- 3) Washed with distilled water and dried by supplying hot air.
- 4) Then iron sheet is dipped in molten bath of Zn at $419^\circ C$ and surface is covered with NH_4Cl flux which prevents the oxidation of Zn metal.
- 5) The excess of coated metal is removed by passing through a pair of hot rollers and cooled gradually.

Metal Finishing

Introduction: Metal finishing covers the wide range of processes carried out in order to modify the surface properties of a metal. These processes involve deposition of a layer of another metal or a polymer, conversion of a surface layer of atoms into oxide films which ultimately modify the surface of the metal.

Definition: “It is a process of modifying surface properties of metals by the deposition of a layer of another metal or polymer on its surface or by the formation of an oxide film”.

Technological importance of metal finishing:

The main technological importance of metal finishing include

- [1] Imparting the metal surface to higher corrosion resistance.
- [2] Providing electrical and thermal conducting surface.
- [3] Imparting thermal resistance and hardness.
- [4] In the manufacture of electrical and electronic components such as PCB's, capacitors contacts, etc.
- [5] To increase the decorativeness of metal surface.

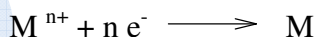
Principles of electroplating

1) Polarization:

The polarization is an electrode phenomenon. The electrode potential is determined by the Nernst equation,

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

M^{n+} is the concentration of the metal ions surrounding the electrode surface at equilibrium. When there is a passage of current, the metal ion concentration near the electrode surface decreases due to the reduction of some of the metal ions into metal atoms. There exist a concentration gradient between electrode surface and bulk concentration. Therefore there is a shift in the equilibrium and a change in electrode potential. However equilibrium is re-established due to the diffusion of metal ions towards the electrode.



Therefore polarization can be defined as the process where there is a variation of electrode potential due to the inadequate supply of species from the bulk of the solution to the electrode is known as “polarization”.

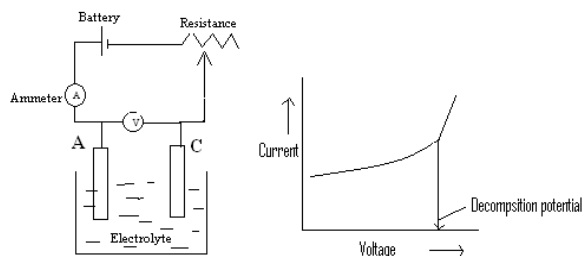
2) Decomposition potential: It is defined as “The minimum voltage that must be applied in order to bring about continuous electrolysis of an electrolyte”. The decomposition potential is represented as

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

This can be determined by an electrolytic cell.

Determination of decomposition potential: The decomposition potential is determined using an electrolytic cell as shown in the figure. The cell consists of two platinum electrodes immersed

in a dilute solution of an acid or a base. The voltage is varied along the wire and the current passing through the cell is measured using an ammeter. At low voltage no reaction occurs and there is a very slight increase in the current & small amount of hydrogen & oxygen are liberated at the cathode & anode respectively. On increasing the voltage to slightly above 1.7V, there is an abrupt increase in the current and process of electrolysis begins. A plot of the current against the applied voltage is shown.



3) Over voltage: It is defined as “The excess voltage that has to be applied above theoretical decomposition potential to bring the continuous electrolysis of an electrolyte is known as over voltage”. For example theoretical potential of oxygen at platinum electrode is 1.23V. But the actual discharge potential of oxygen is 1.68V. The excess 0.45V is the over voltage of oxygen on platinum electrode surface.

Over voltage = (Experimental decomposition potential – Theoretical decomposition potential)

Electroplating

Definition: “It is a process of deposition of a metal by electrolysis, over the surface of substrate. The substrate may be another metal, polymer, ceramic, or a composite”.

Electroplating of chromium

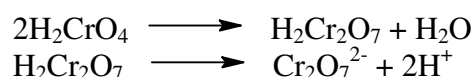
Chromium is one of widely used metal in electroplating industries. In the field of electroplating two types of Chromium are employed, decorative Chromium and hard Chromium.

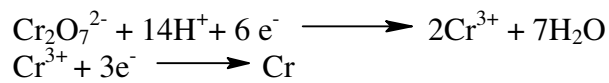
Pretreatment: Before the application of the electroplated coatings, it is essential to clean the surface of the base metal. The impurities present on the surface like grease, oil, oxide layer, dust etc are removed by solvent cleaning or alkali cleaning or mechanical cleaning.

Decorative / hard chromium:

Bath composition	: 250g Chromic acid + 2.5g H ₂ SO ₄ proportion/dm ³
Temperature	: 45-60°C. / 45-55°C
Current Density	: 145- 430 A m ⁻² / 290-580 A m ⁻²
Anode	: Insoluble anodes like pb-sb
Cathode	: Object to be electroplated.

Mode of plating: The plating bath contains CrO₃ in which Cr is in +6 oxidation state. This is reduced to +3 oxidation state in the presence of SO₄²⁻ furnished by H₂SO₄. Cr³⁺ ions are reduced to elemental Cr which gets deposited on the surface of cathode. The reactions taking place are given below.



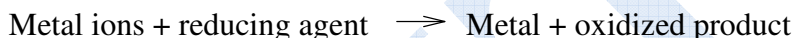
SAI VIDYA INSTITUTE OF TECHNOLOGY**Applications:**

1. Decorative chromium provides a durable finish on cycles, automobiles, furniture's, household fittings, air craft, surgical instruments etc.
2. Hard chromium is used in the manufacture of cutting tools, piston rings, cylindrical liners etc.

Note: Chromium anodes are not used in Chromium plating because Chromium metal deactivates strongly in acid medium.

Electroless plating (Auto catalytic redox reaction)

Definition: "The process of depositing a metal over substrate by controlled chemical reduction of metal ion by a reducing agent without using electric current is called electroless plating"

**Differences between electroplating and electrolessplating:**

Property	Electro plating	Electroless plating
1) Driving force	Passage of current	Auto catalytic redox reaction
2) Anode	A separate anode is used	Catalytic surface of the substrate acts as anode
3) Reducing agent	Electrons bring about reduction	Chemical reagents bring about reduction
4) Applicability	Applicable only to conductors	Applicable to both conductors and nonconductors

Electroless plating of nickel : Electroless plating of nickel involves the following features.

Pretreatment and activation of the surface:

The surface to be plated is first degreased by using organic solvents followed by acid treatment.

Metals and like Al, Cu, Fe, and Brass etc be directly nickel plated without any activation.

Stainless steel surface is activated by dipping in hot solution of 50% dilute H₂SO₄.

Activation of Mg alloy surface is carried out by giving a thin coating of Zn and Cu over it.

Activation of nonmetallic articles is carried out by first dipping in SnCl₂ solution containing HCl, followed by dipping in palladium chloride solution.

Composition of bath:

Acid nickel bath:

Coating solution	: NiCl ₂ solution 20g/L
Reducing agent	: Sodium hypophosphite 20g/L
Buffer	: Sodium acetate 10g/L
Complexing agent	: Sodium succinate 15g/L
pH	: 4.5
Temperature	: 93°c

Alkaline nickel bath:

Coating solution	: NiCl ₂ solution 30g/L
Reducing agent	: Sodium hypophosphite 20g/L
Buffer	: Ammonium chloride 50g/L
Complexing agent	: Ammonium citrate 55g/L
pH	: 8 – 10
Temperature	: 90°c
Chemical Reactions:	
Anodic Reaction	: $\text{H}_2\text{PO}_2^- + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{PO}_3^- + 2\text{H}^+ + 2\text{e}^-$
Cathodic reaction	: $\text{Ni}^{2+} + 2\text{e}^- \longrightarrow \text{Ni}$
Net Reaction	: $\text{Ni}^{2+} + \text{H}_2\text{PO}_2^- + \text{H}_2\text{O} \xrightarrow{\text{Catalytic surface}} \text{Ni} + \text{H}_2\text{PO}_3^- + 2\text{H}^+$

Note: Buffer is added because, the above redox reaction involve the liberation of H⁺ ions, so pH of the solution goes down as the reaction proceeds, there by adversely affecting the quality of the deposit as well as plating rate.

Advantages:

1. Electroless nickel deposits are free from pores and possess better corrosion resistance than electro plated nickel deposit.
2. It gives rise to harder surface with better wear resistance.

Applications:

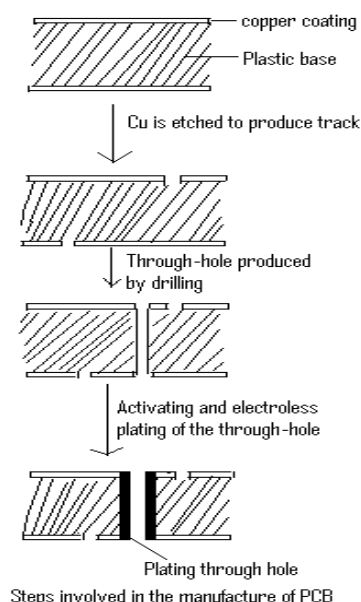
1. Used to plate on industrial components such as pumps and valves, shafts, gears, reaction vessels and other tools.
2. Electroless nickel coated polymers finds preferred decorative applications.
3. Electroless plating of nickel finds applications in domestic as well as automotive fields.

Electroless plating of copper over PCB: Electroless plating of copper involves the following features.

Pretreatment and activation of the surface: The surface to be plated is first degreased by using organic solvents followed by acid treatment. PCBs are activated by first dipping in SnCl₂ solution containing HCl followed by dipping in palladium chloride solution.

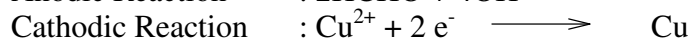
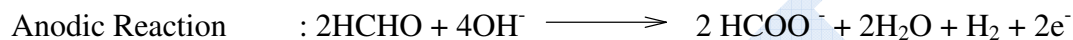
Composition of the bath:

Coating solution	: CuSO ₄ .5H ₂ O (15g/L)
Reducing Agent	: Formaldehyde (8g/L)
Buffer	: NaOH (15g/L) + Rochelle salt (14g/L)
Complexing agent	: EDTA solution (20g/L)
p ^H	: 11
Temperature	: 25 °c



Procedure:

A thin layer of copper is first electroplated over the PCB. Then selected areas are protected by employing electroplated image and the remainder of the plated copper is etched away so as to get required type of circuit pattern. Usually double sided tracks are made in order to pack more number of components in a small space. Finally, the connection between 2 sides of PCB is made by drilling holes. The holes are activated and followed by electroless copper plating through holes.

Chemical Reactions:

Note: Buffer is added because; above redox reaction involves the consumption of OH^- ions, so the p^{H} of the solution decreases as the reaction proceeds.

Application:

- [1] Widely used for metalizing printed circuit boards.
- [2] For plating on non-conductors.
- [3] As an undercoat for electroplating.
- [4] For decorative plating on plastics.

Module-3ENERGY SYSTEMS

Chemical Fuels: Introduction, classification, definitions of CV, LCV, and HCV, determination of calorific value of solid/liquid fuel using bomb calorimeter, numerical problems. Knocking of petrol engine – Definition, mechanism, ill effects and prevention. Power alcohol, unleaded petrol and Biodiesel.

Fuel Cells: Introduction, differences between conventional cell and fuel cell, limitations & advantages. Construction, working & applications of methanol-oxygen fuel cell with H₂SO₄ electrolyte, and solid oxide fuel cell (SOFCs).

Solar Energy: Photovoltaic cells- introduction, construction and working of a typical PV cell. Preparation of solar grade silicon by Union Carbide Process/Method. Advantages & disadvantages of PV cells.

(RBT Levels: L3)

Course outcome: Production & consumption of energy for industrialization of country and living standards of people. Electrochemical and concentration cells. Classical, modern batteries and fuel cells. Utilization of solar energy for different useful forms of energy.

Chemical Fuels

Fuel: Fuel is defined as naturally occurring or an artificially manufactured carbonaceous substance which serves as a source of heat and light.

Classification of fuels

1) Primary fuels: They are naturally occurring fuels

Ex: Solid – coal, wood, lignite, peat
 Liquid – crude oil
 Gas – biogas

2) Secondary fuels: They are derived from primary fuels

Ex: Solid – charcoal, coke, etc
 Liquid – kerosene, diesel, synthetic petrol, benzene, etc
 Gas – water gas, producer gas, LPG etc

Calorific value

“The amount of heat liberated by burning a known mass of fuel in presence of air” is called *calorific value*.

Gross calorific value or High calorific value (GCV or HCV):

The amount of heat liberated when a unit mass of a fuel is burnt in excess air & the products of combustion are cooled to room temperature” is called *Gross Calorific Value*.

