BCHEM 102/202: Applied Chemistry For ME Stream

Module-1: Energy; Source, Conversion and Storage

Fuels: Introduction, calorific value, determination of calorific value using bomb calorimeter, numerical problems on GCV and NCV.

Green fuels: Introduction, power alcohol, synthesis and applications of biodiesel.

High energy fuels: Production of hydrogen by electrolysis of water and its advantages. **Energy devices:** Introduction, construction, working, and applications of Photovoltaic cells, Li-ion battery, and methanol-oxygen fuel cell.

Self-learning: Plastic recycling of Fuels and its monomers or other useful products.

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Chemical fuel:

Definition: A chemical fuel is defined as a combustible carbonaceous substance, which on burning in presence of air/oxygen produces significant amount of heat energy. Energy obtained can be used economically for industrial and domestic purposes.

Classification on the basis of their origin:

Primary or natural fuel is the one, which occurs naturally and requires no chemical processing before utilization. Ex: wood, coal, peat, crude petroleum and natural gas.

Secondary or artificial (derived) fuels are produced from primary fuels by subjecting them to treatments before utilization. Ex: coke, coal gas and gasoline.

Classification of fuels on the basis of state of aggregation:

State of phase	Primary fuel	Secondary fuel
Solid	Wood, peat, lignite, coal, anthracite	charcoal, coke
Liquid	Crude petroleum	Petrol, kerosene, fuel oil, diesel oil
Gaseous	Natural gas	Coal gas, water gas, producer gas, biogas.

Characteristics of a good fuel:

- The fuel should have high calorific value.
- It should have a moderate ignition temperature and burn efficiently.
- The fuel should have low moisture content.
- The fuel should leave a low ash content after the combustion.

- The fuel must not produce harmful combustion products such as CO, SO_2, H_2S, NO_2 etc & smoke.
- Fuel must be readily available in abundant amount in natural form or any other form.
- Storage, transportation and handling of the fuel should be easy.
- Combustion rate should be low (combustion should not be rigorous).
- It should be possible to regulate combustion rate properly.

Calorific value of a fuel:

Definition**:** Calorific value of a fuel is defined as the amount heat released when unit quantity (mass or volume) of a fuel is burnt completely in air or oxygen.

Types of calorific value:

1. **Gross calorific value (GCV) or Higher calorific value (HCV):** GCV is defined as the total amount of heat produced when unit quantity (mass/volume) of the fuel is burnt completely in air or oxygen and the products of combustion are cooled to room temperature.
2. **Net calorific value (NCV) or Lower calorific value (LCV):** NCV is defined as the amount of heat produced when a unit amount of a fuel is burnt completely in air and products of combustion are allowed to escape.

NCV = GCV – Latent heat of water vapour formed
= GCV – Mass of hydrogen × 9 × Latent heat of steam
NCV = GCV – (9 × % Hydrogen × Latent heat of steam)/ 100
NCV = GCV – (0.09 × % Hydrogen × Latent heat of steam)

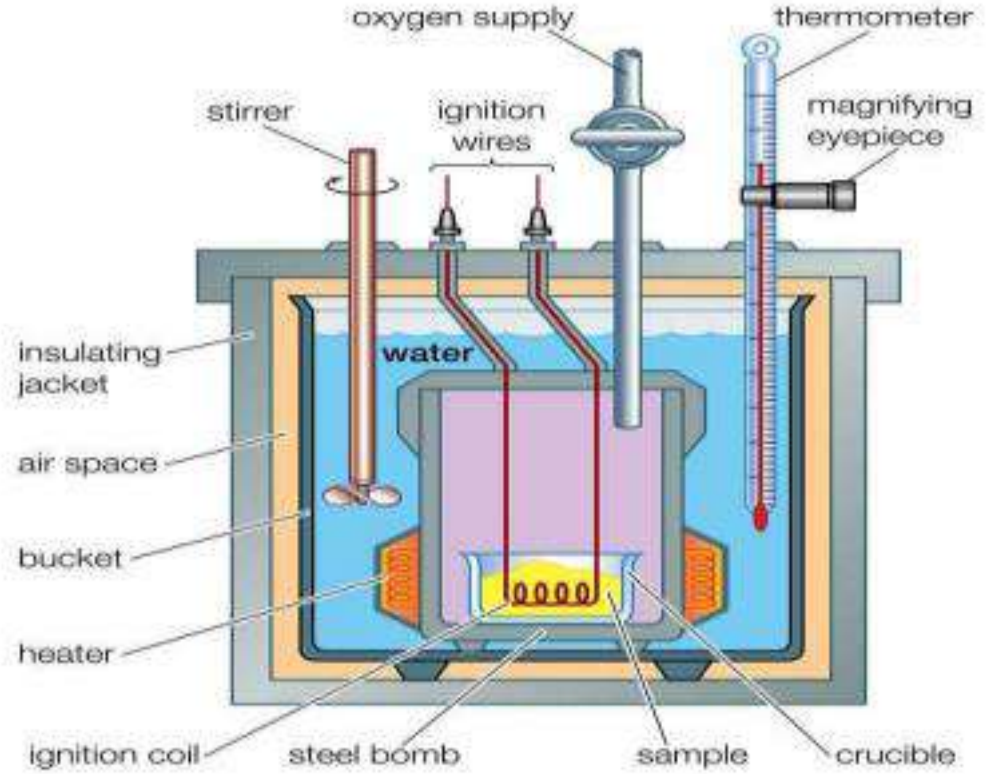
Units of calorific value: The calorific value is generally expressed in joules per kg (KJ/kg) for solid fuels and joules per cubic meter (KJ/m^3) for gaseous fuels in SI units.

Determination of calorific value of a solid/liquid fuel by using Bomb calorimeter:

Principle**:** A known mass of solid or liquid fuel is completely burnt in excess of oxygen in a bomb calorimeter. The heat liberated is absorbed by surrounding water and calorimeter. Thus the heat liberated by burning fuel is the heat gained by water and copper calorimeter.

Construction**:** A simple sketch of bomb calorimeter is shown in Figure. It consists of a strong airtight cylindrical stainless steel bomb in which the combustion of fuel takes place. The bomb is provided with two stainless steel electrodes connected to battery and an oxygen inlet valve. Ignition wire with coil is attached to the electrodes for the combustion process of the fuel. The bomb is placed in copper calorimeter, surrounded by air-jacket and water-jackets to prevent heat losses due to radiation. The calorimeter is provided with an electrically operated stirrer and a thermometer, to read accurately temperature difference.

Working: A known mass (about 0.5 to 1.0 g) of the given fuel is taken in clean crucible and ignition wire, stretched across the electrodes through ignition coil is placed in the stainless steel bomb. The bomb lid is tightly screwed and oxygen is filled in bomb at a pressure of 25-30 atms. The bomb is then lowered into copper calorimeter, containing a known mass of water. The stirrer is worked and initial temperature (t_1) of the water is noted. The electrodes are then connected to 6-volt battery and the combustion of fuel is initiated. The sample burns and heat is liberated. Uniform stirring of water is continued and the maximum temperature attained after the combustion is recorded.



Calculation:

Mass of the fuel sample taken in the crucible = ‘m’ Kg

Mass of water in the calorimeter = W_1 Kg

Water equivalent of calorimeter, stirrer, thermometer, bomb, etc. = W_2 Kg

Initial temperature of water in calorimeter = $t_1{}^0C$

Final temperature of water in calorimeter = $t_2{}^0C$

Specific heat; $S = KJ/ Kg / {}^0C$

Higher calorific value of the fuel = Q KJ/Kg

Heat liberated by burning 'm' Kg of fuel = mQ kJ/ kg

Heat absorbed by water & equipment = $(W_1 + W_2) \times S \times (t_2 - t_1)$ KJ Kg^{-1}

But, heat liberated by the fuel = heat absorbed by water

i.e., $mQ = (W_1 + W_2) \times S \times (t_2 - t_1)$ KJ Kg^{-1}

$$\therefore GCV = Q = \frac{(W_1 + W_2) \times S \times (t_2 - t_1)}{m} \frac{KJ}{Kg}$$

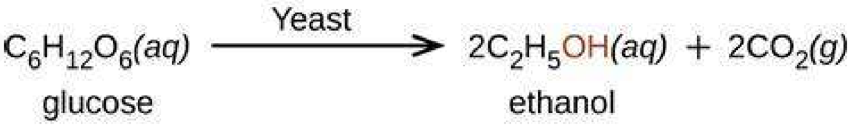
NCV = GCV – (0.09 x %H x Latent heat of steam) KJ Kg^{-1}

GREEN FUELS:

A fuel derived from biomass is called as green fuel. They are considered as renewable, eco-friendly, relatively less flammable compared to fossil fuel, has better lubricating properties and reduce greenhouse gases up to 65 percent. It can be manufactured from wide range of materials. Most common forms of green fuels are solar power, wind power, hydropower, biofuel such as power alcohol, biodiesel, biomass etc.

POWER ALCOHOL (GASOL):

Power alcohol is gasoline blends containing ethanol which can be used as a fuel in internal combustion engines. Blend containing up to 25% of alcohol with petrol are used. The main objective of the power alcohol is to reduce oil imports and provide an alternative to non renewable energy source i.e. gasoline.



$$\underset{\text{glucose}}{C_6H_{12}O_6(aq)} \xrightarrow{\text{Yeast}} \underset{\text{ethanol}}{2C_2H_5OH(aq)} + 2CO_2(g)$$

The importance of power alcohol as fuel is:

- Octane number of alcohol is 90 whereas the octane number of petrol is 60-70.
- Addition of alcohol to petrol increases the octane number of power alcohol. Hence, power alcohol possesses better anti-knocking properties.
- Because of the higher octane number, power alcohol can be used in engines with higher compression ratio without any change in engine design.
- No engine starting difficulties with power alcohol as fuel.

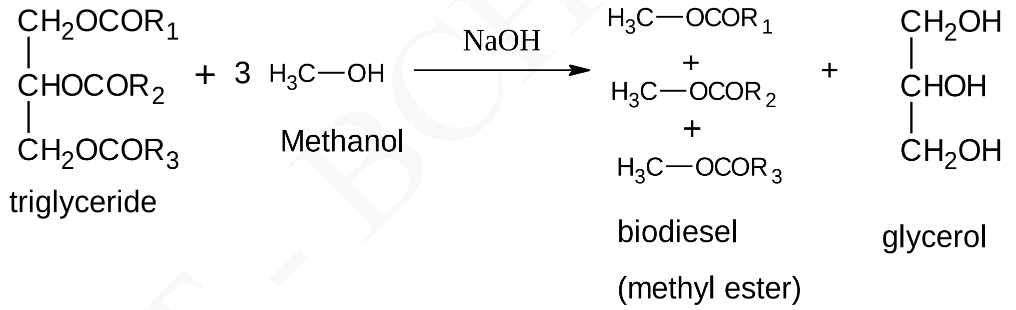
Disadvantages of power alcohol:

- The calorific value of alcohol is low. Hence, power alcohol has low calorific value.
- Due to oxidation of alcohols to acids, it is liable to cause corrosion in fuel storage tanks.
- At low temperature, there is a difficulty in starting the engine due to lower pressure of alcohol.

BIODIESEL:

Biodiesel is a renewable, oxygenated fuel obtained from a variety of vegetable oils and animal fats. Chemically biodiesel is a mixture of mono alkyl esters of long chain fatty acids. Biodiesel is produced from vegetable oils such as soya bean, jatropha, corn, sunflower, cotton seed, rubber seed etc., and animal fats like tallow, yellow grease, lard etc

Oils are triglycerides i.e. esters of fatty acids. These triglycerides are converted into biodiesel by a process called transesterification. Oils and fats are reacted with CH_3OH in the presence of base catalyst (NaOH) at 60-70 ^0C to produce fatty acid methyl esters (biodiesel) and the co-products such as glycerol.



ADVANTAGES:

- It is made using renewable sources and readily undergoes biodegradation.
- Biodiesel has a higher cetane number (48-60) compared to diesel (40-55).
- Use of biodiesel reduces greenhouse gases (eco-friendly).
- Addition of 20% of biodiesel (B20) to diesel brings down the pollutants greatly without any engine modification.

APPLICATIONS:

- Transportation
- Generating energy and electricity
- Provide Heat
- Charging Electronics

- Cooking
- Remove paint and adhesive
- Reduce cost and need for imported oil
- Create energy when fossil fuel runs out
- Biodiesel has higher lubricity can reduce engine wear

HIGH ENERGY FUEL: HYDROGEN FUEL

Green hydrogen produced from electrolysis is a high energy process.

Hydrogen fuel that is created using renewable energy instead of fossil fuels. It is a universal, light, and highly reactive fuel. Hydrogen has the highest energy content per unit of mass of any chemical fuel and can be substituted hydrocarbon in a broad range of applications. It can be easily produced from water found in abundance. Hydrogen produced via electrolysis can result in zero greenhouse gas emissions.

Production of hydrogen by electrolysis of water:

Photocatalytic water splitting:- is an artificial photosynthesis process. The photocatalytic process splits water (H_2O) into hydrogen (H_2) and oxygen (O_2) in the presence of a catalyst and natural light.

Principle: Photo electro catalytic water splitting is based on the conversion of the light energy into electricity within a cell containing two electrodes (or three), immersed in an aqueous electrolyte. Out of two electrodes at least one electrode or both electrode is made up of a semiconductor and able to absorb the light. This electricity is then used for water electrolysis. TiO2 based photo catalysts is used for these processes. In a photocatalytic water splitting reaction, photocatalyst plays a crucial role. Titania (TiO_2) has been a widely used.

Working / Reaction mechanism

1. The generation of a charge (electron or hole) at the semiconductor photoelectrode surface from photon excitation (Light-induced intrinsic ionization) – yielding electron-hole pairs.

$$\textbf{Potocatalyst } (TiO_2/ZnO) + 2h^{\upsilon} \text{ ----------}\rightarrow 2e^- + 2h^+$$

Where, h is the Planck's constant, $^{\upsilon}$ is the frequency, e^- is the electron, h^+ is the hole.

2. Oxidation of the water at the photo anode by photogenerated holes at the photoanode surface to generate molecules of oxygen.

$$\textbf{Oxidation :} \quad 2h^+ + H_2O \text{ -----------}\rightarrow \tfrac{1}{2} O_2 + 2H^+$$

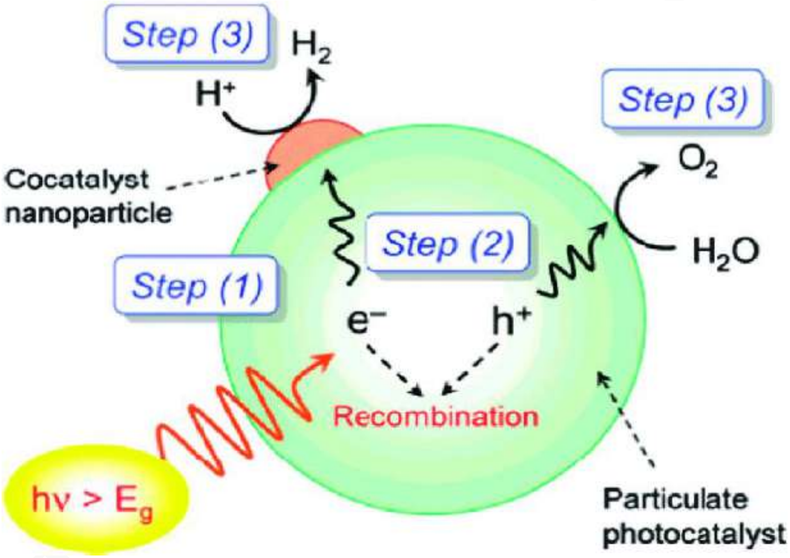
3. Transport of H^+ ions from the photoanode to the cathode through the electrolyte and transport of electrons from photoanode to the cathode through the external circuit reduce protons found at the surface of electrode, completing the electrical circuit.

$$\textbf{Reduction : } 2H^+ + 2e^- \text{ -----------}\rightarrow \quad H_2$$

The produced hydrogen can be used as the fuel in hydrogen fuel cell.

Overall Reaction: $H_2O + h^{\upsilon}$ **(1.23 eV)** -------→ $H_2 + \frac{1}{2} O_2$

This means that the photocatalyst (TiO_2 or ZnO) must have a bandgap > 1.23 eV, or else the electrons will not have enough energy to start the reaction. In practice, this limit should be 1.6 eV to 1.8 eV due to some overpotentials. In general, the efficiency of the catalyst can be enhanced by including dopants or co-catalysts that include metals or metal oxides, such as Pt, NiO, and RuO_2, which can act as the active sites via enhancing electron mobility.



ENERGY DEVICES:

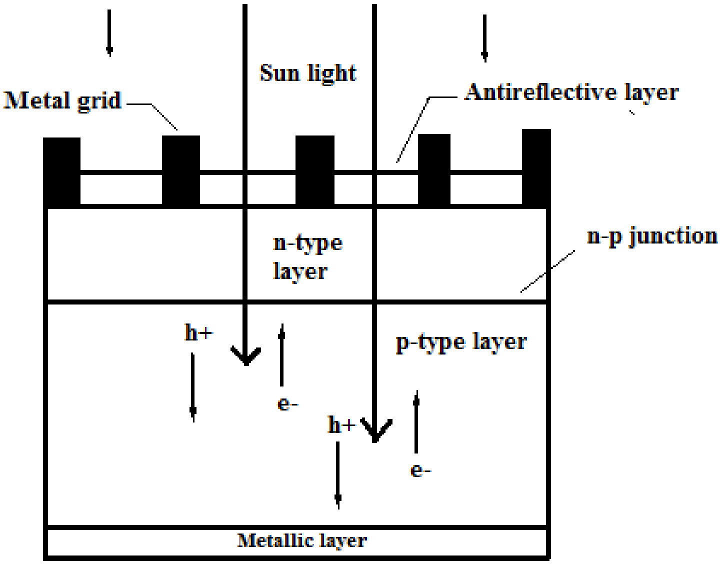
SOLAR CELL :

Solar energy is the radiant energy due to illumination of the sun. It can be converted into various forms of energy such as thermal and electrical energies. The main advantage of using solar energy as a source of energy are that it is readily available, free of cost and eco-friendly. Solar energy alone can supply much more energy than the earth demands, but the only disadvantage that the sun does not shine all the time and not everywhere equally. Most of the other power sources like wind energy, wave energy and hydroelectricity have a common origin in sun.

PHOTOVOLTAIC CELLS OR SOLAR CELLS :

Definition: Photovoltaic cells are the semiconductor devices that generate direct current from sunlight. When semiconductors such as silicon are illuminated by photons (eg. from sun light), electricity is generated.

Construction of photovoltaic cells:-



A silicon photovoltaic cell is composed of a thin wafer of polycrystalline silicon wafer. Cell contains a very thin layer of phosphorous doped silicon (n-type) which is kept above boron doped silicon (p-type). So p-n junction is formed between these two layers. The anti-reflective layer containing silicon nitride or titanium dioxide is applied by plasma enhanced chemical vapour deposition technique, which increases the amount of light transmitted to the semiconductor. Metallic grids are placed above P-doped silicon forms electrical contact of the diode and allows the light to fall on the semiconductor between the grid line. The other electrical contact is made using metallic layer back side of the solar cell.

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

Working of a photovoltaic cell:

The solar cell is a semiconductor diode. Photovoltaic cell is based on photoelectric effect. When semiconductors such as silicon are illuminated by photons (eg. From sunlight), electricity is generated. Semiconductors have the capacity to absorb light and a part of the energy of the absorbed photons act as a charge carries electrons and holes. When light radiation falls on the p-n junction diode, electron-hole pairs are generated by the absorption of the radiation. The electrons are drifted and collected at n-type end (metal grids) and holes are drifted and collected p-type end (metal layer). When these two ends are electrically connected, there is a flow of current between the two ends through the external circuit. Thus photoelectric current is produced and available for use such as lighting spinning of fans, working of motors. A silicon photovoltaic cell produces an open circuit DC volt of about 0.5 to 0.6V, The current output depends on its efficiency, size and proportional to the intensity of sunlight.

Advantages of PV cells::

- Energy source is vast and essentially infinite.
- Solar cells need no recharging like batteries and produce electrical energy as long as sunlight is available
- Solar cells have no movable parts and hence do not suffer from wear and tear.
- The materials used in PV cells do not corrode and serve for long duration.
- They operate at ambient temperature.
- PV cells involve no emissions, no combustion or radioactive residues for disposal.
- PV cells are environment friendly,
- low operating costs and quick installation

Disadvantages of PV cells:

- Poor reliability of auxiliary elements including storage
- The installation cost is high.
- PV cells generate only DC current and must be converted into AC power when used in distribution grids.
- Sun light is diffuse source, i.e , it is relatively low density energy.

Applications of Photovoltaic Cells

- Telecommunication repeater stations/tower
- Water pumps
- Navigational aids
- Laptop computers
- Cottages and remote residences
- Parks in remote regions
- Supplying occasional power
- Satellites
- Toys, watches

BATTERY

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

Batteries can thus generate power and can act as portable sources of electrical energy.

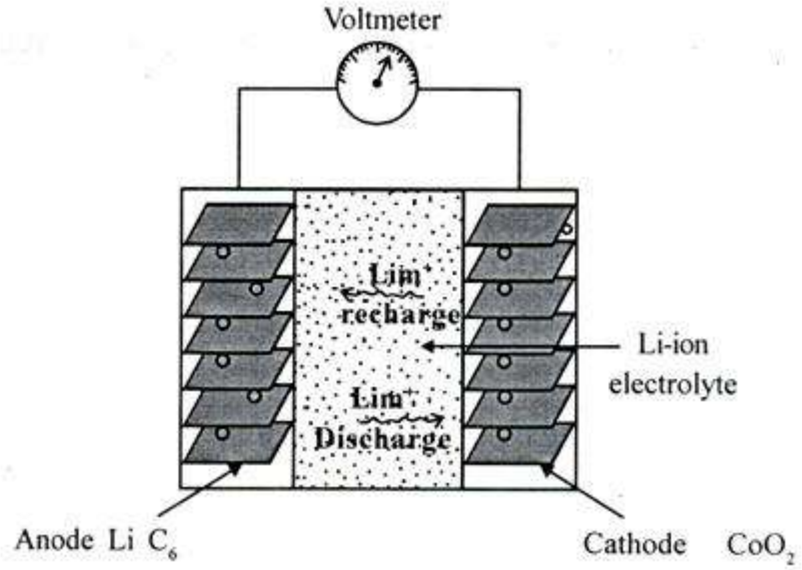
Batteries are classified as Primary, Secondary and Reserve batteries.

LITHIUM ION BATTERY

Definition: The batteries in which lithium ions are used instead of lithium metal and movement of lithium ion through electrolyte takes place from one electrode to another electrode are called lithium ion batteries.

