COURSE TITLE – APPLIED CHEMISTRY FOR CIVIL ENGINEERING STREAM

COURSE CODE: BCHEC102/202

MODULE 1- STRUCTURAL MATERIALS

Metals and Alloys: Introduction, Properties and application of Iron and its alloys, Aluminum, and its alloys
Cement: Introduction, composition, properties, classification, manufacturing process of cement, process of setting and hardening of cement, additives for cement and testing of cement
Refractories: Introduction, classification based on chemical composition, properties, and application of refractory materials.
Glass: Introduction, Composition, Types, Preparation of Soda-lime glass, properties, and applications of glass.
Self-learning: Chemistry of reinforced concrete from various sources of water (seawater, groundwater, treated water).

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Properties of Iron Metal:

- It is malleable and ductile.
- Iron is ferromagnetic at ordinary temperatures.
- Good conductor of heat and electricity.
- Prone to undergo corrosion due to low electrode potential.

Applications of iron:

- It is used in buildings, bridges, dams, pillars etc.
- Used in machinery tools and equipment.
- Used in transformers, electric motors, engines etc.
- Used in making of steel of various types by alloying with carbon and various metals.

Properties of Heat-Treatable Stainless Steel

- Tough, magnetic and can be worked in cold state.
- They have water and weather resistance.
- corrosion resistance.
- They can be rolled, forged and cold drawn.

Applications:

- Heat treatable stainless steels are used in making surgical instruments, scissors, blades, and cutlery.
- Non heat treatable magnetic type stainless steel is used in making automobile parts and chemical equipment.
- Non heat treatable nonmagnetic type stainless steel are used in making dental and surgical instruments, household utensils, decorative pieces, sinks etc.

Properties of Aluminum

- It is soft, malleable, and ductile.
- Has low density.
- High electrical and thermal conductivity.
- Corrosion resistance is due to the formation of protective oxide layer.

Applications:

- Used in daily used products like cans, foils, kitchen utensils, window frames airplane parts etc.
- Used in electrical transmission lines.

Properties of Duralumin:

- It has mechanical strength like steel but lightweight with density one-third of stainless steel.
- Good conductor of heat and electricity.
- It is tough, ductile, easily castable and machinable.
- Exhibit very high tensile strength.

Applications of Duralumin

- Used in aircraft, automobile, and locomotive industry.
- Used in surgical instruments.
- It is used as sheet and plate in structural components for aerospace, and military equipment.

Properties and applications of magnalium

- Magnalium alloys with lower magnesium content exhibit greater mechanical strength, greater corrosion resistance and lower density than pure aluminum.
- They are more easily workable and easily weldable than pure aluminum hence they are used in aircrafts, automobile parts, alloys with higher magnesium content are brittle, low corrosion resistance, more reactive and used as metal fuel and also to produce sparks.

Cement

Cement can be defined as a material possessing adhesive and cohesive properties which is capable of bonding materials like stones, bricks, building blocks iron etc.

Composition

1) CaO --- 60- 69% if CaO content is too less the strength of cement will be lesser and may set too quickly and chances of expansion nd cracking is more in such cases.
2) SiO_2 – 17 – 25%, higher SiO_2 will increase the strength of cement but prolongs the setting period.
3) Al_2O_3 ---- 3-8% higher the % of SiO_2 will increase the strength and reduce the setting period.
4) Fe_2O_3 ---- 2- 4%, it imparts strength, hardness and grey colour to the cement.
5) Other constituents: MgO (1-5% So_3(1-3%), $Na_2O + K_2O$ (0.3-1.5%)

Properties of cement:

1) Initial setting time of cement should not be less than 30 minutes and final setting time should not be more than 600 minutes.
2) Compressive strength of cement should not be less than 1.6kg/mm^2 after 3 days. It should not less than 2.2 kg/mm^2 after 7 days.
3) Soundness: this is the measure of volume change in cement in hydration. The smaller the volume change cement is said to be sounder. The volume change of the cement set in 24 hours between 25ºC and 100ºC for unaerated cement should not be more than 10 mm and for aerated cement should not be more than 5 min.
4) Fitness: fitness refers to the particle size of cement. Cement with lesser particle size will have more surface area. Finer the cement particles, the larger will be surface area and cement

undergoes fast reactions generating large heat resulting in early setting, early development of strength and is likely to develop cracks.

Types of cement

1. Natural cement
2. Pozzolana cement
3. Slag cement
4. Portland cement

Natural cement: natural cement is made by high temperature calcination of naturally occurring limestone such as clay containing Al_2O_3 and SiO_2.natral cement is quick setting and of relatively low strength.

Pozzolana cement: it is made by simple mixing and grinding of slaked lime and volcanic ash which is obtained by rapid cooling of lava which contains silicates of calcium, iron and aluminum.

Slag cement: it is made up of hydrated lime and blast furnace slag (mixture of calcium and aluminum silicates) slag cement sets very slowly and has low strength also poor abrasion resistance. They ae just used in making bulk concrete.

Portland cement: it is a finely ground powder obtained by calcinating together, at about 1500^0C a mixture of argillaceous (clay containing) and calcareous (lime containing) materials in known proportion. It contains compounds of lime, silica, alumina, and iron. All Portland cement is hydraulic in nature as they set and harden under water. It readily forms paste when mixed with water. This paste tends to form a hard mass called concrete. Due to this it's being used everywhere.

Wet Process :

Materials required:

- Source of lime, CaO (limestone, chalk, calcite)
- Source of aluminaAl_2O_3 (clay, slate, shale)
- Source of silica SiO_2 (clay, slate, shale)
- Source of Fe_2O_3 (clay, iron ore)
- Gypsum ($CaSO_4.2H_2O$)

Steps

1. Mixing
2. Burning
3. Grinding

Mixing: in wet process limestone is powdered and stored in separate tank. Alumina, silica source is washed with water to remove organic material and is stored in separate basin. These are sent to grinding mills where they are mixed with water to form a paste called slurry. This slurry contains 38% to 40 % water. This slurry is stored in tanks and kept ready for feeding to a rotary kiln.

Burning: the slurry is taken in a rotary kiln where it is subjected to burning. During burning it undergoes actual chemical changes. Rotary kiln is a long steel cylinder with 30-160 meters and diameter of 2-4 meters. The kiln is kept in slanted position and is rotatable. The upper end is cooler and lower end is hotter. Slurry is passed from upper end and made to flow slowly from upper to lower end with slow rotation.

The following changes takes place based on temperature:

a) The upper part of kiln is called drying zone where the temperature is around 400^0 C, where the water evaporates.
b) The central part is called calcination zone where the temperature is around 1000^0 C, here the limestone is decomposed to quick lime and carbon dioxide.
$CaCO_3 \longrightarrow CaO + CO_2$

c) The lower part is called clinkering zone where the temperature is between 1500^{o} C to 1700^{0} C. Here lime and clay undergo chemical fusion to form calcium, aluminate, and silicates.
   $2CaO + SiO_2 \longrightarrow 2CaO.SiO_2$ (dicalcium silicate)
   $3CaO + SiO_2 \longrightarrow 3CaO.SiO_2$ (tricalcium silicate)
   $3CaO + Al_2O_3 \longrightarrow 3CaO.Al_2O_3$ (tricalcium aluminate)
   $4CaO + Al_2O_3 + Fe_2O_3 \longrightarrow 4CaO.Al_2O_3.Fe_2O_3$ (tetracalcium aluminoferrate)
   These fused products are hard greyish stones called clinkers.

Grinding: Cooled clinkers are subjected to grinding by ball milling or tube milling method. 2-3% gypsum is added to prevent the early setting of cement when mixed with water.

Setting and hardening of cement:
When cement is mixed with water to form a paste, it undergoes hydration reactions. Initially, paste is converted into gel and later it is converted into hard mass.
There are two steps in the process of solidification of cement paste:

1) Setting
2) Hardening

1) Setting: in the initial setting of cement paste it is converted into gel. The gel formation is due to the following reactions.

a) Hydration of tricalcium aluminate
   $3CaO.Al_2O_3 + 6H_2O \rightarrow 3\ CaO.Al_2O_3.6H_2O$

b) Hydration of tetracalcium aluminoferrate
   $4Cao.Al_2O_3.Fe_2O_3 + 7H_2O \rightarrow 3\ CaO.Al_2O_3.6H_2O + CaO.\ Fe_2O_3.H_2O$
   Hydration of tricalcium aluminate and tetra calcium aluminoferrate reactions are important as it is responsible for initial setting and early strength of cement.

2) Hardening: the gel formed in the initial setting of cement undergoes crystallization which undergoes crosslinking resulting in hardening of cement.

a) Hydration of tricalcium silicate
   The hydration of tricalcium silicate begins within 24 hours and completes in 7 days.
   $$2\ [\ 3\ Cao.\ SiO_2] + 6\ H_2O \rightarrow 3\ Cao.2SiO_2.\ 3H_2O + 3\ Ca(OH)_2$$
   This reaction is mainly responsible for the development of the strength of cement in the first 7 days.
   Dicalcium silicate hydrate between 7 to 28 days.
   $$2\ [\ 2\ CaO.SiO_2] + 4\ H_2O \rightarrow 3\ CaO.2SiO_2.6H_2O + Ca(OH)_2$$

Additives for Cement:
Role of accelerators, retarders, extenders, and dispersants in cement.

1) **Accelerators:** these are added to cement to speed up the initial setting time and to start curing earlier. These are very much required in cold conditions where concrete can be frozen before attaining the initial strength. Commonly used accelerators are calcium chloride calcium nitrate, calcium nitrite, calcium formate and aluminum compounds.
2) **Retarders:** these are added to prevent the setting of cement too rapidly. These are used in conditions like high pressure and high temperature like in deep wells. Commonly used retarders are polysaccharides, lignosulphonates, cellulose etc.
3) **Extenders:** these are light weight additives added to reduce the weight of the cement slurry. These have specific gravity lower than that of cement. They decrease density of concrete with acceptable compressive strength. Commonly used extenders are crushed coal, ground rubber, fly ash, sodium silicate.

4) **Dispersants:** these are added to cement slurries to facilitate blending at high densities without the demand for more water. They improve the flow behaviors of cement slurry and help in pumping of slurry. Commonly used dispersants are poly naphthalene sulphonates and poly melamine sulphonates.

Determination Of Cao by rapid EDTA method

Principle: calcium ions present in the solution of cement is determined by titrating a known volume of the cement solution with standard solution of EDTA. The solution is treated with dimethylamine to maintain the pH at 12-14.4 NaOH is added to precipitate the Mg^{+2} present in the solution as magnesium hydroxide. Glycerol is added to get the sharp end point. Patton and Reeder's indicator is used here.

Procedure:

1) Transfer 25 cm^3 of cement solution into a clean conical flask.
2) Add 5 mL of dimethylamine buffer.
3) Add one test tube full of 4N NaOH.
4) Add 5 cm^3 of glycerol.
5) Add 2 drops of Patton and Reeder's indicator
6) Titrate against the standard EDTA solution taken in the burette.

Calculations:

1 cm^3 of 1M EDTA = 1 millimole of CaO = 56.08×10^{-3} g of CaO
y cm^3 of z M EDTA contains = (0.05608x y x z) g og Cao
0.05608 x y x z g of CaO = weight of CaO in 25.0 cm^3 of cement sample solution.
% og CaO in the cement sample = (weight of Cao in cm^3 / weight of cement in 25cm^3 of solution) x100

Refractories:

Refractories are ceramics materials which can withstand high temperatures with high abrasion and corrosion resistance without undergoing any change in their strength and shape.

They are mainly made up of oxides, carbides, nitrides of silicon, aluminum, magnesium, calcium, boron, chromium and zirconium.

Classification based on Chemical composition.

1) **Acidic refractories** : these refractory materials exhibit high resistance to acidic materials but are readily attacked by basic slags like CaO, MgO etc. these used to handle acidic materials under acidic environments. Silica bricks, fireclay refractories and high alumina refractories are commonly used acidic refrctories.
2) **Basic refractories**: these refractory materials exhibit high resistance to basic materials but are readily attacked by acidic slags like silica, alumina, zirconia etc. these are used to handle basic materials under basic envioronmnet. Magnesite and dolomite refractories are the common types of basic refractories.
3) **Neutral refractories**: These refractories are made from weakly basic/ acidic materials. Silicon carbide, carbon refractories and chromite bricks are commonly used neutral refractories.

Properties and applications of refractory materials

Properties

1) Refractoriness: It is the measure of ability of a material to withstand heat without undergoing deformation. A good refractory material will withstand very high temperature.
2) **Load-bearing capacity:** refractories must show high load-bearing capacity at higher temperatures.
3) **Dimensional stability:** dimensional stability is the resistance of a material to any change in the volume when it is exposed to high temperature over a prolonged period. Refractories must exhibit high dimensional stability.
4) **Chemical inertness:** the refractories should not react with reactants, slags, gases, fuel ashes, furnace and the products involved inside the furnace. These should be chemically inert.

Applications:

1) **Fire clay refractories** are used in steel manufacturing industries as lining for blast furnaces, ovens and crucible furnace.
2) **Silica bricks** are used in lining roofs of electric furnaces, glass furnace and walls of coke ovens.
3) **Alumina refractories** are used in linings of cement rotary kilns, reheating furnaces.
4) **Silicon carbide refractories** are used in muffle furnace due to their high thermal conductivity. Low thermal coefficient of expansion.

Glass

Glass is an amorphous, hard, brittle transparent material. It is considered a super cooled liquid with very high viscosity.

It is obtained by fusing a mixture of several silicates of metals like Na, K, Ca and Pb.

Types of Glasses.