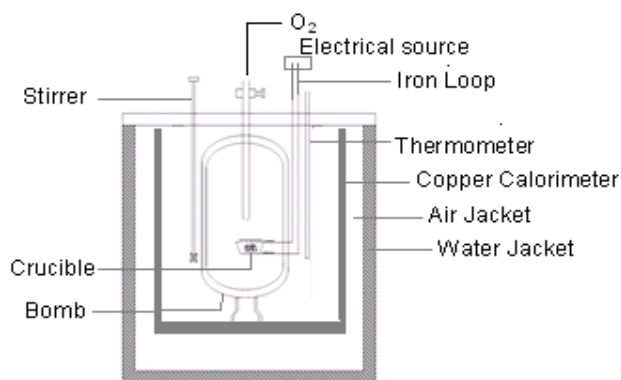
Net calorific value or Less calorific value (NCV or LCV):

The amount of heat liberated when a unit mass of a fuel is burnt in excess air and the product of combustion is allowed to escape in the atmosphere is called *Net Calorific Value*.

Net calorific value = Gross calorific value – Latent heat of steam of H₂O.

Determination of Calorific Value of fuel using Bomb Calorimeter

Construction: A bomb calorimeter consists of a cylindrical vessel fixed with inlet valve for pumping of O₂. A Ceramic or platinum crucible is placed at the bottom of the vessel connected with iron wire, the end of the wire is connected to battery. The bomb is then placed in known weight of H₂O taken in a copper calorimeter and enclosed in air & water jacket to prevent heat exchange with the surrounding. Electrical stirrer is placed one side to maintain uniform temperature and thermometer on the other side.



Working: A known weight of a fuel is taken in crucible Oxygen is pumped into a bomb at a pressure of 25-30 atm. Initial temperature of H₂O is noted. The fuel is ignited through spark produced by iron wire. The heat liberated is absorbed by surrounding water and calorimeter. The water in a jacket is continuously stirred. The maximum temperature attained by water is noted.

Principle: The amount of heat liberated by the fuel is equal to amount of heat absorbed by water and calorimeter.

Observation and calculation:

Let weight of fuel taken	= 'm' kg
Initial temperature of water	= T ₁ ° c
Final temperature of water	= T ₂ ° c
Change in temperature	= (T ₂ -T ₁) = ΔT °c
Weight of water taken in calorimeter	= 'W' kg
Water equivalent of calorimeter	= 'w' kg
Specific heat of H ₂ O	= 'S' J kg ⁻¹ c ⁻¹

$$GCV = \frac{(W + w) \text{ kg} \times S \text{ J kg}^{-1} \text{ c}^{-1} \times \Delta T \text{ } ^\circ\text{c}}{m \text{ kg}}$$

$$GCV = \frac{(W + w) S \Delta T \text{ J kg}^{-1}}{m}$$

Knocking and its mechanism

It is the rattling sound being produced in an internal combustion engine due to the explosive combustion of fuel.

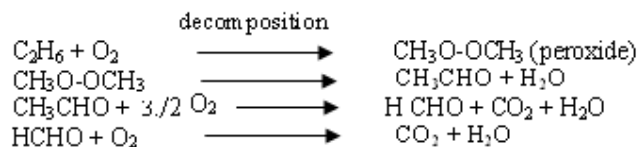
The efficiency of an IC engine depends on the *Compression ratio*.

$$\text{Compression ratio} = \frac{\text{Volume of cylinder at end of suction stroke}}{\text{Volume of cylinder at end of compression stroke}}$$

The petrol-air mixture drawn in the cylinder is compressed and ignited. Under ideal conditions (eg, CR- 5 to10) the hydrocarbons undergo combustion and the flame propagates smoothly to produce power.



But, if the hydrocarbon present is unable to withstand pressure at high compression ratio (CR > 10), then hydrocarbons of the fuel combine directly with oxygen to form unstable peroxides which decompose and burst suddenly into flames by pre ignition producing shock waves. The shock wave hits the walls of the engine part producing sound. This is called as knocking. The knocking mechanism is as follows.



Ill effects of knocking: Decreases in life of engine, causes mechanical damage to engine parts such as spark plug, piston and engine walls, more consumption of fuel and power output decreases

Prevention of Knocking using anti-knocking agents

The substances that are added to gasoline in order to decrease the knocking tendency is called “anti-knocking agents”.

The commonly used anti-knocking agent is Tetra ethyl lead (TEL), usually 1-1.5 ml of TEL is added to petrol along with ethylene dichloride or ethylene di-bromide.

Unleaded Petrol: The gasoline in which the antiknocking properties are increased without addition of lead substance is called unleaded petrol. In orders to improve the octane number of unleaded petrol some compounds like methyl tertiary butyl ether (MTBE) is added.

Addition of MTBE: Methyl tertiary butyl ether (MTBE) added to petrol (unleaded petrol) provides oxygen for combustion, thereby reduces the formation of peroxy compounds. MTBE can be used as anti knocking agent in IC engines with catalytic converter.

Advantages of Unleaded petrol

- 1) It increases the efficiency of the engine.

It permits the attachment of catalytic converters to the exhaust pipe of automobiles. The catalytic converters convert toxic gases like carbon monoxide and nitric oxide to CO₂ and N₂.

Additional information

Leaded petrol: The Petrol containing Tetra ethyl lead (TEL). Tetraethyl Lead decomposes the peroxides formed and prevents knocking. In the process, lead gets deposited on the inner walls of the engines and at spark plugs. Hence ethylene di-chloride or ethylene di-bromide is added along with tetraethyl lead. These convert the lead into PbCl₂ or PbBr₂, which are volatile and escape with exhaust gases. The release of lead compounds pollutes the atmosphere. TEL cannot be used as anti knocking agent in IC engines with catalytic converter.

Power alcohol

Power alcohol is alcohol petrol blend containing 25% of alcohol and 75% of petrol. It is used as fuel in internal combustion engine.

Advantages:

- Alcohol petrol blend processes better anti-knocking properties.
- Alcohol petrol blend can be used in an engine with higher compression ratio.
- There is no starting difficulty with alcohol petrol blend.
- Air required for the complete combustion is less.

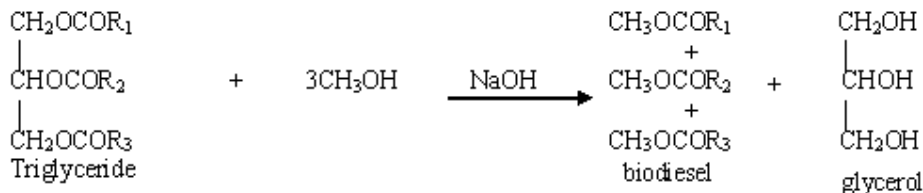
Disadvantages

- a) Alcohol lowers the calorific value of petrol
- b) Alcohol easily oxidizes to acids. Hence alcohol may cause corrosion.
- c) Alcohol absorbs moisture. As a result, separation of alcohol petrol layers takes place. To avoid these blending agents such as benzene or toluene are used.

Biodiesel: It is a mixture of mono alkyl esters of long chain fatty acids which can be produced by transesterification of the vegetable oil. The vegetable oils like soya bean oil, palm oil, sunflower oil etc.,

Preparation: It is a mixture of esters produced by the process of transesterification of vegetable oil with excess of methanol in presence of NaOH as catalyst. The resultant mixture containing glycerol is

removed by gravity separation method; the esters are used as an alternative fuel to diesel in automobiles.



Where R1, R2 and R3 are long chain fatty acids in oil.

Advantages: It has higher cetane number (48-60) compared to diesel (40-55), non toxic and eco friendly products are formed.

Disadvantages: Cost of production is high, Release nitrogen oxide which can lead to the formation of smog and As Biodiesel cleans the dirt from the engine, this dirt can then get collected in the fuel filter, thus clogging it. So, filters have to be changed after the first several hours of biodiesel use.

FUEL CELLS

INTRODUCTION:

Fuel cell is a device, which converts chemical energy of the fuel, and oxidant into electrical energy. Electrical energy is obtained by the combustion of fuels in these galvanic cells. Here, the fuels are supplied from outside and do not form integral part of the cell. These do not store energy. Electrical energy can be obtained continuously as long as the fuels are supplied and the products are removed simultaneously. In these aspects, fuel cells differ from conventional electrochemical cells.

“Fuel cells are galvanic cells which converts chemical energy of the fuels into electrical energy through catalyzed redox reactions with elimination of minimum harmful biproducts”.

Fuel is represented as

Fuel / electrode / electrolyte / electrode / oxidant

At anode, fuel undergoes oxidation, When battery discharge potential, the following reactions takes place at respective electrodes.

Fuel \longrightarrow oxidized product + ne

At cathode, oxidant is reduced, oxidant + ne \longrightarrow reduced product

Difference between conventional cell and fuel cell

S. No	Conventional battery	Fuel cells
1	Battery makes electricity from the energy it has stored inside the battery	Fuel cell makes its electricity from fuel in an external fuel tank
2	Battery may run dead	Fuel cell will make electricity as long as fuel is supplied
3	Store chemical energy	Do not store chemical energy
4	Reactants are not supplied and the products are not removed	Reactants are supplied continuously and the products are removed simultaneously
5	Construction cost is high	Construction cost is low
6	Life time is less	Life time is higher than battery
7	Battery produce electricity depends on concentration of the electrolyte	fuel cell will produce electricity as long as it has a fuel supply
8	Recharge of the cell is required.	Recharge of the fuel cell is not required.

Limitation of Fuel cell

1. Power output is moderate.
2. Fuels are to be stored in tanks under very high pressure in tanks.
3. The refueling and the starting time of fuel cell vehicles are longer and the driving range is shorter than in a “normal” car.
4. It generates only DC and should be converted to AC.

Advantages of fuel cells:

1. Do not pollute the atmosphere
2. Electrical energy can be obtained continuously.
3. Fuel cell provides high quality of DC power.
4. Fuel cells have a higher efficiency than diesel or gas engines.

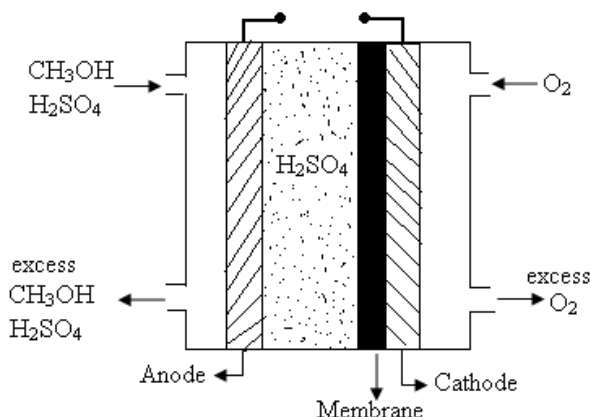
Methanol – oxygen fuel cell

Fuel: CH₃OH

Oxidant: Oxygen

Electrolyte: H₂SO₄

Voltage: 1.2V

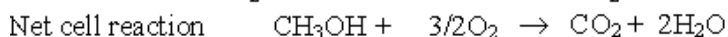
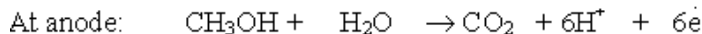


Construction:

1. It consists of anodic and cathodic compartments. Both the compartments contain platinum electrode.
2. Methanol containing H₂SO₄ is passed through anodic compartment. Oxygen is passed through cathodic compartment.
3. Electrolyte used is of sulphuric acid.
4. A membrane made of cellulose is provided which prevents the diffusion of methanol into the cathode.
5. The output voltage is 1.2V.

Working:

Reactions:



Application:

- Used in military applications
- Large-scale power productions.

Note:

1. *KOH is not used as electrolyte as it reacts with CO₂ and gets converted into carbonate. Thus, conductivity of the electrolyte decreases as well as the efficiency.*
2. *The advantage of acid electrolyte is that the CO₂, a product of the reaction can be easily removed.*

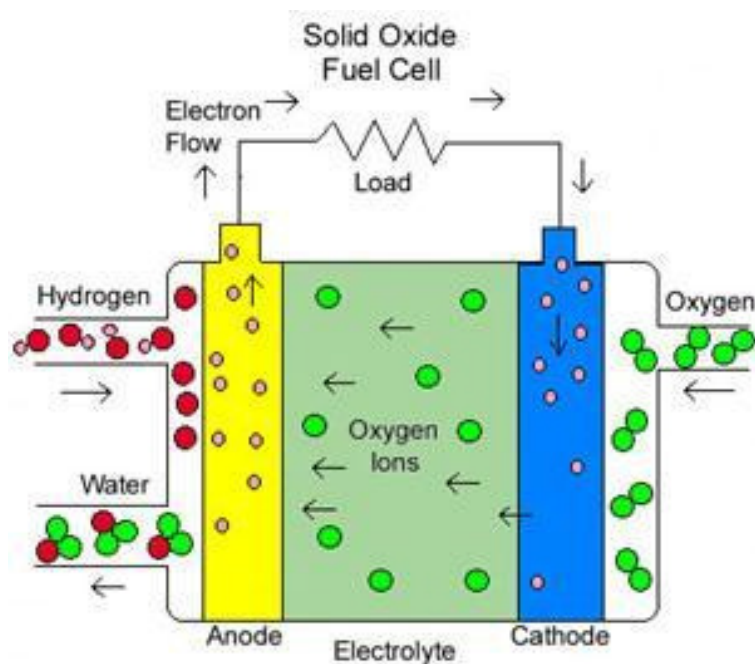
Solid oxide fuel cell (SOFCs): Solid oxide fuel cell is a device which converts gaseous fuel via an electro chemical process directly into electricity.

