

A textbook of

Engineering Chemistry

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For the Students of FY B.Tech

Circuit Branches

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PREFACE

Dear Readers,

It is with great pleasure and enthusiasm that we present to you the book "**Engineering Chemistry**" tailored specifically for first-year engineering students. This endeavor stems from our deep-seated commitment to providing a comprehensive and accessible resource that meets the diverse academic needs of budding engineers.

This book is meticulously crafted to cater to the requirements of first-year degree courses in engineering institutes. With six meticulously curated chapters, it covers essential topics that form the cornerstone of the engineering curriculum. From the fundamental principles of chemical bonding to the application of chemistry in engineering materials, each chapter is designed to provide a robust understanding of key concepts.

We are immensely grateful to Hon. Management, Director & HOD of Sanjivani College of Engineering for their unwavering support throughout the process of writing this book. Their encouragement and understanding sustained us during the long hours of writing and revising.



Dedicated to
Honourable
Late Shri. Shankarraoji Kolhe Saheb,
(Former Minister, Government of Maharashtra,
Founder, Sanjivani Group of Institutes.)
Source of our inspiration





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Water Processing And Environment Sustainability

Water parameters: Introduction, TDS, Dissolved oxygen (DO), COD, pH, Hardness of water, types & units. Determination of hardness by EDTA method, Numerical on hardness. Boiler troubles: Scale, Sludge, Priming, Foaming, Caustic embrittlement, Water treatment: Ion exchange, Ultra filtration, Zeolite Process.

Sustainability: Introduction, Importance, Sustainability in different Industries related to Environmental Parameters such as Air, Water, Land and Noise etc

Water is a common substance found throughout nature, constituting a significant portion of the Earth's crust at approximately 75%. Its unique property of existing as a gas, liquid, or solid under natural conditions on Earth makes it stand out. This versatility is crucial for the planet's various processes.

Our bodies rely on water both internally and externally, emphasizing its vital role in maintaining our health. However, despite its abundance, over 96% of water is locked in oceans and is too salty for most practical uses, restricting its availability for daily life, industries, and agriculture.

Some water sources contain dissolved salts, such as calcium and magnesium, giving rise to what is known as "hard water." This hardness can affect everyday tasks, as these salts react with soap, diminishing its effectiveness. Additionally, certain impurities like calcium carbonate and silicate in water can pose challenges in industrial settings, reducing heat transfer efficiency.

Beyond hardness, water may contain varying amounts of sodium salts, silica, alumina, iron, or manganese. These additional elements contribute to the overall composition of water and can impact its suitability for different purposes.

Industrially, water plays a crucial role, finding applications in sectors like textiles, paper production, sugar refinement, and pharmaceuticals. It also serves as a coolant in power and chemical plants while functioning as a solvent in various processes.

Despite its abundance, the challenges lie in obtaining usable water due to the high salt content in oceans. Moreover, impurities present in water can create complications in industrial processes and affect the efficiency of heat exchange mechanisms. Addressing these challenges is essential for ensuring the sustainable and effective use of this precious resource.

Properties of Water:

- Boiling and Freezing Points:** Water boils at 100°C and freezes at 0°C.
- Colorless and Odorless:** Water has no color or smell.
- Density:** At room temperature, water has a density of 1 gm/cm³.
- Viscosity:** Water has high viscosity, meaning it flows slowly.

5. **Heat of Fusion:** Water has a high heat of fusion, which is the energy needed for it to change from a solid to a liquid.
6. **Bond Angle:** The bond angle in water is 104.5 degrees.

Impurities in Water:

Natural water has different impurities that must be removed for safe use at home or in industries.

1. Biological Impurities:

Water may contain bacteria, protozoans, viruses, etc.

These can cause diseases like cholera, typhoid, dysentery, polio, cold, and hepatitis.

2. Suspended Impurities:

Water might have suspended impurities like leaves, branches, twigs, and dead waste.

Inorganic impurities such as sediments, clay, and sand could also be present.

3. Colloidal Impurities:

Inorganic impurities like iron and aluminum hydroxides may be in the water.

Organic impurities such as globules, animal matter, and humic acid could also be present.

4. Dissolved Impurities:

These include dissolved gases and inorganic salts.

Dissolved O₂, NO₂, and CO₂ may cause corrosion in boilers.

Inorganic salts like bicarbonates, chlorides, and sulphates of Ca and Mg can make water hard.

Total Dissolved Solids (TDS):

Definition:

Total Dissolved Solids (TDS) refers to the amount of particles dissolved in water, which may include all suspended solids, whether or not they pass through a filter. Dissolved solids can originate from various sources, such as organic materials like leaves, silt, industrial waste, and sewage. Inorganic materials from rocks and the air, containing substances like calcium bicarbonate, nitrogen, iron, sulfur, and other minerals, can also contribute to TDS. Rainwater is nearly pure, with TDS levels usually below 10mg/L.

Levels of Total Dissolved Solids:

1. Drinking Water: Ideal TDS for drinking water ranges from 25-250mg/lit.
Drinking water should not exceed 500mg/lit TDS.
2. Distilled water typically has a TDS reading between 0.5-1.5mg/lit.
River and Groundwater:TDS levels vary from 100-20,000mg/l in rivers.
3. Groundwater may have even higher TDS.
4. Seawater:Seawater has a high TDS level of 35,000mg/l.
Lakes & Streams:TDS in lakes and streams generally falls within the range of 50- 250mg/lit.

Dissolved oxygen

Dissolved oxygen in water is the oxygen that aquatic plants and animals can use. We measure it as dissolved oxygen (DO), expressed in parts per million (ppm), indicating the number of oxygen molecules (O₂) in a million total molecules in a sample. This is also *defined as the number of moles of molecular oxygen (O₂) dissolved in a liter of water at a specific temperature, measured as mg O₂/l.*

Temperature plays a crucial role in the ability of oxygen to dissolve, with varying solubilities at different temperatures. Low dissolved oxygen (DO) levels can result from fertilizer and manure runoff from streets, lawns, and farms.

Chemical Oxygen Demand (COD)

COD is a test that measures how much organic stuff is in water. It is in milligrams per liter (mg/l), which indicates how much oxygen is used per liter of water.

In wastewater, COD shows us the oxygen needed to clean it up. It's like saying how much oxygen is used to remove impurities in 1000 ml of water, using strong stuff like acidified $K_2Cr_2O_7$. COD gives us a total measure of the oxygen needed to clean up all the dirty stuff in sewage water.

pH

pH is a measure of the acidity or basicity of a solution. It is a scale ranging from 0 to 14, where values below 7 indicate acidity, 7 is neutral, and values above 7 indicate alkalinity or basicity. The pH level is determined by the concentration of hydrogen ions in the solution.

Hardness of Water

When soap was discovered, it was noticed that water from different places behaved differently with it. Rainwater made a soft and creamy lather, but water from wells left a sticky, curd-like residue, making it hard to clean. Water has sodium and potassium salts, which are okay. But, if it has calcium and magnesium salts, they need to be removed for industrial use. Water that doesn't make good lather with soap is called hard water. If it forms good lather, it's called soft water. Hardness is because of dissolved salts of heavy metals like Ca^{2+} , Mg^{2+} , Fe^{2+} , Al^{3+} , Mn^{2+} in the water.

Causes of Water Hardness

1. Dissolution of Minerals: When rainwater goes through hard rocks, it picks up salts. Sodium, potassium, and lithium salts don't make water hard.

2. Action of Dissolved CO₂:

Rainwater with dissolved CO₂ meets rocks like CaCO₃ and MgCO₃.

It forms soluble salts: Ca(HCO₃)₂ and Mg(HCO₃)₂.

Example: CaCO₃ + H₂O + CO₂ → Ca(HCO₃)₂ (soluble)

3. Dissolution of O₂:

O₂ in water reacts with minerals like FeS₂, forming hardness-causing salt.

Example: FeS₂ + 2H₂O + 7O₂ → FeSO₄ + 2H₂SO₄

Types of Water Hardness

1. Temporary or Carbonate Hardness:

This hardness is from carbonates and bicarbonates.

Boiling can remove it:



2. Permanent or Non-Carbonate Hardness

Caused by chlorides, sulphates, and nitrates of Ca and Mg.

- **Boiling doesn't work; needs specific methods like:**

1. Lime soda method

2. Soda Ash method
3. Sodium Aluminate Addition
4. Sodium phosphate addition
5. Zeolite or permutit or base exchange method
6. Demineralization or De-ionization or Ion exchange method

Water Hardness Categories

1. **Very Soft Water (0-25 ppm):** Extremely low hardness.
2. **Soft Water (25-50 ppm CaCO₃ equivalent):** Low hardness, good for various uses.
3. **Moderately Soft Water (50-100 ppm CaCO₃ equivalent):** A bit more hardness than soft water.
4. **Slightly Hard Water (100-150 ppm CaCO₃ equivalent):** A small amount of hardness.
5. **Moderately Hard Water (150-200 ppm CaCO₃ equivalent):** More hardness than slightly hard water.
6. **Hard Water (200-250 ppm CaCO₃ equivalent):** Water with a considerable level of hardness.
7. **Very Hard Water (Above 250 ppm CaCO₃ equivalent):** Water with a high level of hardness.

Water Hardness Limits for Various Uses :

1. High-Pressure Boiler, Pharmaceutical Industry: Suitable range: 0 to 10 ppm CaCO₃ equivalent.
 2. Drinking Purpose: Recommended range: 150-200 ppm CaCO₃ equivalent.
Sugar Industry, Dye Industry, Paper Industry, Textile Mill: Acceptable range: 0 to 50 ppm CaCO₃ equivalent.
 3. Bakery and Food Processing: Recommended range: 150-200 ppm CaCO₃ equivalent.
 4. The hardness of water is measured using CaCO₃ equivalent hardness because CaCO₃ (calcium carbonate) has a molecular weight of 100, and it doesn't dissolve in water.
- **CaCO₃ eq. hardness =**
Mass of hardness producing substance × (molecular weight of CaCO₃)/(molecular weight of hardness producing Substance)
 - **CaCO₃ eq. hardness =**
Mass of hardness producing substance × (Equivalent weight of CaCO₃)/(equivalent weight of hardness producing Substance)

Units of Hardness:

Various units are used to express the hardness of water:

1. **Parts per Million (ppm):**
It is the number of equivalent parts of CaCO₃ present per million (10^6) parts by weight of water.
2. **Milligrams per Liter (mg/lit):**
It is the number of milligrams of CaCO₃ dissolved in 1 liter of water.
1 mg/lit = 1 mg of CaCO₃ per 10^6 mg of water.
1 mg/lit = 1 part of CaCO₃ per 10^6 parts of water.
1 mg/lit = 1 ppm.
3. **Degree Clarke (°Cl):**
It is the number of equivalent parts of CaCO₃ present per 70,000 parts by weight of water.

4. Degree French (${}^0\text{Fr}$):

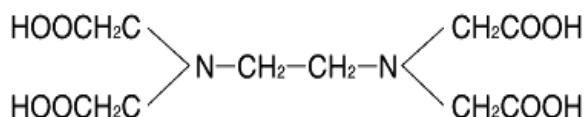
It is the number of equivalent parts of CaCO_3 present per 10^5 parts by weight of water.

$$1 \text{ ppm} = 1 \text{ mg/lit} = 0.07 {}^0\text{Cl} = 0.1 {}^0\text{Fr}.$$

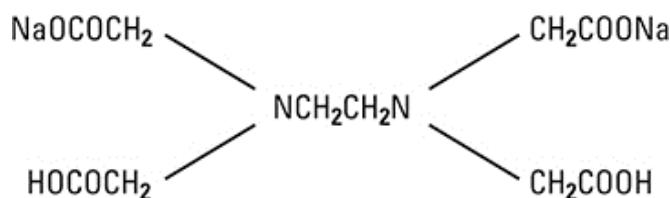
Determination of Water Hardness:

The most common method for determining the total hardness of water is complexometric titration using ethylenediaminetetraacetic acid (EDTA) as a complexing agent. The disodium salt of EDTA is used with Eriochrome Black-T as an indicator.

- **Structure of EDTA:**



- **Structure of Di sodium salt of EDTA**



In this titration, a buffer solution $[\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}]$ with a pH of 10 is utilized. When Eriochrome Black-T is added to the water sample, it reacts with metal ions to form unstable wine-red colored complexes.



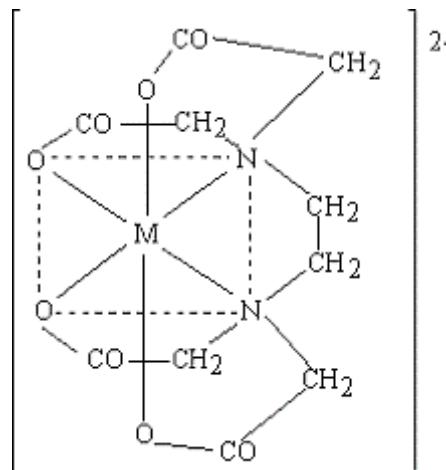
Titrating these unstable complexes with a standard EDTA solution results in the formation of M-EDTA complex, which is more stable than M-EBT complex.



[unstable wine red colored complex] [colorless complex] [blue dye]

A sharp color change from wine-red to blue marks the endpoint. The volume of EDTA required to reach this endpoint allows the calculation of water hardness.

- **The structure of M-EDTA complex :**



- **Experimental Procedure for determination of total hardness:**
 1. Pipette 50 ml of the water sample into a conical flask.
 2. Fill the burette with EDTA solution.
 3. Add about 15 ml of buffer solution ($\text{pH} = 10$) and 4-5 drops of EBT indicator solution.
 4. Titrate the pink-red/wine-red colored solution against EDTA until the color changes to sky blue at the endpoint. Note the reading as 'y' ml.

- **Formula used,**

Hardness of water = $y/v \times Z \times 100 \times 1000$ ppm CaCO_3 eq. hardness

y = volume of EDTA (Burette reading)

v = vol. of water sample

Z = Molarity of disodium salt of EDTA solution

Determination of Alkalinity :

Water in lakes, rivers, and underground is usually a bit basic because of alkaline substances. The main ions responsible for this are OH^- , CO_3^{2-} , and HCO_3^- . Hydroxides and carbonates are stronger bases than bicarbonates.

Alkalinity is the measure of these ions in water.

OH^- : $\text{Ca}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$ and NH_4OH .

CO_3^{2-} : MgCO_3 , Na_2CO_3 , CaCO_3

HCO_3^{2-} : $\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$, NaHCO_3 etc

To find alkalinity volumetric analysis method is used. Here the water sample is titrated with strong acids using indicators like phenolphthalein and methyl orange.