Construction:

Li-ion batteries use lithiated carbon intercalation material as anode and transition metal oxide as active material for cathode.



Anode : Porous carbon intercalated with lithium ions. Copper foil is used as current collector.

Cathode: cobalt oxide compound. Aluminium foil is used as current collector.

Separator: Porous polymer film.

Electrolyte: A lithium salt in an organic solvent. This electrolyte effectively **transport** Li+ ion to cathode during discharge of battery.

The voltage of LIB is about 3.6-3.7 V

Working principle:

Discharge reactions: During discharge, Li ions are dissociated from anode and migrate through the electrolyte to cathode.

At anode: $LiC_6 \rightarrow C_6 + Li^+ + e^-$
At cathode: $CoO_2 + Li^+ + e^- \rightarrow LiCoO_2$

Overall reaction: $LiC_6 + CoO_2 \rightarrow LiCoO_2 + C_6$

Recharge reactions: During charging an external electrical power source applies a higher voltage than that produce by the battery, forcing the current to pass in reverse direction. Lithium ions then migrate from cathode to anode, where they become embed in the porous electrode material in a process known as intercalation.

$$LiCoO_2 + C_6 \rightarrow LiC_6 + CoO_2$$

Applications of lithium ion battery: They are used in cardiac pacemakers, laptops, cell phones, portable LCD, TV and aerospace applications.

FUEL CELL

Definition: Fuel cells are defined as galvanic cells in which chemical energy of a fuel isdirectly converted into electrical energy by means of redox reactions involving fuels and oxidants. Fuel cells give direct current as long as fuel and oxidant are supplied.

A general fuel cell is represented as: **Fuel│electrode│electrolyte│electrode│oxidant**

Working principle:

At anode: fuel undergoes oxidation as **Fuel → Oxidized product + ne$^-$**

At cathode: the oxidant gets reduced as **Oxidant + ne$^-$ → Reduced product**

The electrical output is a result of flow of electrons from anode to cathode through the external circuit.

Advantages of fuel cells:

- High efficiency of energy conversion process (75%).
- They are eco-friendly as the products of the overall reactions are not toxic and hence pose no pollution problems.
- They can produce direct currents for long periods at a low cost.
- Recharging of fuel cells is not needed
- No moving parts and so elimination of wear and tear

Limitations of fuel cells:

- The electrode used is Pt, Ag or alloys of noble metals, which are costly.
- The power generated is moderate.

METHANOL-OXYGEN FUEL CELL:

Methanol is used as fuel in methanol oxygen fuel cell.

Methanol is one of the most electro active organic fuel. Because it has low carbon contents possess readily oxidizable hydroxyl group and highly soluble electrolyte. Methanol is an excellent hydrogen carrier fuel, packing more hydrogen in its simple alcohol molecule.

Construction of MeOH-Oxygen fuel cell:

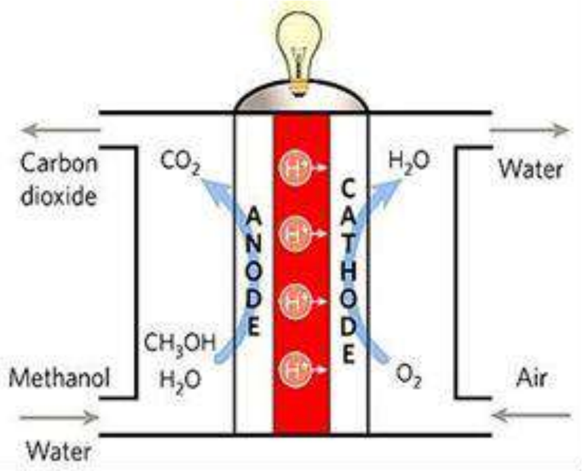
Anode **:** Porous Ni electrode impregnated with Pt/Pd catalyst

Cathode **:** Porous Ni electrode coated with Ag catalyst

Fuel **:** Methanol

Oxidant **:** O2/Air

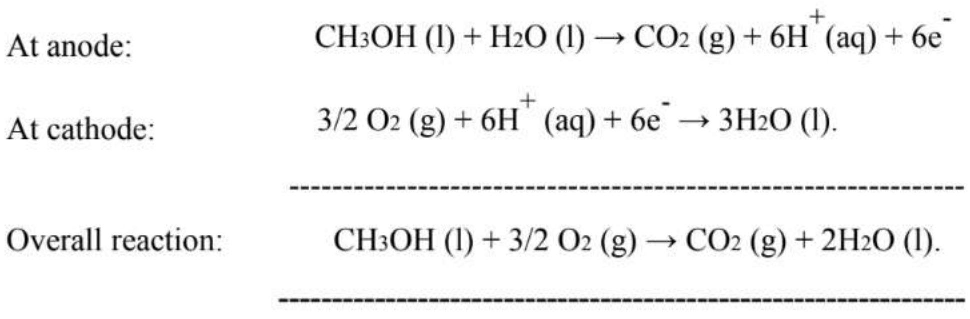
Electrolyte **:** H2SO4



Working principle:

- Methanol mixed with sulphuric acid (3.7M) is circulated through the anode chamber.
- Pure oxygen is passed through the cathode chamber and sulphuric acid (electrolyte) is placed in the central compartment.
- A membrane is inserted adjacent to the cathode on the inner side to minimize diffusion of methanol into the cathode thereby reducing the concentration of methanol near the cathode. In the absence of a membrane, methanol diffuses through the electrolyte into the cathode and undergoes oxidation.
- Methanol absorbs at the electrode(anode) and react with electrolyte form carbon dioxide with the liberation of electron. At cathode oxygen gets reduced in the presence of H^+ ion form water.The EMF the cell is 1.20V at 25^0C

The electrode reactions are:



At anode: $CH_3OH\ (l) + H_2O\ (l) \rightarrow CO_2\ (g) + 6H^+(aq) + 6e^-$

At cathode: $3/2\ O_2\ (g) + 6H^+\ (aq) + 6e^- \rightarrow 3H_2O\ (l)$.

Overall reaction: $CH_3OH\ (l) + 3/2\ O_2\ (g) \rightarrow CO_2\ (g) + 2H_2O\ (l)$.

Applications:

- Military applications since they have low noise and no toxic effluent.
- Large scale power production.
- Transportation, material handling and stationary, portable, and emergency backup power.

Differentiate between fuel cell and a conventional battery:

	Fuel cell	**Battery (conventional cell)**
1	In Fuel cells reactants are fed from outside and the products are removed Constantly.	Batteries are not being supplied with reactants constantly. Reactants are the integral part of the battery
2	They do not store chemical energy.	They store chemical energy.
3	Fuel cells are energy conversion Devices	Batteries are energy storage devices
4	They offer high energy conversions i.e, are more efficient	Efficiency of a battery is low.
5	They operate as long as the reactants are supplied to the electrodes from outside and do not need recharging	They operate until reactants stored in it are completely used up and secondary batteries need recharging
6	No toxic species are formed in a fuel cell and are more eco-friendly	Less eco-friendly

Important Questions:

1. What is a chemical fuel? Give its classification with an example.
2. What is calorific value of a fuel? Explain the types of calorific value.
3. Explain the determination of calorific value of a solid/liquid fuel by using Bomb calorimeter.
4. What is fuel cell. Explain the construction, working, applications of Methanol oxygen fuel cell.
5. Explain the construction and working, Applications of Li-ion battery.
6. Define Solar cell. Explain the construction, working and applications of PV cell.

MODULE 2: CORROSION ENGINEERING AND METAL FINISING

Corrosion: Introduction, electrochemical theory of corrosion, types of corrosion-differential metal, differential aeration (waterline and pitting), stress corrosion (caustic embrittlement). Corrosion control: Metal coating-galvanization, surface conversion coating - anodization and cathodic protection-sacrificial anode method. Corrosion testing by weight loss method. Corrosion penetration rate (CPR)-numerical problems.

Metal finishing: Introduction, technological importance. Electroplating: Introduction, Electroplating of chromium (hard and decorative). Electroless plating: Introduction, electroless plating of nickel.

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CORROSION

Corrosion is a natural process that converts a refined metal into a more chemically stable oxide. It is the gradual deterioration of materials (usually a metal) by chemical or electrochemical reaction with their environment.

Definition

A process of deterioration or destruction of metal / alloy from its surface through an unwanted chemical or electrochemical attack by its environment is called corrosion.

Example:

- Formation of a layer of reddish scale of hydrated ferric oxide on the surface of iron is called rusting of iron when Fe is exposed to moist air.
- Formation of green film of basic carbonate ($CuCO_3$ + $Cu(OH)_2$) on the surface of copper, when it is exposed to moist air containing carbon dioxide.

Cause of corrosion:

- The combined state of metals(ore) has low energy and is stable
- The extracted metal through metallurgy process has higher energy and hence highly unstable
- Hence metals has the natural tendency to react with the environment to become stable that is how corrosion occurs.

Effects of Corrosion/global loss

- Loss of metals/equipment
- The corrosion of steel reinforcing bars in concrete can occur without being noticed. It can cause the failure of a section of highway, damage to buildings, bridges, parking

structures, and the collapse of electrical towers, etc., resulting in significant economic loss and jeopardizing public safety.

- Corrosion that occurs in major industrial plants, such as chemical processing plants or electrical power plants, is perhaps the most dangerous.
- Corrosion can cause severe failures in boiler tanks, pressure basins, blades of motors/turbines, harmful/aggressive chemical containers, airplane parts, automotive routing devices, and bridges.

RUST:

Rust is a mixture of **iron** oxides, on the surface of **iron** when reacts with oxygen and water.

$2[Fe_2O_3.3H_2O]$ (yellow rust) - hydrated ferric oxide

$Fe_3O_4.3H_2O$ (black rust) - ferrous ferric oxide

ELECTROCHEMICAL THEORY OF FORMATION OF RUST:

When a metal, such as iron, is exposed to the environment, according to electrochemical theory the following electrochemical changes occur gradually.

- Anodic and cathodic areas are formed resulting in minute galvanic cells
- Oxidation (corrosion) takes place at the anodic area and electrons are liberated.
- The electrons released at the anodic area migrate to the cathodic area and reduction takes place.

Step I: Reaction at anodic area

Metal Fe dissolves to give Fe^{+2} ions and electrons

$$Fe \rightarrow Fe^{+2} + 2e^{-} \quad \textbf{(oxidation reaction)}$$

Step II: Reaction at cathodic area

Electrons released at the cathodic area are conducted to the cathode and are responsible for various cathodic reactions.

1. ***In the presence of oxygen***: oxygen in the environment dissolves in the moisture
   a. In acidic medium, H^+ ions reduced to H_2O

      $4H^+ + 4e^- + O_2 \rightarrow 2H_2O$

   b. In neutral or slightly alkaline medium, dissolved oxygen reduced to hydroxyl ions.

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

      Both reactions involve absorption oxygen.

2. ***In the absence of oxygen:***
   a. In acidic medium, H^+ ions reduced to hydrogen gas

      $2H^+ \quad + \quad 2e^- \quad \rightarrow \quad H_2\uparrow$

   b. In neutral or slightly basic medium, moisture reduced to hydroxyl ions hydrogen gas

      $2H_2O \quad + \quad 2e^- \quad \rightarrow \quad 2OH^- \quad + \quad H_2\uparrow$

      Both the reactions involve evolution of hydrogen gas.

Step III: Formation of $Fe(OH)_2$

Smaller Fe^{+2} ions diffuses faster than the larger OH^- ions to the cathodic area through the moisture and converted into $Fe(OH)_2$. Hence, the corrosion current flows between the anodic and cathodic areas through conducting media (metal).

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

Step IV: Formation of Rust

a. In the presence of excessive amount of oxygen, $Fe(OH)_2$ is converted into yellow rust (hydrated ferric oxide), $Fe_2O_3.3H_2O$.

   $4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 2[Fe_2O_3.3H_2O]$ (yellow rust)

b. In the limited amount of DO, $Fe(OH)_2$ is converted into black rust (ferrous ferric oxide), $Fe_3O_4.3H_2O$.

   $3Fe(OH)_2 + \frac{1}{2} O_2 \rightarrow Fe_3O_4.3H_2O$ (black rust)

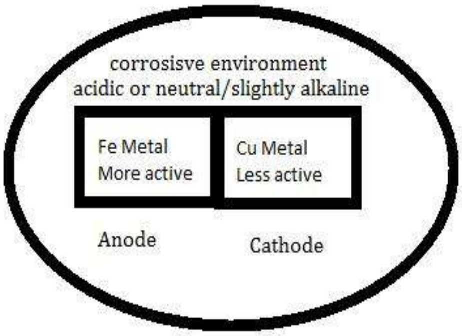
TYPES OF CORROSION

1. **DIFFERENTIAL METAL CORROSION/GALVANIC CORROSION**

Definition: Galvanic corrosion is a type of corrosion caused when two dissimilar metals are in contact with each other in a corrosive environment.

- The metal with lower reduction potential undergoes oxidation that acts as anode whereas the metal with higher reduction potential undergoes reduction acts as cathode and it is free from corrosion.
- The potential difference between the two metals is the cause for corrosion, higher the difference faster is the rate of corrosion.

Let us consider a bimetallic sample of iron and copper.



- The standard electrode potential of Fe is – 0.44 V which is less than that of Cu whose standard electrode potential is 0.34 V
- Hence in this case iron acts as anode and undergoes corrosion whereas copper acts as cathode and remains un attacked.

The following are the reactions which occur during differential metal corrosion when Fe is in contact with Cu

At anode

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

At cathode either hydrogen evolution or oxygen absorption

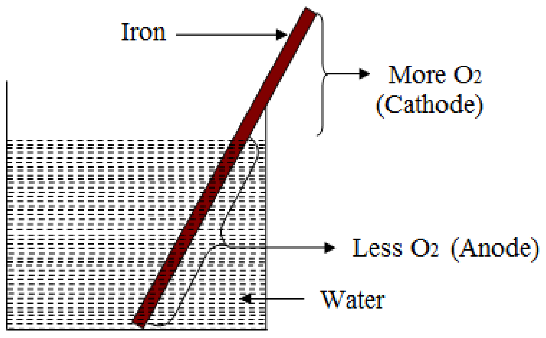
$2H^+ + 2e^- \rightarrow H_2\uparrow$

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

Examples

- Steel screws in copper sheet
- Lead-tin solder around copper wire
- Buried iron pipeline connected to Zinc bar.
- Steel pipe connected to copper plumbing

2. DIFFERENTIAL AERATION CORROSION

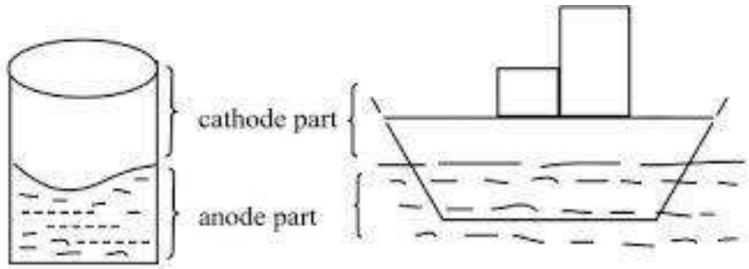


Definition: It is a type of corrosion that occurs when a metal surface is exposed to differential air (or) oxygen concentration in a corrosive medium.

- Part of the metal exposed to lower concentration of oxygen will have lower potential and therefore acts as anode. This part undergoes corrosion.
- The other part of the metal exposed to higher concentration of oxygen acts as cathode and remains unaffected.
- ***At the anode*** (less O_2 concentration): $M \rightarrow M^{n+} + n\,e^-$
- ***At the cathode*** (more O_2 concentration): $H_2O + \frac{1}{2} O_2 + 2e^- \rightarrow 2OH^-$

Example: Waterline corrosion and pitting corrosion

a) WATER LINE CORROSION



Water storage steel Tank

Ship in sea

- Waterline corrosion is a case of differential aeration corrosion that occurs in ocean going ships, water storage steel tanks, in which a portion of the metal is always under water.
- The part of the metal below the water line is less aerated while the part above the water is more aerated.
- Thus part of the metal below the water acts as anode and undergoes corrosion and part above the waterline is free from corrosion. Rusting is observed along a line just below the level of the stored water.

At anode $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation)

At cathode $H_2O + \frac{1}{2} O_2 + 2e^- \rightarrow 2OH^-$ (reduction)

$2Fe(OH)_2 + \frac{1}{2} O_2 + H_2O \rightarrow Fe_2O_3.3H_2O$ (Rust)

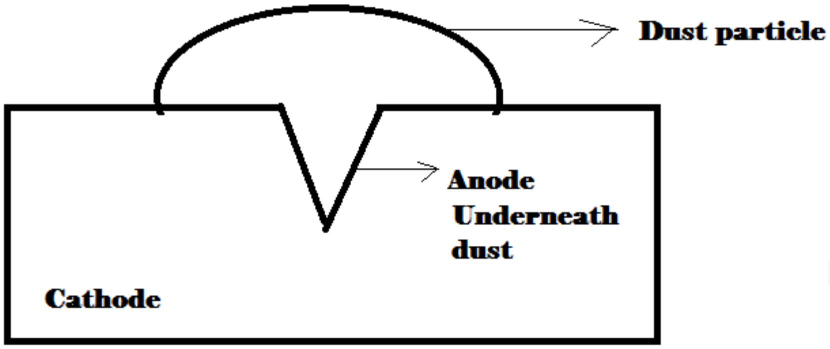
b) PITTING CORROSION:

- Pitting corrosion is a localized corrosion on the small area of the metal surface resulting in the formation of pits or holes.
- The pitting corrosion is generally initiated by the deposition of sand, water drop, dust etc. or due to the breakdown of the protective film.
- The metal below the deposit is exposed to lower oxygen concentration acts as anode and the metal surrounding the deposit acts as cathode since it is exposed to higher concentration of oxygen.
- Corrosion starts under the dust resulting in a pit. The pit grows and ultimately may cause failure of the metal.

Corrosion reactions:

At anode $Fe \rightarrow Fe^{2+} + 2e^-$ (oxidation)

At cathode $H_2O + \frac{1}{2} O_2 + 2e^- \rightarrow 2OH^-$ (reduction)



3. Stress corrosion in civil structures

Definition: The term `stress corrosion' stands for the process of crack initiation and crack propagation under the influence of a specific corrosive environment and static tensile stresses. Stress in the metals arises during fabrication of the articles or when metal is subjected to mechanical operations such as riveting, welding, bending, pressing, hammering and servicing.

- At the stressed area, the atoms of the metal are at higher energy state as compared to metal atoms in the stress-free part and have higher oxidation potential.
- The stressed areas are attacked even by a mild corrosive environment and undergo corrosion.

Stress corrosion occurs only in the presence of specific *corrosive environment*. The corrosive agents are highly specific and selective such are: (a) caustic alkali and strong nitrate solution for mild steel (b) traces of ammonia for brass (c) acid chloride solution for stainless steel.

Examples:

- Caustic embrittlement in boilers. Mild steel boilers undergo corrosion at the stressed portion when the pressure is 10 to 20 atm.

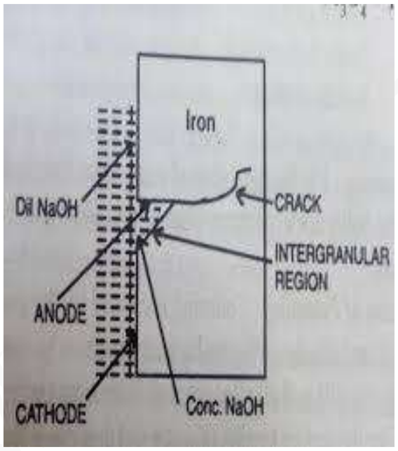
Caustic Embrittlement:

Caustic embrittlement is a phenomenon that occurs in boilers where caustic substances accumulate in boiler materials. It also can be described as the cracking of riveted mild steel boiler plates. This occurs at temperatures of 200°-250°C as a result of local deposition of concentrated hydroxides.

It is a very dangerous form of stress corrosion, occurring in boilers at high pressure and temperatures.

- Boiler-water usually contains sodium carbonate, added for water softening purposes.
- Sodium carbonate undergoes hydrolysis to give sodium hydroxide and carbon dioxide and hence boiler water becomes alkaline.

$$Na_2CO_3 + H_2O \rightarrow 2NaOH + CO_2\uparrow$$



- The alkaline water flows into the cracks present at the inner surface of the boilers due to capillary action. Eventually the concentration of NaOH in the cracks increases.
- The boiler material is thus under two different concentrations of NaOH, higher inside the cracks and dilute outside. The iron in the main body containing dilute NaOH acts as cathode whereas the iron of the cracks surrounded by concentrated NaOH behaves as anode.
- The anodic iron is corroded by the action of NaOH forming sodium ferroate.

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

- Sodium ferroate decomposes as

$$3Na_2FeO_2 + 4H_2O \rightarrow 6NaOH + Fe_3O_4 + H2\uparrow$$

- Fe_3O_4 is precipitated and NaOH is regenerated causing further corrosion.

CORROSION CONTROL

Corrosion control refers to measures that are implemented in various fields to control corrosion.

The following methods are used to protect metals against corrosion:

- Cathodic Protection
- Protective metal coatings
- Proper Design and selection of materials
- By modifying environment
- Use of corrosion inhibitors

METAL COATING

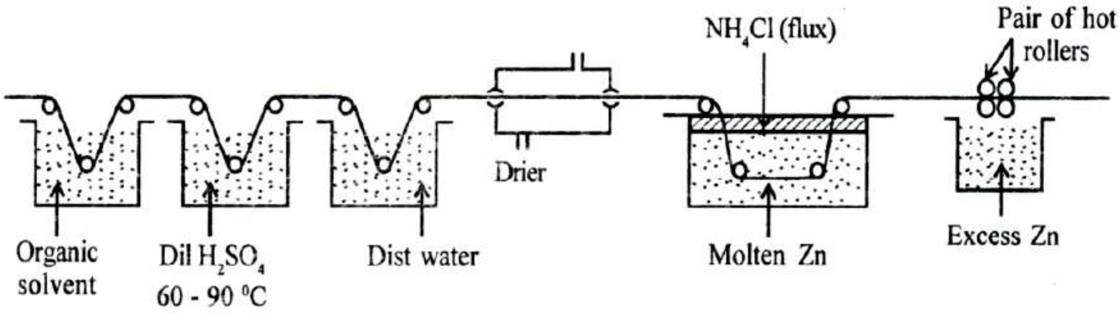
Definition: Deposition of a protective metal over the surface of a base metal is called metal coating. Examples: Galvanization (anodic metal coating) and Tinning (cathodic metal coating).

GALVANIZATION: Is an example for metal coating that is deposition of a protective metal over the surface of a base metal.

Galvanizing (Galvanization) is a process of coating a base metal surface with **zinc** metal. Galvanization is carried out by **hot dipping method**.

The galvanization process involves the following steps.