Fuel: Any gaseous fuel (Natural gas)

Oxidant: Oxygen

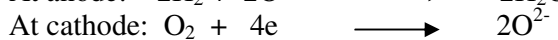
Electrolyte: Mixture of yttrium dioxide and zirconium dioxide

Voltage: 1.1V



Construction: It consists of anodic and cathodic compartments. The anodic compartment is made of Nickel oxide or zirconium oxide whereas cathode is made of lanthanum manganate. Electrolyte used is a solid electrolyte like a mixture of yttrium dioxide and zirconium dioxide. Any gaseous fuel (H₂, CO, CH₄ or H₂+CO) is used as a fuel and oxygen is used as oxidant. The cell operates at a temperature of about 1000°C.

Working:



Applications:

- It is used for space heating, water heating, etc.,
- It is used as locomotives.

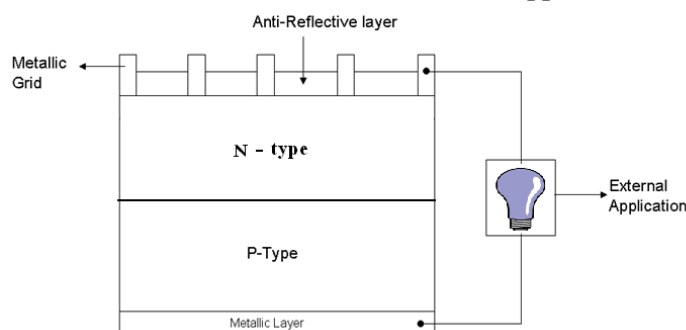
Solar Energy

Photovoltaic cells: (Solar cells) The device which converts solar energy into electrical energy is called photovoltaic cell and the phenomenon is called photovoltaic effect.

Principle: The principle involved is the ejection of electrons from metal surface by striking with photons of solar radiation.

Construction: The device consists of p-n junction diode coated with anti reflective layer (TiO₂). Two electrical contacts is provided, one in the form of metallic grid at the top of the junction and the other is a layer silver on the bottom of the cell. The antireflective layer coated in between the metallic grids allows light to fall on the semiconductor.

Working: The photons of solar radiations enters n-type semiconductor breaks barrier potential and moves to p-type semiconductor where photons knocks the electrons in p type to form electron hole pair. The free electrons so formed will travels through the circuit from n-type and recombines with holes again in p-region. The movement of electrons from n type to p type generates electric current. The electrical energy produced from the solar cell is used for various applications.



Advantages of PV cells: Eco friendly energy conversion devices do not undergo corrode and no moving parts in PV cell, hence no wear and tear

Disadvantages of PV cells: Installation cost is high, produced only during the day time and generates only DC current

Importance of photovoltaic cells: PV cell directly convert sunlight into electricity, do not pollute the nature, to improve remote area communication systems and in transportation systems, milling, sawing etc.,

Production of solar grade silicon (union carbide process)

The production of solar cell grade silicon is carried out in different stages:

In this process SiO₂ is treated with carbon in electric arc furnace at 1500-2000°C to produce Silicon.

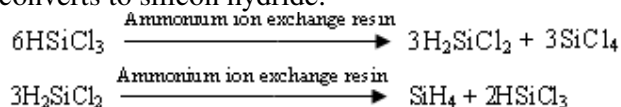


The molten silicon obtained is treated with O₂ and fresh silica as flux to remove impurities Al, Ca and Mg.

Metallurgical grade silicon is treated with HCl at 300°C to form trichlorosilane



Trichlorosilane is then passed through fixed bed columns containing ammonium ion exchange resin catalyst where trichlorosilane converts to silicon hydride.



The products are separated by distillation and trichlorosilane are recycled. The poly silicon is obtained through pyrolysis of SiH₄ in silicon seed rods mounted in a metal bell jar reactor..



MODULE 4**Environmental Pollution and Water Chemistry**

Environmental Pollution: Air pollutants: Sources, effects and control of primary air pollutants: Carbon monoxide, Oxides of nitrogen and sulphur, hydrocarbons, Particulate matter, Carbon monoxide, Mercury and Lead. Secondary air pollutant: Ozone, Ozone depletion.

Waste Management: Solid waste, e-waste & biomedical waste: Sources, characteristics & disposal methods (Scientific land filling, composting, recycling and reuse).

Water Chemistry: Introduction, sources and impurities of water; boiler feed water, boiler troubles with disadvantages -scale and sludge formation, boiler corrosion (due to dissolved O₂, CO₂ and MgCl₂). Sources of water pollution, Sewage, Definitions of Biological oxygen demand (BOD) and Chemical Oxygen Demand (COD), determination of COD, numerical problems on COD. Chemical analysis of water: Sulphates (gravimetry) and Fluorides (colorimetry). Sewage treatment: Primary, secondary (activated sludge) and tertiary methods. Softening of water by ion exchange process. Desalination of sea water by reverse osmosis.

(RBT Levels: L3)

Course outcome: Environmental pollution, waste management and water chemistry.

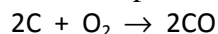
ENVIRONMENTAL POLLUTION**Air pollution**

Air pollution occurs due to the presence of harmful gases, dust, smoke which enters into the atmosphere and makes it difficult for plants, animals and humans to survive as the air becomes dirty. The main pollutants in the atmosphere are SO₂ (sulphur dioxide), CO (carbon monoxide), oxides of nitrogen, particulate matter, mercury, lead etc.,

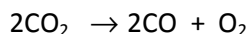
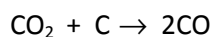
Primary air pollutant: Pollutants that are emitted directly from either natural events or from human activities are called primary air pollutant.

1. Carbon monoxide**Sources:**

- Oxidation of methane: Methane is formed during decay of vegetable matter. Oxidation of methane releases carbon monoxide into the atmosphere.
- Automobile exhaust- carbon monoxide is formed during the combustion of fuel such as petrol and is released into the atmosphere through the exhaust
- Incomplete combustion of fossil fuels: coal when undergoes incomplete oxidation, forms carbon monoxide and pollutes the atmosphere.



- Industries: carbon monoxide is released by industries such as iron and steel and petroleum .

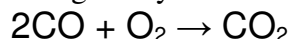


Ill effects:

- Haemoglobin in blood can form a complex with oxygen and hence functions as carrier of oxygen.
- When the atmosphere is polluted with carbon monoxide, on inhalation, CO combines with the hemoglobin to form carboxy haemoglobin and hence oxygen carrying capacity of the blood decreases.
- This causes, headache, dizziness, unconsciousness.
- When inhaled for a long duration it may cause even death.

Control:

- Using catalytic converter in automobiles.

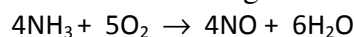
**2. Oxides of nitrogen**

Nitric oxide, nitrogen dioxide and nitrous oxide are the three main oxides of nitrogen found in the atmosphere

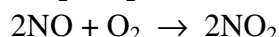
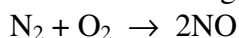
Sources:

The sources for the oxides of nitrogen are:

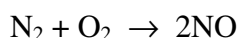
- Bacterial decomposition of nitrogenous compounds – bacteria in the soil act on the ammonium compounds present in the soil, convert them to ammonia and finally release oxides of nitrogen into the atmosphere.



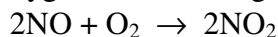
- Combustion during lightning – during lightning, oxygen and nitrogen in the atmosphere combine to give oxides of nitrogen.



- Industries and automobile exhaust - Air is sucked into the IC engines. At high temperatures, nitrogen and oxygen in the air combine to form nitric oxide.



Nitric oxide escapes through the exhaust. It gets cooled rapidly and combines with oxygen in the air to give nitrogen dioxide.

**Ill effects:**

Pollution due to oxides of nitrogen affects human and plant life:

The oxides of nitrogen combine with moisture in the atmosphere to form nitrous and nitric acid. This leads to increase in the acidity of rain water

Formation of photochemical smog: oxides of nitrogen combine with hydrocarbons present in the atmosphere forming peroxyacyl nitrate.

Peroxyacyl nitrate causes injury to plants and in human beings it causes fatigue and infection of the lungs

Peroxyacyl nitrate formation leads to smog (fog + smoke). Smog reduces visibility.

Fading of dyes is caused in textiles .

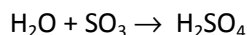
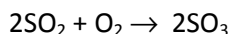
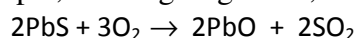
Control:

Using catalytic converter in automobiles. Catalytic converters use Pt/ Rh catalyst. in the presence of the catalysts, the oxides of nitrogen are converted to nitrogen and oxygen .

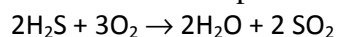
**3. Oxides of sulphur****Sources:**

- Combustion of fossil fuels – coal and crude oil contain up to 3% sulphur.
- roasting of ores – sulphide ores on roasting, are converted to sulphur trioxide. This, when let into the atmosphere, combines with the moisture in the atmosphere to form sulphuric acid.

for example, roasting of galena , the sulphide ore of lead



- oxidation of H_2S – Hydrogen sulphide is formed during the decay of plants. This, on oxidation releases sulphur dioxide into the atmosphere.



- Volcanic eruptions also emit sulphur dioxide.

Ill effects of SO_2 :

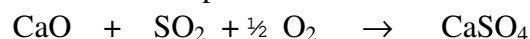
- Sulphur dioxide pollution in the atmosphere affects causes the following damages :
- In humans : it causes eye irritation, cough, lung diseases including lung cancer and asthma
- In plants: it causes damage of leaves, bleaching of chlorophyll which turns leaves brown, damage to crops and to growth of plants.
- Others: Yellowing of paper and wearing away of leather are other ill effects.

Control:

- The gases evolved during combustion of fossil fuels are passed through calcium carbonate when SO_2 is converted to calcium sulphite.



- lime is added to coal and roasted at high temperature so that CaO formed combines with SO_2 to form calcium sulphate.



4. Particulate matter

Particulate matters are solid or liquid suspensions in air. They are also called aerosols. These comprise of dust particles, ash, smoke, fumes and mist.

Sources:

- Volcanic eruptions.
- Soil erosion: wind blows away soil and the dust particles are introduced into the atmosphere.
- Industrial operations such as crushing of solid materials- solid materials are crushed, ground and powdered in industries. During these operations dust is released into the atmosphere.
- Burning of coal: The noncombustible matter in coal is left behind as ash during the combustion of coal.
- Incomplete combustion of compounds containing carbon, processing of coal, cement asbestos: These operations also release dust into the atmosphere.
- Mist – condensation of vapours, sprays etc lead to dispersion of liquids in the atmosphere thus forming mist.

Ill effects

- Presence of particulate matter in the atmosphere has the following effects:
- Decrease in visibility: Particulate matter interfere in the transmission of light and hence affect visibility.
- Particulate matters enter the lungs causing wheezing, bronchitis, and asthma in human beings.
- In plants the particulate matter settle on the leaves blocking the stomata thereby affecting the plant growth.

Control:

Reduce vehicle emissions and increase fuel efficiency:

- Diesel vehicles, including trucks, are a key source of fine particles. Reduce diesel emissions by replacing older engines with newer and cleaner engines
- Walk, cycle, take public transit and carpool whenever possible

Reduce the amount of particulate matter produced through smoke:

- Stop smoking; if you do smoke, do not smoke indoors
- Mulch garden refuse instead of burning it
- Limit the use of fireplaces and wood stoves. When using these appliances, make sure that wood is burned properly. Use wood that is well seasoned instead of wet or green. Stoves should also meet CSA (Canadian Standards Association) or EPA (Environmental Protection Agency) emission standards

- Switch to cleaner burning appliances. For example, pellet stoves produce less particulate matter than traditional wood stoves
- Take action to reduce wildfires. Practice safe backyard burning and careful use of campfire

5. Mercury pollutant

Sources:

Mercury occurs naturally in the earth's crust, but human activities, such as mining and fossil fuel combustion, have led to widespread global mercury pollution. Mercury emitted into the air eventually settles into water or onto land where it can be washed into water.