When water sample is titrated with standard strong acid (e.g. HCl), hydroxide ions present in water will be neutralized and carbonate ions (CO_3^{2-}) will be half neutralized to bicarbonate ions (HCO_3^{2-}).

First, OH^- and CO_3^{2-} react with the acid until the phenolphthalein endpoint, shown by a color change to pink. This is called phenolphthalein alkalinity.

Then, only HCO_3^- is left. We titrate again with acid until the methyl orange endpoint, when the color changes to orange. This is methyl orange alkalinity.

- **Experimental Procedure:**

1. Fill a burette with standard acid.
2. Take a fixed volume of water in a flask.
3. Add phenolphthalein; if the pH is over 8, it turns pink.
4. Titrate with acid until pink disappears. Record the volume (V_1).
5. Add methyl orange; the water turns yellow.
6. Titrate again until the water turns orange. Record the volume (V_2).

Phenolphthalein alkalinity = $(V_1 \times Z \times 50 \times 1000) / V$ ppm of CaCO_3 equivalent

Methyl orange alkalinity = $(V_2 \times Z \times 50 \times 1000) / V$ ppm of CaCO_3 equivalent

- **Where:**

V_1 = Phenolphthalein endpoint volume

V_2 = Methyl orange endpoint volume

V = Volume of water in flask

Z = Normality of the acid

Once P and M are found, we can calculate the amounts of individual ions using a table.

Alkalinity (ppm)	$[\text{OH}^-]$ ppm	CO_3^{2-} ppm	HCO_3^- ppm
$P = O$	0	0	M
$P = M$	M	0	0
$P = \frac{1}{2} M$	0	2p	0
$P > \frac{1}{2} M$	$2P - M$	$2(M-P)$	0
$P < \frac{1}{2} M$	0	2P	$M-2P$

Disadvantages of Hard Water in Boilers:

Industries use water for various purposes, and one crucial application is generating steam in boilers. However, if the water has dissolved salts like carbonates, sulphates, bicarbonates, chlorides, and nitrates of calcium and magnesium, it can cause problems in boilers. For smooth operation and to avoid issues like:

- Boiler Corrosion:** Hard water with certain salts can lead to corrosion, damaging the boiler's metal surfaces.
- Caustic Embrittlement:** Some salts in hard water can make the boiler material brittle, risking fractures.
- Priming and Foaming:** Hard water contributes to priming (carryover of water with steam) and foaming, disrupting normal boiler operation.
- Scale and Sludge Formation:** Hard water causes the build-up of scale (hard deposit) and sludge (semi-solid slurry), reducing boiler efficiency.
- Using softened water and regular maintenance are crucial to prevent these problems and ensure boilers work efficiently and last longer.

Scale and Sludge Formation:

During continuous water evaporation in the boiler, dissolved salts become concentrated. When their concentration reaches saturation, they precipitate on the inner boiler wall. If the precipitate is loose and slimy, it's called sludge. If it forms a hard coating, it's known as scale, with types such as carbonates, sulphates, silicates, phosphates, and oxides. The most problematic scales arise from sulphates and silicates of calcium due to being non-porous, hard, adherent, and poor heat conductors.

- Difference between scales and sludge.**

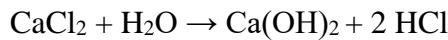
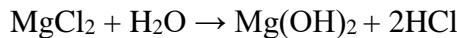
Sr. No.	Scale	Sr. No.	Sludge
1	Hard, adherent coating on the inner boiler wall	1	Loose and slimy.
2	Bad conductor of heat.	2	Poor conductor of heat
3	Formed through contact with water surface.	3.	Formed at cooler positions in the boiler.
4.	Formed by substances like CaCl_2 , MgCl_2 , MgSO_4 , & MgCO_3 .	4.	Formed by substances like CaSO_4 , Mg(OH)_2 , CaCO_3 & CaSiO_3

- **Formation of Scales and Sludges:**

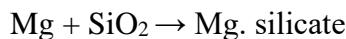
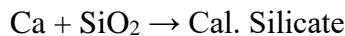
1. **Chemical Decomposition of Salts:**



2. **Hydrolysis of Magnesium and Calcium Salts:**



3. **Presence of Silica:**



- **Disadvantages of Scale Formation:**

1. **Wastage of Fuel:** Scales require more heat, leading to increased fuel consumption.

2. **Lowering Boiler Safety:** Overheating due to scale formation weakens the boiler material.

3. **Danger of Explosion:** Uneven expansion of scale and boiler material can cause sudden steam generation, leading to boiler explosion.

4. **Shortening Boiler Life:** Acid liberation shortens the boiler lifespan.

- **Preventive Actions Against Scale Formation:**

1. Remove hardness-causing impurities from water.

2. Make boiler feed water silica-free.

3. Regularly remove water saturated with impurities (blown down operation).

4. Physically remove scales using tools like hammers, chisels, scrapers, knives, or blades.

Priming & Foaming:

Priming:

When steam is produced rapidly in boilers, some liquid water droplets are carried along with the steam, creating wet steam in a process known as priming.

- **Causes of Priming:**

1. Presence of considerable quantities of dissolved solids.

2. Sudden boiling.

3. Faulty design of the boiler.

- **Prevention of Priming:**

1. Control rapid changes in steaming velocities.

2. Maintain low water levels in boilers.

3. Ensure efficient softening.

4. Regularly blow off sludge and scales.

Foaming:

Foaming is the persistent formation of small bubbles or foam at the water surface in boilers.

- **Causes of Foaming:**

Foaming is caused by the presence of oil and alkalies in boiler feed water. Alkalies react with oil to form soaps, reducing water surface tension and increasing foaming.

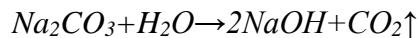
- **Prevention of Foaming:**
 1. Addition of antifoaming agents counteracts the reduction in surface tension (e.g., castor oil).
 2. Removal of foaming agents like oil impurities by adding compounds like sodium aluminate.
- **Disadvantages of Priming & Foaming:**
 1. Wet steam produced carries dissolved salts, depositing them on turbine blades and heaters, reducing efficiency.
 2. Dissolved salts from wet steam may enter other machinery parts, decreasing machinery life.
 3. Difficulty in accurately judging the actual height of the water column, making boiler maintenance challenging.

Caustic Embrittlement:

Deterioration of Boiler Material by Caustic Soda

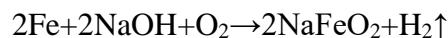
Caustic embrittlement is a type of boiler corrosion that occurs when highly alkaline water, treated with Na_2CO_3 (sodium carbonate) for softening, is used in the boiler. The sodium carbonate undergoes hydrolysis to form NaOH (caustic soda), making the water alkaline.

- **Hydrolysis Reaction:**



The alkaline water penetrates cracks on the boiler walls through capillary action and contacts the red-hot boiler plate. As water evaporates, the concentration of NaOH increases, leading to the formation of sodium ferrate (NaFeO_2) at grain boundaries. This causes embrittlement, especially in stressed areas like joints and rivets.

- **Reaction Leading to Embrittlement:**



During caustic embrittlement, two types of cells are formed: Galvanic Cell and Concentration Cell.

- **Preventive Measures:**

1. **Use Sodium Phosphate:** Replace sodium carbonate with sodium phosphate for water softening.
2. **Add Lignin and Tannins:** Add these substances to block minute cracks, preventing caustic soda infiltration.
3. **Add Na_2SO_4 :** Introduce sodium sulfate to prevent crack formation.
4. **Maintain pH:** Keep the pH between 8 to 9 to prevent excessive alkalinity in boiler feed water.

Treatment Of Hard Water

External Treatment :

This type of treatment is given to water ,before entering it in the boiler.

- a) Zeolite / Permutit /base exchange method
- b) De-ionization / De-mineralization/ Ion exchange method
- c) Ultrafiltration

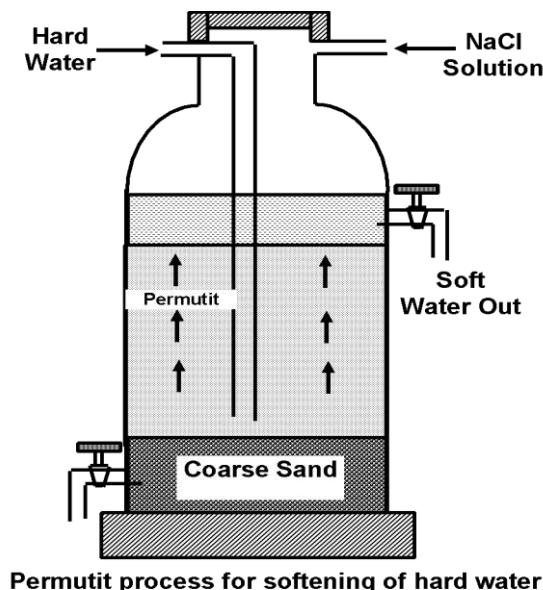
Zeolite / Permutit / Base Exchange method is highly effective for removing both temporary and permanent hardness from water. Zeolite or permutit refers to complex silicates containing various metallic and non-metallic oxides. The approximate chemical formula of zeolite is $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{Si}_2\text{O}_8 \cdot 6\text{H}_2\text{O}$. These silicates have a loose hold on sodium ions, so called sodium permutit (Na_2P) or sodium zeolite (Na_2Ze).

- There are two main types of zeolite:
 - a) **Natural Zeolite:** This type is obtained by treating greenstone with NaOH. It is non-porous in nature.
 - b) **Synthetic Zeolite:** Prepared by treating sodium silicate, sodium aluminate, and aluminum sulfate, synthetic zeolites are porous and offer effective hardness removal from water.

1. Zeolite / Permutit / Base Exchange method

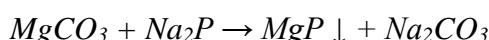
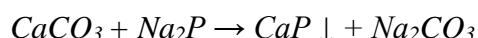
• Principle:

The sodium permutit interact with hard water by exchanging its Na^+ ions with Ca^{2+} and Mg^{2+} ions. This exchange results in the formation of insoluble compounds known as calcium permutit or magnesium permutit.

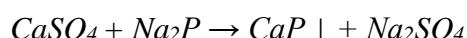
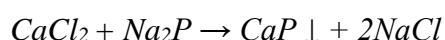


Sodium permutit, placed in a container, is used to treat hard water. As hard water flows through it, sodium permutit exchanges its sodium ions with calcium and magnesium ions, forming insoluble compounds like calcium permutit or magnesium permutit. These insoluble salts stay in the filter bed, leaving the water free from calcium and magnesium salts. The only remaining substances in the water are harmless sodium salts

• For Temporary Hardness:

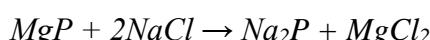
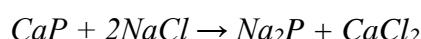


• For Permanent Hardness:



• Regeneration of Permutit/Zeolite:

When the permutit is exhausted it is regenerated by treating with 10 % brine solution (NaCl).



• Limitations:

1. Difficulty in regenerating if Mn^{2+} or Fe^{2+} ions are present in large quantities.
2. Zeolite bed may be destroyed if the hard water contains mineral acids.

3. Turbidity in hard water may clog pores of permuntit.
4. Only removes cations from hard water.

- **Advantages:**

1. Achieves water with 15 ppm hardness.
2. Compact equipment with minimal space requirements.
3. A clean and quick process.
4. Removal of cations from hard water.

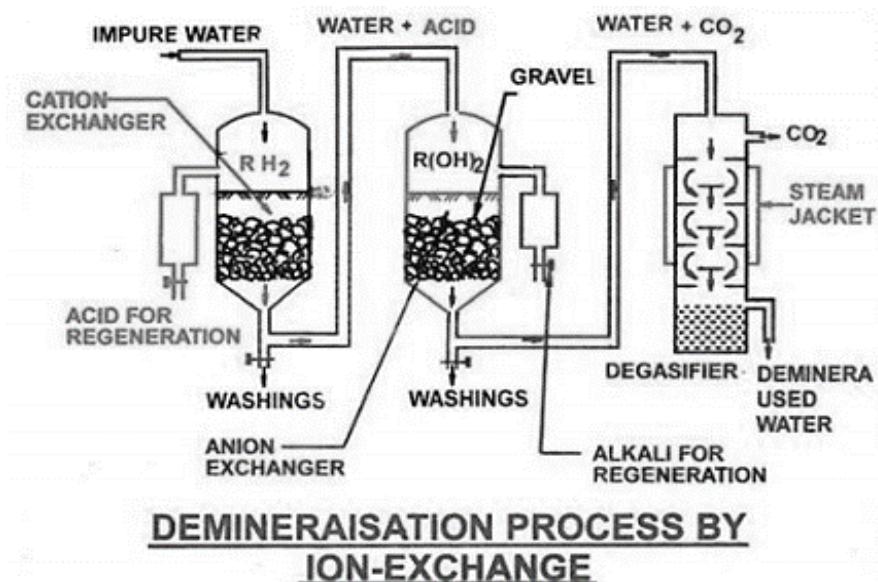
2. De-ionization or De-mineralization or Ion exchange method :

Ion-exchange water softening removes both cation and anion impurities. The method uses polymer-based ion exchangers with exchange sites. There are two types of ion-exchange resins:

- **Cation Exchange Resin/Cation Exchanger:**

This resin replaces Na ions or protons to eliminate Ca^{2+} or Mg^{2+} ions in hard water.

Typically, these are styrene divinyl benzene co-polymers that, through sulphonation or carboxylation, can exchange protons or sodium ions with cations in water. Representation: RH_2 .



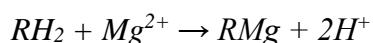
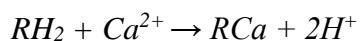
- **Anion Exchange Resins/Anion Exchanger:**

These resins capture anion impurities in hard water with loosely bound OH^- ions.

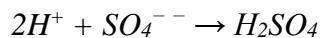
They are styrene divinyl benzene copolymers containing quaternary ammonium hydroxide groups.

Representation: $\text{R}'(\text{OH})_2$.

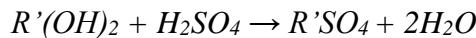
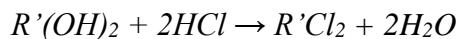
Two cylindrical towers are used in the ion-exchange method: one with a cation exchanger, $[\text{RH}_2]$ and the other with an anion exchanger $[\text{R}'(\text{OH})_2]$. Hard water passes through the cation exchanger, removing cations like Ca^{2+} , Mg^{2+} , Na^+ , Fe^{2+} and releasing H^+ ions. The first tower reactions are:



The anions (Cl^- , SO_4^{2-} , CO_3^{2-}) are converted to acids in the reaction between the two towers:

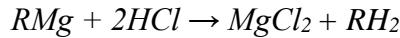
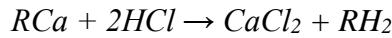


The acidic water then passes through the second tower with an anion exchange resin, converting acids into water. Second tower reactions:

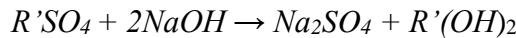
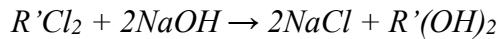


Dissolved gases like CO₂ and O₂ are removed by passing water through a degasifier.