1. **Soda–Lime glass:** The composition of soda- lime glass is $Na_2O.\ CaO.6SiO_2$ they are low in cost, resistance to devitrification and relatively resistance to water. They melt easily.
2. **Potash- lime glass**: the composition of potash- lime glass $K_2O.CaO.6SiO_2$. it is known as hard glass. They possess high melting points. Fuse with difficulty and are less acted upon acids, alkalis and other solvents. These are costlier than soda lime glasses.
3. **Glass Or Flint Glass:** the composition of lead glass is $K_2O.PbO.6SiO_2$. It is bright and luster. Has a low melting point and is more expensive than lime soda glass. Easier to shape and work with it.

4. **Borosilicate glass or Pyrex glass or Jena glass:** These are very hard glass. Contains silica and boron with small amount of alumina and some alkali oxides. They have high chemical resistance and low thermal coefficient of expansion.

Preparation of Soda- Lime Glass

Soda-lime glass is the most used glass.

Raw materials:

1. Soda ash (Na_2CO_3) used as source of sodium
2. Limestone (Cao) chalk, lime is used as source of calcium
3. Quartz, white sand used as source of silicon
4. pieces of broken glass (cullet's)used to increase fusibility
5. For imparting colour, various salts are used such as ferric salt for yellow, nickel salts for red, cobalt salts for blue etc.

Steps:

1. **Melting**: raw materials such as sand, soda ash and limestone are taken with proper proportion and mixed with cullets, the mixture is finely powdered and taken in a open hearth furnace maintained at 1800ºC. at this temperature the mixtres melts and fuses.

   $CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2 \uparrow$

   $Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2 \uparrow$

   Coloring salts are added at this stage. Heating continues until the molten mas is free from bubbles and glass balls. Then the mixture is cooled to 800º C
2. **Forming and shaping**: molten glass ae subjected to forming and shaping obtain the desired articles. This is done by blowing or molding or pressing between rollers.
3. **Annealing**: the process of cooling glass articles slowly and gradually by passing through different chambers with descending temperatures is called annealing. This is an important step in manufacturing glass. If the glass is cooled rapidly then the outer layer cools down first, leaving the interior side portion in strain. Due to this unequal expansion the article is likely to crack to pieces. The longer the annealing period the better the quality of glass.
4. **Finishing**: All glass articles are subjected to a finishing process after the annealing such as grinding, polishing, cutting and sandblasting

Properties And Applications of Glasses

Properties of glasses:

- Glasses are amorphous, brittle, transparent solids without definite melting point.
- They can absorb, reflect, and transmit light.
- They are very good electrical insulators.
- They have good chemical resistance and are not affected by air, water, acids and chemical agents except HF which converts its silica into SiF_4.
- They can be formed and moulded into articles.

Applications of Glasses

1. Soda lime glasses are used in window glasses, electrical bulbs, plate glasses, bottles, jars building blocks, table wares etc.
2. Lead glasses are used for high quality table wares, optical lenses, neon sign tubing, cathode ray tubes , electrical insulators and in art objects, in extra dense optical glasses for windows, and I shields to protect personnel from X-rays and gamma-rays in medical and atomic energy fields etc.
3. Borosilicate's glasses are used for pipelines for corrosive liquids, gauge glasses, laboratory apparatus, kitchen wares, chemical plants, television tubes, electrical insulators etc.
4. Silica glasses are used in chemical plants, electrical insulating materials in electrical heaters, furnaces etc.

Question Bank

1. Write the properties and applications of iron and its alloy.
2. Write the properties and applications of aluminum and its alloy.
3. Describe the manufacture of the cement by wet method.
4. Describe the process of setting and hardening of cement.
5. Explain the testing of cement by EDTA method.
6. Define refractories. Mention the properties and applications of refractories materials.
7. Describe the classifications of refractories based on chemical composition.
8. Explain the preparation of soda lime glass. Write the properties and applications of glass.

Module 2: Energy Conversion and Storage, Corrosion

Energy conversion: Introduction, construction, working, and applications of Photo voltaic cells, methanol-oxygen fuel cell.

Storage devices: Introduction, construction and working of Li-ion battery.

Corrosion: Introduction, electrochemical corrosion of steel in concrete, types (differential metal and aeration), Stress corrosion in civil structures, corrosion control (design and selection of materials, galvanization, anodization, and sacrificial anode method).

Self-learning: Corrosion inhibitors

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Solar Energy

The energy obtained by the sun is called solar energy. Solar energy, based on its utilization, can be of two types:

1. Director solar power
2. Indirect solar power
   1. **Director solar power:** Director solar power in walls only one step transformation into a usable form.
      Example 1) A photovoltaic cell converts solar energy to electrical energy.

      Example 2) solar thermal collector
   2. **Indirect solar power:** Indirect solar power requires more than one transformation to reach usable form.
      E.g. 1: Plants convert solar energy into chemical energy when they are burned.

      E.g. 2: Fossil fuels are obtained from plants which produce heat energy that can later be burned as fuel to generate electricity.

      E.g. 3: Ocean thermal energy production uses the thermal gradient that is present across the ocean depths to generate power.

Advantages of Indirect Solar Power

- Solar power is pollution-free
- Low operating costs
- Facilities can operate with little maintenance
- High public acceptance and excellent safety
- Solar power is economical, except the initial setup

Disadvantages of indirect solar power

- Sunlight is diffuse source
- High installation costs
- Energy can be produced only during the day.

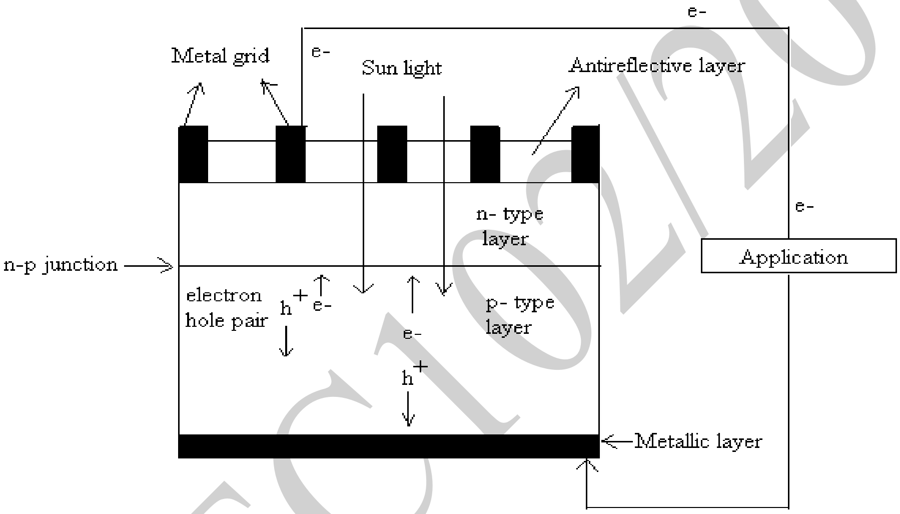
Construction and working of a photo voltaic cell

- A photovoltaic cell consists of 'n' type semiconductor at the top and 'p' type semiconductor at the bottom. Hence, the p-n junction is formed between the two.

- A metallic grid above the diode forms one of the electrical contacts and allows the light to fall on the semiconductor.
- An anti-reflexive layer made up of titanium dioxide present between the metallic grid increases the transformation of sunlight into semiconductors.
- Another metallic layer is present at the back of the semiconductor, which forms another electrical contact.

Working

When electromagnetic radiation falls on the ‘p-n’ junction diode, the electron pair hole is generated. Electrons move towards the ‘n’ type semiconductor, and the holes move towards the ‘p’ type semiconductor. On connecting these to ends, current flows between them to an external circuit.



Applications

1. For producing electricity using solar power plants
2. To provide electricity to satellite
3. Remote sensing techniques from space using satellite with objectives
4. To provide reliable weather monitoring and forecasting by monitoring the climatic factors

Fuel cells:

Introduction: The electrochemical conversion of the free energy change of a redox reaction into electrical energy is the working principle of any type of cell. The electrode reaction of a primary battery is irreversible, and the cell produces EMF as long as the active material is present in the cell.

Conventional Batteries	Fuel cells
1. Batteries are energy storage device. 2. Secondary batteries need charging. 3. The reactance and products from an internal part of batteries 4. Waste product in a battery may be harmful that is less eco-friendly.	1. Fuel cells are energy conversion devices. 2. Fuel cells do not need charging. 3. Reactance is continuously supplied, and the products are continuously removed. 4. More eco friendly

Fuel cells:

A fuel cell is defined as a galvanic cell in which chemical energy is converted into electrical energy.

The Fuel cell can be represented as follows Fuel electrode/electrolyte/electrode/oxidant.

In a fuel cell

At anode: the fuel undergoes oxidation
Fuel ⇒ oxidized product + ne^-

At cathode: the oxidant gets reduced.

Oxidant + ne^- ⇒ reduced product

Advantages of a fuel cell

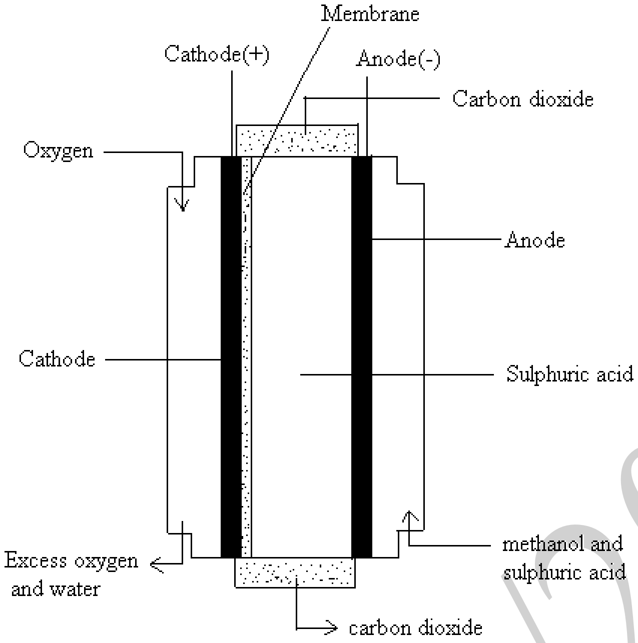
1) They offer high energy conversion
2) Energy as long as fuel and oxidants are supplied
3) Silent operation
4) They are ecofriendly
5) No need of charging

Methanol – Oxygen Fuel Cell

Methanol is one of the most electroactive organic fuels in the low-temperature range. It is mainly because:

- It has low carbon content.
- It possesses a readily oxidisable OH group and
- It has high solubility in aqueous electrolytes

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



The electrode reactions are,

$$\text{At anode: } CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$$

$$\text{At cathode: } 3/2\ O_2 + 6H^+ + 6e^- \longrightarrow 3\ H_2O$$

$$\text{Net cell reaction is: } CH_3OH + 3/2\ O_2 \longrightarrow CO_2 + H_2O$$

Advantages

1. Stable at all atmospheric conditions.
2. CO_2 produced by the reaction can be easily removed.
3. Easy handling
4. Methanol has low carbon content.
5. Readily oxidizable OH group.
6. Low-cost liquid fuel.

Applications

1. It is used in military applications and in large scale power production.
2. It's also used in fuel cell vehicles and space shuttles.
3. It is ideal for powering smaller vehicles such as forklift etc.

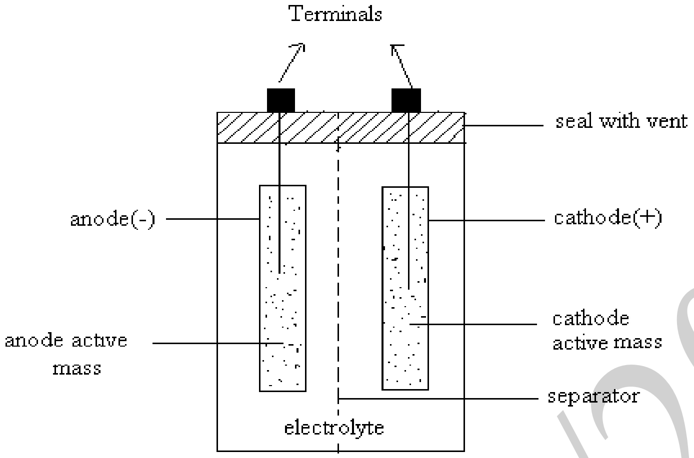
Storage Devices

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

Batteries generate power and acts as portable sources of electrical energy. Batteries are used in calculators, digital watches, pacemakers for heart, hearing aids, portable computers, digital cameras, car engines, emergency lighting, electroplating, industrial, military and space applications.

Basic concepts

The basic electrochemical unit in a battery is a galvanic cell. The components of such a cell are shown in the fig.



The principal components of a battery are

The anode or negative electrode – it gives electrons to the external circuit by undergoing oxidation during electrochemical reaction.

The cathode or positive electrode – it accepts electrons from the external circuit and reduction of the active species occurs.

The electrolyte – an ionic conductor. The electrolyte (active mass in the anode and cathode compartments) is commonly a solution of an acid, alkali or salt having high ionic conductivity. Solid electrolytes having ionic conductivity at the operating temperature of the cell are also used.

The separator – the material that electronically separates the anode and cathode in a battery to prevent internal short-circuit is referred to as a separator. It is permeable to the electrolyte to maintain the desired ionic conductivity. Thus the main function of the separator is to transport ions from the anode compartment to the cathode compartment and vice versa.

Eg: fibrous forms of regenerated cellulose, vinyl polymers and polyolefin's, cellophane and nafion membranes.