Effects:

- Health effects: Deteriorates nervous system, imparts hearing, speech and vision, causes involuntary muscle movements and corrodes skin and membrane.
- Environment effects: Animals that eat fish contaminated with mercury are affected the same way as humans. When pH values are between 5 and 7 the mercury concentration of mercury in the water will increase due to mobilization of mercury in the ground. Once mercury has reached surface water or soils micro organisms can convert it to methyl mercury, a substance that can be absorbed quickly by most organisms and known to cause nerve damage.
- Control:

6. Lead pollutant

Sources:

- The exhaust from automobiles which use lead tetraethyl as antiknocking agent-
- when TEL is used as antiknocking agent, lead is converted to halide and released into the atmosphere. This leads to increase in the concentration of lead in the atmosphere.
- Paint pigments : Litharge and red lead (oxides of lead) and lead chromate are used as pigments. These cause lead pollution
- Plumbing systems- lead pipes are used for plumbing and these may cause lead pollution

Ill effects:

- Lead competes with calcium and enters the blood and bone marrow.
- The lead interferes in the manufacture of red blood corpuscles and abnormal multiplication of blood cells and thus leads to anaemia and blood cancer in human beings.
- Lead enters the blood and various organs of the body including the brain and the Kidneys leading to dysfunction of the kidney and damage to the brain.

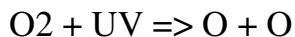
Control:

Lead smelting plants should their storage piles in such a way that the movements of lead materials are minimized to lessen exposure to wind and air.

Fixed conveyors rail cars and rail dampers in all transfer points should be enclosed using dry type dust collecting materials and design.

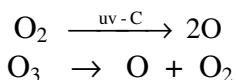
Secondary pollutant: A secondary pollutant is not directly emitted as such, but forms when other pollutants (primary pollutants) react in the atmosphere.

Ozone: Ozone is a gas found in the atmosphere consisting of three oxygen atoms: O₃. Ozone is formed in the atmosphere when energetic ultraviolet (UV) radiation dissociates molecules of oxygen, O₂, into separate oxygen atoms. Free oxygen atoms can recombine to form oxygen molecules but if a free oxygen atom collides with an oxygen molecule forms ozone. Ozone molecules can also be decomposed by ultraviolet radiation into a free atom and an oxygen molecule. Ozone is thus continuously created and destroyed in the atmosphere by UV radiation coming from the sun. This highly energetic UV radiation is called UVC (wavelength 280 nm) and is very harmful for human health.

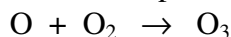


Ozone depletion

Formation of ozone in the atmosphere: Ozone absorbs uv radiations and is broken into atomic and molecular oxygen.



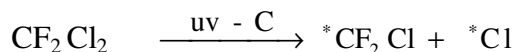
The products formed combine again to form ozone and hence a dynamic equilibrium is set up due to which the concentration of ozone in the atmosphere remains constant.



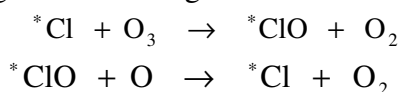
The ozone layer protects the earth from the harmful uv radiations. If the concentration of ozone is reduced (ozone depletion), the concentration of uv radiations reaching the earth increases. This leads to irritation of the eyes, skin cancer and damage to immune system in human beings. In agriculture it causes decrease in productivity.

Causes of ozone depletion

Chlorofluorocarbons (CFCs) are used as refrigerants, aerosols and as industrial solvents. CFCs are noncombustible and volatile. They reach the atmosphere and are broken down into chlorine free radicals by uv radiations.



The chlorine free radical brings about the degradation of ozone



Thus CFCs reduce the concentration of ozone in the atmosphere causing ozone hole.

Ill effects

- Due to ozone hole, the uv radiation increases causing eye infections, skin cancer in human beings and decrease in photosynthesis in plants.
- The temperature on the earth's surface is raised and this leads to global warming.

Control of ozone depletion:

Ozone depletion can be controlled by using alkanes that immobilize the chlorine atoms of CFC's by forming halo alkanes with them.

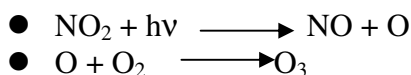
Using hydrogen containing CFC's which are destroyed in the troposphere itself and not taken to stratosphere for ozone depletion.

Photochemical Smog:

Photochemical smog is when photons of sunlight hit molecules of different kinds of pollutants in the atmosphere. It is a mixture of pollutants that are formed when nitrogen oxides and volatile organic compounds (VOCs) react to sunlight, creating a brown haze above cities. It tends to occur more often in summer, because that is when we have the most sunlight.

Mechanism of Photochemical smog:

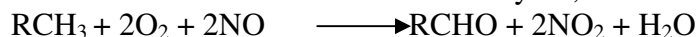
1. Troposphere Ozone:



Sources: Exhaust gases From Motor vehicles and Unburnt Hydrocarbons

2. Volatile Organic Compounds (VOC)

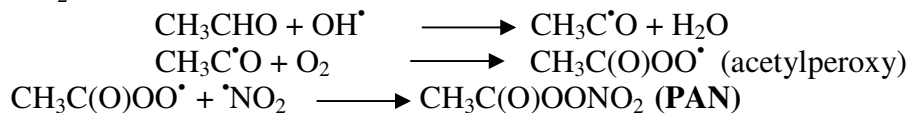
Carbon-based molecules such as Aldehydes, Ketones and Hydrocarbons



Sources: Paint thinners, solvents and petroleum constituents, Trees: emits isoprene and terpenes

And methane from termites, cows and cultivation

3. Peroxy acetyl Nitrates (PAN): Are secondary pollutants formed from peroxyacid radicals and NO_2

**Effects on human health:**

- Headaches, Eyes, nose, chest and throat irritations, Birth defects and low weight birth, impaired lung function, Coughing and wheezing, Limits visibility, Decreases UV radiation, Yellow/black color over cities, Causes respiratory problems and bronchial related deaths.
- Smog inhibits the growth of plants and can lead to extensive damage to crops, trees and vegetation. When crops and vegetables are exposed to smog, it interferes with the ability to fight infections, thus increasing susceptibility to diseases.

Note:

Ozone - Cause acute respiratory problems, Aggravate asthma, Cause temporary decreases in lung function in healthy adults, Lead to hospital admissions and emergency room visits, Impair the body's immune system

Peroxy acetyl nitrate (PANs)

- Respiratory and eye irritants, Mutagenic- causing skin cancer

Volatile organic compounds (VOCs)

- Global warming- Methane, Carcinogenic- benzene, Form Ozone

Control:

Minimize the usage of vehicles and frequently check engines smoke emission.

Prevent high usage of coals

Reduce pesticides use.

WATER CHEMISTRY**INTRODUCTION:**

Water is one of the most basic and essential component of all life. It covers nearly 72% of the earth's surface. It is the second most important substance required to sustain human, animal, and plant lives. Water is essential resource for living system, industrial processes, agricultural production, and domestic use.

Pure water is a clear, colorless, and odorless liquid that is made up of one oxygen and two hydrogen atoms. The chemical formula of the water molecule, H₂O, was defined in 1860 by the Italian scientist **Stanislao Cannizzarro**. Water is a very powerful substance that acts as a medium for many reactions, which is why it is often referred to as the "universal solvent." Although pure water is a poor conductor of electricity, impurities that occur naturally in water transform it into a relatively good conductor. Water has unusually high boiling (100° C/212° F) and freezing (0° C/32° F) points. It also shows unusual volume changes with temperature. As water cools, it contracts to a maximum density of 1 gram per cubic centimeter at 4° C (39° F). Further cooling actually causes it to expand, especially when it reaches the freezing point. The fact that water is denser in the liquid form than the solid form explains why an ice cube floats in a beverage, or why a body of water freezes from the top down. While the density property of water is of little importance to the beverage example, it has a tremendous impact on the survival of aquatic life inhabiting a body of water. Water exists in many forms in the nature. i.e. in the form of clouds, rain, snow, ice and fog. The distribution of water on the earth is as follows.

Sources of water:

1. Surface water: It is available on the surface of the earth either still form or in flowing form. Example: rain water, river water, lake water and sea water.

2. Under ground water: It is developed by any type of well or spring from beneath the surface of the ground whether the water flows from the well or spring by natural force or is withdrawn by pumping, other mechanical device, or artificial process. Example: Springs, well and tube wells.

Impurities in water:

1. Dissolved impurities: Dissolved gases like oxygen, carbon dioxide, hydrogen sulphide etc.,.

2. Suspended impurities: These are mostly insoluble minerals such as clay, sand etc. These cause turbidity to water.

3. Microscopic matter: These consist of mainly bacterial and other micro organisms like algae and fungi.

4. Dissolved impurities: Dissolved salts are mainly the carbonates, bicarbonates, chlorides and sulphates of Ca, Mg, Fe, Na and K. The presence of these salts imparts a sort of hardness in water.

5. Organic matter: It includes vegetable and animal matter.

6. Colloidal impurities: It consist of proteins, amino acids, ferric hydroxide, clay etc.

Boiler feed water

The boilers are used in industries to generate steam. This steam is used in power production, sterilization etc. The water used to generate steam in boiler s called boiler feed water.

Boiler Troubles:

Water used to generate steam is contaminated; it brings problem to boiler and reduces its efficiency. The major boiler troubles are

1. Scale and sludge formation
2. Boiler corrosion

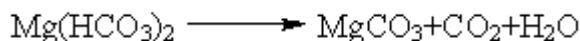
1. Scale formation:

During the production of steam, water evaporates continuously leaving behind the dissolved salts in the boiler. Concentration of the salt increases and reaches saturation level to get precipitated. If the precipitate is hard and strongly adhering on the inner walls of the boiler is known as scale.

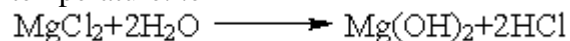
Causes for scale formation:

The various dissolved salts of water are responsible for scale formation

1. Decomposition of bicarbonates: bicarbonates undergo decomposition and forms insoluble carbonates. i.e.



2. Presence of silica: Impurities like calcium silicates, magnesium silicates are highly insoluble in hot water, they precipitate and deposit as scale
3. Hydrolysis of salts of magnesium: Magnesium salts are precipitated as their hydroxides at high temperature. i.e

**Prevention of scale formation:**

The scale formation in boilers can be controlled by two methods.

1. By feeding soft water (external treatment): Water used in boilers is purified by removing suspended and hardness impurities. Suspended impurities are removed by sedimentation and filtration process and hardness is removed by lime soda or ion exchange methods.

Prevention of sludge formation:

2. By internal treatment: Process of adding chemicals directly to water in boilers to remove the scale forming impurities which were not removed during external treatment methods is known as internal treatment. In this process, an ion is prohibited to exhibit its original character by complexing or by converting into more soluble salt by adding appropriate reagent.

Example: colloidal conditioning, phosphate conditioning, carbonate conditioning.

Disadvantages of Scale:

1. Wastage of fuel: Scales have a poor conductor of heat, so the rate of heat transfer from boiler to water is greatly reduced.
2. Reduces boiler efficiency: Decomposition of scales in the valves and condensers of the boiler, choke them partially.
3. Increase in cleaning expenses: Scales must be removed regularly and this cleaning process is very expensive.

4. Lowering of boiler safety: The overheating of the boiler tube makes the boiler material softer and weaker.

5. Danger of explosion: The scale formation also leads to uneven expansion of boiler material.

Sludge formation:

During the production of steam, water evaporates continuously leaving behind the dissolved salts in the boiler. Concentration of the salt increases and reaches saturation level to get precipitated. If the precipitate is soft, loose and suspended in boiler feed water is called as sludge.

Causes for sludge formation:

The impurities of water which causes sludge formation are $MgCO_3$, $MgSO_4$, and $MgCl_2$ etc. If the sludge is not removed periodically, then it will form scale.

Prevention of sludge formation:

Sludge formation can be prevented by using softened water, more over sludge can be removed by flowing off technique i.e. by drawing off some of the concentrated water from the bottom of the boiler through a tap.

Disadvantages of scale and sludge formation:

1. The sludge is bad conductor of heat. So it requires more heating of boiler to produce steam which results in wastage of fuel.
2. Because of more and more heating of boiler, there is a chance of explosion of the boiler
3. It reduces the efficiency of boiler.
4. Sludge's need to be removed regularly and this cleaning process is expensive.

2. Boiler corrosion

The decay of boiler material due to the presence of impurities in boiler feed water is called boiler corrosion.