Cation exchange resin is regenerated with dilute acid in the first tower:



Anion exchange resin is regenerated with a dilute alkali solution in the second tower:



When hard water is passed through both resins, the resulting water is deionized or demineralized.

- **Advantages:**

1. Easy to operate and control.
2. Requires less space compared to lime soda process.
3. Produces better quality water and is more economical.

- **Disadvantages:**

1. Using a hydrogen exchanger may reduce effluent pH, leading to corrosion.
2. Using a sodium exchanger does not reduce TDS, alkalinity, and silica content.

Ultrafiltration (UF):

Introduction:

Ultrafiltration (UF) is a water purification method similar to reverse osmosis, utilizing hydrostatic pressure to push water through a semipermeable membrane. This single-membrane filtration process acts as a barrier against viruses, bacteria, particulates, endotoxins, and other suspended microbes, producing pure water with low silt density.

Definition:

Ultrafiltration membrane filtration (UF) is a low-pressure water treatment process that eliminates turbidity-causing particles, including suspended solids, germs, colloidal debris, and proteins.

Explanation:

UF involves forcing water through a semipermeable membrane, with suspended solids and high-molecular-weight solutes retained on one side (retentate), while water and low-molecular-weight solutes pass through to the other side (permeate). UF effectively removes organic molecules, viruses, and various salts. Its advantages include stable water quality regardless of the source, a compact footprint, 90-100% pathogen removal, and minimal chemical use, mainly for membrane cleaning.

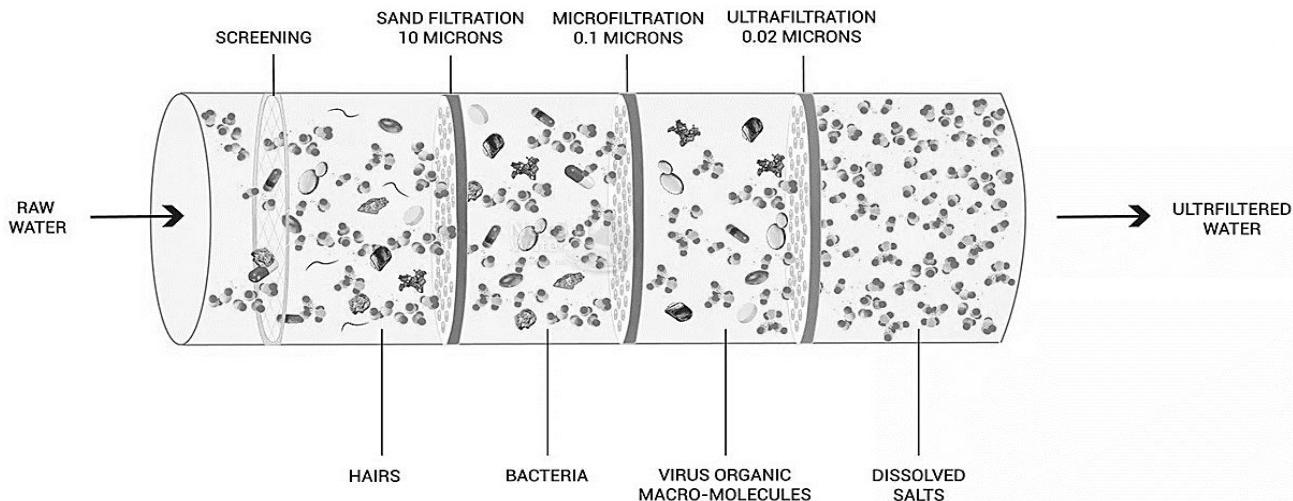
UF Membrane Characteristics:

UF membranes have pore sizes ranging from 0.1 to 0.01 microns, described by "molecular weight cut-off" (MWCO). MWCO represents the molecular weight at which 90% of a macromolecular solute is blocked by the membrane. UF sits between microfiltration and nanofiltration. Maintenance cleaning is required to prevent fouling, scaling, and contamination by microbes and algae. Disposal of separated contaminants condensed in the UF retentate is necessary.

Typical UF Applications:

1. Treatment and recycling of wastewater and industrial process water
2. Removal of particulates and macromolecules (e.g., 90-95% arsenic removal) for potable water.
3. Augmentation or replacement of secondary and tertiary filtration stages in water treatment Plants.
4. Filtration of paper pulp mill effluent.
5. Applications in the food and beverage industry
6. Water softening.

- **Process of Ultrafiltration:**



Ultrafiltration utilizes a well-known semi-permeable membrane to repel harmful chemicals, bacteria, particles, and organic components, resulting in the production of drinkable water. Its primary goal is to remove contaminants affecting water color, taste, and odor.

Basic Separation Process:

UF membrane filtration relies on size exclusion or sieving, effectively eliminating particles in the size range of less than 0.01 to 0.1 mm. The filtrate produced is ideal for downstream reverse osmosis treatment (RO).

Applications of Ultrafiltration:

1. **Chemical and Pharmaceutical Manufacturing:** Used to recycle flow or add value to products.
2. **Beverage and Food Processing:** Employed for filtration and concentration processes.
3. **Wastewater Treatment:** Applied to recycle water or enhance product value.
4. **Dialysis of Blood:** Utilized in medical applications.
5. **Drinking Water Treatment:** UF is employed to make water potable by removing particles and macromolecules from raw water. It can replace or act as an independent system in water treatment plants, particularly in areas with high suspended particles.
6. **Concentration of Proteins:** Widely used in the dairy sector, especially in producing whey protein (WPC) and lactose-rich permeate from cheese whey. UF can concentrate whey 10–30 times in a single step.

Advantages of Ultrafiltration System:

1. **Zero Power Requirement:** Operates without electricity, utilizing natural pressure for filtration.

2. **Elimination of Viruses and Bacteria:** Removes particle materials, ensuring clean and safe water.
3. **Deep Cleaning:** Effectively purifies even muddy water, removing solid particles and germs.
4. **Ensures Pure Drinking Water:** Generates consistently safe drinking water due to the robust membrane.
5. **Low Maintenance, High Performance:** Requires minimal maintenance and lasts for many years with manual flushing.
6. **Excellent Purification:** Removes chlorine-resistant eggs of gastrointestinal parasites, ensuring pure drinkable water.

Environment Sustainability

Definition:

Sustainability means making sure we meet our needs now without hurting the ability of the next generations to meet their needs. It's not just about the environment; it also involves taking care of people and making smart economic choices.

Pillars of Sustainability:

1. Environmental:

Taking care of nature, like plants and animals, and using resources wisely.

2. Economic:

Making sure our money and jobs last in the long run without causing harm.

3. Social:

Treating everyone fairly, making sure people have what they need, and keeping communities strong.

So, sustainability is about keeping a good balance between nature, money, and people for today and the days to come.

Environmental Pollution:

- **Definition:**

Environmental Pollution is any unwanted change in the air, water, soil, or sound that can harm living things or property. It includes the introduction of harmful substances causing discomfort or damage to the environment.

- **Pollution:**

The influence of any substance causing problems, harm, or discomfort to living things.

- **Pollutant:**

Any substance causing problems, harm, or discomfort to living things.

Types of Environmental Pollution:

- **Air Pollution:**

Introduction of harmful chemicals or particles into the air, causing discomfort or damage to humans and the environment.

Sustainable Approach: Use natural gases, avoid bursting crackers, use less fuel for vehicles, and adopt electric stoves.

- **Water Pollution:**

Alteration of water's characteristics through natural or human activities, making it unsuitable for its

intended use.

Types:

Surface water pollution, groundwater pollution, microbiological pollution, oxygen depletion pollution.

Sustainable Approach:

Practice organic farming, enforce laws, reduce plastic use, treat agricultural and industrial wastewater, control pollution.

- **Noise Pollution:**

Undesirable sound disrupting normal activities and causing harm to human well-being.

Examples: Loudspeakers, machinery, appliances.

Sustainable Approach: Plant trees around sound sources, service automobiles regularly, design noise-absorbing buildings, provide protective equipment, regulate loudspeakers.

- **Land Pollution:**

Destruction of Earth's land surfaces by human activities and improper waste disposal.

Sustainable Approach: Increase farming land, plant more trees, dispose of waste properly, avoid excessive drilling, reduce fertilizer and pesticide use, implement integrated waste management, practice good agricultural methods.

Environmental pollution harms our well-being and the planet. Adopting sustainable practices helps us live better while preserving nature for the future.

NUMERICALS ON EDTA METHOD

1. It was found that, 100 ml of water sample requires 12.7 ml of 0.01 M EDTA during titration. Calculate hardness of water.

Solution :-

$$\begin{aligned}\text{Total hardness} &= y/v \times Z \times 100 \times 1000 \text{ ppm CaCO}_3 \text{ eq. hardness.} \\ &= 12.7/100 \times 0.01 \times 10^5 \text{ ppm CaCO}_3 \text{ eq. hardness} \\ &= 127 \text{ ppm}\end{aligned}$$

2. 100 ml. of water sample requires 14.6 ml of 0.01 m EDTA in titration. 100 ml of the same water sample when titrated after boiling and filtration, requires 10.7 ml of the EDTA solution. Calculate carbonate and non-carbonate hardness.

Solution :-

$$\begin{aligned}\text{Total hardness} &= y/v \times Z \times 100 \times 1000 \text{ ppm CaCO}_3 \text{ eq. hardness.} \\ &= 15.6/100 \times 0.01 \times 10^5 \text{ ppm CaCO}_3 \text{ eq. hardness} \\ &= 156 \text{ ppm CaCO}_3 \text{ eq. hardness}\end{aligned}$$

After boiling and filtration carbonates get removed from water and the titration reading corresponds to permanent hardness.

$$\begin{aligned}&= \text{Non-carbonate hardness} \\ &= y/v \times Z \times 100 \times 1000 \text{ ppm CaCO}_3 \text{ eq. hardness.} \\ &= 10.7/(100) \times 0.01 \times 100 \times 1000 \text{ ppm CaCO}_3 \text{ eq. hardness.} \\ &= 0.0107 \times 0.01 \times 100 \times 1000 \text{ ppm CaCO}_3 \text{ eq. hardness} \\ &= 107 \text{ ppm}\end{aligned}$$

$$\therefore \text{Carbonate Hardness} : - \text{Total hardness} - \text{Non-carbonate hardness}$$

$$= 156 - 107$$

$$= 49 \text{ ppm}$$

- 3.** **0.5 gm of CaCO₃ was dissolved in dil. HCl and the volume is made to upto 500 ml with distilled water. 50 ml of the solution required 48 ml of EDTA solution in titration. 25 ml of hard water required 7.5 ml of EDTA and after boiling and filtering 5 ml of EDTA Calculate hardness of water.**

Solution : Weight of CaCO₃ taken = 0.5 gm

Volume of standard water = 500 ml = 0.5 litre

Volume of standard hard water taken for titration = 50ml.

Volume of EDTA = 48 ml

$$\text{Concentration of CaCO}_3 = \frac{\text{weight of CaCO}_3}{\text{Molecular wt.of CaCO}_3 \times \text{vol. of CaCO}_3 \text{ in litre}}$$

$$= 0.5 / (100 \times 0.5)$$

$$= 0.01 \text{ M CaCO}_3$$

Standard hard water Vs EDTA

$$\begin{aligned} M_1 V_1 &= M_2 V_2 \\ 0.01 \times 50 &= M_2 \times 48 \\ \therefore M_2 &= (0.01 \times 50) / 48 \\ &= 0.0104 \text{ M} \end{aligned}$$

Total hardness (before boiling)

$$\begin{aligned} &= y/v \times Z \times 100 \times 1000 \text{ ppm CaCO}_3 \text{ eq. hardness} \\ &= 7.5 / 25 \times 0.0104 \times 100 \times 1000 \text{ ppm CaCO}_3 \text{ eq. hardness} \\ &= \mathbf{312.5 \text{ ppm CaCO}_3 \text{ eq.}} \end{aligned}$$

Permanent Hardness (Non-carbonate hardness) after boiling

$$\begin{aligned} &= y/v \times Z \times 100 \times 1000 \text{ ppm CaCO}_3 \text{ eq. hardness} \\ &= 5 / 2.5 \times 0.0104 \times 100 \times 1000 \text{ ppm CaCO}_3 \text{ eq. hardness} \\ &= \mathbf{208 \text{ ppm CaCO}_3 \text{ eq.}} \end{aligned}$$

Temporary Hardness [carbonate Hardness]

$$\begin{aligned} \therefore \text{Temporary Hardness} &= \text{Total Hardness} - \text{Permanent Hardness.} \\ &= 312.5 - 208 \text{ hardness} \\ &= \mathbf{104.5 \text{ ppm CaCO}_3 \text{ eq.}} \end{aligned}$$

- 4.** **0.8gm of ZnSO₄ is dissolved in water and diluted to 250 ml. 25ml of this ZnSO₄ solution is titrated with Na₂-EDTA solution from burette to obtain end point 14.3 ml. This standardized EDTA solution was titrated with 50 ml of water sample to obtain 8.6 ml burette reading. Calculate hardness of water.**

Solution: =104.5 ppm CaCO₃ equivalent.

Standardization of EDTA.