- The metal surface is first washed with organic solvents to remove oil and grease deposits.
- Rust and other deposits are removed by washing with dilute sulphuric acid (pickling).
- Finally the article is washed with water and air dried.
- The article is then dipped in a bath of molten zinc, maintained at 425-430^{0}C and covered with a flux of ammonium chloride to prevent the oxidation of molten zinc.
- The superfluous (excess) zinc on the surface is removed by passing through a pair of hot rollers, which wipes out excess of zinc coating and produces a thin coating.

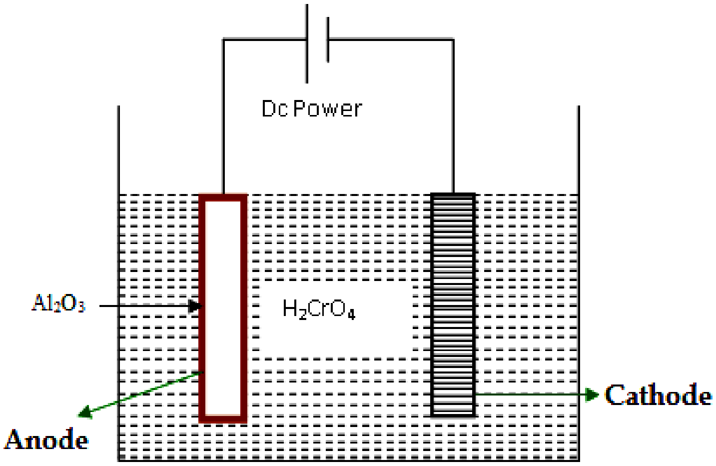


Applications: Galvanization is most widely used for protection of iron from atmospheric corrosion in the form of roofing sheets, wires, pipes, nails, bolts, screws, buckets, tubes etc.

***Disadvantages*:** Galvanized articles are not used for preparing and storing food stuffs since zinc dissolves in dilute acids producing toxic compounds.

ANODIZATION :

Anodizing: It involves the electrolytic oxidation of metal surface to produce a tightly adherent & durable oxide scale by passing electric current through an electrolyte to impart more protection against corrosion. Anodized coating is generally produced on non-ferrous metals like Al, Zn, Mg and their alloys.



Anodizing of Aluminium:

Anode: Aluminum

Cathode: Cu / Steel /Lead

Electrolyte: 5 -10 % chromic acid or 10 % H_2SO_4 (or phosphoric acid, oxalic acid)

Temperature: 35 – 40 ^{o}C

Voltage: 40 V

Current density: 100 A /m^2

Electrode reactions : **At anode** (Oxidation): $2Al + 3\ H_2O \rightarrow Al_2O_3 + 6\ H^+ + 6\ e^-$

At cathode (Reduction): $6\ H^+ + 6\ e^- \rightarrow 3\ H_2$

Overall reaction: $2\ Al + 3H_2O \rightarrow Al_2O_3 + 3H_2$

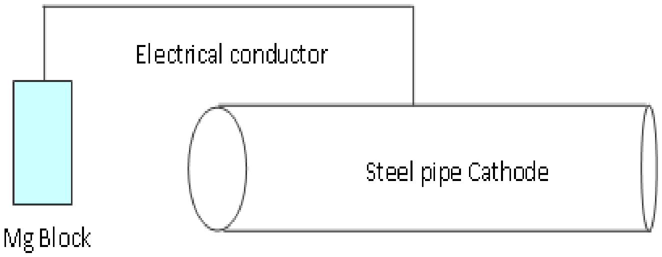
- The metal after pretreatment is made to act as anode and steel copper or lead acts as cathode.
- The electrolyte consists of 5-10 % chromic acid.
- The temperature of the bath is maintained at 35^{o}C
- A current density of 100 A/m^2 is applied which oxidizes the outer layer of Al to Al_2O_3
- An oxide layer of Al_2O_3 with a thickness 2-8 µm is formed.
- The outer part of the oxide film formed may be slightly porous and it is sealed by dipping in boiling water. This treatment converts porous alumina at the surface of coating into its monohydrate ($Al_2O_3.H_2O$) which occupies more volume, thereby the pores are sealed.
- For higher thickness 10% H_2SO_4 is used as the electrolyte.

Applications: It is used providing attractive, highly durable exteriors, roofs, ceilings, floor, lobbies, escalators, and staircases

CATHODIC PROTECTION

Cathodic protection is defined as a method of protecting a metal or alloy from corrosion by converting it completely into cathodic**.** The technique is based on converting active areas on a metal surface to passive, in other words making them the *cathode* of an electrochemical cell.

Cathodic protection can be achieved by the following methods: (i) Sacrificial anode method (ii) Impressed current method.



***Sacrificial anode method*:** In this corrosion control method, the metallic structure to be protected is connected to a more active metal with an insulated copper wire. Thus, the metal structure acts as cathode and more active metal acts as anode.

The more active metal itself gets corroded slowly; while the metal structure (cathodic) is protected. The more active metal so-employed is called sacrificial anode. The corroded sacrificial anode block is replaced by a fresh one, when consumed completely. Metals commonly employed as sacrificial anodes are Mg, Zn, Al and their alloys.

Important applications of sacrificial anodic method: commonly used to protect numerous structures against corrosion, such as ships, offshore floaters, subsea equipment, harbors, pipelines, tanks, underground cables, marine structures, ship-hulls, water-tanks etc.

METAL FINISHING

Definition: The term metal finishing is a process carried out in order to change the surface properties of metal by deposition of layer of another metal or a polymer or by the formation of an oxide film. Electroplating and Electroless plating are the important metal finishing techniques.

Technological importance of metal finishing:

- To offer corrosion resistance.
- To give decorative surface.
- To impart abrasion resistance, wear resistance, thermal resistance impact resistance.

- To provide electrical or thermal conduction.
- To offer the surface a thermal or optical reflectivity.
- To provide thermal insulating properties.
- For manufacturing electrical & electronic components.

Many industries use metal finishing in their manufacturing processes including automotive, electronics, aerospace, hardware, telecommunications etc.

ELECTROPLATING (ELECTRODEPOSITION):

***Definition*:** Electroplating is the deposition of metal, by electrolysis, over the surface of a substrate which may be another metal, polymer, ceramic or a composite.

Electroplating is achieved by passing an electrical current through a solution containing dissolved metal ions and the metal object to be plated. The metal object serves as the cathode in an electrochemical cell, attracting metal ions from the solution. Ferrous and non-ferrous metal objects are plated with a variety of metals, including aluminium, tin, bronze, cadmium, copper, chromium, lead, nickel, zinc etc.

- Metal to be deposited is made as anode: Article to be coated is made as cathode.
- A metallic solution of the metal to be deposited is electrolyzed to have a uniform coating of the metal on cathode.

At the anode, electrode dissolves giving raise to metal ions

$$M \rightarrow M^{+n} + ne^- \quad \text{(At anode)}$$

At the cathode, metal ions get reduced and are deposited as metal atoms

$$M^{+n} + ne^- \rightarrow M \quad \text{(At cathode)}$$

Nature of electrodeposit is mainly affected by current density of deposition, plating bath, metal ion concentration and electrolytes, organic additives, pH, temperature etc.

ELECTROPLATING OF CHROMIUM:

There are two types of chromium coating: Decorative chromium coating and hard chromium coating.

	Chromium plating	Decorative chromium	Hard chromium
1	**Anode**	Insoluble anodes- Pb-Sb or Pb-Sn coated with PbO_2	Insoluble anodes- Pb-Sb or Pb-Sn coated with PbO_2
2	**Cathode**	Object to be plated; pretreated	Object to be plated; pretreated

3	**Electrolyte (bath composition)**	Chromic acid (CrO_3) and H_2SO_4 in 100:1 proportion	Chromic acid (CrO_3) and H_2SO_4 in 100:1 proportion
4	**Operating temperature**	45-55^{0}C	43-66^{0}C
5	**Current density**	100-200 mAcm^{-2}	215-430 mAcm^{-2}
6	**Current efficiency**	8-12%	10-15%
7	**Application**	Provides decorative, durable and corrosion resistant finish to automobile parts, surgical instruments.	Extensively used in industrial and engineering applications such as hydraulic cylinders, diesel engine cylinder, cutting tools, metal forming tools.
8	**Limitations**	Need to reoxidise Cr(III) formed. Poor throwing power	Hard, wear-resistant deposit

Reactions:

***At cathode*:** Plating bath contains chromium trioxide (chromic acid), in which Cr is present in +6 state. During electroplating of chromium, Cr(VI) is reduced to Cr(III) in the presence of SO_4^{2-} catalyst (furnished by sulphuric acid). Cr(III) is reduced to Cr(0), which gets deposited on the article.

$$CrO_3 + H_2O \rightarrow H_2CrO_4 \rightarrow CrO_4^{2-} + 2H^+$$

$$2H_2CrO_4 \rightarrow H_2Cr_2O_7 + H_2O \rightarrow Cr_2O_7^{2-} + 2H^+ + H_2O$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7\,H_2O \text{ (in presence of catalyst } SO_4^{2-}\text{)}$$

$$Cr^{3+} + 3e^- \rightarrow Cr$$

ELECTROLESS PLATING:

Definition: Electro less plating is the controlled deposition of a continuous film of a metal from its salt solution on to a catalytically active surface by a suitable reducing agent without using electrical energy. The reducing agent brings about the reduction of the metallic ions to the metal which gets plated over a catalytic surface.

$$\text{Metal ion} + \text{Reducing agent} \xrightarrow{\text{catalyst surface}} \text{Metal} + \text{Oxidized product}$$

***Advantages*:**

- Use of electrical power and electrical contacts are eliminated.
- Semiconductors and insulators like plastics can also be plated.
- Electro less baths have better throwing power. Intricate parts with irregular shapes, inside parts of tubes, recesses can be uniformly coated.
- Hydrogen gas liberated is not trapped in blind holes.
- Electro less coating are harder than that produced by conventional electroplating.
- No levelers are required.
- Resulting deposits have unique chemical, mechanical and magnetic properties.

NICKEL ELECTROLESS PLATING:

Electro less Nickel Plating (ENP) is the deposit of a nickel-alloy coating by chemical reduction – without the electric current.

Commonly used alloy are Nickel-phosphorus alloy, Nickel – Boron alloy, Nickel – Phosphorous tungsten alloy

The deposition process is autocatalytic; i.e., once a primary layer of nickel has formed on the substrate coated nickel layer itself acts as the catalyst for the further plating reaction and each subsequent layer becomes the catalyst that causes the plating process to continue.

Pretreatment and activation of the surface: Pretreatment process is necessary step to clean the substrate surface and to activate the surface. The surface to be treated is degreased, etched in acid and activated by dipping first in stannous chloride containing HCl and then in palladium chloride.

Electroless plating composition:

Plating bath consists of a source of soluble nickel ions, a reducing agent, complexors, neutralizers/buffers, stabilizers, and brighteners.

- Nickel sulphate ($NiSO_4.6H_2O$) 30 g/ litre – source of nickel ions.
- Reducing agent: Sodium hypophosphite (NaH_2PO_2. H_2O) 20 g/ litre - *source of energy for process*.

- Neutralizers/buffers: ammonium hydroxide, carbonates or sodium or potassium hydroxide (added to control pH to 4.5–5.0).
- Stabilizers: control the plating reaction (Lead as metallic stabilizer)
- Brighteners: to enhance deposit appearance (Cd compounds)

$NiSO_4 + H_2O \rightarrow Ni^{2+} + SO_4^{2-} + H_2O$

$NaH_2PO_2 + H_2O \rightarrow Na^+ + H_2PO_2^- + H_2O$

$\mathbf{Ni^{2+} + H_2PO_2^- + H_2O \rightarrow Ni + H_2PO_3^- + 2H^+}$

$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + H_2$

Overall reaction: $\mathbf{NiSO_4 + NaH_2PO_2 + H_2O \rightarrow Ni + NaH_2PO_3 + H_2SO_4}$

Advantages/ Properties of Ni coating:

Corrosion resistance to common corrodents such as salt water, carbon dioxide, oxygen and hydrogen sulphide, wear resistance, Hardness, Lubricity, Solderability and bondability, Uniformity of deposit regardless of geometries, Nonmagnetic properties of high-phosphorus nickel alloy.

Applications:

Electroless nickel coatings have many unusual properties, which make them very useful in a broad range of functional applications.

- Automotive: gears, gear assembles, heat sink, engine bearings, pistons
- Aircraft :Landing gear, hydraulics, propellers
- Chemicals equipment's : spray nozzles, tanks, heat exchangers
- Rail road – diesel shafts
- Electrical motors

CORROSION TESTING BY WEIGHT LOSS METHOD

Corrosion engineering is the application of science and art to prevent or control corrosion damage in a safe and economical manner.

Corrosion tests are conducted for a number of reasons including:

1. establishing corrosion mechanisms. 2. Defining corrosion resistance of materials and how to develop new corrosion resistant alloys. 3. Estimating service life of equipment. 4. Developing corrosion protection processes. 5. Defining the critical potential values for materials in various environments.

Corrosion involves dissolution of metal, as a result of which the metallic part loses its mass (or weight) and becomes thinner. Corrosion rate expressions are therefore based on either weight loss or penetration in to the metal.

The most widely used corrosion expressions are:

- mm/y (millimeter/year)
- mpy (mils penetration/year)
- g/m2.day (gram/square meter . day)

WEIGHT LOSS METHOD

Weight loss method helps to determine the rate of corrosion.

PRINCIPLE: The simplest, and longest-established, method of estimating corrosion losses in plant and equipment is weight loss analysis. A weighed sample of the metal or alloy under consideration is introduced into the process, and later removed after a reasonable time interval. The metal is then cleaned of all corrosion product and is reweighed. The weight loss is converted to a corrosion rate (CR) or a metal loss (ML), as follows:

$$\text{Corrosion Rate (CR)} = \frac{\text{Weight loss (g)} * K}{\text{Alloy Density (g/cm}^3\text{)} * \text{Exposed Area (A)} * \text{Exposure Time (hr)}}$$

The constant can be varied to calculate the corrosion rate in various units:

Example: Study of weight loss method in steel:

Requirements:

Selected metal for corrosion study : Pure grade Mild Steel

Selected acids as corrosive medium : HCl, HNO_3.

Selected concentration of acids : (1) Different Molar solution of HCl.

(2) Different Molar solution of HNO_3.

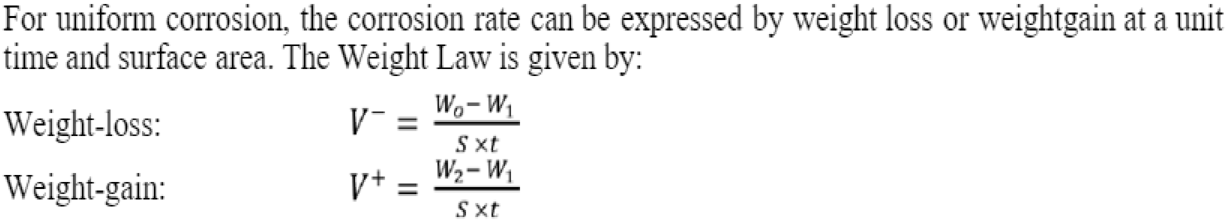
(3) Different Molar Mix. of HCl and HNO_3.

Selected inhibitors : N-containing organic compounds.

Methodology:

The technique requires no complex equipment or procedures, merely an appropriately shaped coupon, a carrier for the coupon (coupon holder), and a reliable means of removing corrosion product without disruption of the metal substrate.

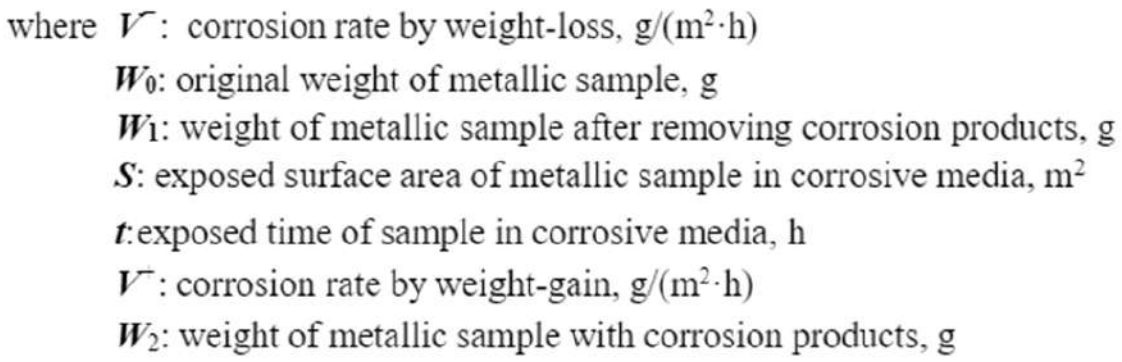
Weight loss method: Mild Steel plates of pure grade material will be used for the measurement of the corrosion rate. Rectangular specimens of Mild Steel of size 5.0 cm (l) x 2.0 cm (b) x 0.12 cm (thickness) with a small hole of ~2 mm diameter just near one end of the specimen will be used for the determination of corrosion rate. These Mild Steel plates will be immersed in 200 ml of test solution at room temperature for 24hour. After the test, the specimens will be cleaned by wash solution [made by 2% Sb_2O_3 (antimony Oxide), 5% $SnCl_2$ (stannous chloride) in concentrated HCl], water and acetone. There after the specimens will be dried in air and weight loss will be measured.



For uniform corrosion, the corrosion rate can be expressed by weight loss or weightgain at a unit time and surface area. The Weight Law is given by:

Weight-loss: $$V^{-} = \frac{W_o - W_1}{S \times t}$$

Weight-gain: $$V^{+} = \frac{W_2 - W_1}{S \times t}$$



where V^-: corrosion rate by weight-loss, g/(m^2·h)

W_0: original weight of metallic sample, g

W_1: weight of metallic sample after removing corrosion products, g

S: exposed surface area of metallic sample in corrosive media, m^2

t: exposed time of sample in corrosive media, h

V^+: corrosion rate by weight-gain, g/(m^2·h)

W_2: weight of metallic sample with corrosion products, g

CORROSION PENETRATION RATE (CPR)

Definition: The Corrosion penetration rate is the speed at which any metal or alloy deteriorates in a specific corrosive environment through chemical or electrochemical reactions.

It is also defined as the amount of weight loss per year in the thickness of metal or alloy due to corrosion.

The Corrosion penetration rate also referred as corrosion rate.

Corrosion penetration rate depends on following factors;

1. Nature of metal.
2. Nature of corrosive environment/medium.
3. Nature corrosion product.
4. Speed at which corrosion spreads in the inner portion of metal.

Following formula is used to determine CPR

$$CPR = \frac{KW}{DAT}$$

Where ,

- K-is constant
- W- Weight loss after exposure time
- D-density of metal/alloy
- A-surface area of exposed specimen
- T-exposure time in corrosive medium

Units-CPR expressed as **mmpy** (millimeter per year) or **mpy** (mils per year)

Note-to remember

	mmpy	mpy
K	**87.6**	**534**
W	**mg**	**mg**
D	**g/cm^3**	**g/cm^3**
A	**cm^2**	**Inch^2**

Conversion factor
1m^2=100*100cm^2
1m^2=1550inch^2
1inch^2=6.45cm^2
1cm^2=0.155inch^2

PROBLEMS

1.A thickness of alloy sheet of area 100 inch^2 is exposed to air near the ocean.After 1 year period it was found to experience a weight loss of 35g due to corrosion. If the density of alloy 8.4 g/cm^3.Calculate CPR in mmpy and mpy.

Given	mmpy	mpy
K	87.6	534
W-35g	35x1000mg	35x1000mg
D-8.4 g/cm^3	8.4 g/cm^3	8.4 g/cm^3
A-100 inch^2	100x6.45cm^2	100 inch^2
T-1 year	365x24 hrs	365x24 hrs

Solution

To find mmpy

$$CPR = \frac{KW}{DAT}$$

= 87.6x35x1000/8.4x100x6.45x365x24

= 0.064mmpy

To find mpy

$$CPR = \frac{KW}{DAT}$$

= 534x35x1000/8.4x100x365x24

= 2.54mpy

2. A piece of corroded steel plate was found in a submerged ocean vessel. It was estimated that the original area of the plate was 10 inch^2 and that approximately 2.6 kg had corroded away during submersion. Assuming a corrosion penetration

rate of 200 mpy for this alloy in sea water, estimate the time of submersion in years. The density of steel is 7.9 g/cm^3.

$$CPR = \frac{KW}{DAT}$$

Given
K =534
W-2.6Kg=2.6x1000x1000mg
D-7.9 g/cm^3
A-10 inch^2
CPR =200mpy
T-?

We can write

T= 534x2.6x1000x1000/7.9x10x200

T = 87873.41/365x24

= 10.03 years

Differentiate between electroplating and electroless plating.

Parameter	**Electroplating**	**Electroless plating**
Driving force	Passage of current	Auto catalytic redox reaction
Site for Anodic reaction	A separate anode is used	Catalytic surface of the substrate acts as anode
Anode reactant	Pure metal (M)	Reducing agent
Anode reaction	$M \longrightarrow M^{n+} + ne^-$	Reducing agent⟶Oxidation product + ne
Site for Cathodic reaction	Object treated to remove surface impurities	Object treated to make the surface catalytically active
Cathodic reaction	$M^{n+} + ne^- \longrightarrow M$	$M^{n+} + ne^- \longrightarrow M$
Throwing power	Throwing power is not satisfactory for intricate parts with irregular shape and inside of	Throwing power is satisfactory irrespective of the shape and inaccessibility of the parts.

	tubes	
Nature of the deposit	Pure metal or alloy	Metals with reducing agents and oxidized products as impurities
Applicability	Applicable only to conductors	Applicable to both conductors and non-conductors

Important Questions

1. What is rust? Discuss the electrochemical theory of corrosion by taking rusting of iron as an example
2. Explain the following type of corrosion: i.) Galvanic Corrosion ii). Differetial aeration corrosion.
3. What is cathodic protection? Explain how the corrosion of a metal is controlled by Sacrificial anode method.
4. Write a note on Stress corrosion and caustic embrittlement.
5. What is metal coating? Write a note on Galvanization.
6. What is anodizing? Write a note on anodizing of aluminium.
7. What is metal finishing? Mention its technological importance.
8. Define electroplating. Explain electroplating of chromium?
9. What is electroless plating? Explain electroless plating of Nickel. Mention its advantages.
10. Write a note on Corrosion penetrate rate? (Numerical problem)
11. Explain briefly about Corrosion study by weight loss method.
12. Differentiate between electroplating and electroless plating.