Causes for Boiler corrosion:

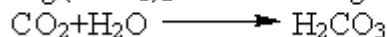
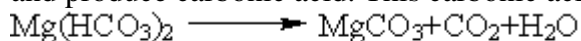
1. Corrosion due to dissolved Oxygen:

When water containing dissolved oxygen is heated in the boiler, the free gas is evolved under high pressure of the boiler and attacks the boiler material and forms the rust.



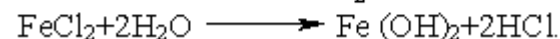
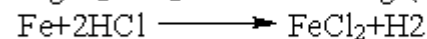
2. Corrosion due to dissolved carbon dioxide:

The CO_2 is obtained from the decomposition of bicarbonates. So formed CO_2 is react with H_2O and produce carbonic acid. This carbonic acid is slightly acid and corrosive in nature.



3. Corrosion due to $MgCl_2$:

The salts like $MgCl_2$ in boiler feed water forms hydroxides and acid. The acid so formed will attack the boiler parts and causes corrosion.



Prevention of boiler corrosion:

Boiler corrosion can be controlled by reducing the quantities of O₂, CO₂ and any acid from the feed water.

1. By removing oxygen: Dissolved oxygen can be removed by treating boiler feed water with sodium sulphite or hydrazine.
2. By removing carbon dioxide: Lime stone easily removes carbondioxide or by adding ammonium hydroxide.
3. Finally acidic impurities if there any can be removed by treating with alkaline agents like ammonium hydroxide.

Sources of water pollution

There are many causes for water pollution but two general categories exist: direct and indirect contaminant sources. Direct sources include effluent outfalls from factories, refineries, waste treatment plants etc.. that emit fluids of varying quality directly into urban water supplies.

Water pollutants sources are of two types.

1. Point sources: point source pollution is defined as any single identifiable source of pollution from which pollutants are discharged, these are discrete and identifiable and hence easy to monitor and regulate.

Example: Industrial discharge, factory smoke, municipal sewage etc.,

2. Non point source pollution: When a source of pollution cannot be readily identified ie. Sources are scattered or diffuse they are called as non point source of pollution.

Examples: Run off from farm lands, parking lots, agriculture logging, animal wastes, etc.,

Additional information:

Sewage And Waste Water: Sewage, garbage and liquid waste of households, agricultural lands and factories are discharged into lakes and rivers. These wastes contain harmful chemicals and toxins which make the water poisonous for aquatic animals and plants.

Dumping: Dumping of solid wastes and litters in water bodies causes huge problems. Litters include glass, plastic, aluminum, Styrofoam etc. Different things take different amount of time to degrade in water. They affect aquatic plants and animals.

Industrial Waste: Industrial waste contains pollutants like asbestos, lead, mercury and petrochemicals which are extremely harmful to both people and environment. Industrial waste is discharged into lakes and rivers by using fresh water making the water contaminated.

Oil Pollution: Sea water gets polluted due to oil spilled from ships and tankers while traveling. The spilled oil does not dissolve in water and forms a thick sludge polluting the water.

Acid Rain: Acid rain is pollution of water caused by air pollution. When the acidic particles

caused by air pollution in the atmosphere mix with water vapor, it results in acid rain.

Global Warming: Due to global warming, there is an increase in water temperature. This increase in temperature results in death of aquatic plants and animals. This also results in bleaching of coral reefs in water.

Eutrophication: Eutrophication is an increased level of nutrients in water bodies. This results in bloom of algae in water. It also depletes the oxygen in water, which negatively affects fish and other aquatic animal population.

Definition of BOD: Biological Oxygen Demand is an important measure of water quality. BOD is defined as “The amount of oxygen required by microorganism to oxidize the organic matter in a water sample over a period of 5 days under aerobic condition at 20 °C”.

Definition of COD: It is defined as “The amount of oxygen required for the complete oxidation of both organic & inorganic matter present in 1 litre of waste water using strong oxidizing agent”.

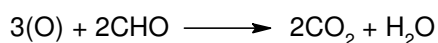
DETERMINATION OF COD OF WASTE WATER:

Definition of COD: It is defined as “The amount of oxygen required for the complete oxidation of both organic & inorganic matter present in 1 litre of waste water using strong oxidizing agent”.

Characteristics of COD:

- 1) The unit of COD is mg/dm³ or ppm.
- 2) In general COD > BOD since both biodegradable and non biodegradable organic load are completely oxidized.

Principle: In this method, the given samples of water containing organic and inorganic impurities are oxidized by K₂Cr₂O₇ in acidic media in the presence of catalyst Ag₂SO₄ and HgSO₄. (Added to prevent the interference the chloride and silver ions). The unreacted K₂Cr₂O₇ is titrated against FAS solution in the presence of a redox indicator, ferroin which shows its color change in the oxidized (bluish green) and reduced states (reddish brown).



Procedure: Preparation of standard solution: Standard FAS solution is prepared by adding dilute H₂SO₄ (Added to prevent hydrolysis of FAS) to a known weight of FAS salt.

1. Pipette out known amount of the waste water into a clean conical flask.
2. Add 10 ml of K₂Cr₂O₇ and 10 ml 1:1 H₂SO₄ into a conical flask.
3. Add 1 g of Ag₂SO₄ followed by 1 g of HgSO₄ and warm if necessary.
4. Titrate with standard FAS using ferroin as indicator till color changes from bluish green to reddish brown.

5. Note down the volume of FAS consumed as 'V₁' ml.

Perform the blank titration without waste water sample. Note down the volume as 'V₂' ml.

Calculations:

Normality of FAS = 'A' N

Volume of FAS consumed during blank titration = B cm³

Volume of FAS consumed during Back titration = C cm³

Volume of FAS consumed for the titration = (B - C) cm³

Volume of water sample = V cm³

1 ml of 1N FAS = 8 mg of oxygen

(B-C) cm³ of 'A' N FAS = A*(B-C)*8 mg of oxygen

Vcm³ of water sample = $\frac{A*(B-C)*8}{V}$ mg of oxygen

Therefore 1000cm³ of water sample = $\frac{A*(B-C)*8*1000}{V}$ mg/dm³ of oxygen

Chemical analysis of water:

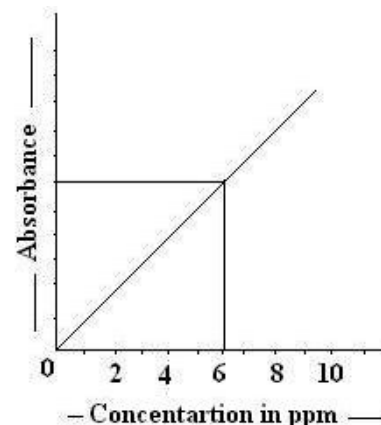
Determination of Fluoride by Colorimetric method

Fluoride contents in water sample are determined by colorimetric method. Fluorides have dual significance in water. High concentration causes *dental fluorosis* and low concentration causes *dental caries*. Significant sources of fluoride are found in coke, glass and ceramic, electronics, pesticides and fertilizer manufacturing, steel and aluminum processing and electroplating industries.

Principle: Fluoride is estimated colorimetrically using SPANDS method. (SPANDS = Sodium 2-(P-Sulphophenyl Azo)-1, 8-dihydroxy-3, 6 Naphthalene Disulphonate trisodium salt). The method utilizes the reaction between fluoride and a complex of Zirconium with SPANDS. The fluoride reacts with the complex, dissociating a portion of it into a colorless anion [ZrF₆]²⁻ and the reagent. As the amount of fluoride is increased the color produced by Zr- SPANDS complex becomes progressively lighter. The decrease in intensity is related to the concentration of fluoride ions.

Procedure:

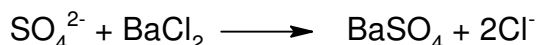
1. Prepare a reference solution by adding 10 ml of SPANDS in HCl and dilute to 100 ml with distilled water. Use this solution to set zero in the colorimeter at 570 nm.
2. Prepare a series of standard solution of NaF in the concentration range up to 2.0 mg/L in 100 ml standard flask.
3. Add 50 ml of distilled water and 10 ml of Zr- SPANDS reagent to each of the standard solution dilute up to the mark, mix well and measure the absorbance at 570 nm.
4. Draw the calibration curve by plotting the concentration of fluoride ion against absorbance.
5. Take the suitable aliquot of water sample to be analyzed and repeat the steps 3 and 4.
6. Calculate the concentration of fluoride ion in the test sample using calibration curve.



Determination of Sulphate by Gravimetric method

Sulphate ions (SO_4^{2-}) in water are due to the dissolved salts such as sulphates of sodium, potassium, magnesium etc.

Principle: In gravimetric method, sulphate ions (SO_4^{2-}) are quantitatively precipitated as BaSO_4 by treating with BaCl_2 in the presence of HCl, separated by filtration, dried and weighed as BaSO_4 .



The precipitate of BaSO_4 is filtered through a quantitative filter paper and is washed with hot water. The precipitate is ignited in silica crucible and weighed as BaSO_4 .

Procedure:

1. Take 1000 ml of water in large beaker, heat it on a hot plate and evaporate to reduce the volume to 100 ml.
2. Add half test tube of dilute HCl and heat the solution nearly to boiling.
3. To the hot solution add 1 test tube of BaCl_2 solution slowly with constant stirring. Digest the solution on water bath for about 30 min.
4. Filter the solution using No.40 quantitative filter paper through a funnel & wash the precipitate with hot water several times to remove chloride ions.
5. Heat the funnel in an aluminium cone till filter is dry. Transfer the filter paper into a previously dried & weighed silica crucible and heat.
6. Transfer the hot silica crucible into desiccators and cool it. Weigh the crucible along with the precipitate of BaSO_4 .
7. Repeat the process of heating, cooling and drying till a constant weight is obtained.

Calculation:

Volume of water taken = 1000 ml

Weight of empty silica crucible = W_1 g

Weight of silica crucible + BaSO_4 precipitate = W_2 g

Weight of BaSO_4 = $(W_2 - W_1)$ g

Amount of Sulphate = $\frac{(W_2 - W_1) \times 96}{233.33}$ g/l

1000 ml of water contains $\frac{(W_2 - W_1) \times 96}{233.33}$ g/l

10^6 ml of water contains $\frac{(W_2 - W_1) \times 96 \times 10^6}{233.33 \times 1000}$ ppm

SEWAGE: Water containing any one of the waste is called as **effluent or sewage**.

SEWAGE TREATMENT: The water containing heavy load of BOD, pathogenic bacteria, colour and annoying smell can't be directly discharged into the rivers as they mainly affect the aquatic life and causes many water borne diseases. The domestic sewage therefore needs proper treatment which is carried out in 3 stages

- Primary treatment
- Secondary treatment
- Tertiary treatment

Primary treatment: It involves

Screening: Removal of large suspended or floating matter in sewage using mesh screens.

Silt and Grit removal: Removal of heavy particles like sand, glass pieces etc. using grit chambers.

Removal of oil and grease: is mainly done using skimming tanks by blowing air through the sewage and oils are lifted to the surface as foams (soapy mixture) which is then skimmed off.

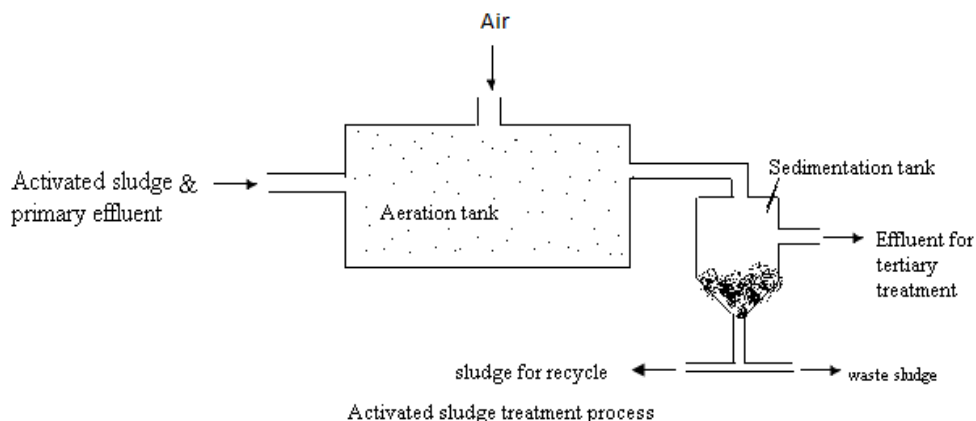
Sedimentation process: involves addition of coagulants like alum, ferrous salts etc. and there by ppt. out the suspended particles by sedimentation process.

Secondary treatment:

It involves aerobic biological oxidation of sewage water. The sewage water after sedimentation is subjected to aerobic oxidation during which the organic matter is converted into H_2O and CO_2 and N_2 to NH_3 and finally to nitrates and nitrites.