Weight of ZnSO₄ = 0.8 gm

Volume of ZnSO_4 = 250 ml = 0.25 litre

Molecular weight of ZnSO_4 = 161.4

$$\begin{aligned}\text{Molarity of } \text{ZnSO}_4 &= \frac{\text{weight of } \text{ZnSO}_4}{\text{Molecular weight of } \text{ZnSO}_4 \times \text{volume of } \text{ZnSO}_4} \\ &= 0.8/(161.4 \times 25) \\ &= 0.0198 \text{ M}\end{aligned}$$

ZnSO₄ Vs EDTA

$$M_1 V_1 = M_2 V_2$$

$$0.0198 \times 25 = M_2 \times 14.3$$

$$\begin{aligned}\therefore M_2 &= (0.0198 \times 25)/14.3 \\ &= 0.0347 \text{ M}\end{aligned}$$

$$\begin{aligned}\text{Determination of Hardness} &= y/v \times Z \times 100 \times 1000 \text{ ppm CaCO}_3 \text{ eq. hardness} \\ &= 8.6/50 \times 0.0347 \times 100 \times 1000 \text{ ppm CaCO}_3 \text{ eq. hardness} \\ &= \mathbf{596 \text{ ppm CaCO}_3 \text{ eq.}}\end{aligned}$$

5. How many grams of MgCl₂ dissolved in water will give hardness of 76 ppm ?

Solution :

$$\begin{aligned}\text{Hardness of } \text{MgCl}_2 &= \frac{\text{Strength of } \text{MgCl}_2 \times \text{Chemical equivalent of } \text{CaCO}_3}{\text{Chemical equivalent of } \text{MgCl}_2} \\ 76 &= \text{Strength of } \text{MgCl}_2 \times 50/47.5 \\ \therefore \text{Strength of } \text{MgCl}_2 &= (76 \times 47.5)/50 \\ &= \mathbf{72.2 \text{ mg/lit or ppm}}\end{aligned}$$

NUMERICALS ON ALKALINITY

1. 100 ml of water sample on titration with N/50 HCl requires 8 ml upto Phenolphthalein end point and 9 ml. of acid upto methyl orange end point. Calculate types and extent of alkalinity in the water sample.

Solution :

$$\begin{aligned}\frac{N}{50} &= \frac{1}{50} = 0.02 \text{ N} \\ P &= \frac{v_1 \times Z \times 50 \times 1000}{v} \text{ ppm of CaCO}_3 \text{ equivalent} \\ &= \frac{8 \times 0.02 \times 50 \times 1000}{100} \text{ ppm of CaCO}_3 \text{ equivalent} \\ &= 80 \text{ ppm of CaCO}_3 \text{ equivalent} \\ M &= \frac{v_2 \times Z \times 50 \times 1000}{v} \text{ ppm of CaCO}_3 \text{ equivalent} \\ &= \frac{9 \times 0.02 \times 50 \times 1000}{100} \text{ ppm of CaCO}_3 \text{ equivalent} \\ &= 90 \text{ ppm}\end{aligned}$$

Here $P > \frac{1}{2} M$, and alkalinity is due to $[\text{OH}^-]$ & $[\text{CO}_3^{2-}]$

$$\begin{aligned}\text{i)} \quad [\text{OH}^-] &= 2P - M \\ &= 2 \times 80 - 90 \\ &= 160 - 90 \\ &= 70 \text{ ppm CaCO}_3 \text{ equivalent}\end{aligned}$$

$$\begin{aligned}\text{ii)} \quad [\text{CO}_3^{2-}] &= 2 [\text{M}-\text{P}] \\ &= 2 [90-80] \\ &= 20 \text{ ppm of CaCO}_3 \text{ equivalent}\end{aligned}$$

2. 100 ml of water sample required 4 ml of N/20 H₂SO₄ for neutralization to phenolphthalein end point. Another 16 ml of the same acid was needed to methyl orange end point. Determine the types and amounts of alkalinites.

Solution:

$$\begin{aligned}\frac{N}{20} &= \frac{1}{20} = 0.05 \text{ N} \\ P &= \frac{v_1 \times Z \times 50 \times 1000}{v} \text{ ppm of CaCO}_3 \text{ equivalent} \\ &= \frac{8 \times 0.05 \times 50 \times 1000}{100} \text{ ppm of CaCO}_3 \text{ equivalent} \\ &= 100 \text{ ppm of CaCO}_3 \text{ equivalent} \\ M &= \frac{v_2 \times Z \times 50 \times 1000}{v} \text{ ppm of CaCO}_3 \text{ equivalent} \\ &= \frac{(4+16) \times 0.05 \times 50 \times 1000}{100} \text{ ppm of CaCO}_3 \text{ equivalent} \\ &= 500 \text{ ppm}\end{aligned}$$

Amounts of Alkalinites

Here $P < \frac{1}{2} M$, alkalinity is due to $[\text{CO}_3^{2-}]$ & $[\text{HCO}_3^-]$

$$\begin{aligned}\text{i)} \quad [\text{CO}_3^{2-}] &= 2P \\ &= 2 \times 100 = 200 \text{ ppm} \\ \text{ii)} \quad [\text{HCO}_3^-] &= M - 2P \\ &= 500 - 2 \times 100 \\ &= 500 - 200 \\ &= 300 \text{ ppm}\end{aligned}$$

NUMERICALS ON ZEOLITE METHOD

1. Hardness of 4500 litres of water was removed completely by zeolite softener . The zeolite had required 30 liters of 100 gm/lit(100mg/lit) of NaCl to regenerate. Calculate hardness of water.

Solution :

As 1 litre of NaCl solution contains 100 gms of NaCl

$$\therefore 30 \text{ litres of NaCl solution contains} = 30 \times 100 \text{ gms of NaCl} \\ = 3000 \text{ gm of NaCl}$$

Quantity of NaCl in terms of CaCO₃ equivalent

$$\begin{aligned}&= \frac{\text{mass of hardness producing substance} \times \text{Equivalent weight of CaCO}_3}{\text{Equivalent weight of hardness producing substance}} \\ &= \frac{3000 \times 50}{58.5} \\ &= 2564.1 \text{ gm of CaCO}_3 \text{ equivalent}\end{aligned}$$

As the hardness of 4500 litres of water = 2564.1gm of CaCO₃ equivalent

$$\therefore \text{the hardness of 1 litre of water} = \frac{2564.1}{4500} \text{ gm of CaCO}_3 \text{ equivalent} \\ = 0.569 \text{ mg/lit or ppm}$$

2. Zeolite softener was completely exhausted and regenerated by passing 100 liters of NaCl solution containing 120 gm/lit of NaCl. How many litres of a sample of water of 500 ppm can be softened by zeolite softener ?

Solution :

As 1 litre of NaCl solution contains 120 gm of NaCl

$$\therefore 100 \text{ litres of NaCl solution contains} = 100 \times 120 \text{ gm of NaCl} \\ = 12000 \text{ gms of NaCl}$$

Quantity of NaCl in terms of CaCO₃ equivalent

$$\begin{aligned} &= \frac{\text{Mass of hardness producing substance} \times \text{Equivalent weight of CaCO}_3}{\text{Equivalent weight of hardness producing substance}} \\ &= 12000 \times 50/58.5 \\ &= 10256.41 \text{ gm of CaCO}_3 \text{ equivalent} \\ &= 10256.41 \times 1000 \text{ mg of CaCO}_3 \text{ equivalent} \\ &= 10256410 \text{ mg of CaCO}_3 \text{ equivalent} \end{aligned}$$

But we know that

500 mg of hardness = 1 litre of water

$$\therefore 10256410 \text{ mg of CaCO}_3 \text{ equivalent hardness} = 10256410/500 \\ = 20512.82 \text{ litres of water}$$

Questions

- Explain what hardness in water means? Additionally, identify and describe the two types of hardness mentioned.
- List and explain the units of hardness used in water quality assessment?
Demonstrate the application of the EDTA method in determining water hardness.
- Provide a detailed procedure, including the specific reagents used and the chemical reactions that take place during the process.
- Simplify Complexometric titration. Illustrate how water hardness is measured using the EDTA method in this titration process. Summarize the key steps involved in determining water hardness.
- Interpret the concept of water hardness in basic terms. Subsequently, execute the application of the Zeolite Method in softening water, breaking down the process into steps and emphasizing the functional role of Zeolite in achieving water softness.
- Explain how we use De-ionization or demineralization to treat water in a straightforward. Describe the steps involved, and clarify how the Ion exchange process helps in this treatment.
- Explain briefly what scale and sludge formation are in water systems and why they occur.
- Describe 'Caustic Embrittlement' in an easy way. Why is it important in water treatment?
- Provide a simple explanation of sustainability. Additionally, give an example to illustrate the concept.



Battery Technology

Batteries: Electrode potential, Nernst equation. Batteries, characteristics, types of batteries:- construction & working of Zn-Carbon cell, recent technologies in Lithium based batteries ,Li-cells – $LiMnO_2$, $LiFeS_2$ batteries , Li ion batteries ,Li-Polymer battery, next generation Li battery, Lead acid cell Na-ion battery, Nicad Battery, Specialty batteries for satellites

- **Capacitors:** Introduction, Electrochemical capacitors, Pseudo capacitors, Symmetrical & unsymmetrical capacitors, Ultra capacitors vs batteries.

Introduction:

In the dynamic landscape of modern technology, the demand for efficient and sustainable power sources has never been more pressing. As we stand at the crossroads of an energy revolution, the focus on clean and renewable energy solutions has intensified. Among the myriad options available, electrochemical power sources have emerged as pivotal players, embodying the convergence of scientific innovation and practical application.

Batteries:

Batteries are a collection of one or more cells whose chemical reactions create a flow of electrons in a circuit. All batteries are made up of three basic components: an anode (the '-' side), a cathode (the '+' side), and some kind of electrolyte (a substance that chemically reacts with the anode and cathode).

Types of batteries:

There are two basic kinds of batteries:

1. Primary Batteries:

These are the batteries in which the electrode reactions are effectively **irreversible** and which cannot be recharged.

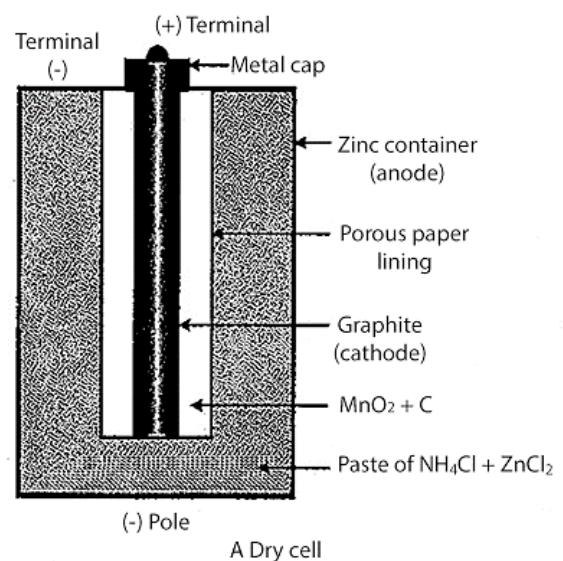
2. Secondary Batteries:

These are the batteries in which the electrode reactions are **reversible** and which can be recharged.

1. Primary Batteries:

a) Dry Cell / Zinc - dry cell :

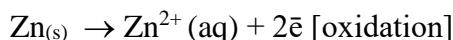
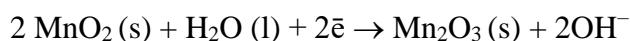
- This cell is also known as ‘**Leclanche cell**’.
- This is the most familiar of all batteries. The cell consists of cylindrical zinc container which acts as an anode.



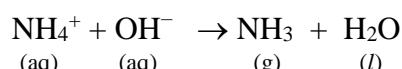
- A graphite rod surrounded by a paste of Manganese dioxide, NH_4Cl and ZnCl_2 acts as the cathode.
- Here starch is being added to make the paste of electrolyte thick.

Anode: Zinc container**Cathode:** Graphite Rod**Electrolyte:** MnO_2 , NH_4Cl and ZnCl_2

- **Reactions:**

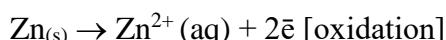
The anode half reaction is :**The cathode half reaction is :**

However, an acid base reaction between OH^- and NH_4^+ (derived from NH_4Cl) evolves $\text{NH}_3 \text{ (g)}$ which disrupts the current flow.

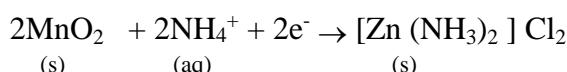


This is prevented by a reaction of $\text{NH}_3 \text{ (g)}$ with Zn^{2+} (from ZnCl_2) to form the complex ion $[\text{Zn}(\text{NH}_3)_2]\text{Cl}_2 \text{ (s)}$. Hence the reactions at two electrodes are :

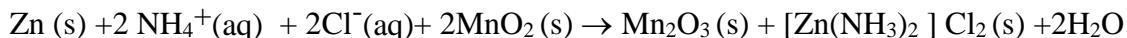
- **At anode :**



- **At cathode:**



- **Net cell Reaction :**



- **Properties:**

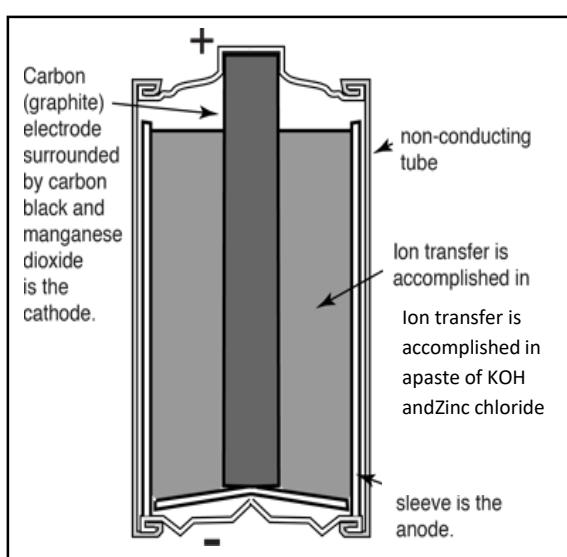
1. Cheap
2. Gives voltage of 1.5

- **Applications:**

Dry Cells are used in flash lights, transistors, radios, tape recorders, calculators etc.

- b) **Alkaline battery:**

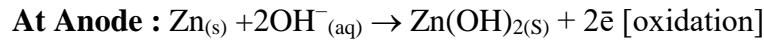
It is an improved form of the dry cell in which NH_4Cl is replaced by KOH .



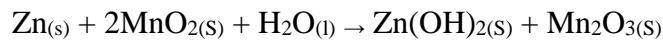
Anode : Zinc container

Cathode: Graphite Rod

Electrolyte : MnO_2 , KOH and $ZnCl_2$



- **Net Reaction:**



- **Properties:**

1. Cheap
2. Gives voltage of 1.5

- **Advantages:**

1. Zn does not dissolve in basic medium
2. Maintains better voltage
3. It is a long life battery (No corrosion of Zn is takes place)

- **Applications:**

It is used camera exposure device, calculators, watches, transistors, radios, tape recorders, etc.

2. Secondary batteries:

Lithium batteries:

Basically these are Primary batteries. These may be classified as primary or secondary as per the choice of cathode and electrolyte used. That's why it is also known as **Modern battery**.

Lithium is a light metal with low electrode potential and good conductivity. The group of batteries where lithium is used as an anode and known as lithium batteries. Different kind of batteries is used.