Additional problems:

A piece of corroded metal alloy plate was found in a submersed ocean vessel ,it was estimated that the original are plate was 800 cm^2 and that approximately 7.6 Kg had corroded a way during the submersion , assuming a corrosion penetration rate of 4 mm/yr for this alloy in seawater , estimate the time of submersion in years , the density of alloy is 4.5 g/cm^3 .

$$CPR = \frac{KW}{DAT}$$

$$T = \frac{87.6W}{DA(CPR)}$$

$$= \frac{87.6 \times 7.6 \times 10^{6}\, mg}{4.5g/cm^{3} \times 800cm^{2} \times 4mpy} = 46233.3hr$$

=5.27 year

A thick steel sheet of area 100 in2 is exposed to air near the ocean , after one year period it was found to experience a weight loss of 485 g due to corrosion , to what rate of corrosion in mpy and mm/yr does this correspond?

MODULE 3 - POLYMER AND COMPOSITES

SYLLUBUS

Polymers: Introduction, methods of polymerization (Condensation and Free radical), molecular weight; number average and weight average, numerical problems. Synthesis, properties and industrial applications of polyvinylchloride (PVC) and polystyrene.

Fibers: Introduction, synthesis, properties and industrial applications of Kevlar and Polyester. Plastics: Introduction, synthesis, properties and industrial applications of poly(methylmethacrylate) (PMMA) and Teflon. Composites: Introduction, properties and industrial applications of carbon-based reinforced composites (graphene/carbon nano-tubes as fillers) and metal matrix polymer composites.

Lubricants: Introduction, classification, properties and applications of lubricants. ==

Polymers

Polymer- A polymer is defined as a macromolecule formed by the repeated combination of several simple molecules (Monomers) through covalent bonds

Mainly there are two types of polymers:

1) Natural polymers: Rubber, resins, cellulose etc.
2) Synthetic polymers: Nylon, PVC, Bakelite etc.

Monomer: Monomer is defined as a simple molecule with two or more binding sites through which it forms covalent linkages with other monomer molecules to form the macromolecule.

Ex. Ethene $CH_2=CH_2$

Hence monomers are often called as the building blocks of a polymer chain. The properties of polymers are different from that of the monomers from which they are formed. Polymers have high molecular weight (Ranging from 10,000 to 1,00,000)

Types of Polymers

- There are many types of polymers based on origin: natural (silk, collagen, keratin cellulose, starch, glycogen) and synthetic polymers Plastics Fibers
- Based on the type of monomer unit: homo polymer (polystyrene) and Copolymer : [A-B-A-B-A-B]- type
- **Homopolymers:** These consist of chains with identical bonding linkages toeach monomer unit. This usually implies that the polymer is made from allidentical monomer molecules. These may be represented as : -[A-A-A-A-A- A]- Homopolymers are commonly named by placing the

prefix poly in frontof the constituent monomer name. For example, polystyrene is the name for the polymer made from the monomer styrene (vinylbenzene).

- Copolymers: These consist of chains with two or more linkages usually implying two or more different types of monomer units. These may be represented as : -[A-B-A-B-A-B]-

Polymers classified by mode of polymerization

- **Addition Polymers:** The monomer molecules bond to each other without the loss of any other atoms. Addition polymers from alkene monomers or substituted alkene monomers are the biggest groups of polymers in this class. Ring opening polymerization can occur without the loss of any smallmolecules.
- **Condensation Polymers:** Usually two different monomer combine with the loss of a small molecule, usually water. Most polyesters and polyamides (nylon) are in this class of polymers. Polyurethane Foam in graphic above.

Polymerization:

The chemical process by which monomers are converted into polymers is known as polymerization. To convert monomer into polymer, small quantity of chemicals known as initiators are needed. Temperature and pressure should be maintained.

$$\text{Monomer} + \text{Initiator} \xrightarrow[\text{Pres.}]{\text{Temp}} \text{Polymer}$$

$$\underset{\text{Ethylene monomer}}{nCH_2{=}CH_2} + \text{Peroxide initiator} \longrightarrow \underset{\text{Polythene}}{[CH_2\text{-}CH_2]\text{-}_n}$$

Examples for initiators: dibenzoyl peroxide, Zieglar Natta catalyst, aliphatic azo compounds. Temperature and pressure should be maintained.

Methods of Polymerization:

There are mainly two methods of polymerization which are classified as:
1) Addition polymerization
2) Condensation polymerization.

1) Addition polymerization: [chain growth polymers]-**Free radical polymerisation**

- An addition polymer is a polymer formed by chain addition reactions between monomers that contain a double bond without the elimination of byproduct.
- Unsaturated monomers [containing double bond or triple bond] normally undergo addition polymerization.
- Addition polymerization is initiated by initiators such as hydrogen peroxide, dibenzoyl

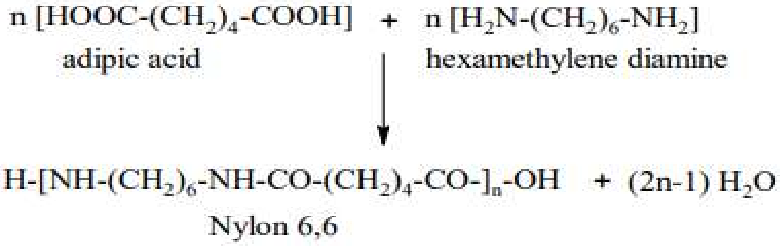
peroxide [$C_6H_5CO\text{-}O\text{-}O\text{-}OCC_6H_5$], or Zeigler-Natta catalyst [$TiCl_4 + (C_2H_5)_3\,Al$], heat or pressure.

- Eg: Molecules of ethene can polymerize with each other under the right conditions to form the polymer called polyethylene.
- Addition process proceed through free radical mechanism. Free radical polymerization proceeds in three different steps: initiation, propagation and termination.

$$\underset{\text{Ethene}}{n\ H_2C{=}CH_2} + \text{initiator} \xrightarrow{\text{Polymerization}} \underset{\text{Polyethene}}{\left[-CH_2-CH_2-\right]_n}$$

2. **Condensation polymerization** :[Step growth polymers]

- A polymerization reaction in which two or more monomers (similar or dissimilar) undergo intermolecular condensation with continuous elimination of byproducts such as H_2O, HCl, NH_3, alcohol etc is called condensation polymerization.
- Thus the resulting material is a copolymer. e.g. Nylon is made by the condensation of adipic acid with hexamethylene-diamine



$$\underset{\text{adipic acid}}{n\,[HOOC\text{-}(CH_2)_4\text{-}COOH]} + \underset{\text{hexamethylene diamine}}{n\,[H_2N\text{-}(CH_2)_6\text{-}NH_2]} \longrightarrow \underset{\text{Nylon 6,6}}{H\text{-}[NH\text{-}(CH_2)_6\text{-}NH\text{-}CO\text{-}(CH_2)_4\text{-}CO\text{-}]_n\text{-}OH} + (2n\text{-}1)\,H_2O$$

Degree of polymerization (DP):

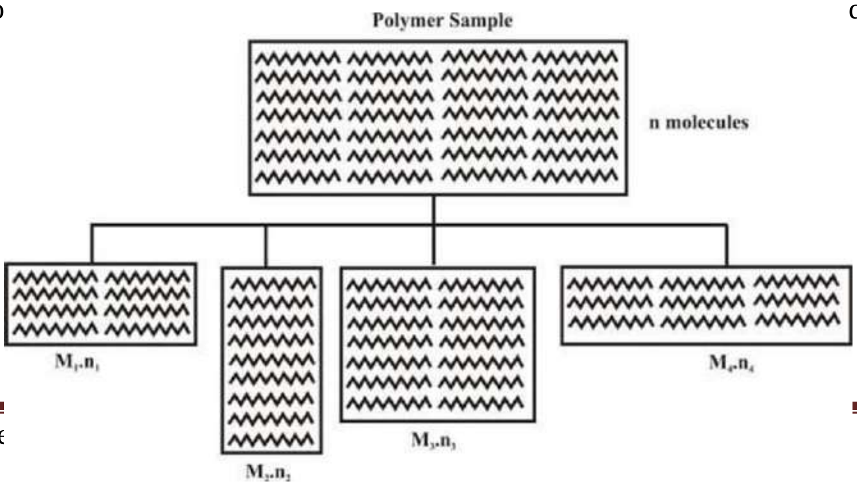
Degree of polymerization is the number of repeating monomeric units present in a polymer. Degree of polymerization is related to the molecular weight of the polymer [M] by the equation,

M = m x DP (where m: Molecular weight of monomer unit)

Molecular weight of a Polymer:

"Molecular weight of a polymer is defined as sum of the atomic weight of each of the atoms in the molecules, which is present in the polymer"

As the polymers are made up of mixture of molecules having different properties, its molecular weight can be determined in two different ways:



Different molecular weights

1. Number – average molecular mass (**$\bar{M}$**n)
2. Weight average molecular weight (**$\bar{M}$**w)

Number – average molecular mass ($\bar{M}$n): Number average molecular weight is the mole fraction of molecules in a polymer sample. It is a way of determining the molecular mass of a polymer. It gives the average of the molecular masses of the individual macromolecules.

It is defined as total mass of all the molecules in a polymer sample divided by total number of molecules present.

$$M_n = \sum N_i M_i / \sum N_i$$

$$\overline{Mn} = \frac{N_1M_1+N_2M_2+N_3M_3+\cdots}{N_1+N_2+N_3\ldots..}$$

Here, M_n is the number average molecular weight, N_i is the number of molecules having M_i weight in the polymer sample, and M_i is the weight of a particular molecule of the sample

1. **Weight average molecular weight ($\bar{M}$w):** Weight average molecular weight is the weight fraction of molecules in a polymer sample. It is another way of determining the molecular mass of a polymer. It gives the average of the molecular masses of the individual macromolecules in the polymer sample. We can find this parameter using the following equation:

$$M_w = \sum N_i M_i^2 / \sum N_i M_i$$

$$\overline{Mw} = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + \cdots}{N_1M_1 + N_2M_2 + N_3M_3 + \cdots}$$

Where M_w is the weight average molecular weight, N_i is the number of molecules of molecular mass M_i.

Poly Dispersity index [PDI]: Index of polydispersity or PDI is used as a measure of molecular weight distribution and is defined as

$$PDI=\frac{\overline{Mw}}{\overline{Mn}}$$

If, PDI =1 polymer is mono disperse & Homogeneous.

PDI >1 polymer is poly disperse & less Homogeneous.

Problems on Molecular weight

1. In a sample of a polymer, 100 molecules have molecular mass 10^3 g/mol, 250 molecules have molecular mass 10^4 g/mol, and 300 molecules have molecular mass 10^5 g /mol, calculate the number average and weight average molecular mass of the

polymer, Calculate PDI and comment on it.

Solution:

Sl. No	No of Molecules(N)	Molecular Mass(M)
1	N_1= 100	$M_1= 10^3$
2	N_2=250	$M_2= 10^4$
3	N_3= 300	$M_3= 10^5$

Number average molecular mass (**M̅**n) is given by:

$$\overline{Mn} = \frac{N_1M_1 + N_2M_2 + N_3M_3 + \cdots}{N_1 + N_2 + N_3 \ldots\ldots}$$

$$\overline{Mn} = \frac{100 * 10^3 + 250 * 10^4 + 300 * 10^5}{100 + 250 + 300}$$

= 50153 g/l

Weight average molecular mass (**M̅**w) is given by:

$$\overline{Mw} = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + \cdots}{N_1M_1 + N_2M_2 + N_3M_3 + \cdots}$$

$$\overline{Mw} = \frac{100*(10^3)*(10^3)+250*(10^4)*(10^4)+300*(10^5)*(10^5)}{100*10^3+250*10^4+300*10^5}$$

= 92794 g/l

PDI **=** $\frac{\overline{\boldsymbol{Mw}}}{\overline{\boldsymbol{Mn}}}$

= 92794/50153

=1.85

PDI >1 , the given polymer is less homogeneous and poly disperse in nature.

2. In a sample of a polymer, 20% molecules have molecular mass 15000 g/mol, 35% molecules have molecular mass 25000 g/mol, and remaining molecules have molecular mass 20000 g /mol, calculate the number average and weight average molecular mass of the polymer, Calculate PDI and comment on it.

Solution. It is given that,

Sl No	No of Molecules(N)	Molecular Mass(M) g/mol
1	$N1$= 20	$M1$= 15000
2	$N2$=35	$M2$= 25000
3	$N3$= 45	$M3$= 20000

Number average molecular mass (**M̅**n) is given by:

$$\overline{Mn} = \frac{N_1M_1+N_2M_2+N_3M_3+\cdots}{N_1+N_2+N_3\ldots..}$$

$$\overline{Mn} = \frac{20 * 15000 + 35 \ * 25000 + 45 * 20000}{20 + 35 + 45}$$

= **20750g/l**

Weight average molecular mass (**M̅**w) is given by:

$$\overline{Mw} = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + \cdots}{N_1M_1 + N_2M_2 + N_3M_3 + \cdots}$$

$$\overline{Mw} = \frac{20 * (15000)^2 + 35 * (25000)^2 + 45 * (20000)^2}{20 * 15000 + 35 * 25000 + 45 * 20000}$$

= 21385 g/l

PDI = $\frac{\overline{\boldsymbol{Mw}}}{\overline{\boldsymbol{Mn}}}$

= 21385/20750

= 1.03

PDI >1, the given polymer is less homogeneous and poly disperse in nature.

Note: For additional problems refer class notes

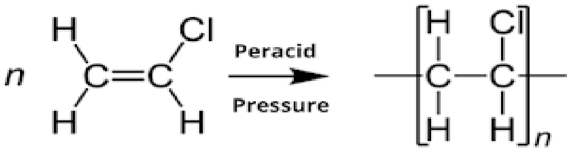
Synthesis, properties applications of polyvinyl chloride (PVC):

Properties:

- PVC is a **lightweight, durable, and abrasion-resistant material** by nature.
- PVC material is used in place of ceramics, metal, concrete, wood, rubber, and many others.
- Since PVC is amorphous in nature, it can be easily mixed with various chemicals/substances.
- Due to its high dielectric strength and vapor barrier capacity, PVC is an excellent insulation material.
- It is resistant to adverse weather conditions, stress, and corrosion.
- PVC materials have an inherent flame-retardant property.
- It has high tensile strength and is naturally stiff.
- It requires less maintenance and is resistant to grease and oil.
- Because the durability is higher, the product will last longer.

Synthesis polyvinyl chloride:

PVC is prepared by addition polymerization in which monomers are added in a chain. Vinyl chloride is treated with per acid (peroxide) under pressure, to obtain polyvinyl chloride (PVC).

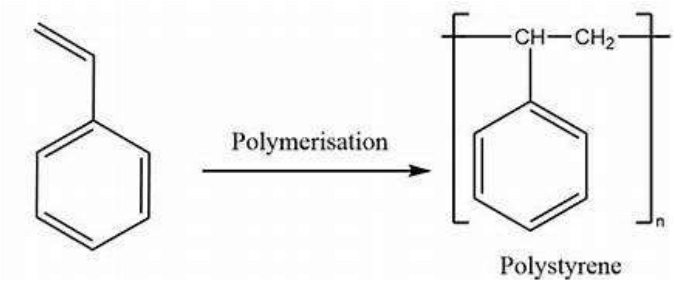


Polyvinyl chloride can be produced through free radical polymerization

USES:

- PVC is utilized in flooring, to make window frames.
- PVC is used to make sewage pipes and other pipe applications where the usage of metal is prohibitively expensive or vulnerable to corrosion.
- It is utilized in various industries, including construction, electronics, electrical cables, automotive, medical, and packaging.
- Aprons, shower curtains, raincoats, jackets, and sports bags are all made from PVC fabric.
- It is utilized in garden hoses and faux leather upholstery.
- PVC is used in the construction industry for electrical wire insulation or flooring in hospitals, schools, houses.

POLYSTYRENE:



Properties:

- Polystyrene is non-polar in nature.
- The polystyrene melting point is 240 degrees Celsius.
- Polystyrene density is 1.05 g/cm3
- Polystyrene has a good optical property like it is a transparent polymer allowing high transmission of all wavelengths.
- Due to the chain stiffening effect of the benzene ring, polystyrene is hard but brittle.
- Polystyrene has a low tendency for moisture absorption. Moreover, it has good electrical insulation characteristics

Applications:

- polystyrene sheets, polystyrene foam, brush handles, and combs.

- plastic like small jars, bottle caps, polystyrene cups, and storage containers.
- Polystyrene has been declared safe for use in food contact by the Food and Drug Administration for decades
- Foam polystyrene cups, plates, and sandwich containers require substantially less energy and water than comparable paper-based or corn-based alternatives, owing to foam polystyrene's significantly lower weight.

Fibres:

Fibres are the polymer which have strong intermolecular forces between the chain. These forces are either hydrogen bonds or dipole-dipole interaction.

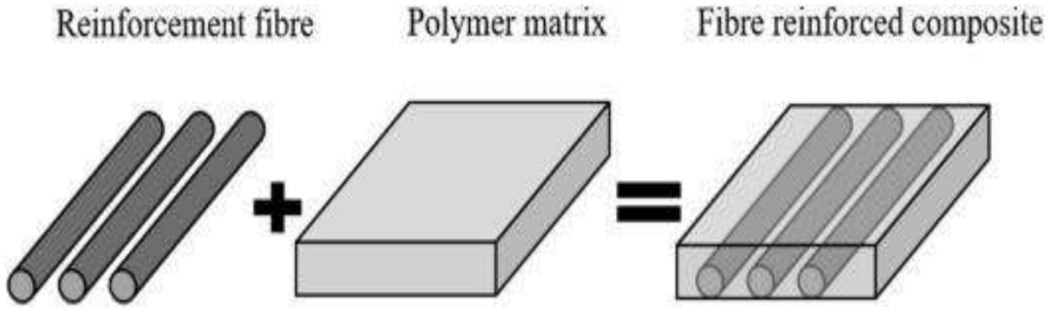
Example: Propylene fibre , Nylon 6,6, Kevlar, polyester

Fiber Reinforced Polymer Composite

Polymer Composite: A polymer composite is a material made of two or more types of polymers with different physical and chemical properties that, when combined, produce a material with characteristics different from the individual components.

Fiber Reinforced Polymer Composite is a composite material made of polymer matrix reinforced with fiber.

- Fiber is embedded in the matrix to make the matrix stronger.
- Commonly used fibers are glass, carbon, aramid etc
- Polymer matrix – epoxy, vinyl ester, polyester, wood, asbestos etc,



Properties

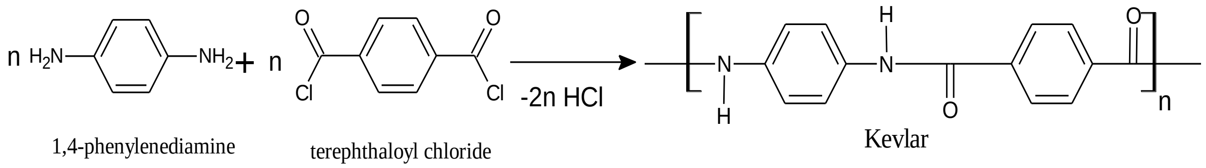
- High strength to weight ratio -Light weight-easy to handle and transport
- high durability.
- high stiffness.
- high damping property - material's ability to dissipate elastic strain energy during mechanical vibration, high flexural strength-the capacity of the concrete (usually beams) to resist deformation under bending moment, resistance to corrosion, wear and fire, Nonmagnetic

The widely used polymer matrices are epoxy, polyester, phenolic resin, etc. The commonly used reinforcements are glass, carbon and aramid (Kevlar- trade name of Du Pont Company) fibres. The glass epoxy composite is popularly known as GFRP- Glass fibre reinforced plastic, and the carbon- epoxy composite is called CFRP – Carbon fiber reinforced plastics.

Kevlar Fibre

- Kevlar is invented by Stephanic Kwolek, the DuPont chemist. Kevlar is an aromatic polyamide (aramide) (IUPAC name is poly- paraphenyleneterepthalamide).
- It is formed the reaction of para-Phenylene diamine and terephaloyl chloride. The individual chloride of Kevlar are held together by hydrogen bonding with amide groups.
- it was the first organic fiber with sufficient tensile strength and structural rigidity to be used in advanced composites.

Kevlar is synthesized in solution of n-methyl-pyrrolidone and calcium chloride from the monomers 1,4-phenylene-diamine (para-phenylenediamine) and terephthaloyl chloride through a condensation reaction with the liberation of hcl.



***Properties*:**

- High tensile strength (five times stronger per unit weight than steel)
- High modulus of elasticity
- Very low elongation up to breaking point
- Low weight
- High chemical inertness
- Very low coefficient of thermal expansion
- High fracture toughness (impact resistance)
- High cut resistance
- Flame resistance

Uses:

- Used as reinforcement in tyre and rubber mechanical goods.
- Industrial applications are as cables, in asbestos replacements, break linings, and body armor.
- Used in plastic reinforcements for boat hulls, airplanes and bicycles.
- Kevlar is well known component of personal armor such as combat helmets, ballistic face masks etc.
- Used as inner lining for some tyres to prevent punctures.
- The Kevlar fiber is used in woven rope and in cables.
- Aramid fibers are widely used for reinforcing composite materials, often in combination with carbon fiber and glass fiber. The matrix for high performance composite is usually

epoxy resin. Typical applications include bodies for F1 racing cars, helicopter rotor blades, tennis, table tennis, badminton and squash rackets, cricket bats, and hockey sticks.

Polyester Fiber :

- Polyester fiber is a “manufactured fiber in which the fiber forming substance is any long chain synthetic polymer composed at least 85% by weight of an ester of a dihydric alcohol (HOROH) and terephthalic acid. (p-HOOC-C_6H_4COOH).

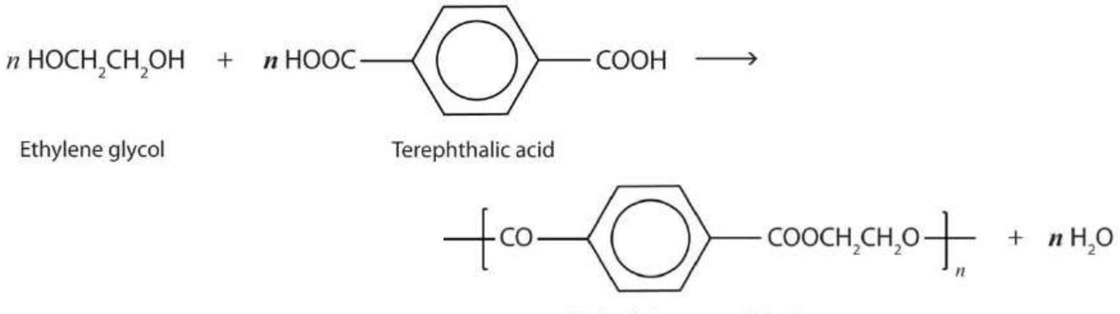
- The most widely used polyester fiber is made from the linear polymer poly (ethylene terephthalate), and this polyester class is generally referredto simply as PET.
- High strength, high modulus, low shrinkage, heat set stability, light fastness and chemical resistance account for the great versatility of PET.