Classification of batteries

Batteries are classified as

a) Primary (irreversible) batteries

b) Secondary (reversible) batteries

c) Reserve batteries

a) **Primary batteries**: In primary batteries the cell reaction is not completely reversible. They are also referred to as irreversible batteries. These are not rechargeable and once discharged after that it has no further electrical use.
Eg: Leclanche cell(Zn-MnO_2) and Li-MnO_2battery

b) **Secondary batteries:** Secondary batteries are rechargeable. The cell reactions are reversible and these are also referred to as storage or reversible batteries. After discharge secondary batteries can be recharged electrically to their original condition by passing current through them in the direction opposite to that discharge current.
Eg: Lead acid battery, Ni-Cd battery

c) **Reserve batteries:** Reserve batteries are the batteries which are stored in an inactive state and made ready for use by activating them before the application. The activation involves adding electrolyte or any other cell component. One of the components is isolated and stored separately and is filled just before it is needed. Electrolyte is the component that is usually isolated and hence the battery has long term storage capacity.
Eg: Mg water activated batteries (Mg-AgCl and Mg-CuCl), Zn- Ag_2O batteries.
Lithium-Vanadium Pentoxide battery (Li-V_2O_5)

Li- ion Battery

The three components of a lithium-ion battery are the positive and negative electrodes and electrolyte. The negative electrode of a lithium-ion cell is made of carbon (graphite). The positive electrode is a layered metal oxide such as lithium cobalt oxide or lithium manganese oxide. The electrolyte is typically a mixture of organic carbonates such as ethylene carbonate or diethyl carbonate containing lithium salts, such as $LiPF_6$, $LiBF_4$ or $LiClO_4$. A liquid electrolyte acts as a carrier between the positive and negative electrodes when current flows through an external circuit.

Electrode reactions

While discharging, lithium atoms present in the graphite layer are oxidized, liberating electrons and lithium ions. Electrons flow through external circuit to the cathode and lithium ion moves through the electrolyte towards cathode. At cathode lithium ions are reduced to lithium atoms and are inserted into the layered structure of metal oxide.

At Anode

$$\text{Li-C}_6 \longrightarrow \text{Li}^+ + 6\text{C} + e^-$$

At Cathode

$$\text{Li}^+ + e^- + \text{MO}_2 \longrightarrow \text{Li-MO}_2$$

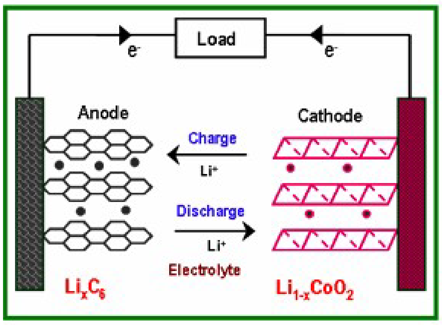
When the cell is charging, the reverse occurs. Lithium present in the layered metal oxide oxidized, liberating electrons and lithium ions. Electrons flow through external circuit to the cathode and lithium ion moves through the electrolyte towards anode.

At Anode

$$\text{Li-MO}_2 \longrightarrow \text{Li}^+ + e^- + \text{MO}_2$$

At Cathode

$$Li^+ + 6C + e^- \longrightarrow Li\text{-}C_6$$



Applications

- Used in mobile phones and smart phones, laptops and tablets, digital cameras and camcorders, electronic cigarettes, handheld game consoles and torches (flashlights).
- Used in electric vehicles like electric cars, Pedelecs (pedal electric cycle), electric wheelchairs, radio-controlled models etc.

Corrosion

Corrosion is defined as “the destruction of metals or alloys by the surrounding environment through chemical or electrochemical changes.”

The process of corrosion is the transformation of pure metal into its undesired metallic compounds. The life of a metal object gets shortened by the corrosion process.

The familiar examples of corrosion are

i. Rusting of iron – a reddish brown scale formation on iron and steel objects. It is due to the formation of hydrated ferric oxide.
ii. Green scales formed on copper vessels. It is due to the formation of basic cupric carbonate [$CuCO_3 + Cu(OH)_2$]

Ill Effects of Corrosion

- Loss of efficiency.
- Contamination of product.
- Damage of metallic equipments.
- Inability to use metallic materials.
- Appearance as when corroded material is unpleasing to the eye.
- Loss of valuable materials such as blockage of pipes, mechanical damage of underground water pipes.
- Accidents due to mechanical loss of metallic bridges, cars, aircrafts etc.
- Safety, for example, sudden failure can cause fire, explosion, release of toxic products, and construction collapse.
- Depletion of Natural Resources.
- India Losses 5.7 % GDP due to corrosion.

Chemical corrosion (Dry corrosion)

Chemical corrosion occurs due to the direct chemical reaction between the metal and the gasses present in the corrosive environment. This type of corrosion is generally observed in the absence of moisture or conducting electrolyte medium. Therefore, it is also known as dry corrosion.

Eg: Oxidation of metals or alloys on exposure to oxygen in air. Reaction of corrosive gasses such as HCl, H_2S, SO_2, Cl_2, F_2, NH_3 etc. with metal and alloy surfaces.

Electrochemical corrosion (Wet corrosion)

Electrochemical corrosion involves reactions in aqueous medium. The conducting surface of the metal undergoes an electrochemical reaction with the moisture and oxygen present in the atmosphere. This process can be explained on the basis of electrochemical theory of corrosion.

Electrochemical theory of corrosion of steel in concrete

Steel in concrete is naturally in a passive state, which can be broken under following conditions:

1. Presence of chloride ions, which convert passive steel into active form.
2. When concrete is exposed to air, carbon dioxide in air reacts with surface of concrete, calcium hydroxide in the concrete is carbonated which lowers the pH and converts steel from passive to active.

Corrosion of iron metal in concrete as explained as follows:

i) Formation of galvanic cells. Anodic and cathodic areas are formed resulting in minute galvanic cells.

ii) At anode oxidation takes place so that metal is converted into metal ions with the liberation of electrons and move towards cathode.

iii) Oxygen of the atmosphere is reduced to OH^- ions in the presence of water (moisture) at the cathodic area.

Anodic reaction:

At the anodic area, oxidation takes place resulting in the corrosion of iron.

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

Cathodic reactions:

Electrons flow from the anodic to cathodic area and cause reduction depending on the nature of the corrosive environment. Since the metal cannot be reduced further, metal atoms at cathodic region are unaffected by the cathodic reaction. Some constituents of the corrosion medium take part in the cathodic reaction.

Most common types of cathodic reactions are either liberation of hydrogen or absorption of oxygen.

In acidic medium and in the absence of oxygen, hydrogen liberation takes place.

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

In neutral or alkaline medium and in the absence of oxygen, hydroxide ions are formed with liberation of hydrogen.

$$2H_2O + 2e^- \longrightarrow 2OH^- + H_2\uparrow$$

In neutral or alkaline medium & in the presence of oxygen, hydroxide ions are formed

$$2H_2O + O_2 + 4e^- \longrightarrow 4OH^-$$

The metal ions formed at the anode combine with the OH^- ions and form the insoluble $Fe(OH)_2$. In an oxidizing environment, it is oxidized to ferric oxide and the yellow rust is hydrated ferric oxide.

$$2Fe^{+2} + 4OH^- \longrightarrow 2Fe(OH)_2$$

$$4Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 2[Fe_2O_3\cdot 3H_2O] + H_2$$

Yellow Rust

Types of Corrosion

1. Differential Metal Corrosion (Galvanic Corrosion)

Differential metal corrosion occurs when two dissimilar metals are in contact with each other in a corrosive conducting medium. The two metals differ in their tendencies to undergo oxidation, the one with lower electrode potential or the more active metal acts as anode and the one with higher electrode potential acts as cathode. The potential difference between the two metals is the driving force for corrosion. The anodic metal undergoes corrosion and the cathodic metal is generally unattacked.

The following reactions occur during differential metal corrosion. At the anode:

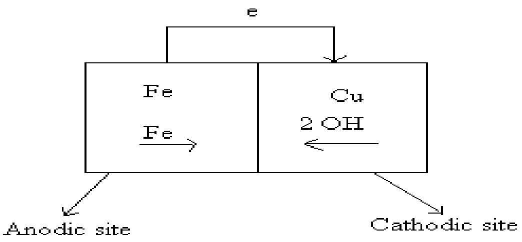
$M \longrightarrow M^{+n} + ne^-$

At the cathode: Depending on the nature of the corrosion environment the cathode reaction is either hydrogen evolution or oxygen absorption.

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

(ii) $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

For example, if a piece of iron combined with copper is exposed to corrosive atmosphere. Iron acts as anode in the presence of copper (iron is placed above copper in the electrochemical series). In such case, iron undergoes corrosion and copper is unaffected.



2. Differential Aeration Corrosion

Differential aeration corrosion occurs when a metal surface is exposed to differential air concentrations or oxygen concentrations, the part of the metal exposed to higher oxygen concentration acts as cathodic region and the part of the metal exposed to lower oxygen concentration acts as anodic region. As a result the part of the metal exposed to lower oxygen concentration undergoes corrosion.

At the anode (less O_2 concentration)

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

At the cathode (more O_2 concentration)

$$O_2 + 2H_2O + 4e- \longrightarrow 4OH^- \text{ (reduction)}$$

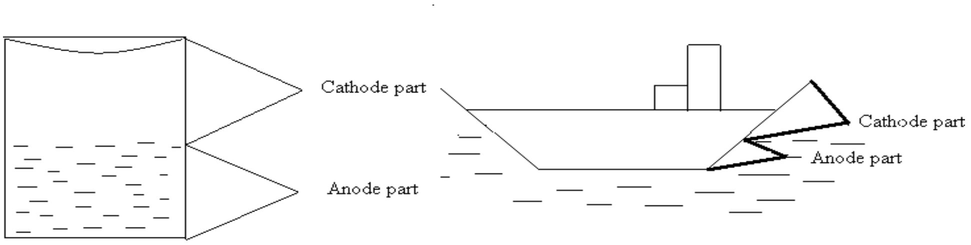
"*Corrosion of metals is due to the formation of an oxygen concentration cell because of the uneven supply of air on the metal surface is known as differential aeration corrosion.*"

Examples

i. Part of the nail inside the wall which is exposed to lower oxygen concentration than the exposed part, undergoes corrosion.
ii. Window rods inside the frame suffer corrosion but not the exposed parts.
iii. Metal under dirt, dust, scale or water undergoes corrosion.
iv. Paper pins inside the paper gets corroded, and the exposed part is free from corrosion. Water line corrosion and pitting corrosion are the two cases of differential aeration corrosion.

3. Water Line Corrosion

Water line corrosion is observed in steel water tanks, ocean going ships etc. The water line corrosion takes place due to the formation of differential oxygen concentration cells. The part of the metal below the water line is exposed only to dissolved oxygen while the part of the metal above the water is exposed to higher oxygen concentration of the atmosphere. Thus part of the metal below water acts as anode and undergoes corrosion and the part above the water line is free from corrosion.



Stress Corrosion In Civil Structure

Example: Caustic embrittlement of water boiler

- This type of corrosion is seen when the metal is under stress.
- Stress can be either applied stress or residual.
- Residual stress is from the process like welding, quenching, bending and deformation.
- Metal alloys are more susceptible than pure metals.
- Stress corrosion is dangerous because it can lead to cracking of the metal without a warning or with little warning.
- Ex: the water boilers made up of mild steel undergo corrosion at the stressed region when exposed to hot concentrated alkaline solution.
- Corrosion mechanism involves passage of alkaline impurities present in water into fine hair like crack made on the boiler.
- When water is boiled the Na_2CO_3 present in the boiler water is hydrolysed to NaOH at high temperature.

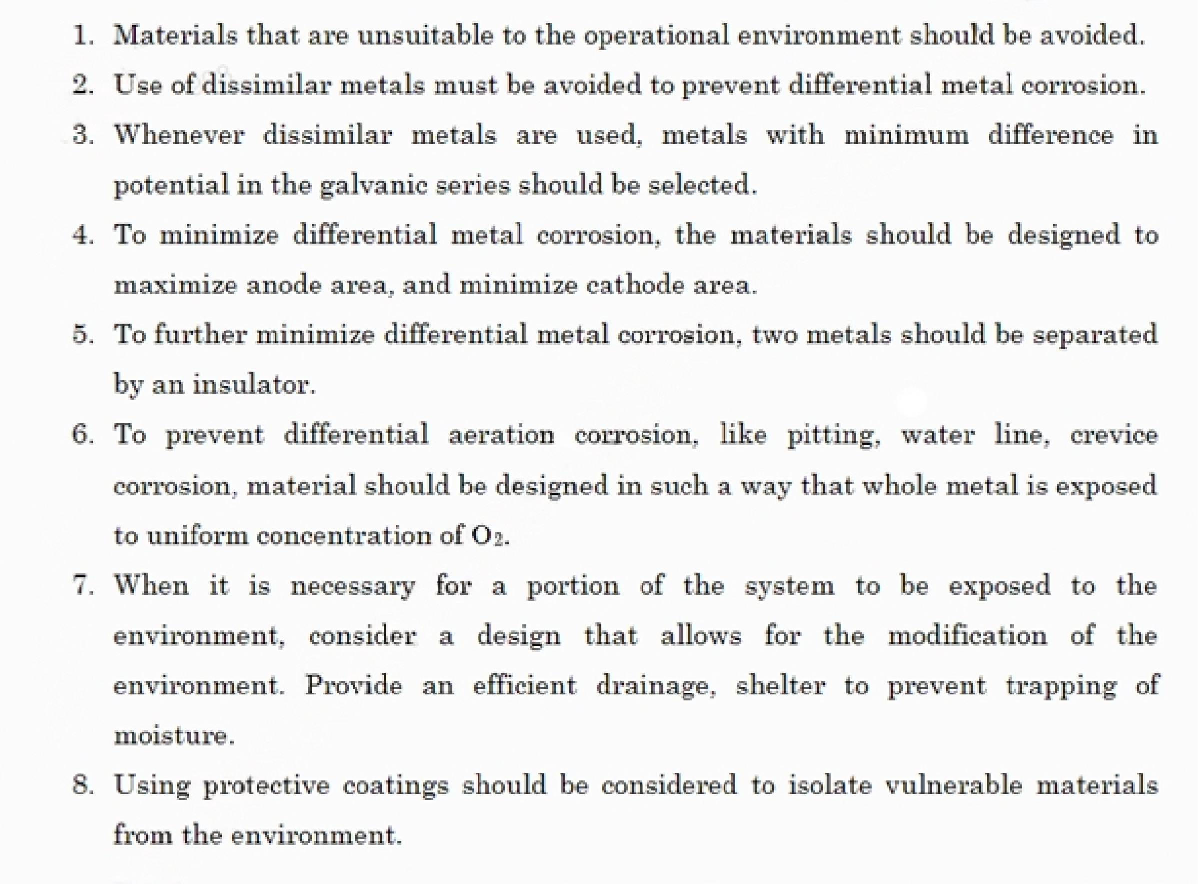
  $Na_2CO_3 + H_2O \rightarrow 2\ NaOH + CO_2$
- NaOH thus formed reaches into the crack and reacts with Fe, forming sodium ferroate and decomposes into Fe_3O_4 and NaOH.