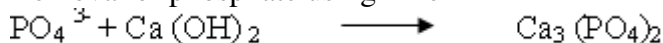
Activated Sludge Method (Biological treatment): Activated sludge is a thick greasy mud containing aerobic bacteria.

This method involves extensive aeration of the sewage water after primary treatment is mixed with activated sludge and allowed to enter in a large aeration tank for biological treatment. Air is continuously passed into tank to maintain the aerobic condition. Under these condition microorganisms present in activated sludge attack on organic matter of sewage and decomposes them into CO_2 and H_2O . The effluent after this treatment is passed to sedimentation tank where sludge will settle down. The clear effluent is sent to tertiary treatment. A part of sludge is used for further treatment and rest is disposed off and used as manure.



Tertiary treatment: It involves

Removal of phosphate using lime



Removal of heavy metals by sulphides.



Degasification of NH_3 , H_2S , and CO_2 by stripping hot water.

Disinfection of microorganisms by chlorine. Acid kills microorganisms.



Softening of water by Ion exchange process:

In this method all the ions present in water are removed. In this insoluble ion exchange resins are used. Resins means it is a long chain organic polymer with functional groups. Depending upon the functional groups attached to resins they are classified into

1. Cation Exchange Resin:

These resins exchange its H^+ ions with cations of water sample. Generally it is expressed as RH^+

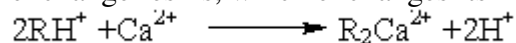
2. Anion Exchange Resin:

These resins exchange its OH^- ions with anions of water sample. Generally it is expressed as ROH^-

Working:

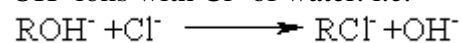
The ion exchange resin contains two compartments. One is cation exchange resin and another is anion exchange resin. For the regeneration of respective resins, acid and alkali regeneration units are connected to compartments. The schematic diagram of ion exchange unit as shown in fig.

The water sample containing high minerals are first allowed to pass through cation exchange resins, which exchanges its H^+ ions with Ca^{2+} ions of water .i.e



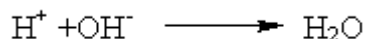
Now the water sample is free from cations.

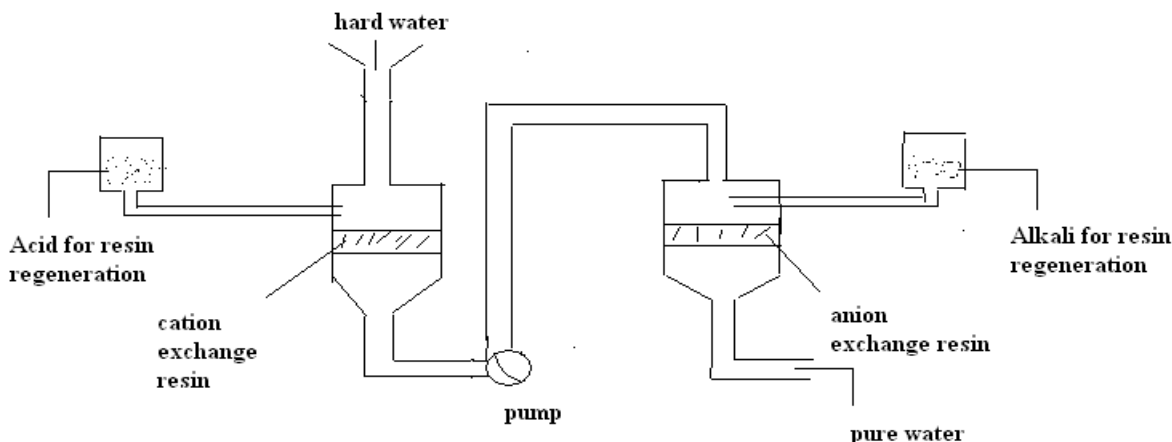
The same water is further allowed to pass through anion exchange resin, which exchanges its OH^- ions with Cl^- of water. i.e.



Now the water is totally free from all the ions.

Now H^+ ions formed at cation exchange resin and OH^- ions formed at anion exchange resin will combine to form pure water.



**Advantages:**

1. The ion exchange apparatus, once set up, is easy to operate and control.
2. Both acidic and alkaline water can be softened.
3. Water of very low hardness is produced.
4. Water produced by this method is used as boiler feed water.

Disadvantages:

1. Equipment and process is costly.
2. Turbid water needs to be filtered first before softening.

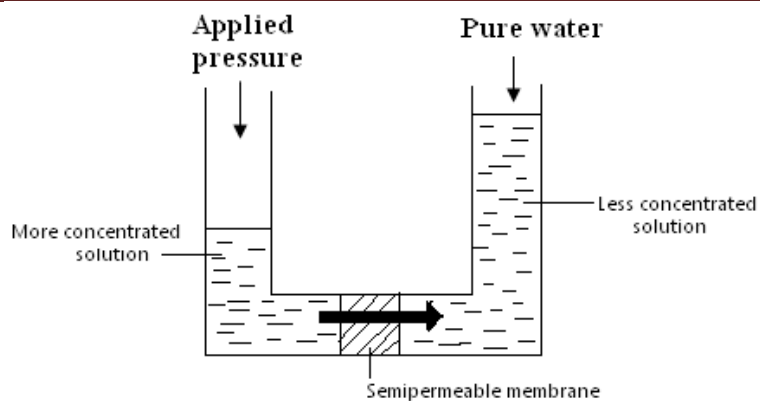
POTABLE WATER-Water that is fit for human consumption and free from pathogenic bacteria and toxic chemicals is called potable water.

DESALINATION-The process of removal of dissolved salts from sea water to the extent that water becomes usable is described as desalination. The important methods of desalination are a) Reverse Osmosis. B) Electrodialysis.

REVERSE OSMOSIS:

Principle: - The principle of osmosis is that water flows from lower concentration to higher concentration side through semi permeable membrane. If the pressure is applied on solution side, the solvent will flow in the reverse direction. This is called reverse osmosis.

It is studied that sea water exerts an osmotic pressure of about 4500-5500 KPa. In reverse osmosis, hydrostatic pressure which is greater than osmotic pressure is applied on the salt solution side then water flows from salt solution to fresh water side. This water can be used for human consumption.



Reverse Osmosis

Application:

1. It is economical, simple and continuous.
2. The process needs extremely low energy.
3. It has long life and membrane is easily replaceable.

MODULE 5**INSTRUMENTAL METHODS OF ANALYSIS AND NANOMATERIALS**

Instrumental methods of analysis and Nanomaterials
Instrumental methods of analysis: Theory, Instrumentation and applications of Colorimetry, Flame Photometry, Atomic Absorption Spectroscopy, Potentiometry, Conductometry (Strong acid with a strong base, weak acid with a strong base, mixture of strong acid and a weak acid with a strong base)
Nanomaterials: Introduction, size dependent properties (Surface area, Electrical, Optical, Catalytic and Thermal properties). Synthesis of nanomaterials: Top down and bottom up approaches, Synthesis by Sol-gel, precipitation and chemical vapour deposition, Nanoscale materials: Fullerenes, Carbon nanotubes and graphenes – properties and applications. (RBT Levels: L1 & L2)
Course outcome: Different techniques of instrumental methods of analysis. Fundamental principles of nanomaterials.

COLORIMETRIC TITRATION:

Introduction: this method is useful to determine the concentration of unknown solution. The concentration of the unknown solution is determined by measuring the absorbance of the light w.r.t known concentration. The instrument name is Photoelectric Colorimeter

Theory: Theory of the colorimeter is explained by Beer – Lambertz Law.

Law of absorption: When light falls upon homogenous medium, a portion of the light is reflected, a portion is absorbed, and remainder is transmitted.

$$I_o = I_t + I_a + I_r$$

Where I_o = intensity of the incident light

I_r = intensity of the reflected light

I_a = intensity of the absorbed light

I_t = intensity of the transmitted light

When glass is used $I_r = 0$ negligible

$$I_o = I_a + I_t$$

$$A = \log (I_o / I_t)$$

Lambert's Law: The intensity of the monochromatic light decreases exponentially as the thickness of the medium increases arithmetically.

$$\frac{dI}{dt} = -K I$$

K is proportion constant.

$$\frac{dI}{I} = -K dt$$

on integrating & Substitute $I = I_o$ when $t = 0$ & $I = I_t$ at t

$$\int \frac{dI}{I} = - \int K dt$$

$$\ln \frac{I_o}{I_t} = K t$$

$$I_t = I_0 e^{-Kl}$$

Beer's law: the intensity of the monochromatic light decreases exponentially as the concentration of the medium increases arithmetically.

$$\frac{dI}{dc} = -Kl$$

$$\frac{dI}{I} = -K \cdot dc$$

on integrating between the $I=I_0$ at $c=0$ and $I=I_t$ at c .

$$\ln \frac{I_0}{I_t} = K \cdot C \text{ or } I_t = I_0 \cdot e^{-Kc}$$

Beer-lambert's law

Absorbance is directly proportional to concentration and thickness.

$$A = \epsilon ct, \quad \epsilon = \text{molar absorption co-efficient.}$$

$$A = \log \frac{I_0}{I_t} = K t c$$

Relationship between absorbance & transmittance

Reciprocal of transmittance, I_0 / I_t is called absorbance.

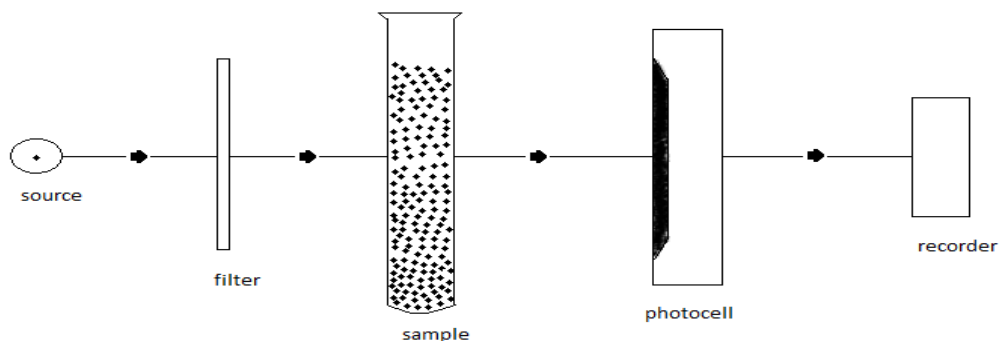
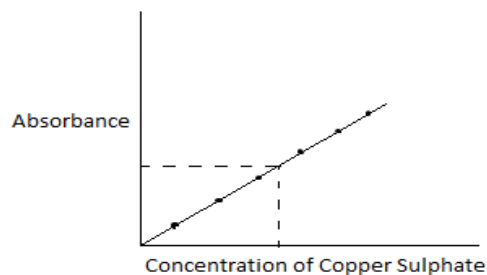
$$A = \log I_0 / I_t = \log I/T = -\log T$$

Reciprocal of absorbance, I_t / I_0 is called transmittance.

$$A = \log I_t / I_0 = \log I/A = -\log A$$

I.e. transmittance of the colored solution is equal to the ration of the intensity of the transmitted radiation to that of intensity of the incident radiation I_0 .

Procedure: Pipette out 2, 4, 6, 8, 10ml of standard copper sulphate solution into 25ml standard flask. Add 2.5ml of ammonia solution into each of them and make up to the mark with distilled water and shake well. Set the filter to 620nm. Adjust the initial reading to zero by using blank solution in the sample tube. Measure the absorbance for each standard flask solution and plot graph of absorbance v/s concentration of copper sulphate.



Instrumentation:**Source:** tungsten bulb is used as a light source.**Filter:** It is a device for isolating monochromatic light.**Sample:** sample is hold in glass cell.**Photocell:** Converts the emitted light into electrical signal.**Applications:**

- In quantitative analysis: large number of metal ions, anions and cations compounds can be determined by in this method
- Photometric Titration i.e. equivalence point can also be determined
- Determination of the composition of colored complex

Advantages:

- Can be determine the concentration of the colored solution
- It is very simple method
- Colorimeter gives most accurate value
- Used for lower concentration

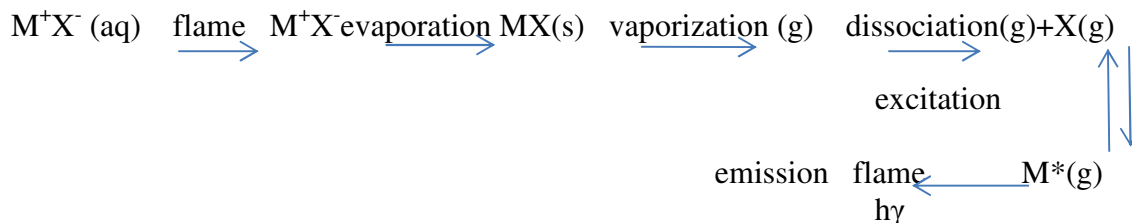
FLAME PHOTOMETRY

Introduction: Elements impart characteristic color with Bunsen flame. The flame photometry is based on the measurement of intensity of the light emitted when a metal is introduced into a flame. The intensity of the emitted light tells about the concentration of the element present.