Synthesis Polymer:

Polyethylene Terephthalate:

- PET is polymerized byone of the following two ways:
- Direct Esterification: Monomers are terephthalic acid and ethylene glycol. Both ester interchange and direct esterification processes are combined with polycondensation steps either batch-wise or continuously.
- Tran’s esterification: Monomers are diethyl terephtalate and ethylene glycol.

Polyethylene Teraphthalate (PET) is a condensation polymer and is industrially produced by either terephthalic acid or dimethyl terephthalate with ethylene glycol.



Polyethylene terephthalate

Properties Polyester Fibre

- Resistant to stretching and shrinking.
- Resistant to most chemicals
- Quick drying
- Crisp and resilient
- Wrinkle resistant
- Mildew resistant
- Abrasion resistant
- Retains heat-set pleats and crease.

Applications of Polyester:

- Polyesters are widely used in clothing fabrics. Several types of clothing apparel are woven from polyester yarns or polyester threads. Examples include polyester shirts, polyester jackets, polyester pants, and polyester hats.
- Polyester is also employed in the manufacture of many home furnishing materials such as bedsheets, curtains, blankets, and pillowcases.
- Polyester is also used in upholstered furniture.
- Polyester is known to play a vital role in the manufacture of certain types of car tyre reinforcements.
- Used In The safety belts that are used in automobiles
- Owing to its insulating properties and its relatively soft texture, polyester is used in the production of cushioning materials for pillows.
- polyester fabrics are highly resistant to staining, they are ideal for use as tablecloth.
- Liquid crystal displays (often referred to as LCDs) are often manufactured with the help of certain polyesters.
- Polyesters are also used in the manufacture of dielectric films that are used in capacitors

Fiber Formation:

- The sequences for production of PET fibers and yarns depend on the different ways of polymerization (continuous, batch-wise, and solid- phase) and spinning (low or high wind up speed) processes.

The Manufacturing Process:

- Polyester is manufactured by one of several methods. The one used depends on the form the finished polyester will take.
- The four basic forms are filament, staple, tow, and fiberfill. In the filament form, each individual strand of polyester fiber is continuous in length, producing smooth-surfaced fabrics.
- In staple form, filaments are cut to short, predetermined lengths. In this form polyester is easier to blend with other fibers.
- Tow is a form in which continuous filaments are drawn loosely together.
- Fiberfill is the voluminous form used in the manufacture of quilts, pillows, and outerwear. The two forms used most frequently are filament and staple.

TEFLON

Teflon is a synthetic fluoropolymer made up of tetrafluoroethylene monomer. The chemical name of Teflon is poly (1,1,2,2 - tetrafluoroethylene). It is a thermoplastic polymer.

Synthesis:

Teflon is produced by a free radical mechanism. The net reaction for the production of Teflon is given below:

$$n\ F_2C{=}CF_2 \rightarrow -(F_2C{-}CF_2)_n-$$

Properties of Teflon:

It is a white solid compound at room temperature.

Its density is about 2200 kg/m^3 2.2 g/cm^3 with melting point is 600 K.

It is a chemical resistance compound; the only chemicals that can affect these compounds are alkali metals.

It shows good resistance towards heat and low temperature.

It has a low water absorption capacity.

It has an anti-adhesion ability due to which it is used as non-stick kitchen utensils.

Uses of Teflon:

It is used in making waterproof fabric.

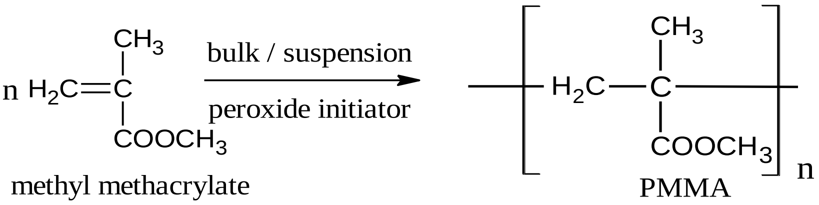
It is used in making non-stick cookware.It is used in making an anti-friction device.

It is used for coating medical appliances (surgical devices).

Due to its high resistance to corrosion, it is used for coating the lining of laboratory appliances.

i) Poly (methyl methacrylate) (PMMA) (plexi glass):

Preparation: Methyl methacrylate is the monomer used in the synthesis of PMMA. PMMA is obtained by subjecting methylmethacrylate to emulsion polymerization at 60-70^{0}C in presence of hydrogen peroxide.



$$n\ H_2C{=}C(CH_3)(COOCH_3) \xrightarrow[\text{peroxide initiator}]{\text{bulk / suspension}} -\!\left[H_2C-C(CH_3)(COOCH_3)\right]_n\!-$$

Properties:

- PMMA is a white transparent thermoplastic polymer.
- It is amorphous in nature due to the presence of bulky group.
- It has an excellent optical clarity, which is not affected by sunlight, but has poor scratch resistance.
- It has resistance to water, alkalis, inorganic salts but dissolves in organic solvents.
- It has good outdoor weathering property and dimensional stability

Applications:

- Used for making light fixtures, aircraft windows, attractive sign boards etc.

- used as paints and adhesives.
- used to make durable lenses for automobile lighting, instrument and dust covers for equipment's.
- In making artificial eyes and teeth.
- In making transparent bottles, moulds, tubes plastic jewellery, toys etc.
- In making TV, computer screens, window screens.

polymer composites:

Introduction of Composite Materials

- Composite material is defined as the material formed by combining two ormore different materials/ constituents macroscopically that is distinct in the properties and they do not dissolve into each other.
- The combination of different constituents in the composites provides the composite material with unique properties which are different from the individual constituent.
- In general, the composite material comprises three main components
  - ➢ The matrix, the continuous phase
  - ➢ The reinforcements, the continuous or discontinues phase used to strengthen the composite,
  - ➢ The fine interface region.

Composites can indeed be found in the majority of common products, including building and engineering projects, medical applications, energy and transportation, sports, aircraft, automotive, and other fields.

Carbon-based reinforced composites:

Composite materials with carbon nanotube and graphene attachments have been regarded as promising materials. Carbon nanotubes (CNT) are the most notable of carbon-based nanomaterials with excellent mechanical properties, characterized by tubular structures . Graphene is a 2D allotropic carbon group consisting of single layers of sp2-hybridized carbon atoms with high structural rigidity and higher thermal stability, and the electrical properties.

Carbon nanocomposites have gained considerable interest in different fields including biomedical applications due to its exceptional structural dimensions and outstanding mechanical, electrical, thermal, optical, and chemical characteristics.

Carbon nanocomposites are applied in various fields such as aviation, batteries, chemical industry, fuel cell, optics, power generation, space, solar hydrogen, sensors, and thermoelectric devices. The recent design, fabrication, characteristics, and applications of carbon nanocomposites such as active carbon, carbon black, graphene, nanodiamonds, and carbon nanotubes are also reported.

- Carbon nanocomposites consisting of graphene and carbon nanotubes have exhibited exceptional catalytic activity in organic chemical processes due to their shape-dependent physical and chemical properties and thickness.
- The catalytic yield from the use of carbon nanocomposites in various fields, including nutritional, pharmaceutical, and materials sciences for biotechnology has been found to be of great value.
- The catalytic products produced using carbon nanocomposites are considered of great value in medicinal, biomedical, agricultural, and material sciences.
- Nanocomposite benefits involve module enhancement, strength, thermal alteration,

Applications of Composite Materials

- Space: antenna, radar, satellite structures, solar reflectors, etc.
- Aircraft: aerofoil surfaces, compressor blades, engine bay doors, fan blades,rotor shafts in helicopters, turbine blades, turbine shafts, wing box structures, etc.
- Automobiles: automobile body, bumper, mudguards, door panels, dashboard, driveshaft, fuel tank, CNG cylinder, chassis, fender, etc.
- Wind turbine blades: rotor blades, nose cone, nacelle cover, accessories forwind electric generators.
- Sports: Skis, surfboards, windsurfing, table tennis boards, slats, and gliding wing spar, Tennis, badminton, fishing rods, golf clubs, baseball bats, hockeysticks, pole shaft, Sword, etc.

Metal matrix polymer composites.

Metal Matrix Composites (MMCs) are materials produced by adding reinforcement in the form of particles (ceramic or metal), fibers, whiskers or even a sheet metal to a metal or alloy matrix.

Properties metal matrix composites

- The matrix phase of an MMC is either a pure or alloy metal as opposed to apolymer or ceramic.

- MMCs evidence higher ductility and toughness than ceramics or CMCs,although they have lower ductility and toughness than their respective unreinforced metal matrix alloys.
- The role of the reinforcement in MMCs is to increase strength and modulusas is the case with PMCs. Reinforcement in CMCs is generally to provide improved damage tolerance.
- MMCs have a temperature capability generally higher than polymers andPMCs but less than ceramics and CMCs.
- Low to moderately reinforced MMCs are formable by processes normallyassociated with unreinforced metals.

Industrial application metal matrix polymer composites:

The following industry and application highlights provide a sampling of the vastrange of applications of polymer matrix composites

- **Transportation vehicles:** find many uses in automotive, aerospace, and marine applications.
- **Automotive vehicles:** used intires and various belts and hoses as well as polymer matrix composite components in automotive bodies.
- **Aerospace vehicles*:*** used in aircrafttires and interiors. Of even greater value, however, is the ability of polymer matrix composites to help satisfy the relentless drive in the aerospace industry to enhance performance while reducing weight
- **Marine vehicles:** find many uses in marine vehicles. Fiberglass boats are among the most familiar examples since fiberglass is a composite where a matrix polymer is reinforced by glass fibers which may be arranged randomly, or as a chopped strand mat, oras a woven fabric
- **Medical devices:** Polymers and composites are essential components of many medical devices and applications. Some examples of these uses areprovided below. Polymer matrix composites are used as components in a wide range of medical devices; such as MRI scanners, C scanners, X-ray couches, mammography plates, tables, surgical target tools, wheelchairs, and prosthetics.
- **Personal protective equipment:** used in protective equipment for use in harsh environments, when exposed to fire, when facing deadly weapons and in many other hazardous situations.
- **Footwear:** The performance and comfort of footwear, as well as the durability of shoe interiors and exteriors, can be improved with the helpof polymer matrix composites.
- **Sporting goods:** find many uses in sportinggoods, performance footwear.

- **Industrial equipment:** used as the main material of construction, or as components of equipment, or in some instances both as the main material of construction and as components.
- Polymer matrix composites are used in many packaging applications.

Lubricants

The word 'Lubricate" came from the Latin lubricus which means slippery.

Lubricants is defines as a substance when interposed between moving parts of machinery make the surface slippery and reduce friction, eliminate asperities and prevent cohesion. Lubrication result in the reduction of friction and wear.

Classifications of lubricants:

Lubricants may be broadly classified as follows

1. **Solid Lubricants:** Soap stone, graphite, talc, chalk, mica Teflon,molybdenum disulfide

Solid lubricants are used in situation such as

- Heavy machinery working on crude job at very high loads and slow speeds.
- Where a liquid or semi-solid lubricant film cannot be maintained or presenceis undesirable as in the case of commutator blades of electric motors and generators.
- Where parts to be lubricated are not easily accessible, and operating temperatures and pressures are too high to use theeasily combustible liquid lubricants

Classification of solid lubricants

The various types of solid lubricants may be conveniently divided into various classes as under

Structural lubricants:

These include materials like graphite, molybdenum disulfide, talc, mica, vermiculite etc. whose lubricating properties are due to their layer lattice structure.

Mechanical lubricants:

These include metals and plastics and are characterized by their sacrificial wear. They form a continuous adherent film on the rubbing surfaces and reduce the wear.

Soaps:

They function both as solid lubricants in their own right and also by formation of compounds 'in situ' in the metal surface by the interaction of fatty acids and themetal.

Chemically active lubricants:

These include extreme pressure additives and other chemicals which interact with the metal surface to produce a lubricating layer. Examples are phosphates, chlorides and oxidizing agents.

Refractories, ceramics and glass:

These are used in defense programmes and rocketry. Combinations of refractory materials work satisfactorily as lubricants for short periods at high temperatures.

2. **Semi-solid lubricants:** Greases, vaselines etc.

Semi solid Lubricating greases are employed in the following situations:

- When a machine is worked at slow speeds and high pressures
- In situations where spilling or spurting oil from the bearings is as in the case of textile mills, paper and food product manufacture, etc.
- In situations where the bearing has to be sealed against entry of dirt, water,dust and grit.
- Lubricating grease is generally defined as semisolid or solid combination of petroleum product and a soap or a mixture of soaps, with or without fillers, suitable for certain types of lubrication.

3. **Liquid lubricants:**
   - Vegetable oil eg. Olive oil, palm oil, castor oil
   - Animal oils e.g., whale oil, lard oil, Tallow oil etc.
   - Mineral oils e.g., Petroleum
   - Blended oils or compound oil e.g., Mineral oils various additives to induce desired properties.
   - Synthetic oils: Silicones

Purpose	Oils recommended as lubricants
Ordinary machinery	lard oil, tallow-oil, medium mineral oil
Steam cylinder	Heavy mineral oils, tallow
Watches, clocks etc.	Mineral oils, olive
For great pressure with low speed	Tallow, Lardoil, palm oil, grease etc.
For great pressure with high speeds	castor oil, medium mineral oils
For loight pressure with high speeds	refined petroleum, cottonseed rape olive and mineral oils.

4. **Emulsions:** An emulsion is a mixture of at least one immiscible liquid dispersed inanother liquid in the form of droplets whose diameters exceed 0.1 µm.

Emulsions are commonly used as lubricants and coolants in metal working andcutting applications.

Two types of emulsions are used for lubricating

Oil-in-water type: cutting emulsion:

- They are prepared by mixing together an oil containing about 3 to 20% of a water soluble emulsifying agent.(e.g., water soluble soap, alkyl or aryl sulfonate,akyl sulfates etc) and suitable quantity of water.

- Chemicals like glycols, glycerol and triethanol amine are also addedsometimes.
- Oil-in-water type emulsions are used as coolant cum lubricant for cuttingtools and in diesel motor pistons and large internal combustion engines.

Water- in – oil type: cooling liquid:

- They are prepared by mixing together water and oil containing 1 to 10% ofwater insoluble emulsifiers (e.g., alkaline earth metal soaps).
- Emulsions containing 50% lube oil and water are used for the lubrication of steam cylinders, giving cooler walls and lesser oil consumption. Such emulsionshave also been successfully used in lubricating compressors handling fuel gases.

Application of Lubricants

i) Lubricants are primarily used to reduce the friction betweentwo moving surface.
ii) Rust and corrosion inhibitors
iii) Used in the soap and paint industries.
iv) Liquid lubricants are used in medicines
v) Lubricants are also used as cutting fluid in cutting, grinding,drilling of metals.
vi) Used as anti-wear, antioxidants, and antifoaming agents.

Important questions

1. Explain addition and Condensation polymerization with example.
2. Define PDI. Explain briefly about number average and molecular average molecular weight of polymer.
3. Explain the synthesis, properties and applications of i) Polyvinylchloride ii). Polystyrene.
4. Explain the synthesis, properties and applications of i). Kevlar ii). Polyester
5. Explain the synthesis, properties and applications of Teflon and PMMA.
6. Explain the synthesis, properties and applications of nylon fiber.
7. Explain the properties and applications of fiber reinforced polymer composites.
8. Explain the properties classification and applications of Lubricants.
9. Explain briefly about properties and industrial applications of carbon-based reinforced composites.
10. Write a note on metal matrix polymer composites.

MODULE 4 : PASE RULE and ANALYTICAL TECNIQUES

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; its application in the estimation of iron, Optical sensors (colorimetry); its application in the estimation of the copper, pH sensor (Glass electrode); its application in the determination of pH of beverages.

Phase rule:

The classification and limitations of phase changes are described by the phase rule, as proposed by the American chemist J. Willard Gibbs in 1876 and based on a rigorous thermodynamic relationship.

Phase rule states that If the equilibrium between any numbers of phases is not influenced by gravitational/electrical/magnetic forces but is influenced by pressure, temperature and concentration, then the number of degrees of freedom (F) is related to the number of components (C) and the number of phases (P) as:

$$F = C - P + 2$$

Explanation of terms used in phase rule:

1) Phase (P):

Phase is defined as “any homogeneous, physically distinct, mechanically separable portion of a system which is separated from other part of system by distinct interface”.

A phase may be gaseous , liquid or solid. It is perfectly homogeneous and distinct from every other phase that is present in the system. There must be a definite boundary between any two phases. This boundary is known as the interface.

Examples:

i. A completely miscible homogenous mixture of gases mixture of gases(O_2 and N_2) and liquids (water and alcohol) gives phase (P=1)

ii. A system consisting of a liquid in equilibrium with its vapor constitutes a two phase system. example : $H_2O_{(l)} \rightarrow H_2O_{(g)}$

iii. Any pair of immiscible liquids (water and Kerosene) gives rise to two phase. P=2

iv. At a specified condition, all the three phases of water co-exists Ice waterand vapour (P=3)

v. All the gases are completely miscible and have no boundary between them. Hence all the gases constitute a single phase. For example O_2, N_2, H_2, CO_2 etc. form air, which constitute a single phase.

vi. The number of liquid phase depends upon the number of liquid present and their miscibility. If two liquid are miscible then they form single phase. If two liquids are immiscible then they form two separate phase.

Alcohol in water. – Single phase

Benzenein water, oil in water etc.- Two phase

2) Component (P):

Component is defined as "number of independent variable like temperature, pressure and concentration by means of which composition of each phase can be expressed in terms of chemical equation".

Example:

i. In water system, the composition of all the three phases can be defined in terms of only H2O. Therefore it is a one-component system, C=1

$$\underset{H_2O}{\text{Ice (s)}} \longleftrightarrow \underset{H_2O}{\text{Water (l)}} \longleftrightarrow \underset{H_2O}{\text{Vapour (g)}} \qquad \mathbf{(C=1)}$$

ii. Lead silver are miscible in all proportions in all proportions in the molten state and gives a homogenous solution of two constituents.Therfore to define the composition of this of this homogenous molten single phase, we need both constituents. Therefore, it is a two component system, C=2

3) Degree of freedom (F):

Degree of freedom is defined as "number of independent variable like temperature, pressure and concentration must be fixed to define the system completely".

$$F = C – P + 2$$

A system having 1, 2, 3 or 0 degrees of freedom is called univariant, bivariant, trivariant and nonvariant respectively.

Example :

i. Consider the water system,

$$\text{Ice}_{(s)} \rightleftharpoons \text{Water}_{(l)} \rightleftharpoons \text{Water vapour}_{(g)}$$

The three phases can be in equilibrium only at particular temperature and pressure. Therefore, when all the three phases are present in equilibrium, then no condition needs to be specified. The system istherefore zero variant or invariant or has no degree of freedom (F=0).

ii. Consider a system consisting of water in contact with its vapour,

$$\text{Water}_{(l)} \rightleftharpoons \text{Water vapour}_{(g)}$$

To define this system completely, we must state either the temperature or pressure.

Thus degree of freedom is one (F=1) and the system is univariant.

iii. Consider any single phase in water system H_2O (s), or H_2O (l) or H_2O (g)

The state of any single phase in water system can be defined by specifying two variables like pressure and temperature. In other words, any single phase of water system has two degrees of freedom. Hence, F= 2

PHASE DIAGRAM

Phase relations are commonly described graphically in terms of phase diagrams.

Phase diagram is a graph obtained by plotting one degree of freedom against another.

If All phases have the same composition (component), then the diagram is a representation of a one-component (unary) system. Based on the number of components two-component (binary), three-component (ternary) can be explained.

If the phase diagram is plotted between temperature against pressure, the diagram is called P-T diagram. P-T diagram is used for one component system.

If the phase diagram is drawn between temperature against composition, the diagram is called T- C diagram. T-C diagram is used for two component system.

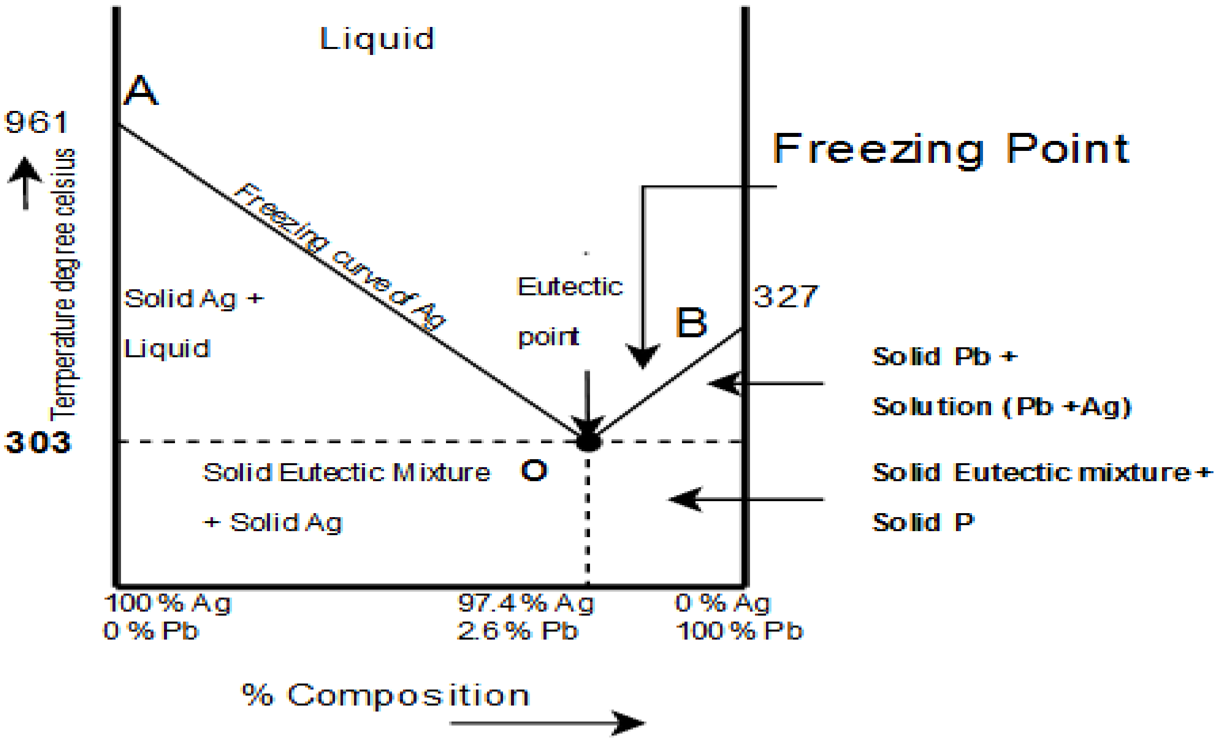
Applications of Phase rule:

- The phase rule is commonly used to describe one component as well as multi-component systems.
- Phase diagram gives a lot of information like the triple point, sublimation temperature, boiling point and freezing point etc.
- From the phase diagram, it is possible to predict whether an eutectic alloy or a solid solution is formed on cooling a homogeneous liquid containing mixture of two metals.
- The phase diagrams are useful in understanding the properties of materials in the heterogeneous equilibrium system.
- The study of low melting eutectic alloys, used in soldering, can be carried out using phase diagrams.