- **Types:**

A) LiMnO₂ Battery:

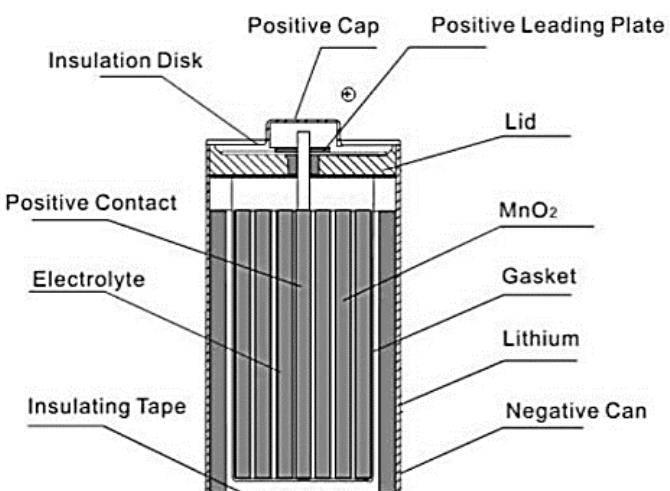
The construction of Li-MnO₂ battery is as follows.

- a) Anode is composed of lithium
- b) Cathode is composed of heat treated MnO_2 .
- c) Electrolyte contains a mixture of LiCl, LiBr, LiAlO₄ and LiClO₄ dissolved in organic solvents like propylene carbonate and 2 dimethoxyethane.

The cell reaction are as follows:



(Oxidation) At the cathode :



The overall cell reaction is : $Li + MnO_2 \rightarrow LiMnO_2$

- Characteristic Properties :**

1. The battery offers an EMF of 3.0 V.
2. The batteries are light in weight and compact.
3. They are known for low maintenance and have high energy density.

- Applications:**

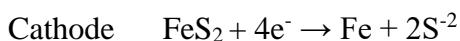
1. Used as pacemakers, and other electronic devices.
2. Used in Clock cameras and calculators, thermometer, car locks etc.

B) Li/FeS₂ batteries:

Iron sulfide, in both the monosulfide (FeS) and the disulfide (FeS₂) forms, has been considered for use in solid-cathode lithium batteries. These batteries have a nominal voltage of 1.5 V* and can therefore be used as replacements for aqueous batteries having a similar voltage.

The Li/FeS₂ battery uses lithium for the anode, iron disulfide for the cathode, and lithium iodide in an organic solvent blend as the electrolyte.

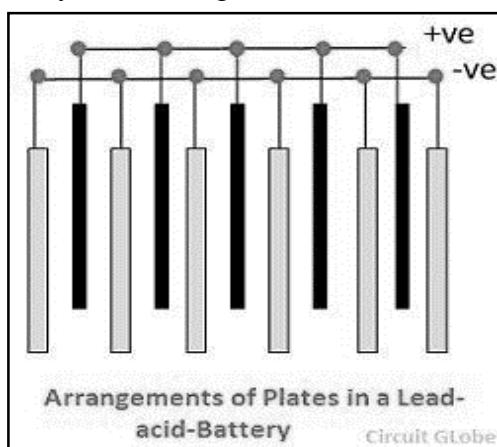
The cell reactions are



C) Li ion battery

D) LEAD ACID CELL: [Lead Acid Storage Cell]:

It is a secondary type of battery and rechargeable.



node: Pb grid with spongy lead Cathode:Pb grid with PbO₂ Electrolyte: 20 % H₂SO₄ solution

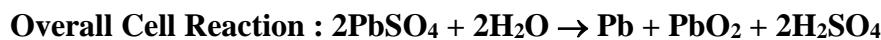
Lead storage cell consists of Pb grid filled with spongy lead which acts as the anode and Pb grid packed with PbO₂ acts as the cathode. A number of (generally six) such electrode pairs are dipped in H₂SO₄ solution (20%) which acts the electrolyte and these are separated by inert and porous partitions.

The cell reaction are : (**During Discharging**)

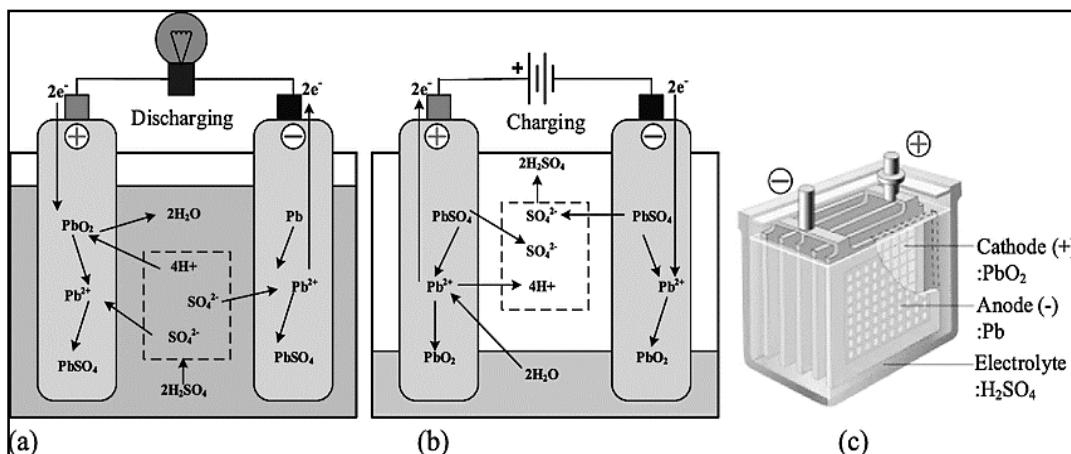


The cell reaction shows that the electrolyte H_2SO_4 is consumed during the reaction, so as the reaction proceeds the concentration of H_2SO_4 decreases. Once the concentration of H_2SO_4 fallen to a permissible level, the battery needs to be recharged by reversing the discharge reaction. For this an external potential higher than the cell potential is applied. The cell then operates like an electrolytic cell and PbSO_4 deposited on the electrodes reverted to Pb and PbO_2 by the following reactions.

During **Charging** of battery reverse reactions takes place.



The cell reaction shows that the conclusion of H_2SO_4 increases during recharging of the cell. The potential developed by each electrode pair is about 2V and higher potential can be obtained by connecting a number of electrode pairs in series.



- **Applications : It is used as**

1. Automobile batteries.
2. Also used in trains, hospitals etc.
3. Also used in telephone exchanges, mines, laboratories, broad casting stations, power stations etc.

Lithium-ion batteries:

(Li-ion) are the most common modern battery type. These are most common in consumer electronics, but these are also being increasingly adapted to other uses and are the lack of innovation in battery technology today.

In Li-ion batteries, lithium ions shuttle through the electrolyte solution from one electrode to the other. The anode is usually made of carbon-based compounds like graphite. The cathode is usually made of transition metal compounds that contains lithium in their molecular structure.

Differences in the battery's cathode, anode, and electrolyte solution give the battery different strengths and weaknesses.

Li-ion batteries tend to outperform the other most common battery type, lead-acid batteries, across every metric, but their increased cost of production and safety concerns have limited broader commercial adoption until the last few years. It remains the focused of most energy storage research today and are

expected to have the broadest range of commercial applications in the near future.

- **Anode:**

Carbon materials, like graphite

- **Cathode:**

Lithium cobalt oxide (LiCoO_2), lithium manganese oxide (LiMn_2O_4), lithium iron phosphate (LiFePO_4)

- **Electrolyte:**

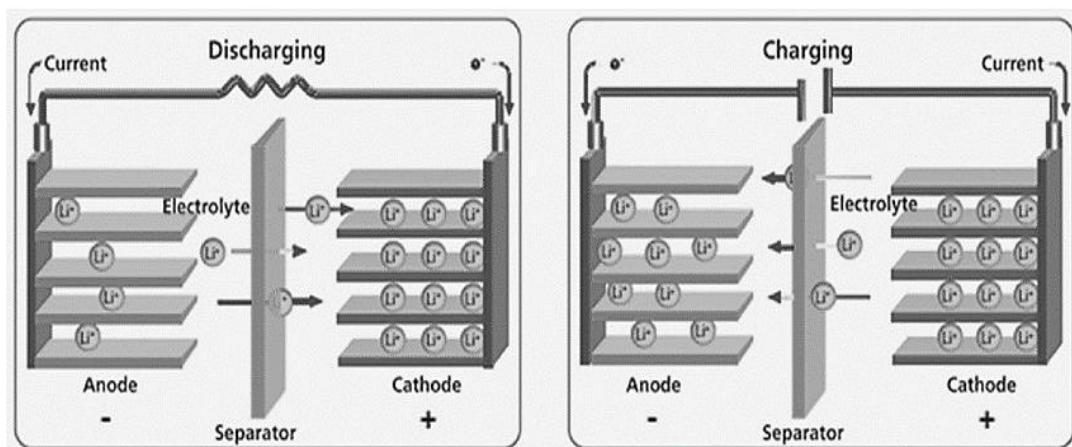
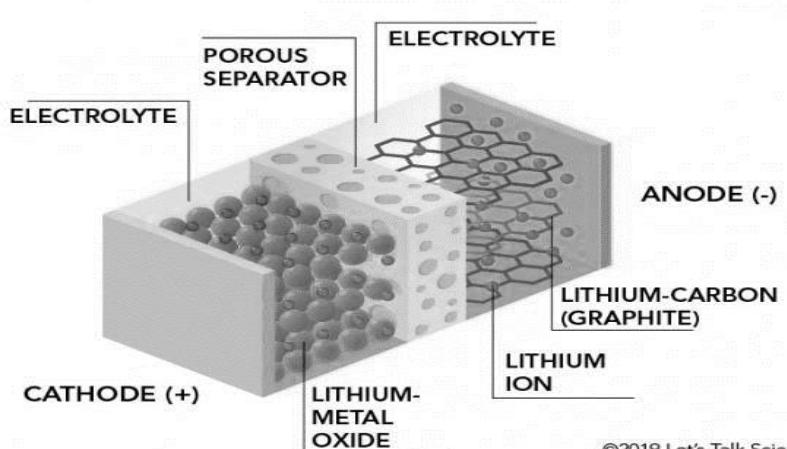
lithium salt dissolved in a solvent, typically an organic solvent.

- **Separator:**

The separator is a porous, insulating material that physically separates the cathode and anode.

- **Casing:**

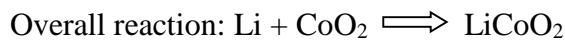
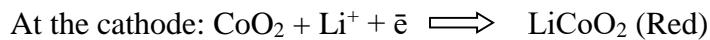
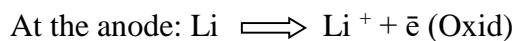
The battery components are enclosed in a casing made of metal or plastic to protect the internal components and provide structural integrity.



- **Reactions:**

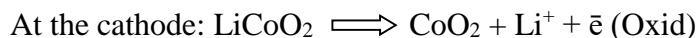
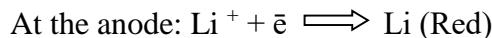
Discharging: Discharging

The cell reaction are as follows:



- **Charging:**

The cell reaction are as follows:



Advantages:

1. **High Energy Density:** Lithium-ion batteries offer a high energy density, which means they can store a large amount of energy in a relatively compact and lightweight package.
2. **Rechargeable:** They are rechargeable and can be charged and discharged hundreds to thousands of times before their capacity significantly degrades.
3. **Low Self-Discharge:** Li-ion batteries have a relatively low self-discharge rate, meaning they can hold their charge for extended periods when not in use.
4. **Improved Safety :** No liquid electrolyte

Applications:

1. **Consumer Electronics : Smartphones :** Laptops and Tablets Digital Cameras
2. **Electric Vehicles (EVs) :** Electric Cars, Electric Bicycles and Scooters
3. **Renewable Energy Storage:** Home Energy Storage , Grid-Level Energy Storage
4. **Aerospace and Aviation:** Drones, Aircraft
5. **Medical Devices:** Implantable Medical Devices, Portable Medical Equipment
6. **Power Tools:** Cordless Power Tools
7. **Marine and Automotive:** Marine Applications, Hybrid Vehicles
8. **Military Equipment**
9. **Smartwatches and Fitness Trackers**
10. **Emerging Technologies Space Exploration Electric Boats Beyond**

Traditional Lithium-ion Batteries :

1. **Lithium-air batteries** currently in the earliest stages of development would use oxygen from their environment as the cathode material. This would make the battery much lighter than other lithium-ion battery and give it much greater theoretical energy density. One obstacle is finding an electrolyte material that can keep the anode from reacting with the air and becoming unstable. Exposing the battery cell to the air can also result in other chemical reactions that produce compounds that cover the electrode's surface and impede it from working.
2. **Lithium-sulfur batteries** have a cathode made of a sulfur-based compound and an anode made of lithium. These batteries have a higher energy density than lithium-ion batteries, and are potentially much cheaper, but commercialization remains a long way off due to a lower capacity, higher self-discharge rate, and worse safety.
3. **Sodium-ion batteries** have a cathode made of a sodium-based compound. Sodium is more abundant and easily sourced than lithium, making this battery potentially much cheaper than Li-ion alternatives, but has less energy density and is still not widely commercially available. This makes sodium-ion batteries more likely to be applied in renewable energy storage than consumer electronics in the future.

4. **Aluminum-ion batteries** could be much cheaper than other alternatives given the ubiquity of aluminum on Earth. In addition, it offers high theoretical capacity and safety. However, the electrochemical reaction associated with aluminum is fairly sluggish, limiting its power output. This technology has seen focused research over the last five years and is probably at least a decade away from feasibly being deployed at scale.
5. **Solid state batteries** refer to lithium-ion batteries where the electrolyte is a solid rather than a liquid. Using a solid electrolyte is safer and lighter than a liquid electrolyte and can be made more compact. This gives solid state batteries higher energy density than traditional lithium-ion batteries. However, this technology is not only more expensive than liquid electrolytes, but also unstable during fast charging when scaled up to the battery pack level. Solid electrolytes come in two variants: solid polymers and ceramics. Solid polymers operate at high temperatures of 220 degrees Fahrenheit or greater, while ceramics operate at room temperature have the advantage of acting like a liquid without the safety concern. In late 2020, a number of companies such as Toyota, QuantumScape and others claimed to have a feasible solid state battery technology that can be potentially scaled up to electric vehicle battery packs in an economically feasible manner.