  $2\ NaOH + Fe \rightarrow Na_2FeO_2 + H_2$

  $3\ Na_2FeO_2 + 4\ H_2O \rightarrow Fe_3O_4 + 6NaOH + 4H_2$
- NaOH thus formed reacts with iron and causes an explosion of the boiler.
- Since NaOH (caustic soda) is the main reason for corrosion this is also called caustic embrittlement.

Corrosion Control

Design And Selection of Materials

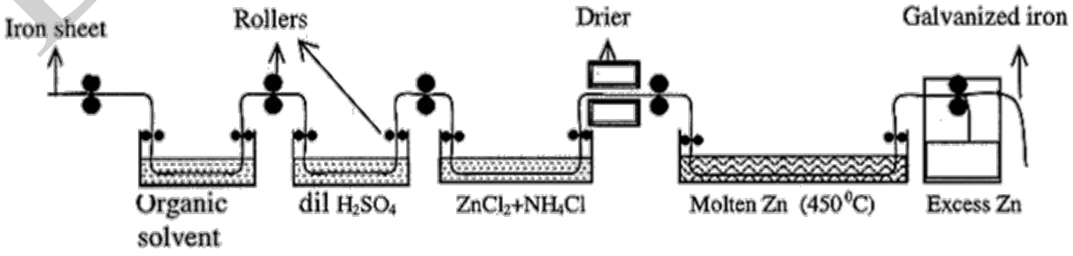


1. Materials that are unsuitable to the operational environment should be avoided.
2. Use of dissimilar metals must be avoided to prevent differential metal corrosion.
3. Whenever dissimilar metals are used, metals with minimum difference in potential in the galvanic series should be selected.
4. To minimize differential metal corrosion, the materials should be designed to maximize anode area, and minimize cathode area.
5. To further minimize differential metal corrosion, two metals should be separated by an insulator.
6. To prevent differential aeration corrosion, like pitting, water line, crevice corrosion, material should be designed in such a way that whole metal is exposed to uniform concentration of O_2.
7. When it is necessary for a portion of the system to be exposed to the environment, consider a design that allows for the modification of the environment. Provide an efficient drainage, shelter to prevent trapping of moisture.
8. Using protective coatings should be considered to isolate vulnerable materials from the environment.

Galvanization:

The coating of anodic Zn metal on iron is called galvanizing. Steps:

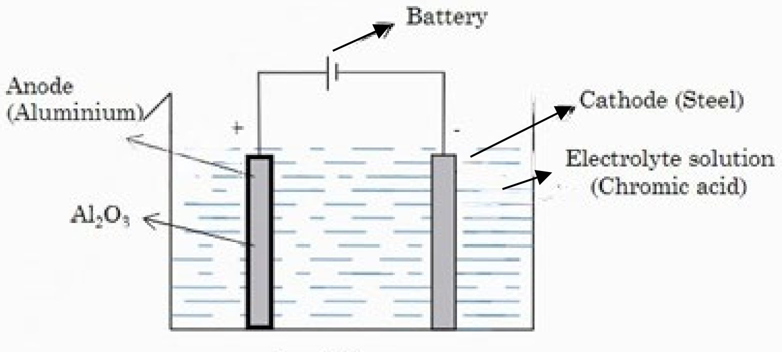
1. Iron sheet is passed through organic solvent to remove oil or grease.
2. Then it is washed with dil. H_2SO_4 to remove any rust.
3. Then it is treated with mixture of aqueous solution of $ZnCl_2$ and NH_4Cl.
4. It is dried then dipped in molten Zinc at 450℃
5. Excess zinc present on iron sheet is removed by passing through rollers.



Galvanization of iron

Anodizing

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

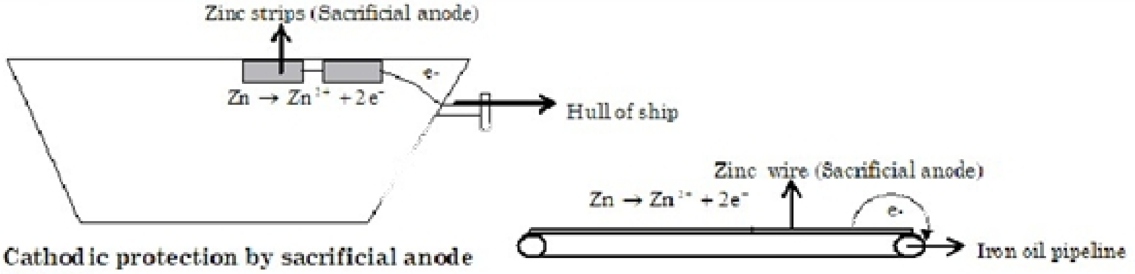


Anodizing

Before subjecting aluminium to anodization, it's surface is cleaned, degreased and polished and then it is taken as anode in an electrolytic cell. It is then immersed in an electrolyte consisting of 5-10% chromic acid. Steel or copper is taken as cathode. Temperature of the bath is maintained at 35°C. A current density of 100 or more A/m^2 is applied which oxidizes outer layer of Al to Al_2O_3 that gets deposited over the metal.

Sacrificial Anode

In **Sacrificial anode** method, metallic material to be protected is connected to a more active metal (anodic metal). Anodic metal like Zn can be employed to protect iron articles. When an anodic metal is in contact with iron specimen, a galvanic cell is set up, where anodic metal becomes anodic area and whole iron article becomes cathodic area. Anodic metal undergoes oxidation and provides electrons to the specimen and the entire specimen becomes cathodic and hence protected from corrosion. In the process, anodic metal undergoes corrosion and sacrifices itself to protect the specimen; therefore it is called as sacrificial anode. Sacrificial anodes have to be replaced in due course of time



Cathodic protection by sacrificial anode method

MODULE 3

WATER TECHNOLOGY AND NANOTECHNOLOGY

Syllabus:

Water Technology: Introduction, water parameters, hardness of water, determination of temporary, permanent and total hardness by EDTA method, numerical problems, Softening of water by ion exchange method, desalination of water by electrodialysis, determination of COD, numerical problems. Forward osmosis: Introduction, Process and applications.

Nanotechnology: Introduction, size dependent properties of nanomaterial (surface area and catalytic), Synthesis of nanomaterial by sol-gel method and co-precipitation method.

Nanomaterials: Introduction, properties and engineering applications of carbon nanotubes, graphene and nanomaterials for water treatment (Metal oxide).

Self-learning: Sewage treatment (Primary, secondary and tertiary)

Hard Water: Hard water is the one which contains salts of calcium and magnesium that is the water which contains sulfate nitrates chloride and bicarbonates of calcium and magnesium, and the hard water doesn't form leather easily with the soap this is because of the precipitation of the soap with the calcium and magnesium.

Types of the Hardness

1) **Temporary hardness:** temporary hardness is caused by the presence of bicarbonates of calcium and magnesium. This can be removed by boiling the water for about the 30 minutes. Upon boiling the bicarbonates of calcium and magnesium gets converted into insoluble carbonates and hydroxide forms which can be later on filtered and removed .
2) **Permanent hardness:** permanent hardness is caused by chloride and sulphate of calcium and magnesium. This cannot be destroyed by boiling.

Total Hardness is the sum of temporary and permanent hardness.

The hardness of the water is expressed in terms of ppm of $CaCO_3$.

Estimation of Hardness:

Principle: Metal ions responsible for hardness of water i.e., Ca^{+2} Mg^{+2} can be estimated by using standard solution of disodium salt of EDTA.

Disodium salt of EDTA is a hexa dentate ligand which forms metal EDTA complex. Which takes place readily at pH=10 to maintain this, NH_3-NH_4Cl.

Eriochrome Black-T indicator is used. When EBT is added to hard water at pH10, it forms wine red complex with few metal ions.

$M^{+2} + \text{EBT} \longrightarrow \text{M-EBT (Wine Red Color)}$

When a water sample is titrated against standard EDTA solution, remaining metal ions react with EDTA forming M-EDTA complex.

$M^{+2} + EDTA \longrightarrow M\text{-}EDTA$

M-EDTA complex is more stable than M-EBT complex, therefore at the end point EDTA replaces EBT from M-EBT complex and free EBT is released to the solution.

$M\text{-}EBT + EDTA \longrightarrow M\text{-}EDTA + EBT$ (Blue color)

Procedure:

Estimation of Total Hardness:

1. Pipette out 25 ml of hardwater into conical flask.
2. Add 5ml of NH_3-NH_4Cl buffer.
3. Add 2 to 3 drops of EBT indicator.
4. Titrate against standard EDTA solution, till the color changes from wine red to clear blue.

Calculation:

$$\text{Total Hardness} = \frac{(100 \times 10^{-3} \times V_1 \times z) \times 10^6}{V_s} = \underline{\qquad\quad} \text{ PPM}$$

Ion Exchange Method

The process of removal of calcium, magnesium, iron, salts and other metallic ions from water is called softening of water.

In iron exchange method, softening of water is done by exchanging the ions causing hardness of water with the desired ions from an ion exchange resin. Ion exchange resins are high molecular weight cross-linked polymer with a porous structure. The functional group which are attached to the chain are responsible for ion exchange properties. The resins containing acidic groups which are capable of exchanging H^+ ions for cations present in water are known as cation exchange resins. The resins containing the basic groups which are capable of exchanging OH^- ions for anions present in water as anion exchange resins.

Process: in this process cation and anion exchange resins are packed in separate columns. Hard water is first passed through cation exchange resin where cations like Ca^{+2}, Mg^{+2} are removed from hard water by exchanging with H^+ ions as follows.

$Ca^{+2} + 2R^- \text{-}H^+ \longrightarrow R_2^{-2}\text{-}Ca^{+2} + 2H^+$

$Mg^{+2} + 2R^- H^+ \longrightarrow R_2^{-2}\text{-}Mg^{+2} + 2H^+$

Hard water is then passed through anion exchange resins where ions like SO_4^{-2}, Cl^- are exchanged with OH^- ions as follows:

$R^+\text{-}OH^- + Cl^- \longrightarrow R^+\text{-}Cl^- + OH^-$

These H^+ and OH^- ions released combine to form water molecules.

Regenerations: When resins are exhausted and lose their capacity to exchange ions, they are regenerated. The process of regeneration is the reverse of the reaction taking place for ionic change. The cation exchange resin is regenerated by passing a solution of dilute HCL or H_2SO_4

$R_2^{-2}\text{-}Ca^{+2} + 2H^+ \longrightarrow Ca^{+2} + 2R^{-}\text{-}H^+$

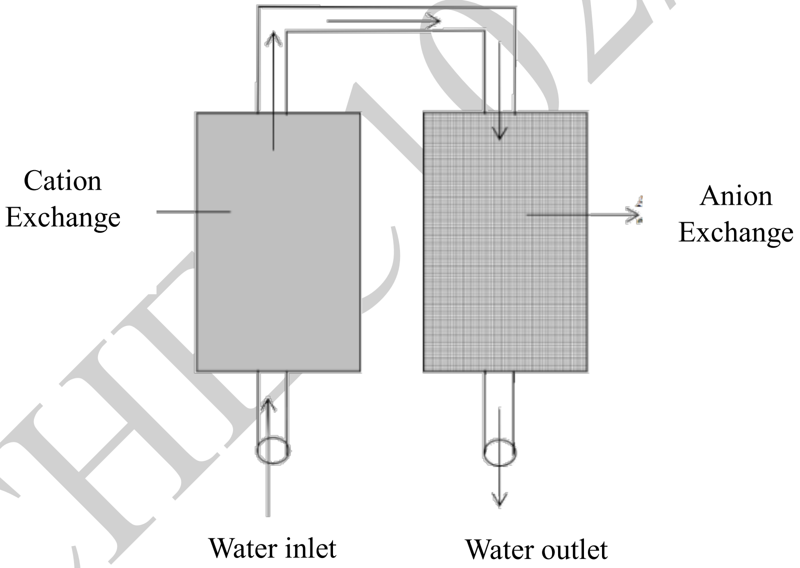
Similarly, anion exchange resin is washed with ammonium or sodium hydroxide solutions.

$R^+\text{-}Cl^- + OH^- \longrightarrow R^+\text{-}OH^- + Cl^-$

The columns are finally washed with deionized water and the washings are discarded.