Principle: When liquid sample containing metallic salt solution is introduced into a flame, the flowing process is involved in that.

- Solution containing the metal is aspirated into flame
- Solvent evaporates leaving behind a solid residue
- Salt is vaporized or converted into a gaseous state
- In the gaseous state salt is dissociates into constitute atoms
- Gaseous atoms get excited from ground state to excited state.
- The excited atoms are unstable quickly emit photons & return to the lower energy level
- The intensity of the emitted radiation is measured using flame photometry

These steps are schematically represented as follows



Relationship between ground state & excited state atoms is given by Boltzmann equation

$$N_1/N_0 = (g_1/g_0) e^{-\Delta E/RT}$$

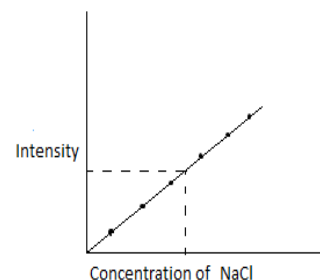
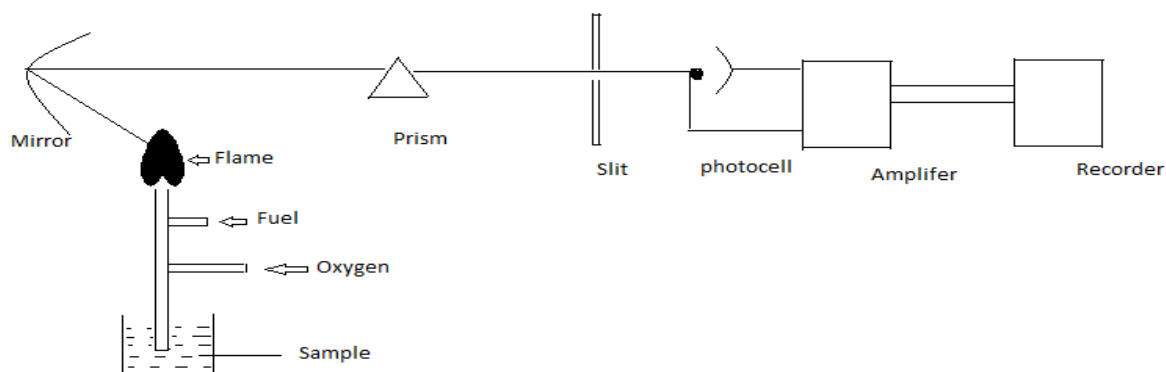
N_1 = atoms in excited state, N_0 = atoms in ground state

g_1/g_0 = ratio of statistical weights for ground & excited states.

ΔE = excitation energy, K = Boltzmann constant, T = temperature.

Procedure: Flame photometric estimation of sodium

Prepare 1ppm NaCl solution by weighing 2.52g of sodium chloride in distilled water. Transfer 2, 4, 8, 10ml of standard NaCl solution into the instrument to zero by using distilled water and hundred by using Measure the emission intensities for other standard solutions. Draw plotting the emission intensity (y axis) and concentration of NaCl in curve find out concentration of NaCl and calculate the amount of Na.

**Instrumentation:****Applications:**

It is used in the quantitative determination of metals in solution, especially alkali & alkaline earth in the given sample.

POTENTIOMETRIC TITRATION

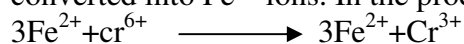
Aim: Determination of the weight of ferrous ammonium sulphate and ferrous iron in the given solution by potentiometric titration method.

Principle: In this titration the amount of substance in the solution is determined by measuring the emf between two electrodes that are dipped into the solution. When the metal M is immersed in the solution containing its own ions M^{n+} ions, the electrode potential is given by Nernst equation,

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

emf of the solution can be measured by combining reference electrode with indicator electrode. The electrode which responds to the change in the concentration of the ion in the solution is called indicator electrode & reference electrode is one whose potential is constant.

The titration of Mohr's Salt solution with $K_2Cr_2O_7$ in the presence of H_2SO_4 is a redox titration. Before the titration is started, the solution contains only ferrous ions in the solution. When a small volume of the dichromate solution is added, equivalent small quantity of Fe^{2+} ions are converted into Fe^{3+} ions. In the process, the Cr^{6+} ion in dichromate is reduced to Cr^{3+} ion.



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In the presence of both Fe^{2+} and Fe^{3+} ions in the solution developing an electrode potential which is picked up by a Pt wire [Pt/ Fe^{3+} ; Fe^{2+}], whose electrode potential is given by

$$E = E^{\circ} + \frac{0.0591}{n} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

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

At the equivalence point, all the Fe^{2+} ions are converted into Fe^{3+} ions, the Pt/ Fe^{3+} , Fe^{2+} electrode ceases to exist. But addition of a slight excess of dichromate solution introduces Cr^{6+} ions into the solution, which along with the Cr^{3+} ions in the solution (formed during the oxidation of Fe^{2+}) form a new oxidation reduction electrode, Pt/ Cr^{6+} , Cr^{3+} .

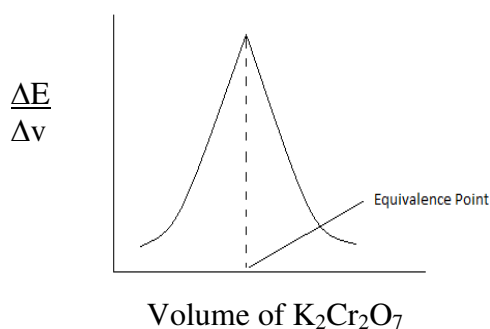
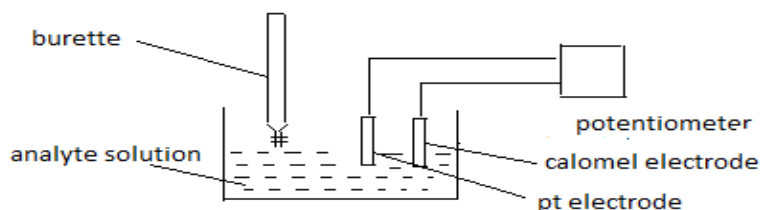
After the equivalence point potential of the redox reaction is determined by the equation

$$E = E^{\circ} + \frac{0.0591}{n} \log \frac{[\text{Cr}_2\text{O}_7^{2-}]}{[\text{Cr}^{3+}]}$$

Procedure: Pipette out 25cm³ of FAS solution into a 50cm³ beaker. Add one test tube full of dil H₂SO₄. Immerse Pt. & calomel electrodes into the solution, & connect the electrodes to a Potentiometer.

Fill the burette with $\text{K}_2\text{Cr}_2\text{O}_7$ solution. Add $\text{K}_2\text{Cr}_2\text{O}_7$ solution from the burette with increment of 0.5cm³, stir well and measure the potential after each addition. Continue the titration till the potential indicates a rapid jump with a drop of titrant.

Plot the graph of $\Delta E / \Delta V$ v/s vol. of $\text{K}_2\text{Cr}_2\text{O}_7$

**Instrumentation**

A potentiometer consists of an indicator electrode (e.g.: Platinum), A standard reference electrode (E.g.: Calomel electrode), & potentiometer to read the values directly as change in potential.

Applications:

1. Coloured solution can also be titrated.
2. Acid-base titration can also be done in this method.
3. In this method Oxidation-reduction titrations can also be carried out.
4. Precipitation reactions can also be carried out potentiometrically.

CONDUCTOMETRIC TITRATION

Conductance is ease with which current flows through the solution. It is reciprocal of resistance.
 $C = 1/R = \Omega^{-1}$ or mho or siemen

Theory:

The Conductance of the solution is explained by considering ohm's law.

According to ohm's law the current flowing through the conductor is directly proportional to voltage and inversely proportional to the resistance.

$$I = \frac{E}{R} \quad \text{or} \quad E = I R$$

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

Therefore $R = S (l/a)$ where S is specific resistance

Therefore $C = 1/R = 1/S (a/l)$, $K (a/l)$, $K = \text{specific conductance}$

It is defined as the conductance of the solution which is place between two electrodes of area 1cm^2 and 1cm apart

The conductance of the solution is depends on mobility of the ion and number of the ion

Types of conductance: There are three type's namely specific conductance, equivalence conductance, and molar conductance.

Specific conductance (K) is conductance of the solution which are placed between two electrodes of area 1cm^2 and at 1cm apart

$$K = 1/R (l/a) \quad K = \text{Siemen } m^{-1}$$

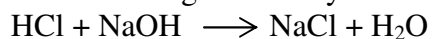
Equivalence conductance (λ) is the conductance of the solution when 1g equivalent weight of solution is placed between two electrodes of area 1cm^2 at 1cm apart.

Molar conductance (μ) is the conductance of the solution when 1g molecular weight of solute is placed between two electrodes of area 1cm^2 at 1cm apart

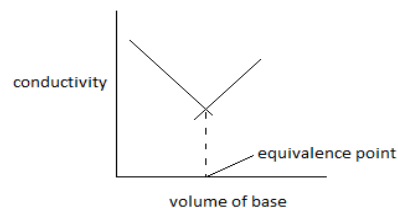
Conductometric titration**Strong acid v/s strong base**

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 H^+ ions by slow moving Na^+ ions



After the neutralization point, conductivity rapidly rises with further addition of NaOH because of continuous addition of fast moving OH^- ions. A plot of conductance against the volume of

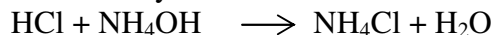


base added is shown in the figure. The point of intersection of two curves gives the neutralization point.

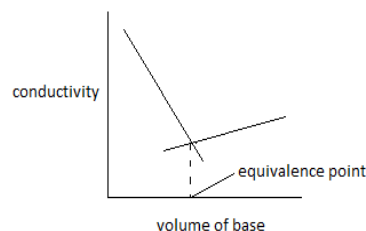
Strong acid v/s weak base

HCl v/s NH₄OH

Conductivity of the solution decreases due to the replacement of fast moving H⁺ ions by NH₄⁺ ions but after equivalence point, conductivity almost remains constant, since NH₄OH is weak electrolyte and ionizes to small extent giving very small conductivity.



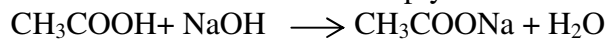
A plot of conductance against the volume of base added is shown in the figure. The point of intersection of two curves gives the neutralization point.



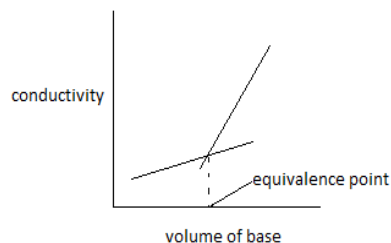
Weak acid v/s Strong base

Consider the titration of acetic acid against NaOH.

The conductance of the acid will be initially low since acetic acid is a weak electrolyte. When NaOH is added to the acid, the salt formed is highly ionized and the conductance increases. On complete neutralization of the acid, further addition of base leads to an increase in the number of mobile OH⁻ ions. Hence the conductance increases sharply.

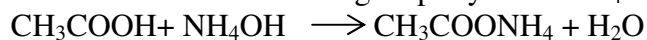


A plot of conductance against the volume of base added is shown in the figure. The point of intersection of two curves gives the neutralization point.

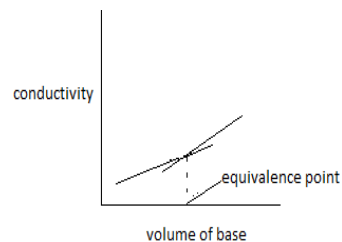


Weak acid v/s weak base

Consider the titration of acetic acid against NH₄OH. The conductance of acid will be initially low since acetic acid is a weak electrolyte. When NH₄OH is added to acid salt is formed and the conductance of the solution increases. On complete neutralization of acid conductance does not change rapidly since NH₄OH is a weak base.



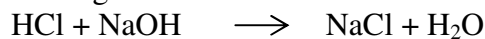
A plot of conductance against the volume of base added is shown in the figure. The point of intersection of two curves gives the neutralization point.



Mixture of strong acid and weak acid v/s strong base

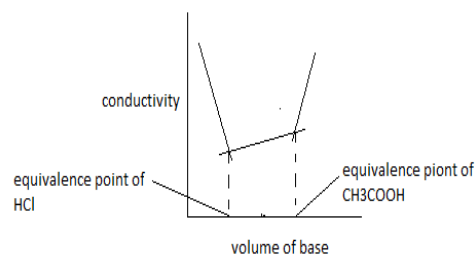
HCl, CH₃COOH v/s NaOH

the strong acid like HCl is titrated against a strong base such as NaOH, the conductance first decreases due to replacement of fast moving H⁺ ions by slow moving Na⁺ ions



The weak acid does not get neutralized initially because of the well known common ion effect.