New-Generation Lithium-Ion Battery

A conventional lithium-ion battery uses lithium-ion as a key component of its electrochemistry. Lithium atoms in the anode are ionized and are separated from their electrons. The next generation of lithium-ion batteries will work on technological innovations in the cathode, enabling higher energy densities and lower costs. There are three types of **lithium-ion batteries which are used in electric vehicles: lithium ferrophosphate, or lithium iron phosphate, lithium nickel manganese cobalt oxide and lithium nickel cobalt aluminum oxide.**

Despite the advantages of eco-friendliness and lower working potential, conventional graphite anode in lithium batteries is facing challenges, such as the limited capacity to fulfill the requirements of emerging trends of electric cars and hybrid vehicles. Next-generation lithium-ion batteries with higher density have novel anode materials. These batteries have the potential to exhibit higher energy capacity and better cycling durability than conventional graphite. Currently, various prelithiation methods for compensating the anode's initial irreversible capacity have been found. However, large-scale commercial applications have not been developed yet. Firms like Tesla, Inc. (NASDAQ:TSLA), Taiwan Semiconductor Manufacturing Company Limited (NYSE:TSM), and General Motor Company (NYSE:GM) are aiding the development of new battery tech like this.

Lithium-Sulfur Battery :

In lithium-sulfur batteries, the positive electrode is sulfur and the negative electrode is made up of metallic lithium. The cell voltage is comparatively lower than lithium-ion cells and is about 2 V.

These batteries have an energy density several times higher than lithium-ion batteries. Li-S have specific energies on the order of 550 Wh/kg. Contrary to that, conventional lithium-ion batteries have a range of 150-260 Wh/kg.

The sulfur used as a cathode in lithium-sulfur batteries is less expensive than the cobalt used in conventional lithium-ion batteries. These batteries are in higher demand in future because of their greater energy storage and cost efficiency.

Lithium-sulfur batteries have a major drawback: These are reusable for around 1000 charge cycles whereas lithium-ion batteries can be recharged 2000 – 3000 times. Lithium-sulfur batteries with more than 1500 charge and discharge cycles were presented in 2017 but their cycle life test at a commercial scale with lean electrolyte is yet to be demonstrated.

Speciality batteries for satellites:

Satellites primarily use batteries with large lithium-ion cells. These batteries provide high-energy levels and long cycle life at a low weight and in small volumes.

Capacitors:

Introduction

Capacitors are the essential electronic components that store and release electrical energy. They are made of two conductive plates separated by a non-conductive material called a dielectric. This setup allows capacitors to store charge. Capacitors come in various types like electrolytic, ceramic, and tantalum, each with its specific applications in devices like power supplies and timing circuits.

Understanding capacitance is crucial; it measures a capacitor's ability to store charge. Factors like plate area, distance between plates, and the dielectric material influence capacitance.

Capacitance is measured in Farads (F).

Capacitors play a vital role in electronics, storing energy for various applications, and understanding their principles is fundamental for engineering students.

Electrochemical Capacitors:

Electrochemical capacitors, also known as supercapacitors or ultracapacitors, are advanced energy storage devices that store electrical energy through electrochemical processes. Unlike the traditional capacitors, which store energy electrostatically, electrochemical capacitors store energy electrochemically, similar to batteries.

These capacitors consist of two electrodes immersed in an electrolyte solution, with a separator between them to prevent short circuits. When a voltage is applied, ions from the electrolyte are attracted to the electrodes, forming a double layer of charge at the electrode-electrolyte interface. This process enables rapid charge and discharge cycles, making electrochemical capacitors ideal for applications requiring high power densities and fast charging/discharging capabilities.

Electrochemical capacitors bridge the gap between conventional capacitors and batteries, offering higher energy densities than traditional capacitors and faster charge/discharge rates than batteries. They find applications in various fields, including renewable energy systems, electric vehicles, consumer electronics, and industrial machinery. Here their unique combination of high power density, long cycle life, and rapid response times is highly advantageous.

Pseudocapacitors:

Pseudocapacitors are a special type of energy storage device that combines the features of both capacitors and batteries. Unlike regular capacitors, which store energy through electrostatic charge on the surface of electrodes, pseudocapacitors store energy through fast and reversible redox reactions at the electrode-electrolyte interface. This enables them to achieve higher energy densities than conventional capacitors while still retaining the fast charge and discharge capabilities of capacitors.

Pseudocapacitors typically use transition metal oxides or conducting polymers as electrode

materials, which undergo reversible redox reactions during charge and discharge processes. This allows pseudocapacitors to store and release electrical energy more efficiently than traditional capacitors, making them suitable for applications requiring both high energy and power densities.

Pseudocapacitors have several advantages like long cycle life, rapid charge and discharge rates, and high power density. They are used in portable electronics, hybrid electric vehicles, renewable energy systems, and grid energy storage applications, where their combination of high energy storage capacity and fast response times is beneficial.

Overall, pseudocapacitors play a crucial role in advancing energy storage technologies towards more efficient and sustainable solutions. They are suitable for applications requiring quick bursts of energy, such as regenerative braking in vehicles and peak power support in renewable energy systems.

Symmetrical and Unsymmetrical capacitors

Symmetrical and unsymmetrical capacitors refer to the arrangement of their electrodes and how they store electrical charge.

- **Definition:**

Symmetrical capacitors have identical electrodes, meaning both electrodes have the same size and material composition. They store charge equally on both sides, resulting in balanced electrical properties.

- **Definition:**

Unsymmetrical capacitors have electrodes of different sizes or materials. As a result, they store charge unevenly, leading to imbalanced electrical characteristics.

The choice between symmetrical and unsymmetrical capacitors depends on the specific application requirements.

Symmetrical capacitors are commonly used in circuits where balanced electrical properties are crucial, such as in filters and tuning circuits.

Unsymmetrical capacitors may be preferred when asymmetrical charge distribution is desired, such as in sensors or impedance matching circuits.

Understanding the differences between symmetrical and unsymmetrical capacitors helps engineers select the most suitable component for their electronic designs, ensuring optimal performance and functionality.

Ultra capacitors vs Batteries :

Aspect	Ultracapacitors	Batteries
Energy Density	Lower energy density compared to batteries.	Higher energy density compared to ultracapacitors.
Power Density	Higher power density, enabling rapid charge and discharge.	Lower power density compared to ultracapacitors.
Cycle Life	Typically have a higher cycle life with thousands to millions of cycles.	Generally have a limited cycle life, typically ranging in the hundreds to thousands of cycles.
Charge/Discharge Rates	Capable of very fast charge and discharge rates, suitable for high-power applications.	Charge and discharge rates are slower compared to ultracapacitors.

Environmental Impact	Tend to be more environmentally friendly due to the absence of toxic materials like lead and cadmium.	Depending on the chemistry, batteries may contain toxic materials and require proper disposal methods.
Temperature Sensitivity	Less affected by temperature variations compared to batteries.	Performance may degrade significantly at extreme temperatures.
Efficiency	Ultracapacitors have high efficiency, typically above 95%, due to minimal internal resistance.	Batteries exhibit lower efficiency compared to ultracapacitors, often below 90%, due to internal resistance and chemical processes.
Size and Weight	Ultracapacitors are generally larger and heavier per unit of stored energy compared to batteries.	Batteries are more compact and lightweight per unit of stored energy compared to ultracapacitors, making them suitable for portable applications.
Shelf Life	Ultracapacitors have a longer shelf life with minimal self-discharge rates.	Batteries may experience significant self-discharge over time, reducing their shelf life.

Primary Batteries vs Secondary Batteries :

Primary Batteries	Secondary Batteries
Cell reaction is irreversible.	Cell reaction is reversible.
Must be discarded after use.	May be recharged.
Have relatively short shelf life.	Have long shelf life.
Functions only as Galvanic cell.	Functions both Galvanic and Electrolytic Cell.
They cannot be used as storage devices.	They can be used as energy storage devices.
They cannot be recharged.	They can be recharged.
Eg. Dry cell	Eg. Lead acid storage cell

Questions

1. What is battery ? How are they classified ? (3M)
 2. Distinguish between Primary and secondary cell. (3M)
 3. Explain the basic components in a battery and their characteristics ? (3M)
 4. Describe the following with respect to a battery
 - a) voltage
 - b) current
 - c) capacity
 - d) energy density and efficiency
 - e) life cycle and shelf cycle
- (5M)

5. Describe the working of dry cell using the example of Leclanche cell.
How does alkaline battery differ from Leclanche Cell.? (5M)
6. Write short note on Leclanche Cell (5M)
7. What is Lithium battery ? Explain the construction and working of Li-M_nO₂ (5M)
8. Give the construction and working of Lithium ion battery. (5M)
9. What is secondary battery ? Give the construction and working of Nickel –cadmium battery (5M)
10. Describe the construction and working of lead acid storage battery .Explain the process of discharging and charging. (5M)
11. Explain in detail Lead acid storage battery. (5M)
12. Explain the construction ,working and applications of lead acid storage battery along with reactions involved during charging and discharging. (5M)
13. Compare Ultracapacitors and Batteries. (3M)
14. Explain different types of Capacitors. (5M)



Fuel Cells & Solar Cells

Solar Cell: Introduction, Importance, Construction & working of Solar PV cell, Monocrystalline & Polycrystalline Solar cell, Types of solar cell- First, second & third generation solar cells. Silicon solar cell, polymer solar cell, thin film solar cell. Dye Sensitized Solar Cells & polymer photo Voltaic materials. Solar cell efficiency & technology.

Fuel cell: Principle, PAFC, PEMFC, Proton exchange membrane, & direct methanol fuel cell, Molten carbonate fuel cell etc

Solar Cell :

Introduction to Solar Cells:

Solar cells, also known as photovoltaic cells or PV cells, are devices that convert sunlight into electricity. They are a crucial component of solar panels and are used to harness solar energy, a clean and renewable source of power. Solar cells have become increasingly important in the transition to more sustainable and environmentally friendly energy sources.

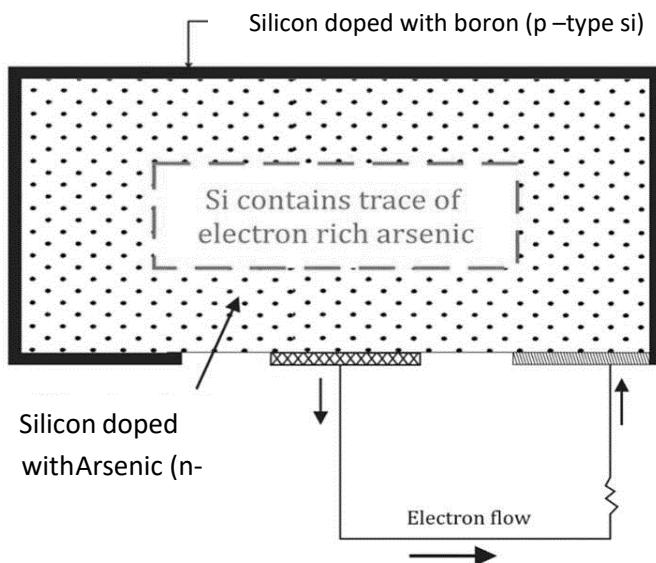


Figure shows photovoltaic cell, in which a p-type semiconductor (such as silicon doped with B) is in contact with an n-type semiconductor, (such as silicon is doped with P). Due to close contact, a limited extent of electrons (from n-type semiconductor) and positive holes (from p-type semiconductor) can cross the boundary or junction between the two type of semiconductors. However such migrations are very limited , because they tend to produce a separation of charge. e.g. When a +Ve hole leaves the p-type semiconductor, build up of – ve charge occurs, due to the presence of immobile B ions.

Construction of Solar PV Cell:

Solar PV cells are typically constructed using semiconductor materials, most commonly silicon. Here's a basic outline of the construction:

1. Silicon Wafers:

The core of a solar cell consists of thin slices or wafers made from high-purity crystalline silicon. These wafers are usually quite thin, typically less than 0.2 millimeters thick.

2. Doping:

The silicon wafers are doped with specific materials to create two distinct layers. The top layer is doped with a material that introduces extra electrons, giving it a negative charge (n-type), while the bottom layer is doped with a material that creates a deficit of electrons, resulting in a positive charge (p-type).

3. P-N Junction:

The interface between the n-type and p-type layers forms a p-n junction. This junction plays a critical role in the photovoltaic process.

4. Contacts:

Metal contacts are added to the top and bottom layers to collect the generated electrical current. These contacts are usually made of aluminum or copper.

5. Anti-Reflective Coating:

A thin anti-reflective coating is applied to the top surface of the cell to reduce reflection and enhance light absorption.

Working of Solar PV Cell:

The operation of a solar PV cell can be summarized in the following steps:

1. Light Absorption:

When sunlight (photons) strikes the surface of the solar cell, it excites electrons in the semiconductor material, allowing them to break free from their atomic bonds and creating electron-hole pairs.

2. Electron Migration:

The electric field created by the p-n junction within the cell causes the energized electrons to move toward the n-type layer, while the holes move toward the p-type layer. This movement generates an electric current.

3. Electric Current Collection:

Metal contacts on the top and bottom of the cell collect the electric current generated by the movement of electrons and holes.

4. External Circuit:

The collected electric current can be used to power electrical devices, charge batteries, or be fed into the electrical grid via an inverter.

Importance of Solar Cells:

Solar cells hold significant importance for several reasons:

1. Clean and Renewable Energy:

Solar energy is abundant and renewable, making it an eco-friendly alternative to fossil fuels. It reduces greenhouse gas emissions and mitigates climate change.

2. Energy Independence:

Solar power reduces reliance on non-renewable energy sources, contributing to energy independence for individuals, communities, and nations.

3. Reduced Electricity Costs:

Solar panels equipped with solar cells can generate electricity for homes, businesses, and industries, potentially leading to lower energy bills.

4. Off-Grid Power:

Solar cells can provide electricity in remote areas where traditional power infrastructure is unavailable or costly to install.

5. Sustainable Development:

Solar technology supports sustainable development goals by providing access to electricity for remote and underserved regions, improving living conditions and economic opportunities.

There are different types of solar cells, including:

First Generation Solar Cells:

- **Crystalline Silicon Solar Cells:**

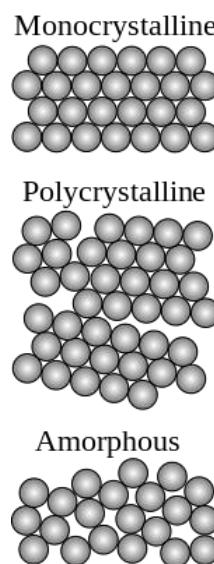
The first generation of solar cells, and still the most widely used, is based on crystalline silicon. There are two main types:

- **Monocrystalline Silicon Cells:**

These are made from single-crystal silicon, offering high efficiency but are more expensive to produce due to the complex manufacturing process.

- **Polycrystalline Silicon Cells:**

These are made from multiple crystalline silicon grains and are less efficient but more cost-effective.