Significance:

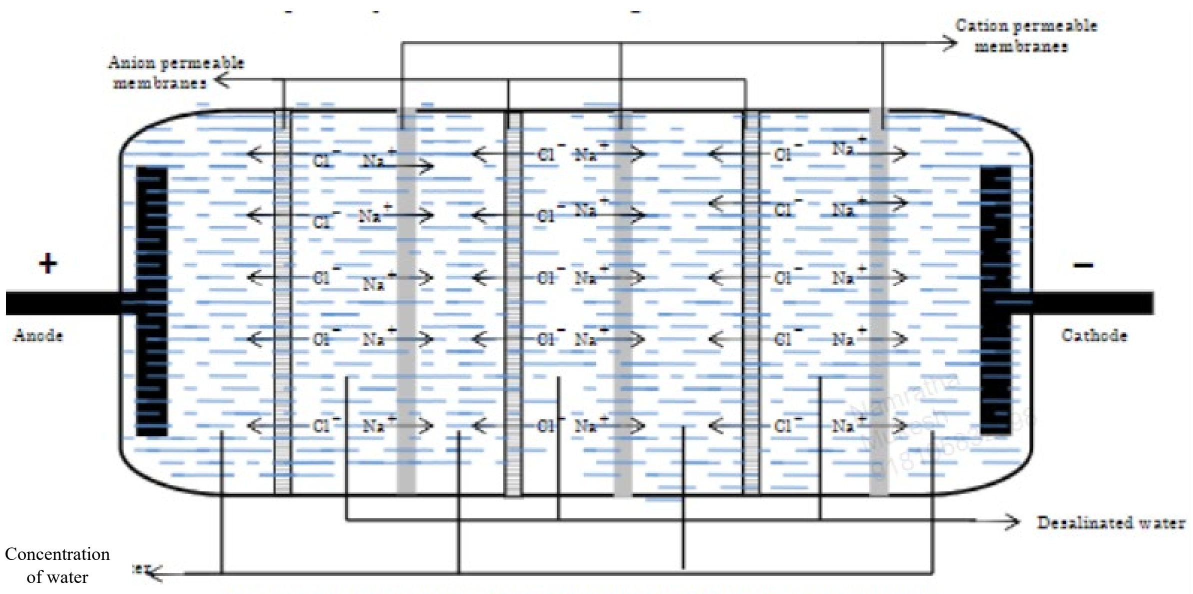
- Both acidic and alkaline water can be softened
- The ion exchange apparatus once set up is easy to operate and control.
- Residual hardness is very low and thus water is suitable for high pressure boilers also.



Softening of water by ion exchange method

Desalination Of Water By Electrodialysis:

1. The process of removal of dissolved salts present in water is called desalination.
2. In electrodialysis method Salts present in water are removed by applying direct current method.
3. The unit consists of alternately placed cation and anion exchange membranes.
4. Two electrodes, a cathode and an anode are placed at two ends.
5. Salt water is taken in compartment and direct current is passed.
6. Under the influence of electric current, the anions move towards anode and cation move towards cathode.
7. This each compartment gets concentrated with anions and cations. Meanwhile other compartments get diluted.
8. Highly concentrated and desalinated water can be removed separately.

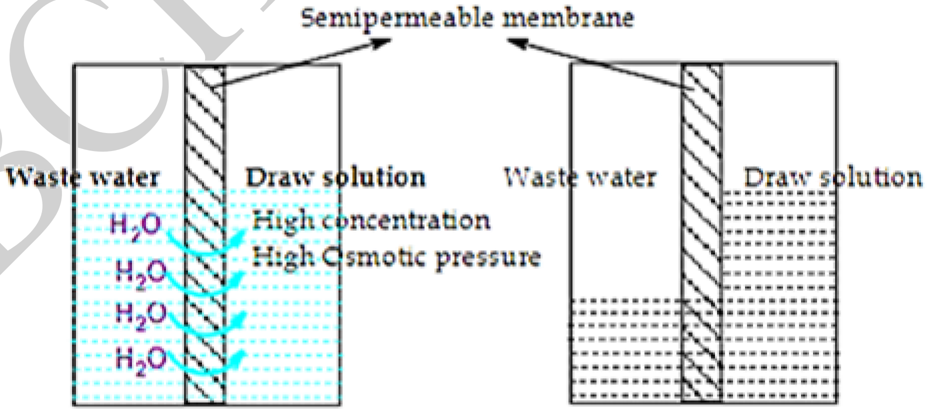


Desalination of water by electrodialysis using ion selective membrane

Forward Osmosis:

Forward osmosis. It's based on the principle of direct osmosis. In this method, Pure water is separated from wastewater without applying hydraulic pressure, just by direct osmosis. In forward osmosis technique, the wastewater sample from which clear water must be removed, is taken in one side of the membrane. On the other side, Solution of higher concentration with higher osmotic pressure is taken. This solution is called draw solution.

The concentration and osmotic pressure of draw solution is higher than the concentration and osmotic pressure of feed solution. Due to this difference, pure water molecules move from waste to feed solution to draw solution. Pure water from diluted draw solution is recovered by conventional process like reverse osmosis. Concentrated, solution is again used for drawing pure water from wastewater. Pure water can be recovered by thermal process as well. For example, when concentrated ammonium carbonate is used as a draw solution, pure water can be recovered by Thermal decomposition of ammonium carbonate.



Forward Osmosis

Applications:

1) Mainly used in industries for the concentration recovery of fruit juices, sugar concentration etc
2) Can be used for desalination of sea water to obtain potable water.
3) Used to extract pure water from sewage water.

Chemical Oxygen Demand (COD)

COD is defined as the amount of oxygen required to oxidize all oxidizable impurities presenting 1 liter of wastewater using a strong oxidizing agent such as acidified $K_2Cr_2O_7$.

Determination of COD

Principle: a known volume of wastewater sample is refluxed with $K_2Cr_2O_7$ solution in sulphuric acid medium. $K_2Cr_2O_7$ oxidizes oxidizers impurities. The amount of unreacted $K_2Cr_2O_7$ is determined by titration with the standard solution of ferrous ammonium sulphate. The amount of $K_2Cr_2O_7$ consumed corresponds to the COD of the wastewater sample to find out this a blank titration without waste water is carried out.

Ag_2SO_4 is used as catalyst for the oxidation of straight chain aliphatic compounds. And mercuric sulphate is added to hinders the interference of chloride ions.

$$Hg^{+2} + 4Cl^{-} \longrightarrow [HgCl_4]^{-2}$$

Procedure:

Back titration: 25 cm^3 of wastewater sample and 25 cm^3 of $K_2Cr_2O_7$ into 250 cm^3 of conical flask and one test tube full of 1:1 sulphuric acid containing the silver sulphate and mercuric sulphate is added. Reflux the mixture for half an hour and cool add two to three drops of ferroin indicator is added and titrate against standard for ferrous ammonium sulphate solution till the colour changes from bluish green to reddish brown.

Let the normality of the sample solution be z N

Let the volume of FAS solution consumed in titration be y cm^3

Blank titration: pipette out 25 cm^3 of $K_2Cr_2O_7$ solution into clean conical flask. Add one test tube full of 1:1 sulphuric acid followed by 2 to 3 drops of ferroin indicator and titrate against the standard FAS solution till the colour of solution turns from bluish green to redish brown.

Calculations:

$$1 \text{ cm}^3 \text{ of } 1 \text{ N FAS solution} = 1 \text{milli equivalent of oxygen} = 8 \text{ mg of oxygen}$$

$$(x\text{-}y) \text{ cm}^3 \text{ of z N FAS solution} = 8 \times (x\text{-}y) \times \text{z mg of oxygen}$$

$$\text{i.e.,} \quad 25.0 \text{ cm}^3 \text{ of waste water sample} = 8 \times (x\text{-}y) \times \text{z mg of oxygen}$$

$$1000 \text{ cm}^3 \text{ of the waste water sample} = \frac{8 \times (x - y) \times z \times 1000}{25} \text{ mg of oxygen}$$

$$\text{COD of waste water sample} = \frac{8 \times (x - y) \times z \times 1000}{25} \text{ mg of } O_2/\text{dm}^3$$

Nanotechnology

Any material with nano size with different properties from their bulk material is called nano material.

Size Dependent Properties

- **Surface area:** if a bulk material is subdivided into individual nano material, the total volume remains same but the collective surface area increases.
- **Catalytic properties**: nano materials have significant proportion of atoms at the surface, properties like catalytic activity, adsorption and chemical activity which are surface phenomenon, which depend on surface area.
- There for nanomaterials show some specific surface related properties which are not observed in bulk materials. Example, bulk gold is catalytically inactive, but gold nano particles are catalytically active.
- **Electrical properties**: the electronic bands in buk material is continuous where as in nanomaterials is discrete due to this even though bulk material is conducting its nano materials may become semiconductor or insulators

SOL-Gel Process

Preparation of SOL:

A sol is prepared by dispersing precursors in suitable solvent. Either a metal salt of metal alkoxide is used as precursor.

Conversion of SOL to gel: Sol further undergoes hydrolysis and condensation reaction forming a gel.

$M(OC_2H_5)_4 + x\ H_2O \longrightarrow M(OC_2H)_{4\text{-}X}(OH)_X + x\ C_2H_5OH$

Condensation:

$M(OC_2H_5)_{4-x}(OH)_x + M(OC_2H_5)_4\text{-}x(OH)_x \rightarrow (OC_2H_5)_{4-x}(OH)_{x-1}M\text{-}O\text{-}M(OH)_{x-1}(OC_2H_5)_{4-X} + H_2O$

Ageing of a gel: gel on ageing of known period, finally condenses to nanoscale clusters of metal hydroxides.

Removal of solvent: the solvent is removed by evaporation.

Heat treatment: the sample thus obtained is calcinated to obtain nano particle.

Co-Precipitation Method

In this method solid nanoparticles are obtained by careful precipitation from their solution.
The process involves 2 steps:

1. **Nucleation:**
   - A solution of metal salt (nitrate or acetate) is obtained by dissolving in water.
   - Precipitating agents like NaOH, NH4OH are added which changes the pH and causes condensation of precursors.
   - Thus, the concentration of the solution increases and reaches a super saturation level and at this stage nucleus formation is initiated.
2. **Growth of particle:**
   - A nucleus further grows into nano particle, which gets precipitated.
   - The product obtained is filtered, washed with water, air dried and finally calcinated at high temperature to remove counter anions like nitrate, acetate which are readily decomposed.
   - Precipitation synthesis can be used to prepare nano particles of metal oxide, metal sulphides and metals.
   - For the production of metallic nanoparticles, reducing agents are added to the solution.
   - Metal sulphides are produced by adding H_2S.

Carbon Nano Tubes (CNT)

Carbon nano tubes are cylindrical tubes with central hollow core, formed by rolling up of graphite sheets.

Types:

1. **Single walled carbon nano tubes (SWCNTs):** They are formed by rolling up of single layer of graphite. The diameter of SWCNT is 1.4 nm and length can go up to few micrometers.
2. **Multi- walled carbon (MWCNTs):** They consist of two or more concentric graphenes cylinders with van der waals forces between them. The diameter of MWCNTs varies from 30 to 50 nm and length can go up to few micrometers.

Properties of CNTs

1. They have high electrical and thermal conductivity.
2. They have low density and very high mechanical strength
3. They can emit electrons when subjected to high electric field
4. They have sp^2 carbon-carbon bonds which ae stronger than sp^3bonds found in diamond and provides CNTs with very good mechanical properties.
5. They are strongest and stiffest
6. SWCNTs efficiently absorb radiation in the near infra red range

Applications

1. As electrode material for lithium ion rechargeble batteries
2. Metallic interconnect between the components of integrated circuits.
3. Used in field emission X-ray tubes.
4. Used to obtain composite material with enhanced mechanical properties.
5. SWCNTs are used in cancer thermotherapy to selectively kill cancer cells without affecting the nearby healthy tissues.

Graphenes

- Graphene is a two-dimensional nano material made up of single atomic layer of carbon atoms present in hexagonal honeycomb like lattice.
- It is just one atom thick but extends in two directions.
- From a layered graphite material if a single layer is separated then it results in graphene.

Properties Of Graphenes

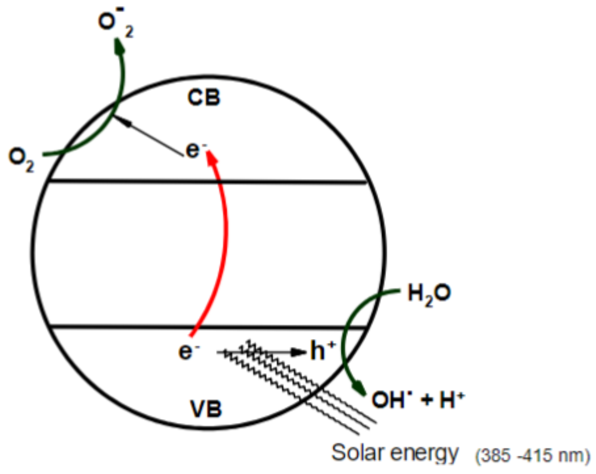
1. Graphene is transparent, flexible material with excellent mechanical, optical, thermal, electronic and chemical properties.
2. It has very high mechanical strength almost 100 times higher than steel
3. It is the best conductor of heat and electricity. Its thermal conductivity is higher than CNT, graphite and almost 10 times higher than Cu metal.
4. It has very wide optical band.it can absorb 2.3% radiation in visible and IR region which is 2-3 times higher than other semiconductors.

Applications

- Graphene is used as reinforcement fiber material in polymer composites.
- Due to excellent electrical and thermal properties graphene is used to improve both energy capacity and charge rate in rechargeable batteries.
- In making superior supercapacitors and in lightweight, flexible photovoltaic cells.
- In biomedical applications such as targeted drug delivery (useful in cancer treatment), bio sensing and biomedical imaging.

Application of TiO_2 nanoparticle in disinfection of water

1. TiO_2 nanoparticle absorbs near visible UV radiation of wavelength 385 to 415 nm.
2. Electrons are ejected from valence band and jump to conduction band leaving behind hole.
3. Hole takes up an electron from water molecule and splits it to hydroxyl free radical.
4. Electron in conduction band reduces oxygen to superoxide radical anion.
5. These hydroxyl radicals can oxidize organic molecules in the cells of microorganisms to carbon dioxide and water and destroy their cell structure and kill them.