LEAD – SILVER SYSTEM:

Lead-silver system is a two component system. The phase diagram of this system is shown in figure. Lead and silver are immiscible with each other in liquid state. And they do not react with each other. In this two component systems there are four possible phases Solid, Ag, Solid Pb, Solution form of Ag & Pb and vapour.

In some system, an equilibrium exists between solid-liquid phase and practically gas phase is considered as absent. Hence the effect on pressure on such system can be neglected, so the system can be represented by temp-concentration diagram at atmospheric pressure. Such system showing soli-liquid equilibrium is called **condensed system** and the phase rule applied for such system is called as **condensed phase rule** i.e $F = C - P + 1$



The melting point of pure silver and pure lead is 961 ^{O}C and 327 ^{O}C respectively. A molten mixture of the two metals on metals on cooling at constant temperature forms a eutectic mixture with a constant composition.

From the figure following salient features are observed:

1. The curve OA(freezing curve of Ag)
2. The curve BO(freezing curve of Pb)
3. The eutectic point 'O'
4. The Area AOB

Curve AO : Freezing curve of Ag:

- It shows the effect on freezing point of Ag on addition of Pb in small quantities.
- The curve starts from 961°C the M.P of Ag, where pure Ag coexists as solid and liquid (Vapors being neglected)
- When Lead Is Added, melting point of Ag gradually decreases till lowest point O is reached i.e at 303^{O}C where the solution gets saturated with respect to the lead..
- If we add the Pb further it will not decrease the freezing point further.
- Along this curve, solid Ag and solution coexist and hence, according to reduced phase rule equation $F = 2 - P + 1$ i.e. $(2-2+1=1)$ system is univariant.
- The point O corresponds to a fixed composition of 2.6% Ag and solution and 97.4% Pb and is known as **eutectic composition**.

Curve BO: Freezing curve of Pb

- It represents the effect on freezing point of Pb on gradual addition of small amount of Ag to it, point B is the M.P of pure Pb 327∘c
- Along BO, the M.P gradually falls on addition of Ag till lowest point O is reached
- At this point solution gets saturated with respect to Ag and Melting Point of Pb does not fall any more.
- On cooling whole mass crystallizes out. Therefore the system is univariant like AO.

Point O: Eutectic point

- The two curve AO and BO meet at O, where all three phases solid Ag, solid Pb and their solution coexist.
- The point of O represents a fixed composition of Ag 2.6% and 97.4 % Pb is called eutectic composition, the temperature corresponding is called eutectic temperature.

At eutectic composition temperature remains constant until the whole of melt solidifies in block to become solid of eutectic composition. However, further cooling results in simultaneous crystallization of a mixture of Ag and Pb in relative amounts corresponding to eutectic point O. On cooling whole mass solidifies into a block.

Below temperature line there are two regions:
Eutectic solid + solid Ag in crystalline - stable.
Eutectic solid + solid Pb in crystalline - stable.

Area above curve AOB:

In this area, silver and lead are present as a homogeneous liquid solution. Thus, there is only one phase in this region. Applying the condensed rule to any point in this area, we obtain $F=C-P+1 = 2-1+1=2$

Applications of Lead silver phase diagram::-

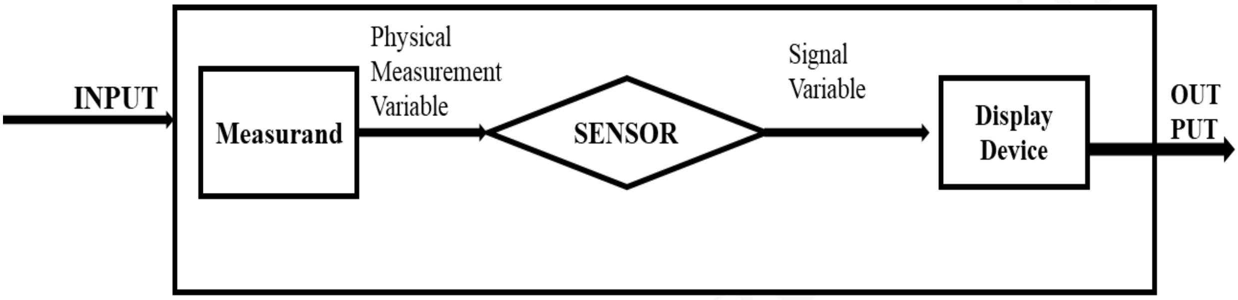
1). Used in Pattison's process of desilverization of Pb. Pattinson's process is the process used for the desilverization of lead. This method is used for purifying lead and removing silver from it. If Pb is less than 2.6 Pb will separate out from solution, If Pb is more than 2.6 Ag will separate out.

Analytical techniques

Introduction:

SENSORS: A sensor is a device that measures or detects a physical quantity, such as temperature, pressure, humidity, light, sound, motion, or position. Sensors are used to convert the physical quantity into an electrical signal that can be processed by a computer or other electronic system.

Sensors - Definition: Sensors are electronic devices or modules that detect and measure physical/chemical phenomena into an electrical signal. Physical/Chemical phenomena: Temperature, pressure, motion, light, or sound/ concentration.



Transducer: is a device that is capable of converting a physical quantity or non-electrical signal into an electrical signal.

Actuator: An actuator is a device that receives a signal or input and produces a physical output.

Measurement process for the instrumentation model

- Sensor input- The physical value is observed by the sensor device.
- Sensor output – The sensor generates a signal variable output which is normally electrical.
- Signal conditioning- The signal is transmitted and conditioned if needed (amplified, converted, filtered, etc.)
- Display of measurement – the measurement is then displayed by the outputdevice.

POTENTIOMETRIC SENSORS

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

Principle

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

Potentiometric sensors mainly determine the analyte concentration by measuring the variation of potential difference between working and reference electrodes at different analyte concentrations. Ion-selective electrodes belong to such sensor.

Potentiometric sensors measure the potential difference between two electrodes under the conditions of no current flow. The measured potential may then be used to determine the analytical quantity of interest, generally the concentration of some component of the solution. The signal of a general potentiometric sensor is based on the Nernst equation. This equation predicts a linear dependence of the sensor response, *E*, on the logarithm of a function of the activity of the ion in solution:

Nernst Equation: The **Nernst equation is often used to calculate the cell potential** of an electrochemical cell at any given temperature, pressure, and reactant concentration.

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

Applications:

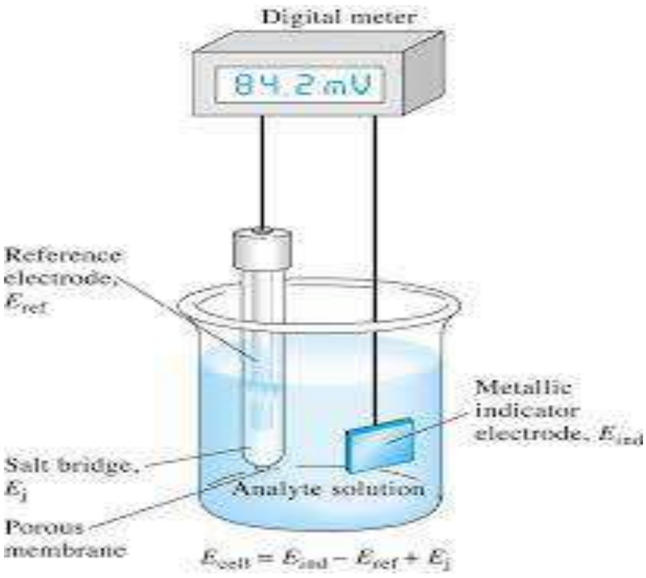
Wearable potentiometric sensors have received considerable attention owing to their great potential in a wide range of physiological and clinical applications. It is employed in several applications including medicine, forensic analysis, environmental assessment, industry, agriculture, and pharmaceutical drug analysis.

Determination of FAS/iron using potentiometry:

Determination of iron can be done using potentiometry method. It is a technique similar to direct titration of a redox reaction. No indicator is used; instead the potential is measured across the analyte, typically an electrolyte solution.

Potentiometer is used to determine the difference between the potential of two electrodes.

- Working or indicator electrode - The potential of which responds to the analyte’s activity
- Reference electrode - has a known, fixed potential.



The typical potentiometric analytical cell has two electrodes immersed in a solution containing the analyte, whose concentration is to be measured. The reference electrode (Calomel, Ag-AgCl electrodes) and indicator electrode is Pt whose response depends on the concentration of the analyte and the instrument used is modern electronic voltmeter or potentiometer.

The potential of a potentiometric electrochemical cell is

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

Where $E_{cathode}$ and E_{anode} are reduction potentials for the redox reactions at the cathode and the anode. Reduction potential is calculated using the Nernst equation:

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

This is redox titration where Mohr's salt is a reducing agent and $K_2Cr_2O_7$ is an oxidizing agent. Titration is carried out read the potential difference. Initially the potential difference is with respect to ferric ferrous system:

$$\mathbf{Pt_{(s)} \mid Fe^{3+}, Fe^{2+}}$$

Potential developed is given by the Nernst equation shown below:

$$E_{Fe3+/Fe2+} = E^0 + 0.0592 \log \frac{[Fe^{3+}]}{[Fe^{2+}]}$$

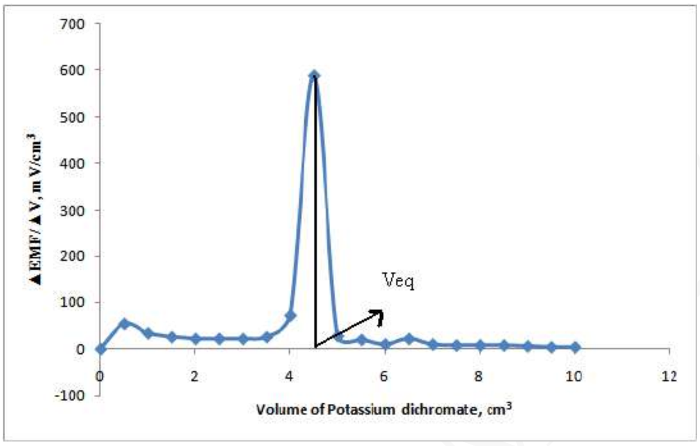
Thus potential of this electrode is determined by the ratio, $[Fe^{2+}]/[Fe^{3+}]$. The formal potential (standard potential under the specified experimental conditions) of this system is +0.68 V in 1M H_2SO_4 with respect to SHE (standard hydrogen electrode).

Fe^{2+} ions are oxidized to Fe^{3+} ions, when dichromate solution is added.

$$Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 6Fe^{3+} + 2Cr^{3+} + 7H_2O$$

Dichromate ions are reduced to Cr^{3+} ions by Fe^{2+} ions. Thus the ratio,$[Fe^{2+}]/[Fe^{3+}]$ gradually decrease and hence $E_{Fe^{3+}/Fe^{2+}}$ gradually increases in accordance with the Nernst equation, when dichromate is added to Mohr's salt solution. This occurs until the end point.

After the endpoint, dichromate remains in solution, because Fe^{2+} ions do not exist in solution to react with it. Hence potential of the redox electrode is determined by $Cr_2O_7^{2-}/Cr^{3+}$coupleinstead of Fe^{3+}/Fe^{2+}couple after the end point. The formal potential of $Cr_2O_7^{2-}/Cr^{3+}$ system is about +1.3V in 1M H_2SO_4 w.r.to SHE. Hence a steep change in the electrode potential results at the endpoint. Then again gradual increase in the EMF.



Applications

- It is used for all types of volumetric analysis: acid base, redox, precipitimetry and complexometry.
- Used to highly colored and turbid solutions.
- For very dilute solutions
- Used when there is no availability of indicator for the titration.

pH SENSOR :

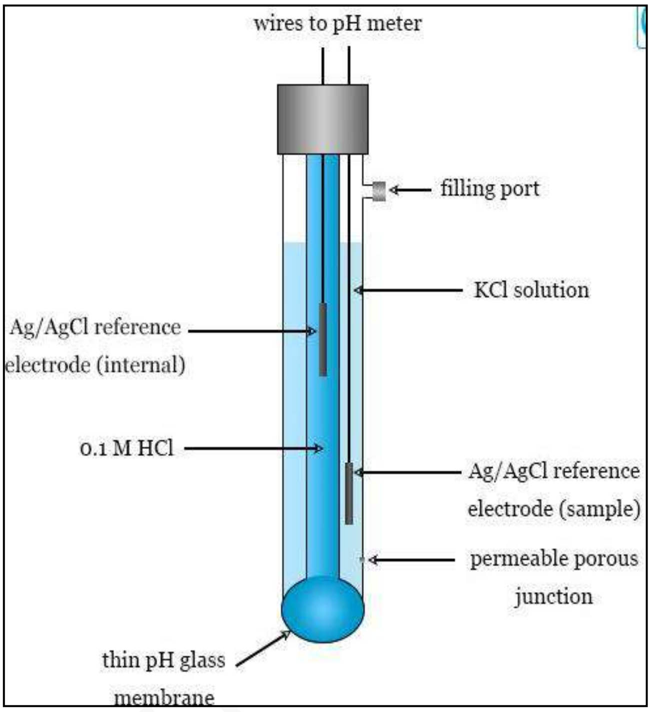
pH sensor is a equipment used in science to determine whether a solution is naturally acidic or alkaline. pH levels can be detected between 0 and 14 by the sensor set.

This pH sensor kit can be used to assess the quality of both soil and water, beverages, food quality.

The pH Sensor is often made of glass bulb membrane that is specifically made to be selective to hydrogen-ion concentration. It contains known concentration of H+ ion. When glass electrode is dipped in an unknown sample concentration, creats an electrochemical potential across the bulb. The electrical potential difference between the two electrodes created during the test is detected by the electronic amplifier, which transforms it into pH units.

GLASS ELECTRODE CONSTRUCTION & WORKING

Glass electrode or Ion-selective electrode is a membrane electrode which is selectively sensitive to a specific ion in a mixture and potential developed at the electrode is a function of concentration of that ion in the solution. The electrode generally consists of a membrane which is capable of exchanging the specific ions with the solution with which it is in contact.



Construction and working principle of Glass electrode

Construction:

A glass electrode consists of a long glass tube with a thin walled glass bulb at one end. This glass can specifically sense hydrogen ions up to a pH of about 9. The bulb contains 0.1 M HCl and Ag/AgCl electrode (as internal reference electrode) immersed into the solution and connected by a platinum wire for electrical contact.

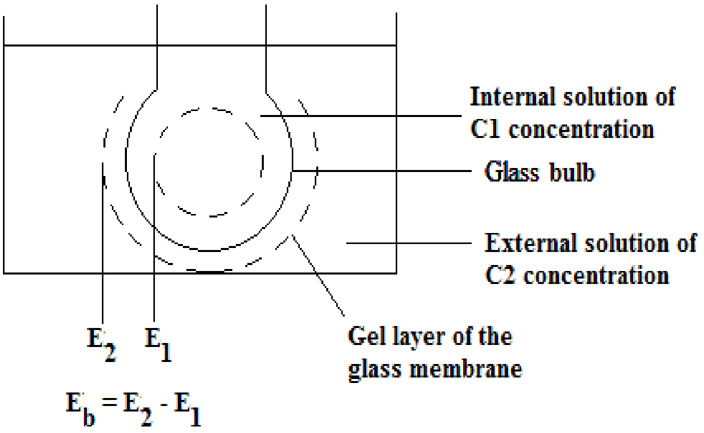
The electrode is represented as: Ag | AgCl (s) | HCl (0.1M)| Glass

Working principle:

A glass bulb containing an acid is immersed in analyte solution, a potential is developed across the glass membrane. The potential difference, E_B at the interface also referred to as the ***boundary potential*** is the result of difference in potential ($E_2 - E_1$) developed across the gel layer of glass membrane between the two liquids.

The boundary potential, E_B can be related to the difference in the hydrogen ion concentration of the two solutions by the relation,

$$E_B = E_2 - E_1$$



$$E_B = (E^{0} + \frac{0.0591}{n}\log C_2) - (E^{0} + \frac{0.0591}{n}\log C_1) - - - - - 1$$

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

$$E_B = -\frac{0.0591}{n}log[C_1] + \frac{0.0591}{n}log[C_2] - - - - 2$$

Since concentration of C_1 is known,

$$E_B = \text{Constant} + \frac{0.0591}{n}\log[C_2]$$

Since $C_2 = [H^+]$ of the solution,

$$E_B = \text{Constant} + 0.0591 \log[H^+]$$

$$E_B = \text{Constant} - 0.0591 \text{ pH}$$

$$\mathbf{E_B = L - 0.0591p^H \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 3}$$

Where, L is a constant, which depends primarily on the pH of the solution taken in the bulb and glass electrode assembly.

The membrane undergoes an ion exchange reaction; Na^+ ions on the glass are exchanged for H^+ ions.

The boundary potential established due to the above reaction is mainly responsible for the glass electrode potential E_G is given by

$$E_G = E_B + E_{Ag/AgCl} \ldots\ldots\ldots\ldots(5)$$

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

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

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

$$\mathbf{E_G = E_G^0 - 0.0591 \text{ pH}}\ldots\ldots\ldots\ldots(6)$$

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

Application of Glass electrode: Glass electrode is used to determine the pH of an unknown solution.

Advantages and limitations of glass electrode.

Advantages of glass electrode:

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

Limitations of glass electrode:

- The glass membrane though it is very thin, it offers high resistance. Therefore ordinary potentiometers cannot be used; hence it requires sensitive electronic potentiometers.
- This electrode cannot be used for solutions for pH less than 1and greater than 9.
- Fluoride ions attack the glass electrode easily.
- In strongly acidic solutions of pH<1, the salt effect due to anions is observed.
- It can be used up to a pH of 13 but being sensitive to Na^+ ions above a pH of 9, the linear relationship between glass electrode is altered. So an alkaline error is introduced beyond a pH of 9, which should be taken into consideration

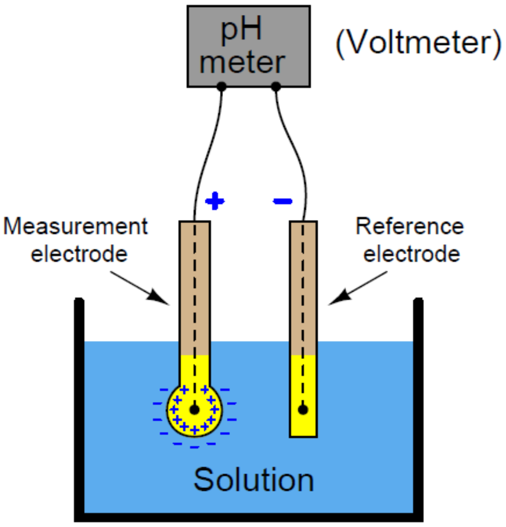
Application: Glass electrode for pH measurement of beverages

Acidity testing is vital in ensuring food products, beverages quality analysis to meet regulatory requirements and concern with health issues for the consumer. Acidity is an important attribute of many foods and drinks. pH indicates a food or beverage's degree of acidity or alkalinity. A pH meter measures this acid strength in terms of the potential difference between a reference electrode (like Calomel or Ag/AgCl) and a pH electrode (glass electrode). This difference is then related to the concentration of H+ ions in the solution and corresponds to the acidity of the solution. pH sensors are used to perform accurate and reliable acidity content determinations in the beverage industry.

Determination the pH of the beverage by using glass electrode

Representation: Calomel electrode || Solution of unknown p^H |glass electrode

The glass electrode is immersed in a solution of beverages whose pH is to be determined. It is combined with a reference electrode such as a calomel electrode through a salt bridge. The cell assembly is represented as:



E_{cell} measured is the difference between potential of glass electrode E_G and calomel electrode (E_{cal}).The potential developed at the indicator glass electrode is higher than the reference calomel electrode ($E_G > E_{cal}$).

Hence, $E_{cell} = E_{cathode} - E_{anode}$

$= E_G - E_{cal}$

$E_{cell} = [E_G^0 - 0.0591\ pH] - E_{cal}$ (Since, $E_G = E_G^0 - 0.0591\ pH$)

$0.0591pH = E^{o}_{G} - E_{CAL} - E_{CE}$

Therefore, pH can be calculated as = $\frac{E^0_G - E_{CAL} - E_{CELL}}{0.0591}$

Where, E^0_G and E_{cal} are constants.
E_G^0 is a constant equal to L + $E_{Ag/AgCl}$ + E_{asy} . By substituting E_{cell} value, p^H of an unknown solution is calculated.

Colorimetry

- Simple technique used to determine the concentration of compounds in a solution.
- This method is used for solution which are themselves colored (or) which gives colour with a suitable reagent.
- The colour intensity of the solution is directly proportional to the concentration of the solution.

Theory/Principle

This method is based on Beer- Lambert law

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

$$\mathbf{A = \varepsilon . C . t}$$

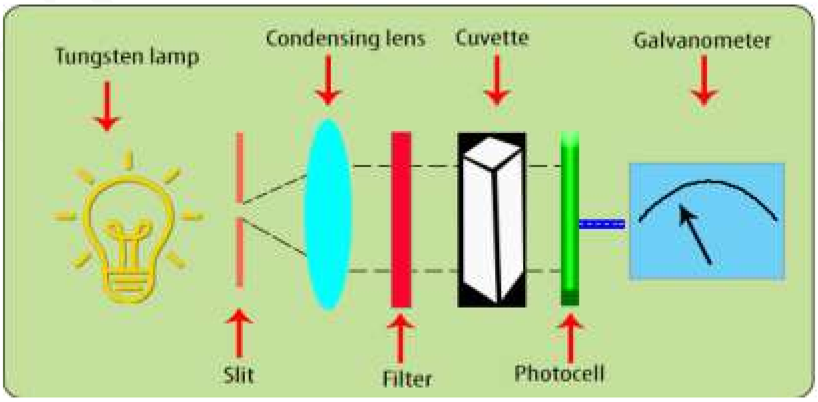
A→Absorbance

C →Concentration of solution.

t → path length

ε → Molar absorption coefficient which is dependent on the material being studied

Instrumentation



1.Light source: In colorimeter, the light source is usually an ordinary filament lamp.

2.Slit: It is a slit between light source and condenser lens which can be adjusted.

3.A lens: A condenser lens is used through which the light beam is passed.