- **Comparison of Monocrystalline and Polycrystalline solar cells**

Factor	Monocrystalline Solar Panels	Polycrystalline Solar Panels
Silicone Arrangement	One pure silicon crystal	Many silicon fragments melded together

Cost	More expensive	Less expensive
Appearance	Panels have black hue	Panels have blue hue
Efficiency	More efficient	Less efficient
Lifespan	25-40 years	20-35 years
Temperature Coefficient	Lower temperature coefficient, making them more efficient in heat	Higher temperature coefficient, making them less efficient in heat
	Monocrystalline solar panels are characterized by their black PV cells with rounded edges.	Polycrystalline solar panels have blue-hued PV cells with straight edges.

Advantages:

- Proven technology with a long track record of reliability.
- Relatively high efficiency.
- Suitable for a wide range of applications, from residential to utility-scale installations.

Disadvantages:

- Higher production costs compared to newer generations.
- Limited flexibility and aesthetics.

Second Generation Solar Cells:

Thin-Film Solar Cells:

The second generation introduced thin-film solar cell technologies, which use thinner semiconductor materials. Some common types include:

- **Amorphous Silicon (a-Si) Thin-Film:**

Offers flexibility and can be integrated into building materials, but has lower efficiency compared to crystalline silicon.

- **Cadmium Telluride (CdTe) Thin-Film:**

Known for its cost-effectiveness and reasonable efficiency, often used in large-scale installations.

- **Copper Indium Gallium Selenide (CIGS) Thin-Film:**

Offers good efficiency and flexibility, making it suitable for various applications.



Thin film Silicon laminates being installed onto a roof

Advantages:

- Lower production costs compared to crystalline silicon.
- Greater flexibility, enabling integration into various surfaces and applications.
- Good performance in low-light conditions.

Disadvantages:

- Generally lower efficiency compared to first-generation crystalline silicon cells.
- Potential concerns over the toxicity of materials like cadmium in CdTe cells.

Third Generation Solar Cells:

Third-generation solar cells represent emerging and innovative technologies aimed at improving efficiency and addressing some limitations of earlier generations. These technologies include:

1. Multijunction Solar Cells:

These use multiple layers of different semiconductors to capture a broader spectrum of sunlight, increasing efficiency. They are often used in space applications and concentrated photovoltaics.

2. Organic Photovoltaic (OPV) Cells:

OPV cells use organic materials as semiconductors. They are lightweight, flexible, and have the potential for low-cost production, but they are currently less efficient than traditional solar cells.

3. Perovskite Solar Cells:

Perovskite materials have gained attention for their high efficiency potential, low production costs, and ease of manufacturing. Research in perovskite solar cells is ongoing to improve stability and scalability.

4. Tandem Solar Cells:

These combine multiple solar cell technologies, such as silicon and perovskite, in a single device to increase efficiency while maintaining cost-effectiveness.

5. Quantum Dot Solar Cells:

Quantum dots, semiconductor nanocrystals, can be engineered to capture specific wavelengths of light, potentially increasing efficiency.

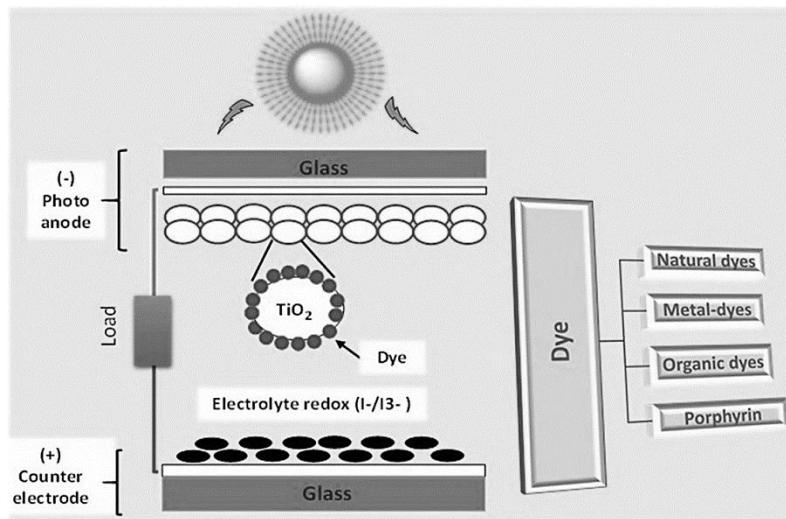
Third-generation solar cells are still in the research and development stage, and while they hold promise for higher efficiency and novel applications, they may not yet be as widely deployed as first and second-generation technologies due to various technical challenges and scalability issues. However, ongoing innovation in solar cell technology continues to drive advancements in the field.

Dye Sensitized solar cells (DSSCs):

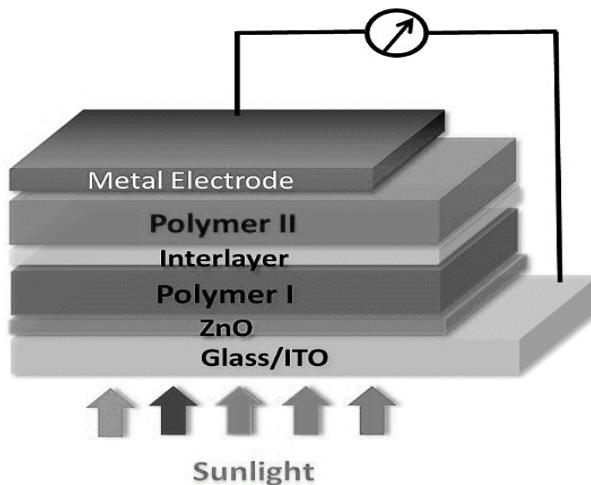
The dye sensitized solar cell (DSSC) follow the photosynthesis -the natural processes plants convert sunlight into energy- by sensitizing a nanocrystalline wide band gap semi-conductor film using natural or synthetic sensitizers. In dye sensitized solar cell DSSC charge separation is accomplished by kinetic competition like in photosynthesis leading to photovoltaic action.

A dye-sensitized solar cell consists of two conducting glass electrodes in a sandwich arrangement as shown in above figure 6. Each layer has a specific function in the cell. The glass electrodes are transparent which allows the light to pass through the cell. The tin dioxide coating is a transparent, conductive layer. The titanium dioxide (or any other nano materials and composites like ZnO, TiO₂-

graphene composites, etc) serves as a holding place for the dye. The dye molecules collect light and produce excited electrons which cause current in the cell. The iodide electrolyte layer acts as a source for electron replacement. The bottom conductive layer is coated with graphite so that light does not pass through the bottom layer.



Polymers in Photovoltaics (Polymer Solar Cells)



A polymer solar cell is a type of flexible solar cell made with polymers, large molecules with repeating structural units that produce electricity from sunlight by the photovoltaic effect. A polymer solar cell includes organic solar cells that are also called "plastic solar cells". They are one type of thin film solar cell, others include the currently more stable amorphous silicon solar cell. Polymer solar cell technology is relatively new and is currently being very actively researched by universities, national laboratories, and companies around the world.

Usually polymer solar cells consist of an electron- or hole-blocking layer on top of an indium tin oxide conductive glass followed by electron donor and an electron acceptor, a hole or electron blocking layer, and metal electrode on top.

Advantages of Polymers in Photovoltaics :

Polymer Photovoltaics are a type of flexible solar cell with a stable, thin-film semiconductor deposited on different types of plastic substrate.

- Polymer solar cells are lightweight compared to silicon-based devices and this is important for small autonomous sensors, easily disposable and low cost for fabricating
- The material is flexible and customizable at molecular level, and has lower potential for negative environmental impact.
- When stress is applied on the front glass, the polymer layer around the cell can influence laminate stiffness, creep and other aspects

Disadvantages :

- The serious disadvantages in using polymer photovoltaic is the efficiency of the best plastic devices is little more than 8%, whereas silicon solar panels can achieve up to 18%
- Currently, plastic photovoltaic is also relatively unstable toward photochemical degradation
- The lifetime of plastic photovoltaic currently doesn't come anywhere near that of silicon solar panels
- Despite the continuing advances in semiconducting polymers, the vast majority of solar cells still rely on inorganic materials.
- Polymer solar cells also suffer from environmental degradation owing the lack of effective protective coatings.

Solar cell efficiency & technology.

Solar cell efficiency refers to the percentage of sunlight that a solar cell can convert into electricity under standard test conditions. Higher efficiency means that a solar cell can generate more electricity from the same amount of sunlight, which is desirable for maximizing the energy output of a solar panel or system. Solar cell efficiency can vary depending on the technology used. Here are some key solar cell technologies and their typical efficiency ranges:

1. Crystalline Silicon (c-Si) Solar Cells:

- **Monocrystalline Silicon:** Typically has an efficiency range of 15% to 22%.
- **Polycrystalline Silicon:** Typically has an efficiency range of 13% to 16%.

Crystalline silicon solar cells, especially monocrystalline ones, are the most common and widely used solar cell technology. They have a proven track record of reliability and performance.

2. Thin-Film Solar Cells:

- **Amorphous Silicon (a-Si):** Efficiency ranges from 5% to 10%.
- **Cadmium Telluride (CdTe):** Efficiency ranges from 9% to 14%.
- **Copper Indium Gallium Selenide (CIGS):** Efficiency ranges from 10% to 22%.

Thin-film solar cells are known for their flexibility and lower manufacturing costs compared to crystalline silicon. While their efficiency is generally lower, they are used in various applications, including building-integrated photovoltaics (BIPV) and large-scale installations.

3. Perovskite Solar Cells:

Perovskite solar cells have shown remarkable progress in recent years. Laboratory efficiencies have reached over 25%, and some commercial products are achieving efficiencies in the 20% range. Perovskite cells are known for their potential to be highly efficient and cost-effective.

4. Multijunction Solar Cells:

These are often used in space applications and concentrated photovoltaics, where high efficiency is critical. Multijunction solar cells can achieve efficiencies above 40%.

5. Organic Photovoltaic (OPV) Cells:

OPV cells are still in the research and development stage, and their efficiencies typically range from 5% to 15%. They offer flexibility and the potential for low-cost production but are currently less efficient than other technologies.

6. Tandem Solar Cells:

Tandem solar cells combine different materials or technologies in a single device to achieve higher efficiencies. They can achieve efficiencies above 30%.

It's important to note that solar cell efficiency can vary based on factors like the quality of materials, manufacturing processes, and environmental conditions. Additionally, the efficiency of a solar cell is just one aspect of overall solar panel performance. Other factors, such as panel design, tracking systems, and maintenance, also play a role in determining the overall energy output of a solar installation.

Advancements in solar cell technology continue to push the boundaries of efficiency, with researchers and manufacturers constantly working to improve the performance of solar cells and make solar energy more accessible and cost-effective.

Fuel Cell Or Flow Battery

Fuel cell is an electrochemical cell that converts the chemical energy from a fuel into electricity through an electrochemical reaction. The first fuel cell were invented in 1838. All fuel cells consists of an anode, a cathode and an electrolyte, that allows positively charged hydrogen ions (protons) to move between the two sides of the fuel cell.

Flow battery or fuel cell :

Fuel cell is the cell in which materials (reactants, products, electrolytes) pass through the battery, which is simply an electrochemical cell that converts chemical energy into electrical energy.

- **Representation of Fuel Cell:**

Fuel | electrode | electrolyte | electrode | O₂

Fuel cell are classified on the basis of electrolyte used in it.

1. Alkaline fuel cell
2. Phosphoric Acid fuel cell
3. Molten carbonate fuel cell
4. Polymer electrolyte membrane fuel cell.
5. Solid oxide fuel cell.

A) **Phosphoric Acid Fuel Cell :**

Fuel :- Hydrocarbons containing hydrogen

Electrolyte :- Phosphoric Acid

Electrodes :- porous carbon or graphite

Catalysts :- Pt / Gold / Tantalum / Rhodium

Charge carrier :- H⁺ ions

Operating temperature :- 150 - 200°C.

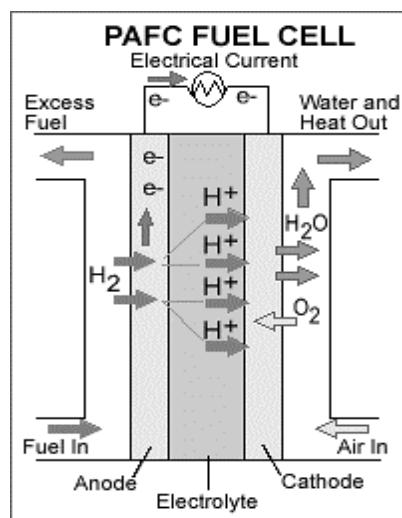
Fuel cell efficiency : 40 - 60%

Power output :- 20 to 200 kw

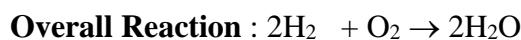
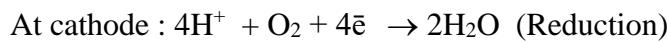
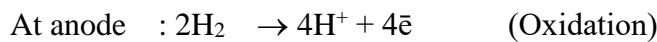
- Set up and working:**

In phosphoric acid fuel cell phosphoric acid is placed between the two electrodes. The electrodes are made up of porous carbon or graphite coated with finely divided platinum catalyst. Hydrogen gas generated from hydrocarbons is used as fuel where air is used as oxidant.

Oxidation of hydrogen gas takes place when it comes in contact with graphite or carbon porous electrode (anode). Positively charged hydrogen ions then migrate through the electrolyte from anode to cathode. Electrons generated at the cathode travel through an external circuit providing electric power and reach to the cathode. At cathode electrons, hydrogen ions and O₂ form water which is discharged from the cell.



The cell reaction can be represented as



- Advantages:**

- As the operating temperature of fuel cell is 150-200°C the expelled water can be converted to steam which is used for to drive the turbines, moisturisation, cleaning, sterilization, heating , atomization, humidification etc.
- Efficiency of fuel cell is 40-60%
- It gives useful waste heat for on site applications.

- Applications :**

PAFC is used in hostels, hospitals, office buildings and large vehicles.

- Limitations :**

- PAFC is less powerful than other fuel cells.
- PAFC's are expensive, because they require expensive catalyst.
- It has lower cell performance than PEMFC.
- At lower temperature, phosphoric acid is poor conductor.

B) Polymer Electrolyte membrane fuel cell [PEMFC] or Proton exchange membrane fuel cell.

These are also known as Ion exchange membrane fuel cell.