TiO_2 photo active material for water disinfection

Silver Nano Particles (SNPs)

The silver nanoparticles has unique optical, thermal, catalytic electromagnetic, adsorbent and anti-microbial activities.

AgNP's have antibacterial activity due to their large surface volume ratio. They penetrate the cell wall of bacteria and lead to cell death.

AgNPs exhibit antifungal and antiviral activity. They are effective in killing viruses and fungus in water. They also exhibit anti-inflammatory and anti-cancer activity. Due to their broad range anti-microbial activities, silver nano particles are used in water purification.

QUESTION BANK

1. Explain the determination of total hardness of water using EDTA method.
2. Explain the process of softening of water by ion exchange method.
3. Explain the determination of COD
4. Explanation of desalination of water by electro dialysis method.
5. Write a note of forward osmosis.
6. Write the properties and applications of CNT and Graphenes.
7. Explain the synthesis of nanomaterials by sol-gel and co-precipitation method.
8. Write the application of nanomaterials in water treatment.
9. Numerical problems on COD and hardness determination.

MODULE 4 – POLYMERS AND COMPOSITES

Syllabus:

Polymer: Introduction, methods of polymerization, molecular weight of polymers, numerical problems. Synthesis, properties, and engineering applications of polyethylene (PE) and Chloro-poly-vinyl-chloride (CPVC).

Fibers: Synthesis, properties and applications of nylon fibers.

Polymer composites: Introduction, properties, and applications of fiber reinforced polymers composites (FRPC), Geopolymer concrete: Introduction, synthesis, constituents, properties, and applications.

Adhesives: Introduction, properties, and applications of epoxy resin.

Biodegradable polymers: Synthesis of polylactic acid (PLA)and their applications.

Self-learning: Biopolymer: Introduction, structural properties, and applications of cellulose and lignin

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Polymers

Polymers are defined as high molecular weight compounds formed by repeated small units of monomers.

Polymerization is defined as the process of linking up monomers to form polymer with or without the elimination of byproducts.

Types of Polymerizations.

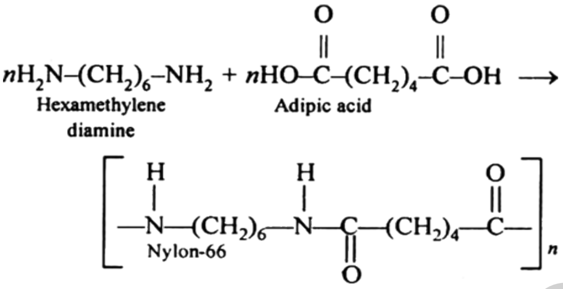
1. **Addition Polymerization**: (chain-growth polymerization)
   The process in which polymer is obtained from simple addition reaction of monomers without eliminating any simple molecule is called addition polymerization.
   Example: polyethylene is obtained by the addition reaction of ethylene monomers.
   n ($H_2C=CH_2$) → --(---H_2C- CH_2--- $)_n$-
   ethylene polyethylene

   Based on the kind of intermediate formed, there are three methods of addition polymerization namely:
   a) Free radical addition polymerization: in this type of polymerization, reaction is initiated by using an initiator. Organic or inorganic peroxides like dibenzoyl peroxide, hydrogen peroxide, potassium persulphates are commonly used as initiators. These initiators undergo photochemical dissociation or thermal decomposition easily when exposed to light radiation or to heating. Free radicals thus generated will initiate polymerization.
   b) Cationic addition polymerization.
   c) Anionic addition polymerization.

2. **Condensation Polymerization:** the process in which a polymer is obtained by condensation reaction of monomers with the elimination of small molecules like H_2O, NH_3, CH_3OH is called condensation polymerization.

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

   Reaction:



$$nH_2N{-}(CH_2)_6{-}NH_2 + nHO{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}(CH_2)_4{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OH \longrightarrow \left[{-}\overset{\overset{\displaystyle H}{|}}{N}{-}(CH_2)_6{-}\overset{\overset{\displaystyle H}{|}}{N}{-}\underset{\underset{\displaystyle O}{\|}}{C}{-}(CH_2)_4{-}\overset{\overset{\displaystyle O}{\|}}{C}{-} \right]_n$$

Expression of molecular masses of polymer:

There are two ways to express molecular masses.

1. Number- average molecular mass ($\bar{M}_n$)
2. Mass - average molecular mass or weight average molecular mass ($\bar{M}_w$)

Number average molecular mass is the mass obtained when total mass of all the molecules of a sample is divided by the total number of molecules.

$$\bar{M}_n = \frac{N_1M_1 + N_2M_2 + N_3M_3 + \cdots}{N_1 + N_2 + N_3 + \cdots}$$

number average molecular weight ($\bar{M}_n$)

$$\bar{M}_n = \frac{\Sigma N_i \bar{M}}{\Sigma N_i}$$

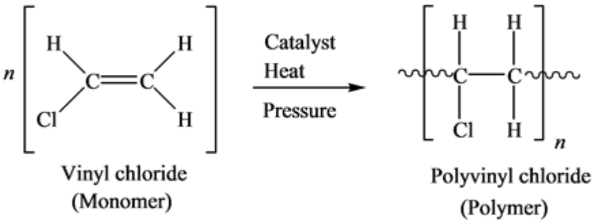
Mass- average molecular mass is defined as mass obtained when sum of the products of total mass of group of molecules and their respective molecular mass is divided by total mass of all the molecules.

$$\bar{M}_w = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + \cdots}{N_1M_1 + N_2M_2 + N_3M_3 + \cdots}$$

$$M_w = \frac{\sum M_i^2 N_i}{\sum M_i N_i}$$

PVC (polyvinyl chloride)

PVC is obtained by emulsion polymerization of vinyl chloride at 40° C - 60° C in the presence of potassium persulphate ($K_2S_2O_8$) as initiator.



Properties:

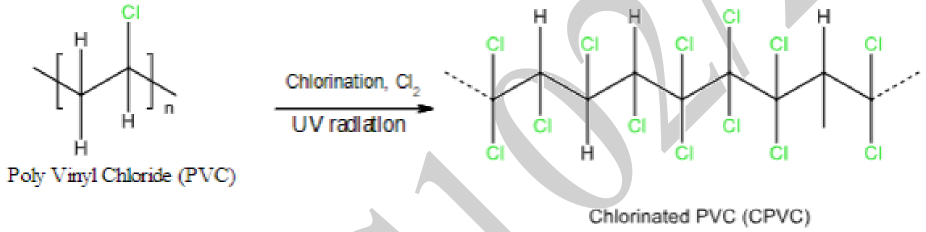
1. PVC is a hard and rigid polymer.
2. It has high impact resistance and chemical resistance.
3. It is a very good electrical insulator.
4. It can be molded to any shape with the addition of plasticizer.

Applications:

1. Used in PVC pipes.
2. Used as covering for cable and wires.
3. Used as thin film and sheets for floor coverings.
4. Used in window frames and bathroom doors.

Chloro Poly Vinyl Chloride (CPVC)

CPVC is obtained by further chlorination of PVC under UV radiation. Chlorine Free radicals produced by UV radiation. Which initiates the reaction and proceeds. Commercial CPVC is chlorinated to get 63% to 69% chlorine content.



Properties:

1. They have high mechanical strength, ductility and flexibility.
2. They have corrosion resistance to water and other chemicals.
3. They have good electrical insulating properties.

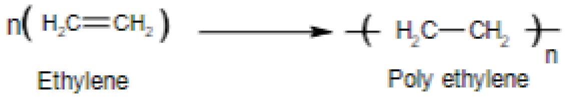
Applications:

1. Used to store industrial chemicals and solvents.
2. Used in water piping systems for hot and cold-water delivery.
3. Used as electrical insulator.

Polyethylene:

Preparation: polyethylene is obtained by addition polymerization reaction of ethylene monomers.

Reaction:



$$n(H_2C{=}CH_2) \longrightarrow -\!\!\left(H_2C{-}CH_2\right)\!\!-_n$$

Polymerization can be carried out by free radical polymerization using dimethoxy peroxide as an initiator.

Low Density Polyethylene (LDPE): Polymer obtained by addition polymerization using dimethoxy peroxide having more branches with less close packing and it is called low density polyethylene (LDPE)

High Density Poly Ethyle (HDPE): when polymerization is carried out by Zeigler -Natta catalyst using $TiCl_4$ and $AlCl_3$, polyethylene with less number of branches with more close packing is called high density poly ethylene.

Properties:

1. LDPE has high degree of branching with low crystallinity
2. LDPE exhibits good flexibility, transparency , good moisture barrier properties.
3. HDPE has very low degree of branching with high crystallinity
4. HDPE exhibits excellent chemical resistance , high tensile strength, excellent moisture barrier

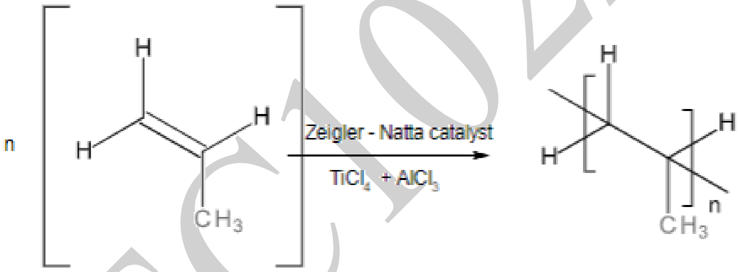
Applications:

1. LDPE is used as carry covers, squeezable bottles, garbage bags and laminates
2. HDPE are used in injection moldings, hollow plastic products and pipes.

Polypropylene:

Preparation: It is prepared from propene monomer by Zeigler – Natta catalyst i.e $TiCl_4$ and $AlCl_3$

Reaction:



Properties:

1. Polypropylene is tough , rigid, light weight synthetic fiber.
2. It has better mechanical properties and thermal stability than polyethene
3. It has good chemical resistance.
4. It has good fatigue resistance.

Applications:

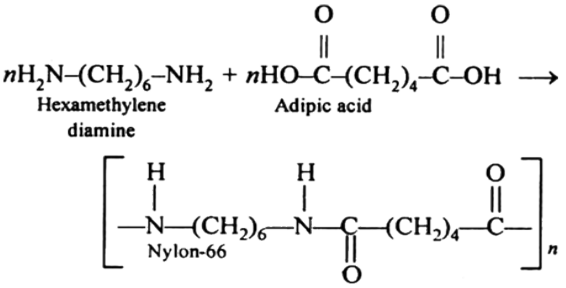
1. It is used in packaging, cast films
2. Due to high thermal stability it is used in laboratory and medical products.
3. Used in piping system
4. Used in water storage containers.
5. Used as materials for ropes.

NYLON:

Preparation:

Nylon 6,6 is obtained by condensation polymerization of hexamethylene diamine and adipic acid under high pressure and temperature (553K).

Reaction:



$$nH_2N-(CH_2)_6-NH_2 + nHO-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-OH \longrightarrow$$

$$\left[-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\underset{\underset{O}{\|}}{C}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-\right]_n$$

Properties:

1. It is a high mechanical strength and high rigidity synthetic fiber.
2. It exhibit high thermal stability.
3. It has high chemical resistance.
4. It has high resistance for abrasion.

Application:

1. Used in the textile industry.
2. Used in tires.
3. Used in conveyor belt, carpets etc
4. Used in making sleeping bags, tents, ropes, bristles for brushes etc.

Polymer Composite Materials:

A composite is a multiple material made by the combination of two or more materials having specific characteristics properties. The constituents of composite materials do not dissolve or merge completely into each other but act together. And retain their individual identities.

Composite materials are made up of only two phases, namely matrix which is a continuous phase and surrounds the other phase called dispersed phase.

Fiber reinforced composites:

1. These are the composite obtained by the combination of matrix and fiber.
2. Matrix is usually a thermosetting plastic like polyester, polyurethane, phenolic and epoxy resins.
3. Commonly used fibers are Kevlar, polyester, polyamide, CNT, graphenes and metal nano particles.
4. The fiber is embedded in between two matrix layers.

Properties:

- They exhibit high strength, stiffness, high abrasion.
- Thry show impact resistance and corrosion resistance.
- They have low weight, low density.

Applications:

These are useful in aerospace and automobile industries.

Geopolymer Concrete:

These are formed by the reactions of alumino silicate and alkaline solutions. Binding phase of geopolymer is because of an alkali aluminosilicates gel, in which Si and Al are linked in a 3D TETRAHEDRAL gel network.

Preparation of Geo Polymer:

Constituents:

1. Fly ash: which is obtained by burning coal from power stations which serve as a source of alumino silicate.
2. Coarse and fine aggregates like Portland cement.
3. Alkaline solution made from sodium silicate and sodium hydroxide solution.
4. Naphthalene sulphonates which acts as super plasticizer.

Preparation:

1. Fly ash and aggregates are mixed in a pan mixer for about 3 minutes.(dry materials)
2. Alkaline liquid and super plasticizer are mixed well with some more water .(liquid component)
3. Liquid component are added to dry materials and mixed well for about 4minutes.
4. Silica and alumina oxides reacts with alkaline liquid to form geopolymer paste. That binds loose coarse aggregates , fine aggregates and other un reacted materials together to form geopolymer concrete.

Properties

1) They have high strength
2) Low shrinkage power
3) Sulphate and corrosion resistance

Applications:

1. Used in construction materials as it emits less carbon dioxide.
2. Used as fire protection coating in cruse ships.
3. Used as resin in carbon-fiber composites.