4.Set of filters: There is a set of filters with different colours which can filter a certain wavelength of light and remaining light can pass through it. Filter is used to select the colour of light that absorbs by solute present in the solution. The colour of light absorbed is always the complimentary to the colour of the solution. In other words if the substance is orange in colour, a blue filter would be appropriate.

5.Cuvette: It is the sample holder. Cuvettes are made of plastic or glass or quartz material. The coloured solution in the cuvette absorbs part of the light and remaining is allowed to pass on the detector.

6.Detector: It is a photo resistor or photocell that measures the light passed through the solution.

7.Meter: It displays the output from the detector in terms of absorbance or transmittance. Here sensors measure the amount of light passed through the solution and compare it with the incident light.

Procedure/ Working

1. Monochromatic light of suitable wavelength can fall on the sample cell.
2. First blank solution is taken in the sample cell and placed in the path of light beam.Its absorbance is adjusted to zero.
3. Series of standard solutions is placed in the path of light and its absorbance is measured
4. Then the analyte solution is placed in the path of light and its absorbance is measured.
5. A plot of absorbance versus standard concentration of analyte is used to find the unknown concentration of analyte in the samples.

Application

1. Colorimetry is used various laboratories including clinical laboratories for biochemical estimation.
2. Colorimetry is used in clinical laboratories for the analysis of biomolecules such as glucose, urea, etc.
3. Colorimetry is used soil testing laboratories for analysis of pesticides, soil nutrients and plant nutrients, metal ion detection.

Determination of Copper using Colorimetry:

A series of standard solutions of copper sulphate pentahydrate is treated with ammonia to get blue cuprammonium complex, $[Cu(NH_3)_4]^{2+}$ and is diluted to a definite volume. The absorbance of each of these solutions is measured at 620 nm since the complex shows maximum absorbance at this wavelength. The absorbance values are plotted against concentration to get a calibration curve.

The given test solution is treated with ammonia and diluted to the same volume as above. The absorbance of this solution at 620 nm is measured and its concentration is determined from the calibration curve.

PROCEDURE:

Transfer the given copper sulphate solution (stock solution) into a burette and draw out 2, 4, 6, 8 and 10 cm^3 of the solution into a 25 cm^3 volumetric flasks and add 5 cm^3 of ammonia solution to each of them, shake well and then dilute up to the mark with distilled water. Stopper the flasks and mix the solutions well.

To the test solution (electroplating effluent) given in a 25 cm^3 measuring flask, add 5 cm^3 of ammonia solution, shake well and then dilute up to the mark with distilled water and mix well. Prepare a blank solution by diluting only 5 cm^3 of ammonia solution in a 25 cm^3 measuring flask up to the mark with distilled water and mix well. After 10 minutes, measure the absorbance of the solutions against blank at 620 nm using a photoelectric colorimeter. Tabulate the readings as shown. Draw a calibration curve by plotting absorbance against volume of copper sulphate solution. Using the calibration curve, find out the volume of copper sulphate solution given in test solution and calculate the amount of copper in the given solution.

RESULT: The weight of copper in the given test solution = ... mg

OBSERVATIONS & CALCULATIONS:

Flask no.	Volume of copper sulphate solution (cm^3)	Volume of ammonia solution (cm^3)	Volume of distilled water (cm^3)	Concentration of copper (mg)	Absorbance/ Optical density
1	2	5			
2	4	5			
3	6	5			
4	8	5			
5	10	5			
T	a =	5			

CALCULATIONS:

1000 cm^3 of stock solution contains 8 g of $CuSO_4.\ 5H_2O$

249.54 g of $CuSO_4.5H_2O$ ≡ 63.54 g of Cu

8 g of $CuSO_4.5H_2O$ ≡ 63.54 x 8 / 249.54 = 2.037 g of Cu per 1000 cm^3 of stock solution

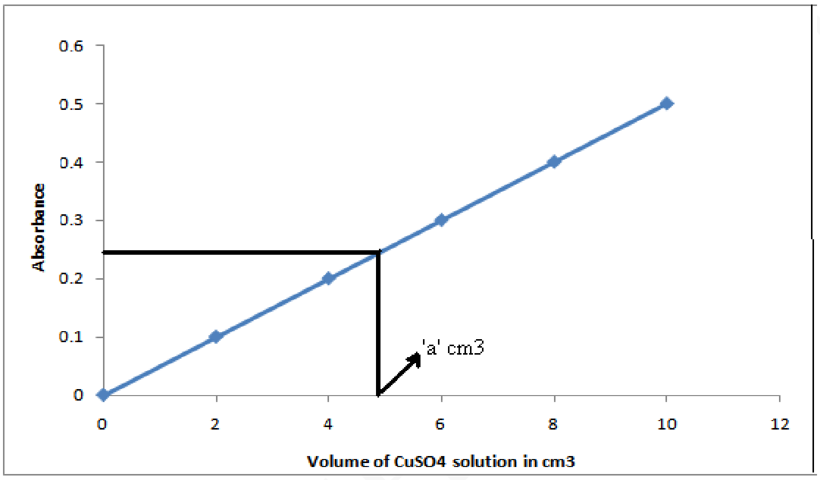
1 cm^3 of $CuSO_4.5H_2O$ ≡ 2.037/1000 = 0.002037 g of Cu = 2.037 mg of Cu

Cu present in 'a' cm^3 of effluent solution = 'a' cm^3 X 2.037 mg

= ………… X 2.037

=………………..mg

Calibration graph:



Course Title: Applied Chemistry for Mechanical Engineering stream

Course Code: BCHEM102/202

Module-5: Structural Materials (8 hr)

Alloys: Introduction, classification, composition, properties and applications of Stainless Steel, Brass and Alnico. Ceramics: Introduction, classification based on chemical composition, properties and applications of perovskites (CaTiO3). Nano chemistry: Introduction, size dependent properties of nanomaterial (surface area, catalytical and thermal), synthesis of nanoparticles by sol-gel, and co-precipitation method. Nanomaterials: Introduction, properties and engineering applications of carbon nanotubes and graphene.

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METALS AND ALLOYS

METAL: A lustrous chemical substance that is good conductor of heat and electricity

True metals are pure elements, while alloys are blends of two or more metals that have been melted together. Alloys have different properties than the metal.

Examples: Aluminium can be altered by alloying it with another soft metal, like copper. Al and Cu metals are very soft and ductile; the resulting aluminium alloy will be much harder and stronger. Gold when combined with copper becomes suitable to make jewels.

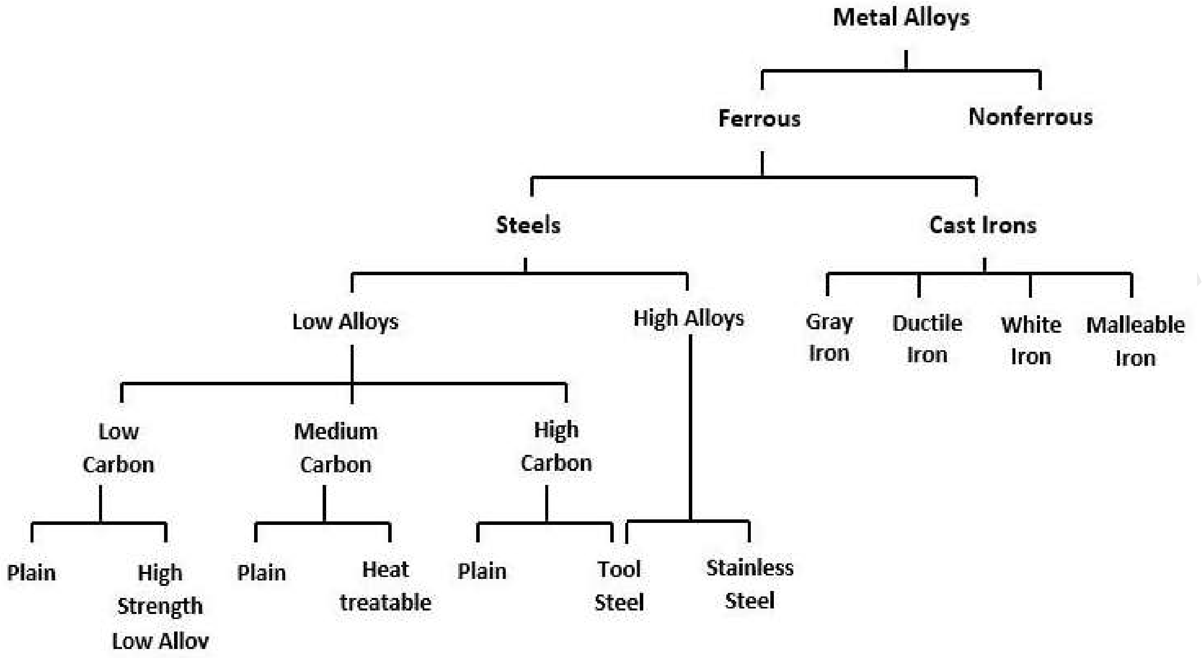
ALLOY:

- Alloys are homogeneous mixture of two or more metals. Alloy is a substance with metallic properties that consist of two or more chemical elements out of which at least one of which is metal. Alloys are prepared by fusing together the different metals in a furnace. The alloys exhibit different properties when compared with the properties of metals in them.
- There are thousands of alloys that have different compositions. The mechanical properties are sensitive to the content of carbon.

Example. Brass, Bronze, Stainless steel, Duralumin, Solder, Amalgum

Alloying: Alloying is a process in which two or more metal elements are melted together in a precise combination to form a specific material, or alloy.

General Classification of Alloys:



Types of alloys:

Alloys are mainly classified into two types.

1. Ferrous Alloys
2. Non-ferrous alloys

Ferrous alloys (Iron based alloys):

Ferrous alloys are alloys in which iron is the principal constituent and alloys of iron with other metals. **Ferrous alloys** are known for their strength and are usually stronger than pure metals. Examples: Stainless steel, chromium steel and vanadium steel. Ferrous based alloys are the most important construction materials due to their high mechanical properties, abundance and reasonable price.

Classification of Ferrous based alloys:

Varying the amount of carbon gives steel different properties. For example, higher carbon content makes hard steel.

Steel is classified based on the alloying element.

Stainless steel: An alloy of iron that contains at least 11% chromium and smaller amounts of nickel and carbon. Iron : 84%, Chromium : 14%, Nickel : 1%, carbon : 1-2%. Applications: Used for making Kitchen utensils, surgical devices, Automobile parts.

Carbon steel: (Based on carbon content)

The carbon steel is generally contested less than 2 % carbon and traces of manganese, sulfur, silicon, phosphorus. The properties and characteristics of carbon steel mainly depend on the carbon content in steel and there is a minor influence on this type of carbon due to the alloying and residual materials. Plain carbon steel is further classified into

- Low carbon steel: Steel containing carbon in percentage ranging from 0.1 – 0.3 %. Used in body panels of vehicles, wire, pipeline, building sheets etc.
- Medium carbon steel: Steel containing carbon in percentage ranging from 0.3 – 0.6 %. Used in Railway wheels, gear, shat, couplings etc.
- High carbon steel: Steel containing carbon in percentage ranging from 0.6 – 1.4 %. Used in cutting holes, drills, cutters etc.

Other important types of steel are:

Alloying steel: Alloy steel is the type of carbon steel in which one or more elements other than carbon have been intentionally added, to produce a desired physical property or characteristic. Generally, molybdenum, manganese, nickel, silicon, boron, chromium, boron and vanadium are added as external elements.

Tool Steels: Tool steels commonly contain tungsten, molybdenum, cobalt and vanadium. Tool steels are commonly used in cutting and drilling equipment due to the higher heat resistance.

STAINLESS STEEL:

Stainless steel is a type of steel that consists of at least 10.5% chromium, less than 1.2% carbon, and other alloying elements. In addition to chromium, stainless steel may contain other alloying elements such as nickel, molybdenum, and copper, which can enhance its strength, ductility, and other properties. Chromium in stainless steel reacts with oxygen in the air to form a thin, transparent chromium oxide layer on the steel surface, which protects the underlying metal from corrosion.

Properties:

- **Corrosion Resistance.** The high chromium content of stainless steel makes it highly resistant to corrosion and rust. When exposed to oxygen, the chromium in stainless steel forms a thin layer of chromium oxide on the surface, which protects the steel from corrosion.
- **Durability:** Stainless steel can withstand high temperatures and heavy loads without deforming or breaking.
- **Low Maintenance.** Stainless steel is easy to clean and maintain and requires no regular maintenance or painting to protect it from the elements.

- **Non-toxic**. Stainless steel is non-toxic and safe for food handling and storage. It does not leach any chemicals or contaminants into the food, making it a hygienic and safe choice for use in kitchen appliances and gadgets.
- **Recyclable.** Stainless steel is fully recyclable and can be melted down and reused without losing its properties.
- **Non-Magnetic.** Some grades of stainless steel are non-magnetic, making them suitable for use in applications where a magnetic field is present.

USES:

Stainless steel is used in a variety of applications for its corrosion resistance, strength, and durability. It is commonly used in the construction of buildings, bridges, and infrastructure, as well as in the manufacture of products such as kitchenware, cutlery, and medical instruments.

Types of stainless steel:

There are different types of stainless steel, classified based on their composition and properties. The most common types include

1. **Austenitic Stainless Steel:** This type of stainless steel contains high levels of chromium and nickel, typically at least 16% chromium and 8% nickel. It has good corrosion resistance and is resistant to stress corrosion cracking. It is used in different sectors depending upon the type of grade as follows:
   - SS 304 / 304 L – Tanks, Storage vessels, Sinks, Cutlery, Architecture.
   - SS 309/ 310 - Furnace, Kiln, Catalytic convertors.
   - SS 200 series – Dishwashers, Washing Machines, Cutlery, Cookware, Food beverage equipment.
2. **Ferritic Stainless Steel:** This type of stainless steel has a lower chromium content, typically less than 16%, and is magnetic. It is strong and has good resistance to high temperatures. It is commonly used in car exhaust systems and other high-temperature applications such as boilers and heat exchangers.
3. **Martensitic Stainless Steel:** This type of stainless steel has a higher carbon content and is difficult to obtain by heat treatment. It has good wear resistance and makes it magnetic is not suitable for use in acidic or humid environments. It is commonly used in cutlery and other applications that require a hard, durable material.

4.Duplex Stainless Steel: This is a combination of ferritic and austenitic stainless steel and has both good corrosion resistance and strength. Duplex stainless steel is commonly used in the oil and gas industry.

5. Precipitation-Hardening Stainless Steel: This type of stainless steel can be hardened through a process called precipitation hardening, which involves aging the material at a high temperature. It is high in chromium and other alloying elements and is widely used in aerospace and military applications.

NON-FERROUS ALLOYS

Alloys which do not contain iron as the main constituent are called as non-ferrous alloys.

Examples: Brass, Alnico, Dutch metal (Cu, Zn), German silver (Cu, Ni, Zn), gun metal (Cu, Sn, Zn) and duralumin (Al, Cu, Mg, Mn).

Brass Alloy:

- Brass is an alloy of copper and zinc with 66 percent copper and 34 percent zinc.
- Brass is strong, easy to cast machinable, tough, conductive, and corrosion resistant. This along with beauty and ease of production make brass one of the most widely used alloys.
- The malleability of brass depends on the zinc content.
- Lead is commonly added to brass at a concentration of around 2% to improve machinability. Also, it may include iron, manganese, aluminum, silicon, or other elements.

Properties:

- Brass often has a bright gold appearance; however, it can also be reddish-gold or silvery-white. A higher percentage of copper yields a rosy tone, while more zinc makes the alloy appear silver.
- Brass has higher malleability than either bronze or zinc.
- Brass has desirable acoustic properties appropriate for use in musical instruments.
- The metal exhibits low friction.
- Brass is a soft metal that may be used in cases when a low chance of sparking is necessary.
- The alloy has a relatively low melting point.
- It's a good conductor of heat.
- Brass resists corrosion, including galvanic corrosion from saltwater.
- Brass is not ferromagnetic. Among other things, this makes it easier to separate from other metals for recycling.

Applications:

- Cartridges, auto-radiator. Musical instruments, coins
- brass became a major material for the manufacture of fine instruments for astronomy, surveying, navigation, and other scientific pursuits.
- Musical instruments, plumbing, decoration, low-friction applications (e.g., valves, locks), tools and fittings used around explosives.

types of brass Alloys with its applications: There are over 40 standard grades of brass with zinc content varying from around 5-40%

Admiralty brass: 70% copper, 29% zinc and 1% tin, Admiralty Brass has good corrosion resistance and is specially used for fresh, salt or brackish water application.

Free Cutting Brass: Used in Nuts, Bolts, Threaded Parts, Terminals, Jets, Taps, Injectors, Valve Bodies.

Gilding Metal (Red Brass): Gilding metal is a form of brass that is made up of 95% copper and 5% zinc. Used in Architectural fascia's, Grillwork, Jewellery, Ornamental Trim, Badges, Door Handles, Marine Hardware

High brass: 65% copper and 35% zinc, has a high tensile strength and is used for springs, rivets, and screws.

Nickel brass: 70% copper, 24.5% zinc, and 5.5% nickel used to make pound coins in the pound sterling currency.

High brass: Copper-zinc alloy containing 20% zinc; ductile brass used for flexible metal hoses and bellows.

Manganese brass: 70% copper, 29% zinc, and 1.3% manganese, used in making golden dollar coins in the United States.

AlNiCo:

AlNiCo magnets are a type of permanent magnet that is made from an alloy of aluminum, nickel, and cobalt. The composition of alnico alloys is typically 8–12% Al, 15–26% Ni, 5–24% Co, up to 6% Cu, up to 1% Ti, and the rest is Fe.

They are characterized by their high magnetic strength, high coercivity, and excellent temperature stability.

Properties:

- **High magnetic strength:** AlNiCo magnets are one of the strongest types of permanent magnets available.
- **High coercivity:** AlNiCo magnets are resistant to demagnetization, even at high temperatures.
- **Excellent temperature stability:** AlNiCo magnets retain their magnetic properties over a wide range of temperatures.
- **Good corrosion resistance:** AlNiCo magnets are resistant to corrosion, even in harsh environments.

Applications:

- **Electric motors:** AlNiCo magnets are used in the stators and rotors of electric motors.
- **Loudspeakers:** AlNiCo magnets are used in the voice coils of loudspeakers.
- **Sensors:** AlNiCo magnets are used in a variety of sensors, such as compasses, proximity sensors, and Hall effect sensors.
- **Aerospace applications:** AlNiCo magnets are used in a variety of aerospace applications, such as gyroscopes, accelerometers, and attitude control systems.

There are three main types of AlNiCo magnets:

- **Alnico 2:** Composition: 8% aluminum, 14% nickel, 22% cobalt, and the remaining 56% is iron. It has a high magnetic strength and a good temperature stability. Alnico 2 magnets are used in a variety of applications, including electric motors, loudspeakers, and sensors.
- **Alnico 5:** Composition: 5% aluminum, 15% nickel, 20% cobalt, and the remaining 60% is iron. They are used in applications where high magnetic strength is required, such as electric guitar pickups and microphones.
- **Alnico 8:** Composition: 3% aluminum, 14% nickel, 21% cobalt, and the remaining 62% is iron. They have highest magnetic strength of the three types, but it is also the most brittle. Used in applications where the highest possible magnetic strength is required, such as aerospace applications.

Ceramics:

- A ceramic is an inorganic, non-metallic solid mainly based on oxide, nitride, boride, or carbide that are shaped and then fixed at high temperatures. Ceramic is hard, brittle, heat-resistant, and corrosion-resistant.

- Traditional ceramics include insulating materials, glass, tiles, pottery, porcelain, bricks refractories, abrasives and enamels, fire clay, fullers earth. Other examples include metal oxides, carbides, borides, nitrides and silicates. Some of their examples are Tungsten carbide, Silicon carbide, Boron oxide, Zirconia, Alumina, Magnesia, Barium titanate, Boron nitride, Earthenware, Porcelain, Silicon nitride, Ferrite.

Properties of ceramics

- Ceramics have high hardness.
- They are brittle and have poor toughness.
- They have a high melting point.
- They have poor electrical and thermal conductivity.
- They have low ductility.
- They have a high modulus of elasticity.
- They have high compression strength.
- They show optical transparency to a variety of wavelengths.

Applications of ceramics

- Silicon carbide and tungsten carbide are technical ceramics that are used in body armor, wear plates for mining, and machine components due to their high abrasion resistance.
- Uranium oxide (UO_2) is a ceramic that is used as a nuclear reactor fuel.
- Zirconia is a ceramic that is used to make ceramic knife blades, gems, fuel cells, and oxygen sensors.
- Barium titanate is a ceramic that is used to make heating elements, capacitors, transducers, and data storage elements.
- Stealite is a ceramic that is used as an electrical insulator.
- Used as cutting tools, refractory materials
- Used as thermal insulator, electrical insulator
- Fire clay is used in refractory (high-temperature) bricks and cement
- Ball clay is a high quality clay prized for its use in ceramics, sanitaryware, and wall and floor tiles.

Classification of ceramics based on chemical composition:

1. **Oxide ceramics:**

Oxide ceramics contains oxide fibers which include a combination of Zirconium dioxide, aluminum trioxide, and titanium dioxide. The oxide fibers help ceramics to withstand oxidation and provide strength and reinforcement.

Following are some types of oxide ceramics:

- **Alumina Ceramics:** Alumina ceramics have high chemical resistance, increased strength, and high-temperature resistance. Alumina ceramics can be manufactured from its powder form then corresponding it and then fired overheat.
- **Beryllium oxide ceramics**: Beryllium oxide ceramics have good thermal conductivity, high insulation, low dielectric constant, low medium loss, and good process adaptability. Beryllium oxide ceramics are used as a component in glass and that glass is used to make X-ray tubes which are used for medical purposes, high-power microwave packaging and high-frequency transistor packaging.
- **Zirconia Ceramics**: Zirconia ceramics are less brittle than other ceramics and have low thermal conductivity, excellent thermal insulation, and very high resistance to crack propagation. They are used for protective coatings, dental services, and making ceramic knives.

2. Non-oxide ceramics:

Non-oxide ceramics offer a great replacement to oxide ceramics because oxide ceramics can't be used in extreme environments and can't bear heavy loads. Non-oxide overcomes all these limitations of oxide ceramics because they have high corrosion resistance, hardness, and oxidation resistance. They even don't degrade till 2400^{o} C temperature. Following are the two most common types of non-oxide ceramics:

- **Silicon nitride ceramics:** Silicon nitride ceramics have low density, high fracture toughness, good flexural strength, and excellent thermal shock resistance. Silicon nitride ceramics are used for rotating bearing balls and rollers, cutting tools, moving engine parts, turbine blades, and weld positioners.
- **Silicon Carbide Ceramics:** Silicon carbide ceramics are much lighter and harder than other ceramics and are resistant to acid. They have a low thermal expansion, high conductivity, and are chemically stable.