In the presence of excess of H⁺ ions, the ionization of the weak acid is suppressed and hence, weak acid like CH₃COOH ionizes gradually after the first end point and the available H⁺ ions are neutralized giving the second end point.



Because of common ion effect dissolution of acetic acid is suppressed. Hence it does not provide H^+ ions which required for neutralization.

After the neutralization point of HCl, CH_3COOH , conductivity rapidly rises with further addition of NaOH because of continuous addition of fast moving 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.

Advantages:

- Mixture of acid can be titrated
- Indicators are not used
- Very weak acids can be titrated
- Can be used with colored solution

NANO MATERIALS

Nano Materials: Introduction, properties (size dependent). Synthesis-bottom up approach (sol-gel, precipitation, gas condensation & chemical vapour condensation processes). Nano scale materials- carbon nano tubes, nano wires, fullerenes, dendrimers, nano rods, & nano composites.

COURSE OUTCOME: Over viewing of synthesis, properties and applications of nanomaterials Program.

INTRODUCTION: Nanotechnology is a multidisciplinary science and technology and encompasses physical, chemical, biological, engineering and electronic processes. It is the study deals with various structures of matter having dimensions of the order of billionth of a meter. These materials or particles are called as nano particle. Nano technology is the making of usage and technique, in order to solve a problem to perform specific functions. The particles which are smaller than about 100nm give rise to enhance properties of nano structures built from them. Matter arranged by exercising control over length of one to hundred nanometers and the formulating structures exhibit characteristics that are specific to their size and dimensions, the resulting materials are called nano materials.

SIZE DEPENDENT PROPERTIES

a) **Surface area:** Nanomaterials have a significant proportion of atoms existing at the surface. Properties like catalytic activity, gas adsorption and chemical reactivity depend on the surface area. Therefore nanomaterials can show specific related properties that are not observed in bulk materials.

b) **Electrical properties:** the electronic bands in bulk materials are continuous due to overlapping of orbitals of billion of atoms. But in the nanomaterials, very few atoms or molecules are present so the electric band becomes separate and the separation between different electric states varies with the size of the nanomaterials. Hence, some metals which are good conductors in bulk semiconductors and insulator as their size is decreased to nano level.

c) **Optical properties:** Nanomaterials have particular optical properties as a result of the way light intersects with their fine nanostructures. The discrete electronic states of nanomaterials allow absorption and emission of light at specific wavelength. Hence, nanomaterials exhibit unique color different from bulk materials.

SYNTHESIS OF NANOMATERIALS

There are two methods of preparing nanomaterials. One is top-down approach & the other is bottom-up approach.



- In top-down approach, the material is reduced from bulk size to nano scale. Examples for top-down approach are ball milling method & nanolithography.
- In bottom-up approach, matter in atomic or molecular level gets assembled to form tiny clusters which grow to reach nano-size. Examples for bottom-up approach are arc discharge method, chemical vapor deposition, physical vapor deposition & sol gel method.

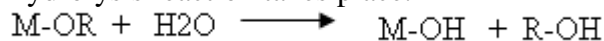
SOL – GEL PROCESSES

Sol gel processes principle is conversion of precursor solution into gel via hydrolysis and condensation reactions.

Sol gel processes allow to synthesis of nano materials of high purity.

This process involves five steps

1. Preparation of sol: sol is prepared by suspended particles in water during suspension hydrolysis reaction takes place.



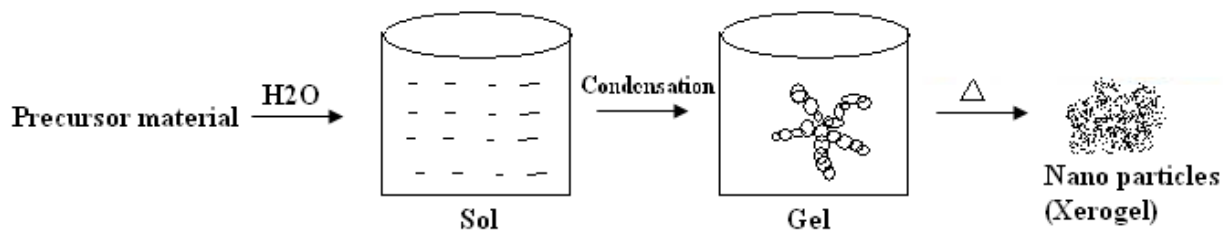
2. Conversion of sol into gel: sol is converted into gel by condensation reaction forming network between oxides. When networking takes place, the viscosity of the solution increases.



3. Aging of gel: during which poly condensation reaction continue until the gel is transformed into solid mass.

4. Removal of solvent: Further the solid mass is isolated from the solvent by thermal evaporation. The product formed is xerogel.

5. Heat treatment: solid mass (xerogel) obtained is dried at nearly to 800C to get fine nano particle powder.



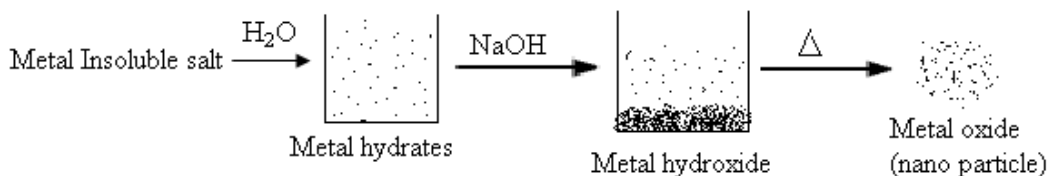
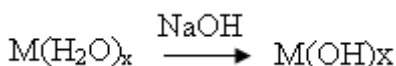
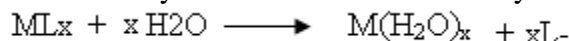
Advantages:

- Nano materials of high purity with good homogeneity can be obtained.
- Samples can be prepared at low temperature.
- Easy to control the synthesis parameters like shape and size of resulting material

PRECIPITATION METHOD

Principle: The principle involved in the precipitation of precursor materials at constant pH via condensation.

Processes: In this method inorganic metal salt such as chloride, sulphate, nitrate ions etc., are used as precursor. Precursor materials is dissolved in water and undergo hydrolysis where metal ions exist in metal hydrates form. On adding base like NaOH/NH₄OH, pH of the solution changes and reaches super saturation level leading to condensation of precursor to form metal hydroxide precipitate. The precipitate is washed with water, filtered and finally calcinated at higher temperature to convert metal hydroxide into metal oxide by dehydrogenation takes place.



Advantages: The process is relatively economical.

- The wide range of single and multi components to oxide nano powders can be synthesized.

CHEMICAL VAPOUR CONDENSATION

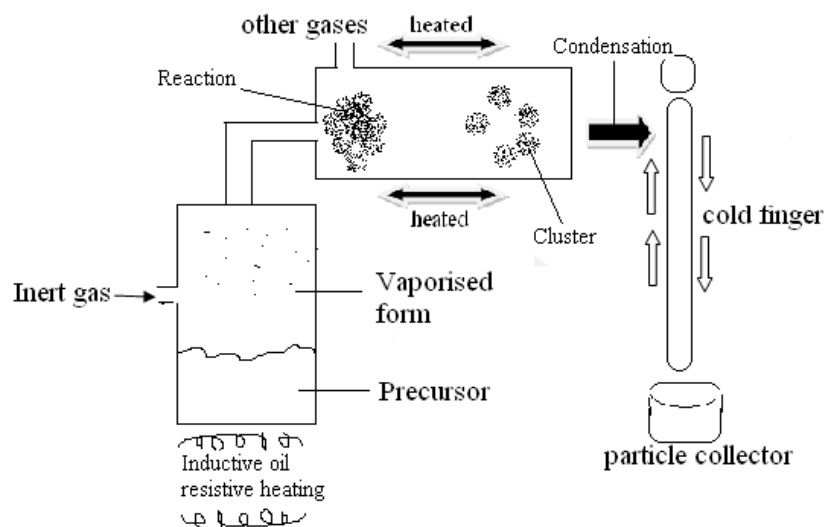
Principle: the process involved is conversion of precursor (metal organic compound) into vapors in reduced pressure atmosphere.

Processes: the precursor (starting material) is vaporized in a bubble and mixed with inert gas like helium to carry vapors into heating furnace. Condensation reaction takes place in heating furnace at a particular temperature. The product formed after the condensation process is in the form of clusters. The clusters are then condensed into nano particles in a cold finger which are removed by scraping.

Advantages:

- Simple technique and does not require high vacuum
- It is possible to deposit nano materials with almost any shape and size.

The byproducts are removed to gas phase. Therefore the product obtained is pure.



NANO SCALE MATERIAL

Nano scale materials are defined as a set of substances where atleast one dimension is less than approximately 100nm. A nanometer is one millionth of a millimeter. Nano materials are of interest because of this scale unique optical, magnetic, electrical and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine and other fields.

FULLERENES: Fullerenes are class of molecules made of only carbon atoms having closed cage like structure. Many number of fullerene molecules with different carbon atoms like C_{60} , C_{70} , C_{74} , C_{76} etc., have been prepared but C_{60} is more stable. The C_{60} molecule had spherical shape resembling a soccer ball (foot ball). It is also commonly called as Bucky ball. The C_{60} molecule consist of 12 pentagons and 20 hexagons and each pentagon is surrounded by five hexagons and each hexagon is surrounded by three hexagons



and three pentagons placed next to each other alternately fold in the form of ball. Each carbon atom on the cage surface is bonded to three carbon neighbors therefore is sp^2 hybridized. The chemical formula for fullerene is C_{20+2n} .

In fullerenes, 12 pentagonal rings are necessary and sufficient to form the cage closure. It is quite stable, breaking the balls requires temperature of about 1000C. Fullerene has high tensile strength and high packing density.

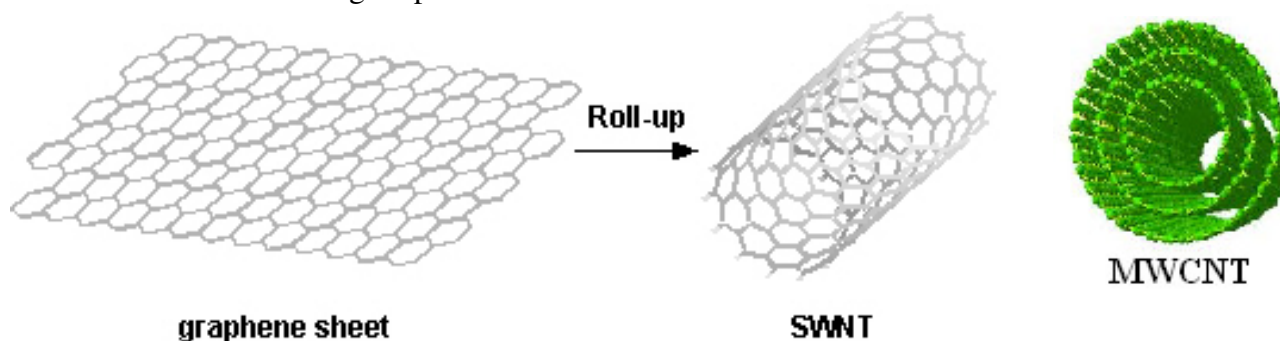
Applications:

- It is used in electrographic imaging, solar cells, non linear optical thin films etc.,
- Used to make carbon films, diodes, double layer capacitor and storage devices.
- Used for the conversion of diamond
- Used as gas sensors, temperature sensors, particle sensors and detection of organic vapors.

CARBON NANO TUBES: Carbon nanotubes are allotropes of carbon with a cylindrical nanostructure having diameter of 1nm and longer than a micrometer. It is one dimensional material like nano wires. CNT is made up of graphite sheet. When the graphite sheet is rolled up hexagonally, it forms a tube like structure is called as CNT.

Types of CNT:

1. Single walled nanotubes (SWCNT): These are formed by rolling up of single graphite layer. Diameter is 1.4nm and length upto few micrometers.



2. Multi walled nanotubes (MWCNT): These are formed by rolling up of two or more graphite layers. Diameter is from 30 to 50nm and length upto few micrometers.

Properties:

- CNTs have High Electrical Conductivity, Tensile Strength, Thermal Conductivity And flexibility and elasticity.

Applications: It can be used in

- Conductive plastics ,Structural composite materials, Flat-panel displays, Gas storage Micro- and nano-electronics, Radar-absorbing coating, Batteries with improved lifetime, Biosensors for harmful gases