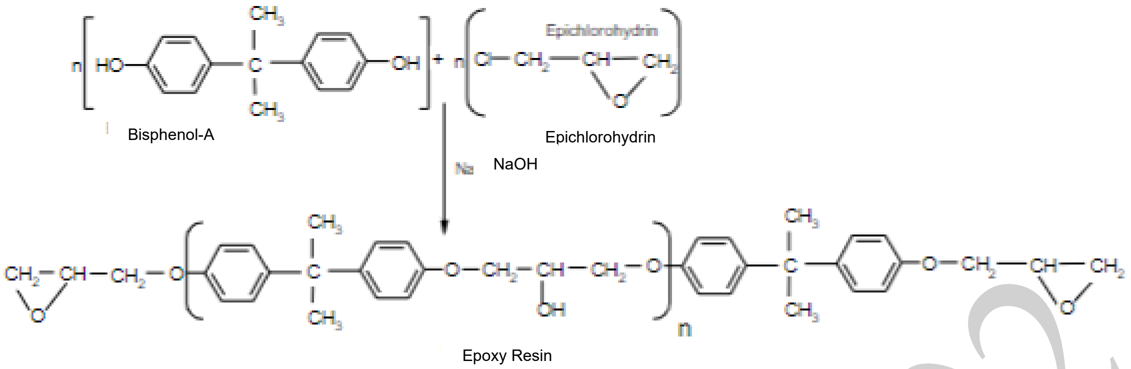
Adhesive: these are the materials used to bind two or more materials like wood, glass, metals etc. .as result of which new material is obtained for usage.

Example: epoxy resin

Preparation of Epoxy Resin:

Epoxy resin is obtained by the reaction of Bisphenol-A and epichlorohydrin in the presence of NaOH as catalyst.

Reaction:



Properties:

a) It has resistance to water, alkali, acids, and various solvents.
b) Cured resins have more toughness, adhesion, and heat resistance.
c) Good electrical insulating properties.
d) Good abrasion and wearing resistance.

Applications:

a) Used to bind metals, glass, wood, ceramics, concrete, leather materials.
b) In industrial floorings.
c) Production of aircraft and automobiles.
d) Used as laminating materials for electrical equipment.

Biodegradable Polymers:

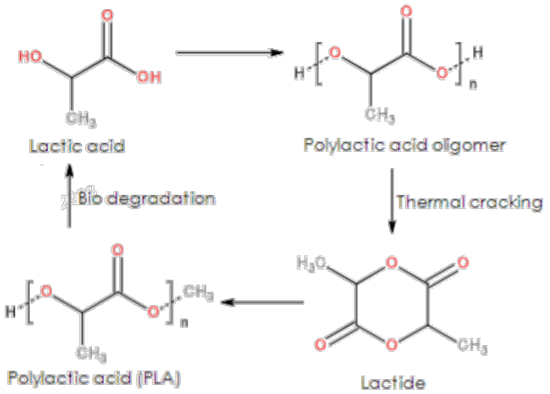
These are the polymers which can undergo degradation (decomposition) by the microbial activities (like bacteria, fungi and algae etc)

Example: poly lactic acid (PLA)

Synthesis of Poly Lacic Acid:

- It is obtained by the polymerization of lactic acid monomers.
- Lactic acid is concentrated and subjected to condensation reaction resulting in poly lactic acid oligomers.
- This oligomer under elevated temperature undergoes cyclization in the presence of catalyst to give Lactide.
- Lactide undergoes ring open polymerization to yield high molecular weight PLA.

Reaction:



Properties:

1) It has resistance to fat, food oil, solvents, humidity etc.
2) It is bright and transparent but brittle in nature.
3) Molecular weight ranges from a few thousands to millions.
4) Can be easily converted into fil fiber.

Applications:

- ✓ Used as dissolvable sutures as materials for drug delivery, bone fracture internal fixation.
- ✓ As plant growth promoters.
- ✓ Used in textiles, diapers, candy wrap, thermoformed cups, and containers etc.

Question Bank

1) Write a note on number average molecular mass and weight average molecular mass and numerical problems.
2) Give the synthesis, properties and applications of polyethylene and PVC.
3) Give the synthesis, properties, and applications of choloropolyvinyl chloride (CPVC)
4) Give the synthesis, properties, and applications of polypropylene.
5) Give the synthesis, properties, and applications of nylon fiber(nylon-6,6)
6) What are polymer composites? Write a note on properties and application of fiber reinforced polymer composites. (FRPC)
7) What are geopolymer concrete? Give the synthesis, properties, and applications of geo polymer concrete.
8) What are adhesive? Give the synthesis, properties and applications of epoxy resins.
9) What are biodegradable polymer? Give the synthesis, properties and applications of poly lactic acid (PLA)

Module 5- Phase Rule and Analytical Techniques

SYLLABUS:

Phase rule: Introduction, Definition of terms: phase, components, degree of freedom, Phase rule equation. Phase diagram: Two component-lead-silver system.

Analytical techniques: Introduction, principle, instrumentation of potentiometric sensors and its application in the estimation of iron, conductometric sensors and its application in the estimation of acid mixture, pH sensors and its application in the determination of soil sample.

Self-learning: Chromatographic technique, application of chromatography (column and thin layered chromatography) in the separation of components

Phase Rule

Phase rule is mathematical equation that relates number of degree of freedom, phase and components.

It is defined as **"for a heterogeneous system in equilibrium, the number phases plus the number of degree of freedom is equal to the number of components plus two"**

i.e **P+ F = C+ 2**

terms involved:

Phase: it is a homogeneous part of heterogeneous system which can be physically separable and remains physically distinct.

Example1: mixture of gas, here only one phase is seen.

Example 2: In a saturated solution of salt two phases are seen. Liquid and solid

Example 3: A equilibrium that exists between ice, water and vapor, here three phases are seen . solid, liquid and gas.

Example 4: mixture of oil and water or benzene and water, here we can see two phases.

Component: it is the minimum number of independent constituents present which are necessary and sufficient to express the composition of all the phase present in the system.

Example: consider the equilibrium between ice ↔ water ↔ vapor, this is one component system as all the phases made up of water.

Degree of freedom: the minimum number of variables like temperature, pressure and composition of the components which must be specified to define the system completely is called degree of freedom.

If F= 1 it is called univariant system.
F= 2 bivariant system.
F= 0 it is invariant system.

Lead- silver system (two component system)

In two component system when the number of phases is one and degree of freedom is three. All the three variables are necessary to define any single phase in a two-component system which is bit difficulty so in order to simplify this pressure is kept constant.

For two component system under constant pressure the phase rule is modified as

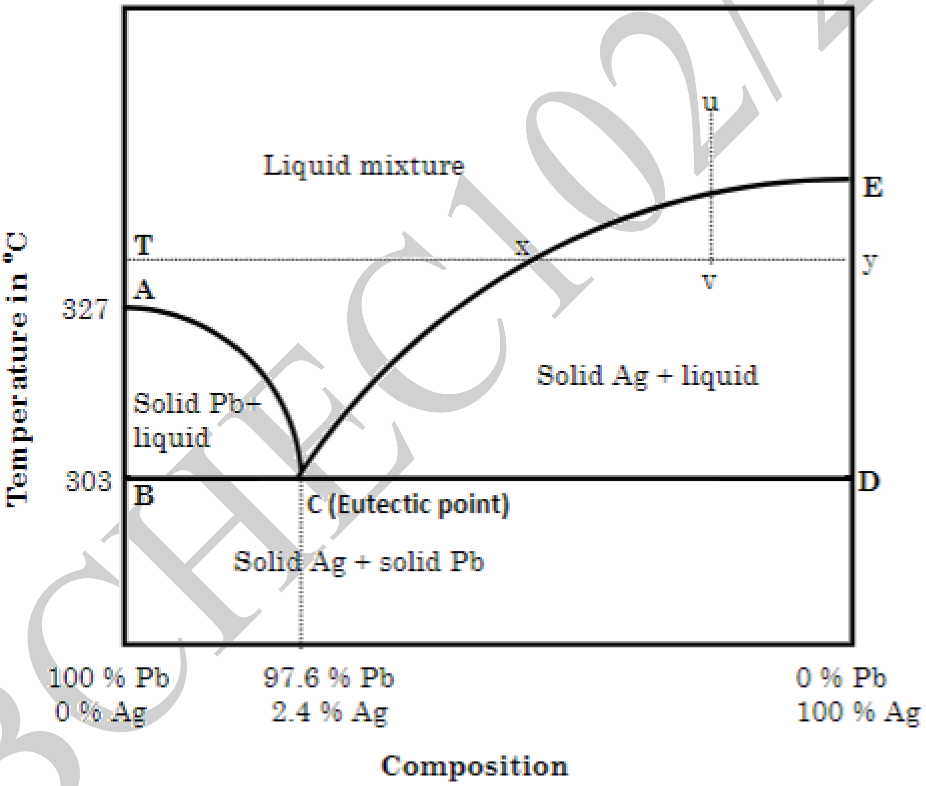
P+ F’ = C+ 1

P + F’ = 2+ 1

P + F’ = 3

The above equation is called **“condensed phase rule.”**

Lead- silver is a two-component system here the two components are completely miscible in the liquid state and pure components crystallize from the solution on careful cooling.



Phase diagram for Pb-Ag system

The phase diagram is obtained by plotting the temperature against the percentage composition of mixture of Pb and Ag.

It consists of:

1) Areas: ACE, ACB and ECD
2) Lines: AC and EC
3) Eutectic point: C

Areas: consider the area ACE, it represents the liquid phase consisting of completely miscible molten Pb and molten Ag.
Here $P= 1, C= 2$
From the condensed phase rule, $P + F' = C+1$
$= 1 + F' = 2 + 1$
$= F' = 2$
There for the system is bivariant and both temperature and % composition is needed to define the system.
Consider the **area ACB and ECD**, it represents solid lead and liquid and solid silver and liquid respectively.
From the condensed phase rule, $P + F' = C + 1$
$= 2 + F' = 2 + 1$
$= F' = 1$
There for the system is univariant. Either temperature or %composition is enough to define the system.

Suppose the liquid mixture is gradually cooled no solid separates out till the point v. at point v the solid Ag separates out.
Lines: AC is the freezing point curve of lead. And line EC is freezing pint curve of silver.
Here $P = 2, C = 2$
From the condensed phase rule
$P + F' = C + 1$
$2 + F' = 2 + 1$
$F' = 1$
There for the system is univariant and hence either temperature or %composition is enough to define the system.
Eutectic point (C): point c is the eutectic point where equilibrium exists between sold Ag , solid Pb and liquid mixture. Here the composition of Ag will be 2.4% and composition of Pb will be 97.6%.
here $P = 3, C = 2$
from the condensed phase rule
$P + F' = C + 1$
$3 + F' = 2 + 1$
$F' = 0$

There for the system is invariant. And no need to specify the temperature or %composition here as it is fixed.

If the temperature at the eutectic point is lowered, the liquid will disappear and the entire mass separates as a mixture of solid Pb and Ag.

Applications of Phase diagram:

- Useful for selection of alloys with a specific composition to produce specific properties.
- To predict the phase changes that have occurred in an alloy that has been exposed to a particular eat treatment.

Analytical Techniques:

Analytical chemistry methods refer to techniques used for the detection, identification, characterization, and quantification of chemical compounds. Qualitative identifies analytes, while quantitative analysis determines the numerical amount or concentration. Several Instruments and sensors are being used for analysis as these methods are faster, accurate and require a minimum quantity for analysis. Instrumental methods such as conductometry and potentiometry are some examples of these methods.

Conductometry

Principle/ Theory

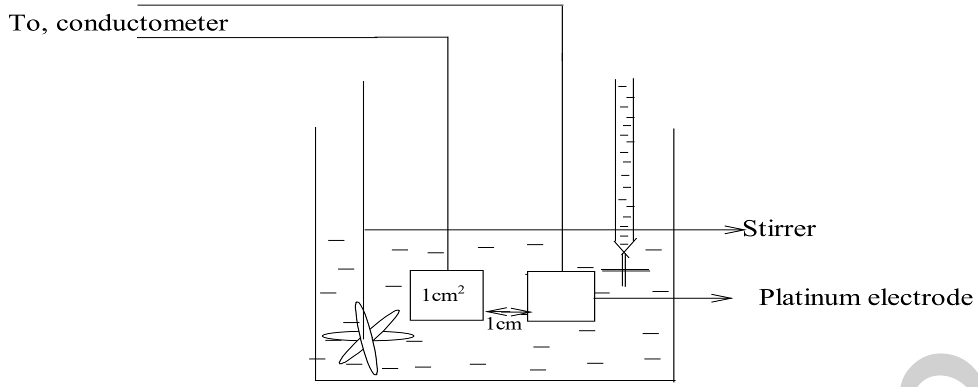
Conductometric titrations are the titrations in which the amount of the analyte present in the given solution is measured by the change in conductance. The principle underlying conductometry is the measurement of replacement of ions of a particular conductivity by ions of different conductivity during a chemical reaction. Conductivity electrodes or sensors are used to determine the end point in acid base titrations. Neutralization point is determined by observing the change in specific conductance of the solution. Specific conductance(K) is the conductance of a solution present between 2 parallel electrodes of area 1cm^2 which are kept 1cm apart. Here R is the resistance.

$$K = \frac{1}{R} \times \frac{l}{a} \qquad \left[\frac{l}{a} = \text{cell constant} \right]$$

The specific conductance of an electrolytic solution at any temperature depends on ions present and hence varies with ionic concentration. The measurement of conductance is used to determine the equivalence point in acid base titrations. In conductometric titration, there is a sudden change in conductance of solution at equivalence point. Hence equivalence point is determined by plotting a graph of conductance versus volume. Therefore, the concentration of the analyte in the solution can be calculated.

Instrumentation

The conductor consists of 2 platinum electrodes and a conductance measuring device. The 2 electrodes have unit area of cross section and are placed unit distance apart. The solution to be estimated is taken in a beaker. The system responds readily to changes in concentration of analyte.