3.Composite Ceramics (CMC’s)

Composite ceramics is made up of two or more constituent materials with different physical or chemicals properties. Composite ceramics have **ceramics fibers** embedded in the ceramic and called as ceramic matrix-based composites (CMC’s).

Ex: silicon carbide fibers in a silicon carbide matrix (SiC/SiC) with boron nitride at the interface between them — a material used in cutting-edge gas-turbine jet engines.

Pervoskites:

A perovskite is a material that has the same crystal structure as the mineral calcium titanium oxide. Perovskite materials have emerged as the most promising and efficient low-cost energy materials for various optoelectronic and photonic device applications.

- The discovery of calcium titanate (CaTiO3) in 1839 by a Russian mineralogist Perovski was considered to be the origin of perovskite, and materials with the same type of crystal structure as that of CaTiO3 were known as the perovskite materials (structure).
- The general chemical formula used to describe the perovskite materials is ABX_3, where A and B are cations with A larger than that of B and X is the anion usually oxides or halogens.

Properties of Perovskite materials:

- high-absorption coefficient
- long-range ambipolar charge transport,
- low exciton-binding energy,
- high dielectric constant,
- Ferroelectric properties, etc. have gained a huge interest in these materials for optoelectronic and photovoltaic applications.

Application of perovskite materials:

- Perovskite materials are also widely used in LEDs, photodetectors, nano lasers, and waveguides.
- In perovskite thin film based optoelectronic and photovoltaic devices, the quality of the perovskite film (morphology, grain size, uniformity, coverage, etc.) plays a significant role in determining the device performance.
- Recently increased interest has been grown in the development of the low-dimensional (LD) perovskite materials and in exploring their properties for the photonic and optoelectronic device applications.
- Unique features of the LD perovskite materials mainly their tunable optical and electrical properties due to the quantum-sized effects and their mechanical flexibility are attaining increased attention in the semiconductor materials and optoelectronic devices.

- Different morphologies of LD perovskites developed are perovskite quantum dots (QDs; zero-dimensional). perovskite nanorods or nanowires (NWs; one dimensional), and perovskite nanoplatelets and nanosheets (two dimensional).
- The advantages of reducing the dimensionality of the bulk perovskite materials are prominent on the optoelectronic properties of LD perovskites.
- These properties of LD perovskites have already been used widely in LEDs, photovoltaics, photodetectors, and lasing applications.

Types of perovskite material (NOTE)

- The different classes of perovskite materials, such as chalcogenide perovskite (AMO_3) and halide perovskite (ABX_3) that is again classified as alkali halide and organometal halide, were widely studied. The superior ferroelectric and superconducting properties of oxide-based perovskites were extensively studied for various applications.
- In the case of metal halide perovskites, mainly cesium lead halide ($CsPbX_3$) and methylammonium lead halide ($CH_3NH_3PbX_3$) perovskites are the most popular ones.
- Halide perovskite structure was first observed in $CsPbX_3$ in 1958.
- Owing to the strong excitonic properties of layered perovskite materials (organic–inorganic lead halides), were studied for thin-film light-emitting diodes (LEDs) and field effect transistor (FET) applications.
- Methylammonium halide (MAX_3) perovskites occurred with their use as light-absorbing materials in the photovoltaic device. The high-absorption coefficient, long diffusion length, superior charge-transport properties, low nonradiative emission, and solution process ability make them suitable materials.

NANO MATERIALS

The term nano is originated from the Greek nanos which means 'dwarf'. Nanotechnology is defined as the design, characterisation, production and use of structures between 1 nanometre to 100 nanometers in size. One nanometer (nm) is one billionth, or 10^{-9}, of a meter.

Nanomaterials – Definition:

The ***nanomaterial*** is a material having structural components with at least one dimension in the nanometer scale, that is, 1-100 nm. Nanomaterials have high *Surface area* to volume *ratio.*

The classification of nanomaterials is based on the number of dimensions as:

Zero dimensional (0D): All dimensions are at nanoscale. (nanospheres and nanoclusters)

One-dimensional (1D) : Two dimensions are at nanoscale and the other is outside the nanoscale. (nanofibres, nanotubes, nanorods, and nanowires)

Two-dimensional (2D): One dimension is at nanoscale and the other two are outside the nanoscale. (nanofilms, nanolayers and nanocoatings with nanometre thickness – plate like shape)

Three dimensional (3D): These are the nano materials that are not confined to the nanoscale in any dimension, composed of a multiple arrangement of nano size crystals in different orientations. (dispersions of nanoparticles, bundles of nanowires and nanotubes as well as multi nano layers – poly crystals).

GENERAL APPLICATIONS OF NANO MATERIALS:

- Carbon nanotubes are used to make bicycle frames and tennis rackets lighter and stronger.
- Nano-sized particles of titanium dioxide and zinc oxide are used in many sunscreens, to block UV radiation more effectively without making the skin look pasty white.
- Nano phase ceramics are of interest because they are ductile at elevated temperature as compared to the coarse-grained ceramics.
- Nano structured semiconductors are known to show various non-linear optical properties.
- Nano sized metallic powders have been used to produce gas tight materials dense parts and porous coatings. Magnetic Nano composites have been used for mechanical Materials in the nanometre scale exhibit physical properties distinctively
- Force transfer, for high density information storage and magnetic refrigeration.
- Nanostructured metal clusters and colloids have a special impact in catalytic applications.
- Nanostructured metal-oxide (MnO_2) finds application for rechargeable batteries for cars or consumer goods.Nanotech batteries last longer and are lighter and more powerful than their current counterparts.
- Nano materials are used in semiconductors as nano capacitors
- They are used in targeted drug delivery, in agriculture, in fuel cells, in chemical and biosensors, in waste water management etc.

Properties of nanoparticles (Size Dependent):

The Nano materials have different properties due their extremely small size. Fundamental electronic, magnetic, optical, chemical and biological properties are also different at nano level.

The properties of nano materials are size dependent due to

1. **The surface area to volume ratio** is relatively larger than the bulk materials of the same mass. The relative concentration of surface atoms is thus greater for nanomaterial's compared to their bulk form, which typically lowers their melting point and increases their reactivity.

- The energy levels (quantum confinement) also changes at nano size that changes the optical, electronic, magnetic, chemical and biological properties of the material. Quantum confinement effects change the electronic structure where nanomaterial's start to have discrete electronic states, while the bulk material has essentially continuous electronic states. For example, this will change the band structure of the nanomaterial and consequently modulate its optical, electrical and thermal properties.

  Due to expanded surface more and more atoms are required to fill the band and hence band gap widens. So a material in bulk which was a metal may behave like an insulator or even as semiconductor.

  The property change may be due to the reason Electromagnetic forces begin to dominate and gravitational forces become negligible. Also due to the electron movement effect.

2. **Catalytic property change:**

- The catalytic property of materials depends on particle size. If the size of the particles reduces from bulk to Nano scale, surface to volume increases drastically, that leads to very high catalytic activity of same material.
- Example: Gold acts as effective catalyst at Nano scale but inert at bulk scale.
- Three factors namely Very small size, very high surface-to-volume ratio, and increasing the number of atoms on the surface are the most important reasons for the emergence of catalytic properties in nanomaterial's.
- Basically, when particles become very small (nanoscale), due to the very high curvature they find, they have many atoms on their surface, which are very weakly bonded to the lattice atoms of the lattice. Therefore, these particles have very high surface energy and are highly active, and are prone to perform many chemical reactions. Determining reason for the emergence of catalytic properties in nanomaterials is their very high The higher the surface-to volume ratio, the higher the catalytic properties in nanomaterial's due to the increase in surface energy.

- Example: Gold is inert at bulk scale but acts as catalyst in nano scale

3. Thermal properties (Melting point)

- Melting point is defined as the temperature at which the atoms, ions or molecules in a substance have enough energy to overcome the intermolecular forces that hold them in a fixed position in a solid.
- Nanomaterials' thermal features rely on material's particle size and such features include the thermal conductivity, melting point and glass-transition temperature.
- As the size of the material decreases to Nano scale, their melting point decreases. Because surface atoms are in contact with only fewer atoms in nanomaterial's and require lesser energy to overcome inter-molecular forces. However, in nanomaterials the melting temperature is size dependent and it decreases with the decrease particle size diameters.

Few examples which show the change in properties with size in nanomaterials:

- Opaque substance may become transparent (Ex: Cu is opaque in bulk state and transparent in nano scale)
- Inert material shows catalytic activity (Ex: Gold is inert at bulk scale but acts as catalyst in nano scale)
- Stable material become combustible (Ex: Al is stable in bulk state but combustible in nano scale)
- The non-magnetic materials becomes magnetic in nano scale (Pd and Pt are non-magnetic in bulk scale but becomes magnetic in nano scale)
- Colour of the material also changes with the size (Gold is known to be a shiny, yellow noble metal which is non-magnetic, however gold nano particle of 10nm size will absorb green light and thus appear as red.
- Mechanical properties are also size dependent including hardness, scratch resistance,
- Thermal properties also changes when size is reduced (Silicon nano wires have much smaller thermal conductivities compared to bulk silicon. Carbon nano tubes are expected to have extraordinary high thermal conductivity)

Preparation Techniques:

Bottom-up and top-down methods of synthesis

In the **bottom-up approach**, molecular components arrange themselves into more complex assemblies' atom-by-atom, molecule-by-molecule, cluster-by cluster from the bottom. Bottom-up approaches; arrange molecular components themselves into some useful conformation using the concept of molecular self-assembly. Synthesis of nanoparticles by colloid dispersions is an example of the bottom-up approach.

In the **top-down approach**, nanoscale devices are created by using larger, externally-controlled devices to direct their assembly. The top-down approach often uses the traditional workshop or microfabrication methods in which externally-controlled tools are used to cut, mill and shape materials into the desired shape and order. Attrition and milling for making nanoparticles are typical top-down process

- Bottom up approach, plays a very important role in preparing nanomaterials having very small size where the top-down process cannot deal with the very tiny objects.
- The bottom-up approach generally produces nanostructures with less defects and homogeneous composition as compared to the nanostructures produced by the top-down approach.
- In spite of the defects, the top-down approach plays an important role in the synthesis and fabrication of nanomaterial's. The present state of nanoscience can be viewed as an amalgamation of bottom-up chemistry and top-down engineering techniques.

Synthesis of Nanomaterial's by Sol-Gel method.

Principle: Conversion of homogeneous solution into a sol by treatment with suitable reagent. Here the hydrolysis of cross linked solid results in the formation of **sol**. The sols are linked to form a three dimensional network called a **gel**. Controlled evaporation of liquid phase results in dense porous solid called the xerogel. When super critical extraction is used, highly porous light weight solids called aerogels are produced. Calcination of the gel produces the metal oxide nano particles.

Sol-Gel process consists of the following steps:

1-Step: Formation of Sol: It involves formation of different stable solutions of alkoxides or solvated metal precursors (sol)

$$\text{M-O-R} + H_2O \rightarrow \text{M-OH} + \text{R-OH (Hydrolysis)}$$

2-Step: Formation of Sol to Gel: In the first stage, metal alkoxide (Precursors) are hydrolysed in water-alcohol mixed solvent. This step involves the transformation of molecular precursor into a highly cross linked solid. (Gel)

M-O-R + M-OH → M-O-M + R-OH (condensation)

Where M= Si, Ti, Al, Zr etc.

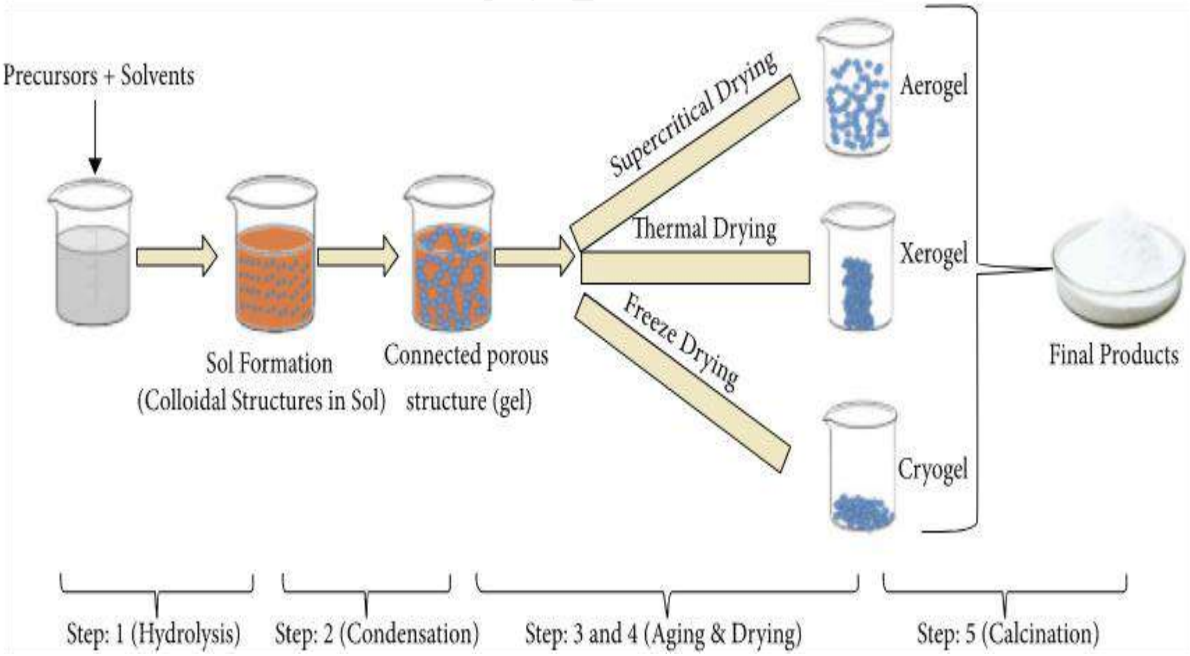
Step 3: Aging of gel: During which the polycondensation of hydrolysed species with each other or with unhydrolysed species continue and gel transforms into a solid mass. It involves contraction of gel network and expulsion of solvent molecules from gel pores.

Step 4: Drying and dehydration: Drying of the gel, when water and other volatile impurities are removed from gel network. Dehydration involves removal of surface bound M-OH groups

6-Step: Calcination: Densification and decomposition of the gel at high temperature > 800°C results in the formation of nano particles. Gel network is collapsed, and remaining organic species are volatized.

Advantages:

- The main advantage is that the mono sized particles can be obtained.
- The nano particles are prepared at comparatively low temperature.
- Simple and inexpensive equipment
- Ease of compositional modifications

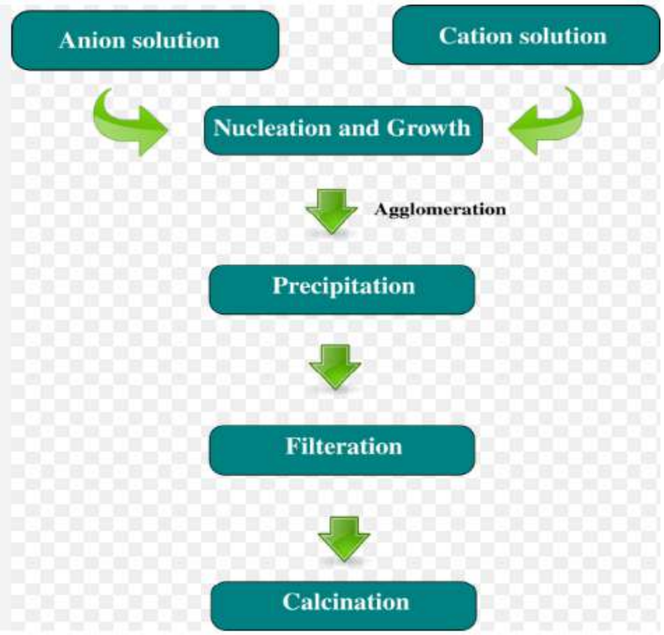


Note: Sol - It is a colloidal suspension of very small solid particles in liquid medium. Ex: Ink and Blood.

Gel - It is a colloidal suspension of very small liquid particles in solid medium Ex: agar, gelatin, jelly and tooth paste.

Synthesis of Nanomaterial’s by Precipitation method:

The Process is mainly used to prepare metal oxide nano particles. Co precipitation technique **involves the precipitation of metal in the form of hydroxide from a salt precursor with the help of a base in a solvent**. The controlled release of anions and cations assists to regulate the nucleation and particle growth kinetics, which helps to synthesize monodispersed nanoparticles



- In this technique, an inorganic metal salt (such as chloride, nitrate, acetate or oxy chloride) is dissolved in water.
- Metal cations in water exist in the form of metal hydrate species such as $[Al(H_2O)]^{3+}$, $[Fe(H_2O)_6]^{3+}$.
- The species are hydrolysed by adding a base solution, such as NaOH or NH_4OH.
- On increasing the concentration of OH^- ions, the hydrolysed species condense with each other to form either metal hydroxide or hydrous metal oxide precipitate.
- The precipitate is then washed, filtered and dried.
- The dried powder on subsequent calcination to obtain the final crystalline metal oxide nano particles.

Advantages:

- The process is relatively economical, simple.
- Wide range of single and multi-components of oxide nano powders can be synthesized.
- Use of more harmful organic solvents are minimized.

Disadvantages:

- Inability to control the size of the particles
- Chances of aggregation of nano particles.

NANO MATERIALS:

Nanostructured materials may occur in several different geometric configurations including wires, tubes, rods, crystals, powder, pores, etc. They possess unique properties and are being developed for specific applications. Some of these interesting and emerging trends in nanostructures are described below.

Carbon Nano Tubes (CNT):

Carbon nanotubes (CNTs) are allotropes of carbon with a cylindrical nanostructure, composed of carbon atoms. CNT is made up of enrolled cylindrical graphitic sheets (named graphene) wrapped up into a seamless cylinder with a nanometer-sized diameter. Graphene sheets are rolled at specific and discrete angles to form carbon nanotubes, and the combination of the rolling angle and radius decides the nanotube properties.

Nanotubes are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs).

Single-walled carbon nanotube (SWCNT): It is obtained by rolling a sheet of graphite into a cylinder. Typical diameters of SWCNTs are in the range of 0.7–1.4 nm and their length can be several micrometres.

Multi-walled carbon nanotubes (MWCNT):

(MWCNTs) can be regarded as a coaxial assembly of SWCNT's. MWCNT's has their diameters in the range of 5–50 nm.

Carbon nanotubes have high thermal conductivity, high electrical conductivity, high mechanical strength, high thermal stability and enhanced chemical reactivity and unique mechanical properties.

Properties:

- **Electrical Conductivity :** Carbon nanotubes (CNTs) are electrically and thermally conductive and have a high mechanical strength.

- **Strength And Elasticity :** In terms of tensile strength and elastic modulus, carbon nanotubes are the strongest and stiffest materials yet found.
- **Thermal Conductivity And Expansion :**The carbon bond's rigidity aids in the transmission of vibrations throughout the nanotube, resulting in excellent heat conductivity. carbon nanotubes have an extremely high melting point.
- **Electron Emission –** Because each carbon atom is connected to three other carbon atoms by strong covalent bonds, carbon nanotubes have an extremely high melting point. This also means that each carbon atom has an extra electron, forming a sea of delocalized electrons within the tube, allowing nanotubes to conduct electricity.

Applications:

- In Field emitter/emission, energy storage
- Carbon nanotubes are utilized in energy storage, device modelling, automotive parts, boat hulls, sporting goods, water filters, thin-film electronics, coatings, actuators, and electromagnetic shields.
- In CNT based RAMs, transistors, fibers, ceramics
- Because of their large surface area, CNTs have been successfully used in pharmacy and medicine to adsorb or conjugate a wide range of medicinal and diagnostic substances.

GRAPHENE:

- Graphene is an allotrope of carbon that exists as a two-dimensional planar sheet. It consists of single layer of carbon atoms arranged in hexagonal lattice.
- Each carbon atom in graphene is covalently bonded (sp^2 hybridized) to three other carbon atoms in a hexagonal array, leaving one free electron per each carbon atom.
- This free electron exists in a p-orbital that sits above the plane of the material. Each hexagon in the graphene sheet exhibits two pi-electrons, which are delocalized, allowing for an efficient conduction of electricity.
- It has high electrical conductivity and acts as semi metal with a small overlap between valence and conduction band.

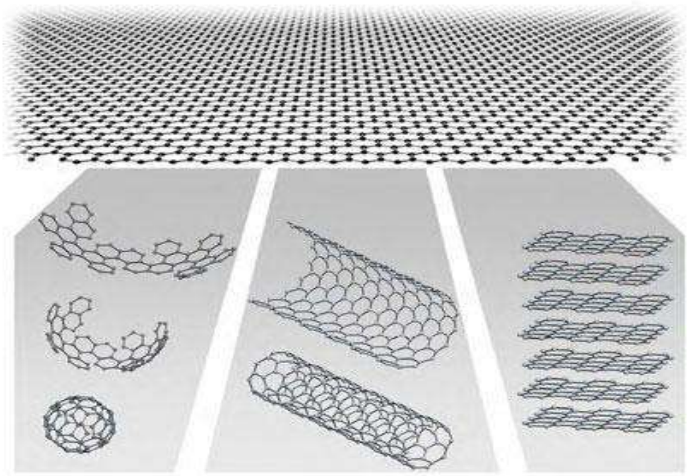
Properties:

- Grapheme has excellent electronic conductivity, because its conduction and valence band meet at the Dirac point.
- It has unique optical property; it shows high opacity for an atomic monolayer in vacuum.
- The holes in the structure gives rise to high thermal conductivity.. it finds application in thermal management applications.

- It melts at nearly 4125 K before transforming into gas.
- Grapheme is the strongest material ever tested, has an intrinsic tensile strength of 130.5GPa

Applications:

- Graphene is a flexible conductor that finds applications in solar cells, Light emitting Diodes, touch screens panels, smart windows etc.
- Used in fundamental electronic devices such as capacitors, field effect transistors.
- Grapheme super capacitors act as energy storage alternatives to traditional batteries.
- Functionalized graphenes are used as biological and chemical sensors.
- It finds application in the field of catalysis because of its high surface area and electronic properties.



Graphene is a 2D building material for carbon materials of all other dimensionalities. It can be wrapped up into 0D buckyballs, rolled into 1D nanotube or stacked into 3D graphite.

Important questions:

1.What are alloys? Explain about ferrous based alloys.

2. Summarize the composition, properties and applications of stainless steel.

3. Mention the composition, properties and applications of brass and Alnico.

4. Explain the Properties and applications of the following: a) Ceramics b) Perovskites

5. What are nanomaterials? Out line the synthesis of nanoparticles by sol-gel method.

6. Explain the precipitation method for the preparation of nanoparticles.

7. Discuss about the size dependent, Catalytic and Thermal property change of nanoparticles.

8. Explain in detail about the engineering applications and properties of carbon nanotubes and Graphene.

9. What are ceramics? Explain the classification of ceramics based on the composition.