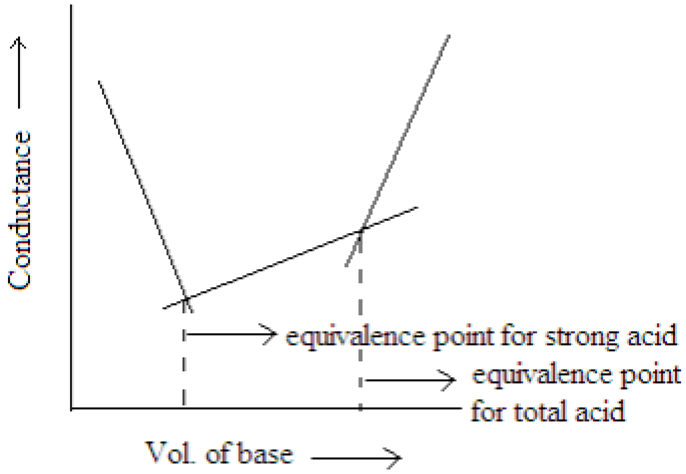
Advantages

- ✓ Mixture of acids can be titrated accurately.
- ✓ Accurate results are obtained in dilute as well as more concentrated solutions.
- ✓ The method can be employed for colored solutions also.

Application: estimation of acid mixture

Titration of acid mixture with strong base:

- In the mixture of strong acid and weak acid, strong acid dissociates completely and is consumed first by the base.
- After the neutralization of strong acid, the weak acid is neutralized.
- During neutralization of the strong acid (Ex: HCl) conductance first falls since highly mobile H^+ ions are replaced by Na_+ of base.
- Later, during the neutralization of weak acid (Ex: acetic acid), the poorly conducting acid is converted. Into salt (Ex. CH_3COONa). The salt undergoes complete dissociation; therefore, **the** conductance increases gradually.
- After the complete neutralization, further addition of base NaOH introduces more and more Na_+ and OH_- ions into the solution, conductance again increases rapidly.
- When conductance of the solution is plotted against volume of base added, three straight lines will be obtained. The first point of intersection corresponds to the volume of base required to neutralize strong acid and second point of intersection is for total acid.



Potentiometry

Principle

In potentiometric titrations, concentrations of the solutions can be calculated by measuring the emf between two electrodes dipped in the analyte solution.

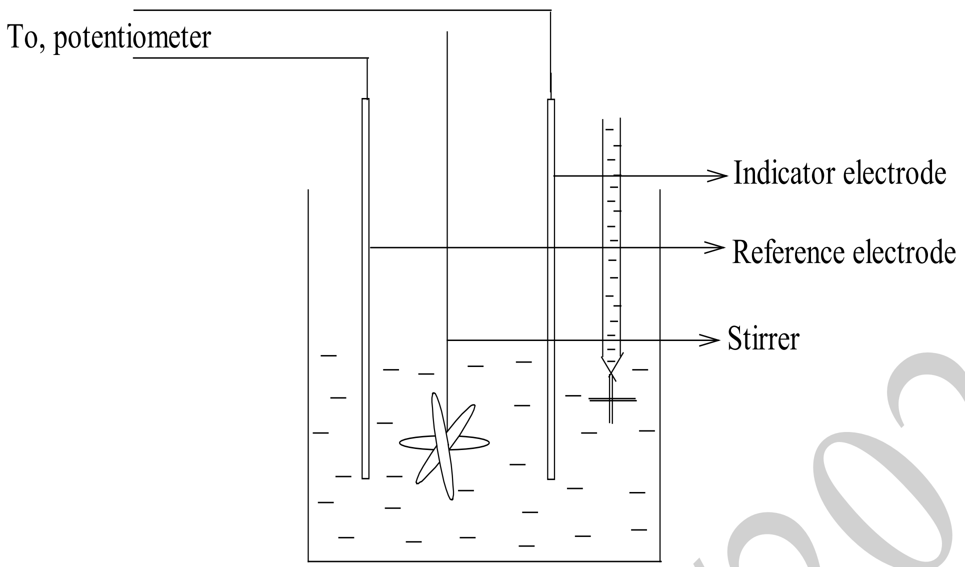
The potential of an electrode is given by Nernst equation,

$$E = E^{o} + \frac{0.0591}{n} \log\left[M^{n+}\right]$$

i.e., The potential of an electrode depends on the concentration of ion to which it is reversible. This method can be used in the determination of end points of acid-base titrations, red-ox titrations etc. When a known volume of analyte is titrated with a standard solution, neutralization or red-ox reaction takes place. During titration, concentration of product will be continuously altered. If a metal electrode, reversible with respect to corresponding ions is placed in the solution, the potential will vary throughout the titration, which can be determined using a suitable device. Initially, the change in potential is very small. At the equivalence point, when the amount of titrant added is equivalent to the amount of analyte present, there will be a sharp rise in potential. Beyond the equivalence point, there will be no significant change in potential. By plotting a graph of change in potential against the volume of titrant added, the equivalence point can be determined.

Instrumentation

Potentiometer consists of a reference electrode, an indicator electrode, and a potential measuring device. The indicator electrode (platinum electrode) responds to the changes in concentration of analyte. A reference electrode like saturated calomel electrode is also used. A known volume of analyte is taken in the beaker and its potential is determined. The titrant is added in increments of 0.5 ml and emf is measured each time. At equivalence point, emf increases rapidly. At this point, titrant is added in small increments of 0.5ml. a few readings are taken beyond the end point. Thus, the changes in potential at different volumes of titrant are recorded.



Advantages:

- ✓ Potentiometric titrations can be carried out in colored solutions where indicators cannot be used.
- ✓ By potentiometry, it is possible to determine the end point in titrations of redox, precipitation and acid-base titrations.

Application:

Estimation of Iron (Fe) using acidified Potassium dichromate solution

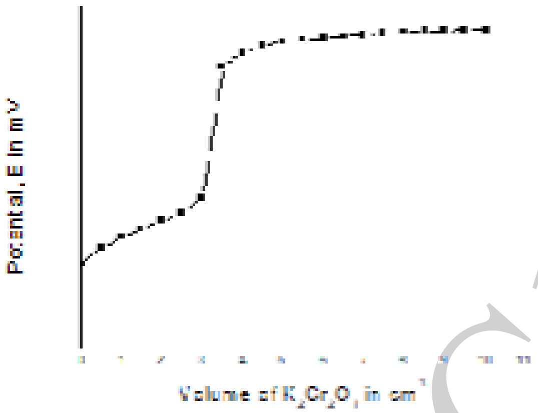
Potentiometry can be used to determine the end point of a redox titration by measuring the change in potential during titration using a platinum-calomel electrode combination.

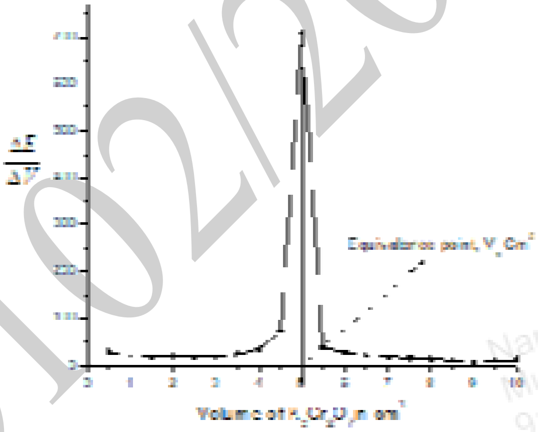
The titrations involving Mohr's salt solution and Potassium dichromate solution can be done by Potentiometry.

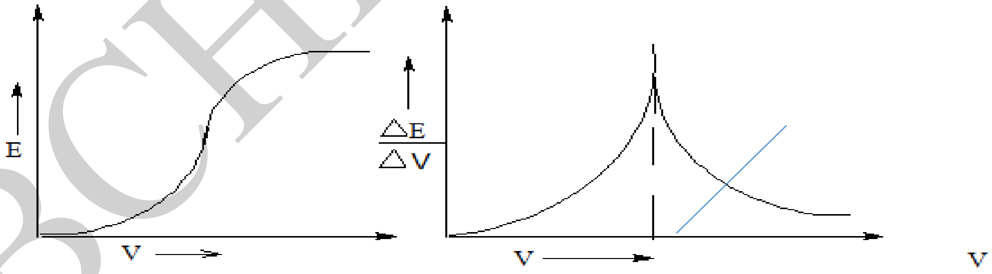
- The platinum electrode is used as an indicator electrode and coupled with a calomel electrode (reference electrode) and dipped in a solution of known volume of analyte (Mohr's salt solution) and connected to potentiometer and emf is measured.
- The titrant (Potassium dichromate) of known concentration is added in increments of 0.5ml from burette to the analyte solution and emf is measured each time after stirring the solution.
- FAS reacts with $K_2Cr_2O_7$ under acidic conditions, the redox electrode potential is set up at indicator electrode. Pt/Fe^{2+}, Fe^{3+}.
- The electrode potential of the redox electrode is given by Nernst equation.

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

- The electrode potential depends upon concentration of Fe^{2+} and Fe^{3+},
- As the titration proceeds Fe^{3+} increases and Fe^{2+} decreases and redox electrode potential increases and emf of the cell goes on increasing and steep rise is seen at equivalence point.
- At equivalence point all the Fe^{2+} is converted to Fe^{3+} ions and redox potential of Pt/Fe^{2+}, Fe^{3+} stops and further addition of dichromate new redox potential comes into existence Pt/Cr^{6+}, Cr^{3+} because the solution contains Cr^{3+} ions produced due to reduction of dichromate by Fe^{2+} ions. This redox electrode Pt/Cr^{6+}, Cr^{3+} has higher potential than Pt/Fe^{2+}, Fe^{3+}.
- Plot a graph of ΔE/ ΔV versus volume of $K_2Cr_2O_7$ gives the equivalent point.





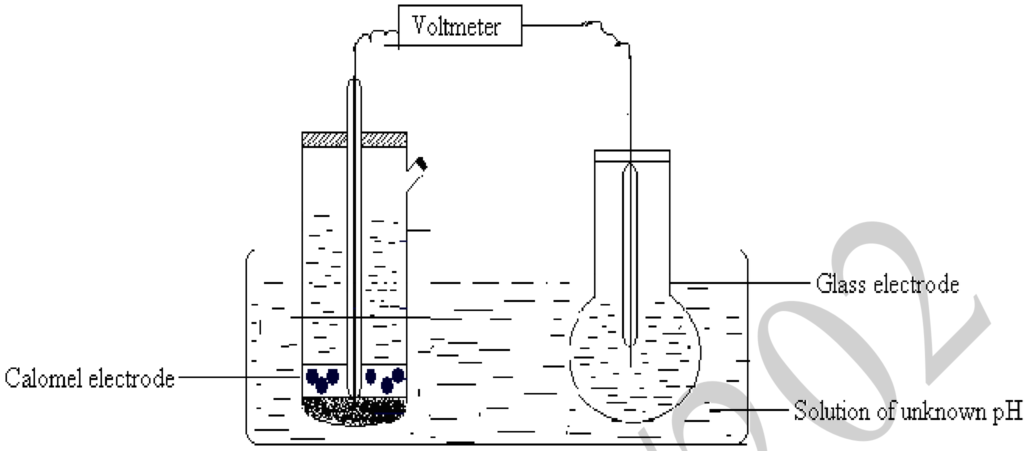


pH sensor and its application in the determination of pH of soil.

- The most accurate method of determining soil pH is by using the pH meter and pH sensor.
- Glass pH electrode is the pH sensor used.
- Glass electrode is an ion selective electrode which is more selective towards H^+ ions.
- In order to measure the pH of a beverage or any other unknown solution a galvanic cell is constructed by using saturated calomel electrode (reference electrode) and a glass electrode.
- Galvanic cell is represented as

Hg/ $HgCl_2$/ KCl / solution of unknown pH / glass membrane/ HCl / AgCl /Ag

Schematic representation



- EMF of the cell is measured using a highly sensitive voltmeter.
- EMF of the cell is measured using two times. First by immersing the cell in an unknown solution and secondly in known pH of buffer.
- EMF of the cell can be calculated using the formula (for unknown solution)

$$E_{cell\,(u)} = E_{cathode} - E_{anode}$$

$$= E_{glass} - E_{SCE}$$

$$= L' - 0.0591\ pH(u) - E_{SCE}$$

$$E_{cell\,(u)} = K - 0.0591 pH_{(u)} \text{ ------> eq1}$$

(where K is a constant and K= L’-E_{SCE})

The value of K can be determined by measuring EMF of the galvanic cell immersed in standard buffer solution of known pH.

$$K = E_{cell\,(b)} + 0.0591\ pH_{(b)}$$

On substituting the value of K in equation 1

$$E_{cell(u)} = E_{cell(b)} + 0.0591 pH_{(b)} - 0.0591\ pH(u)$$

$$0.0591\ pH_{(u)} = E_{cell(b)} + 0.0591 pH_{(b)} - E_{cell\,(u)}$$

$$pH_{(u)} = pH_{(b)} + \frac{E_{cell\,(b)} - E_{cell\,(u)}}{0.0591}$$

Thus pH of soil sample solution can be determined by measuring EMF of the above galvanic cell immersed in buffer solution and then in solution of unknown pH..

Question Bank

1. Define phase rule. Explain the terms involved in it with examples.
2. Explain the phase rule for Lead-Silver system (two component)
3. Explain the principle, instrumentation, and application in estimation of acid mixture using conductometric sensors.
4. Explain the principle, instrumentation, and application in estimation of amount of iron (Fe) /ferrous using potentiometric sensors.
5. What is a pH sensor? Explain the determination of pH of soil sample using pH sensors.