Fuel :- Hydrogen

Electrolyte :- Ion exchange polymer membrane (Nafion)

Electrode :- Carbon of Graphite

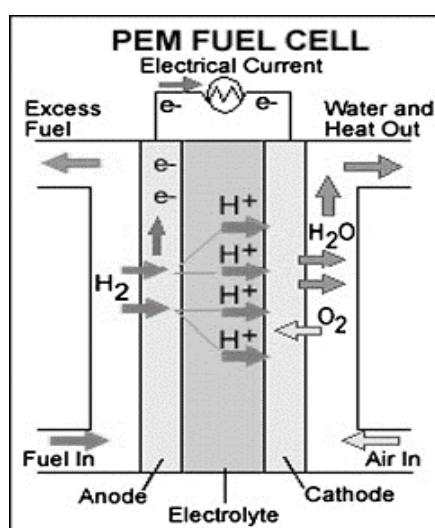
Catalyst :- Platinum

Charge carrier :- H^+

Operation temperature :- $80^{\circ}C$.

Fuel cell Efficiency :- 60%

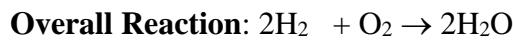
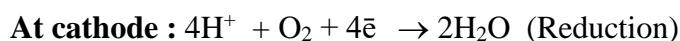
Power output :- 5-200 kw



In this cell electrolyte is a thin synthetic polymeric membrane (25-250 μm thick) which is an excellent conductor of hydrogen ions, known as **Nafion**. **Nafion** is a co-polymer of tetra fluoroethylene and vinyl ether.

Hydrogen is passed from the anode side while O₂ is passed from the cathode side, at a time. At anode hydrogen ions are formed with the liberation of electrons. Hydrogen ion enters the electrolyte. The electrons flow through the external circuit and reach to the cathode. The hydrogen ions migrate through the polymer electrolyte and recombines with the electrons and O₂ at cathode to produce water.

The cell reaction can be represented as



- **Advantages:**

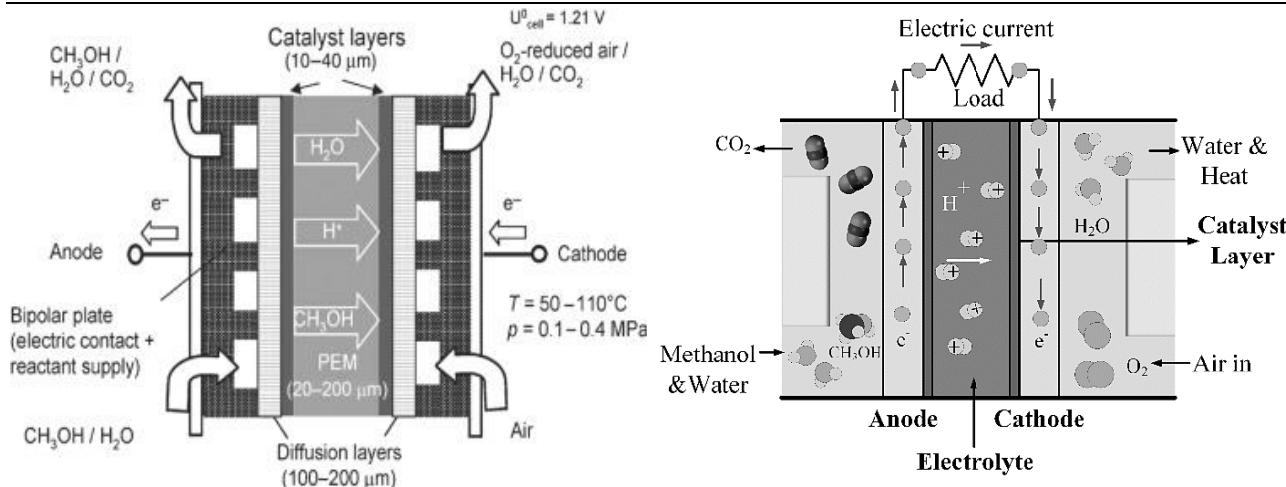
1. Cell has low weight and volume
2. Relatively it operate at low temperature
3. No corrosion of cell is takes place, as the electrolyte is solid polymer membrane.
4. Fuel cell efficiency is 60%

- Applications :**

- Used in cars and vehicles.
- Used for residential and office buildings
- Used in consumer electronics.

C) Direct Methanol Fuel Cell:

Construction:



1. Anode:

The anode is the negative electrode of the DMFC. It is typically made of a porous material, such as carbon paper or cloth, coated with a catalyst, often based on platinum or other noble metals. This catalyst facilitates the electrochemical oxidation of methanol.

2. Cathode:

The cathode is the positive electrode of the DMFC. Like the anode, it is also made of a porous material coated with a catalyst, usually platinum or similar materials. The cathode facilitates the electrochemical reduction of oxygen.

3. Proton Exchange Membrane (PEM):

The anode and cathode are separated by a proton exchange membrane, which is a crucial component of the DMFC. The PEM is typically made of a polymer electrolyte material, like Nafion, that allows protons (H⁺ ions) to pass through while blocking the passage of electrons and other molecules. The PEM also serves to keep the fuel and oxidizer separated.

4. Fuel Supply:

The DMFC requires a supply of liquid methanol, typically stored in a reservoir. A pump or capillary action can deliver methanol to the anode.

5. Oxygen Supply:

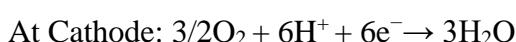
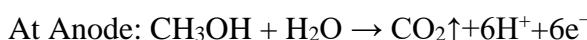
Oxygen or air is supplied to the cathode, usually from the surrounding environment.

6. Electrical Connections:

Electrical connections are made to the anode and cathode to collect the generated electrical current.

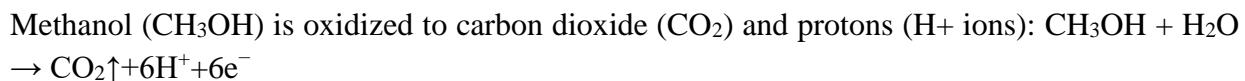
• Working:

Reaction:



1. Methanol Oxidation at Anode:

- Methanol from the fuel reservoir is supplied to the anode.
- At the anode, methanol undergoes electrochemical oxidation, resulting in the following chemical reactions:



Electrons (e^-) are released during this process, creating an electrical current that flows through an external circuit.

2. Proton Transport Through PEM:

- Protons (H^+ ions) generated at the anode move through the proton exchange membrane (PEM) toward the cathode due to its selective permeability to protons.

3. Oxygen Reduction at Cathode:

- Oxygen (O_2) from the air or an oxygen supply is provided to the cathode.
- At the cathode, oxygen undergoes electrochemical reduction, combining with protons from the PEM and electrons from the external circuit to form water (H_2O): $1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$
- This reaction consumes the protons that have traveled through the PEM.

4. Generation of Electrical Energy:

- As protons move through the PEM from the anode to the cathode and electrons flow through the external circuit from the anode to the cathode, electrical current is produced.
- The flow of electrons and protons through their respective pathways generates electrical power that can be used to perform work, such as powering electronic devices or providing backup power.

This process results in the generation of electrical energy, along with water and carbon dioxide as byproducts.

A Direct Methanol Fuel Cell (DMFC) is a type of fuel cell that generates electricity through the electrochemical reaction between methanol and oxygen. Like other fuel cells, DMFCs are highly efficient and produce electricity with minimal emissions. They have several unique characteristics and applications:

1. Operation:

DMFCs work by directly oxidizing methanol at the anode (negative electrode) and reducing oxygen at the cathode (positive electrode). This electrochemical process produces electricity, water, and carbon dioxide as byproducts.

2. Methanol as Fuel:

Unlike hydrogen fuel cells, which require pure hydrogen as fuel, DMFCs can use methanol, a liquid fuel, as their energy source. This makes them more practical for certain applications, as methanol is easier to store and transport than hydrogen.

3. Efficiency:

DMFCs are known for their high energy conversion efficiency, typically ranging from 30% to 40%. This efficiency makes them suitable for various portable and small-scale applications, such as powering electronic devices and backup power systems.

4. Applications:**• Portable Electronics:**

DMFCs have been used to power laptops, smartphones, and other portable electronic devices. They offer longer runtimes compared to traditional batteries and can be refueled quickly by adding

methanol.

- **Backup Power:**

DMFCs are used as backup power sources for critical infrastructure, such as data centers and telecommunications equipment. They provide reliable power during grid outages.

- **Military and Defense:**

DMFCs are used in military applications for portable power generation in remote locations and for soldier-worn equipment.

- **Unmanned Aerial Vehicles (UAVs):**

DMFCs are considered for UAVs, where long flight durations and high energy density are essential.

5. Challenges:

Despite their advantages, DMFCs also face challenges, such as methanol crossover, which reduces their efficiency, and the need for methanol storage and transportation solutions. Additionally, the cost of platinum-based catalysts used in DMFCs has been a limiting factor in commercial adoption.

6. Research and Development:

Researchers continue to work on improving DMFCs by developing more efficient catalysts, membrane materials, and system designs. Non-platinum catalysts, for instance, are being explored to reduce costs and increase sustainability.

Overall, DMFCs offer a promising alternative to traditional batteries and have found niche applications where their unique characteristics, such as their ability to use liquid methanol fuel, make them a viable power source.

Advantages of DMFCs:

1. High energy density: Methanol has a high energy density, making it a compact and efficient fuel source.
2. Ease of fuel storage and transport: Methanol is a liquid at room temperature and can be stored and transported more easily than hydrogen, which is used in some other types of fuel cells.
3. Low emissions: DMFCs produce fewer pollutants compared to traditional internal combustion engines, as their primary byproduct is water.
4. Quiet operation: DMFCs are quiet in operation because they lack moving parts and combustion processes.

QUESTIONS

1. Describe solar cells. (3M)
2. Differentiate between monocrystalline and polycrystalline solar cells. (3M)
3. What is fuel cell ? How fuel cell is represented ? Explain Phosphoric acid fuel cell. (5M)
4. What is fuel cell ? Explain Polymer electrolyte membrane fuel cell. (5M)
5. Explain the construction and working of Phosphoric acid fuel cell with relevant reactions taking place. What are its advantages and applications ? (5M)
6. Explain the construction and working of Polymer electrolyte membrane fuel cell with relevant reactions taking place. What are its advantages and applications? (5M)
7. Explain the construction and working of **DMFCs** with relevant reactions taking place. What are its advantages and applications? (5M)



Flexible Electronic & Optoelectronic Materials

Polymers: Addition polymerization, Condensation polymerization, thermo softening, thermosetting polymers, Tg & Tm of polymer.

Conjugated polymers –Factors influencing charge transport – structural features - defects, molecular weight, crystalline/amorphous nature, doping- oxidative and reductive. Synthesis, properties and applications of polyaniline, polythiophene and polypyrrole, polycarbonate.

Electroluminescence- OLED materials– emitters- charge transfer complexes, metal chelates, Polycyclic aromatic oligomers, Liquid crystalline polymers- classification of liquid crystals, chemical constitution, stability and applications.

CO : Make use of basic knowledge of Flexible electronic materials & Optoelectronic materials with their applications..

■ Polymers :

The word polymer is derived from the two Greek words (poly – many & mer – unit or part.)

Different terms:

1. Polymer :

A polymer is a large molecule which is formed by repeated linking of small molecules called monomers.

e.g. polyethylene, polypropylene, Nylon 6:6, phenol formaldehyde, melamine formaldehyde, epoxy resin, polyvinyl chloride, poly methyl methacrylate etc.

2. Monomer :

Small and simple molecule from which polymer is made called monomer. Monomers are of different types.

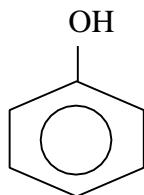
1. Bifunctional Monomers :

These monomers form straight chain polymers. (F = 2)

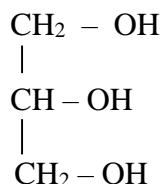
- i) $\text{CH}_2 = \text{CH}_2$ (Ethylene)
- ii) $\text{CH}_2 = \text{CH}$
|
 CH_3 (Propylene)
- iii) $\text{HOOC} - (\text{CH}_2)_4 - \text{COOH}$ (Adipic Acid)
- iv) $\text{CH}_2 - \text{OH}$
|
 $\text{CH}_2 - \text{OH}$ (Ethylene Glycol)

- 2. Trifunctional Monomers :** These monomers are having three reactive sites or bonding sites and forms cross linked polymers. ($F = 3$) e.g.

a) Phenol



b) Glycerol



- 3. Tetrafunctional Monomers :** These monomers are having four reactive sites or bonding sites and forms three dimensional network structure (cross linked) of polymers. ($F = 4$) e.g.

a) Acetylene : $\text{CH} \equiv \text{CH}$

b) 1-3 butadiene : $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$ or

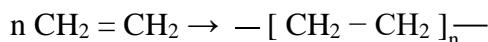
In order to facilitate the polymerization reaction monomer must have at least two reactive sites or bonding sites.

3. Functionality :

Number of reactive sites or bonding sites present in the monomer called functionality.

4. Degree of Polymerization :

Number of repeating unit in the chain is called degree of polymerization. e.g.



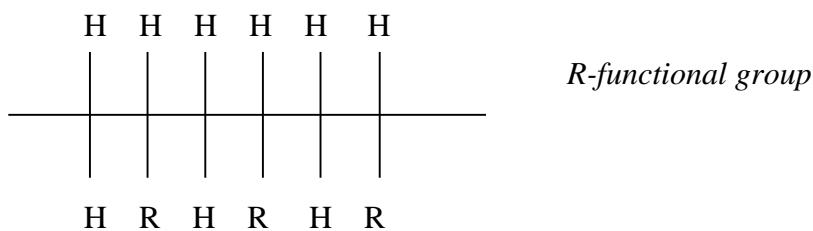
(ethylene) (Polyethylene) n - is the repeating unit.

Polymers with high degree of polymerization are called **high polymers** or **macromolecules** whereas the polymers with low degree of polymerization are called **oligopolymers** (Oligo \rightarrow few).

5. Tacticity :

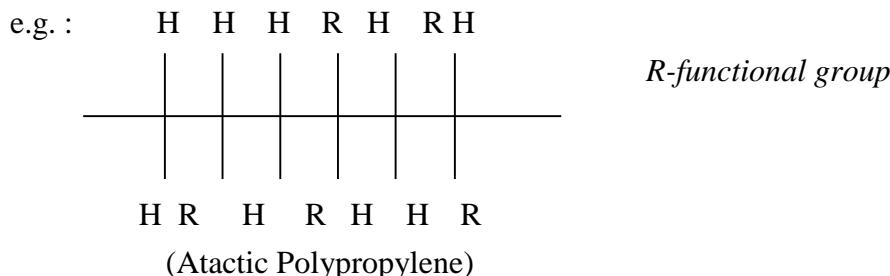
Orientation of monomeric units in a polymer molecule chain with respect to the main chain is called **Tacticity**. The difference in configuration (tacticity) do affect their physical properties.

- i) **Isotactic Polymers** : When the functional groups are, all on the *same side of the chain* is called isotactic polymers.

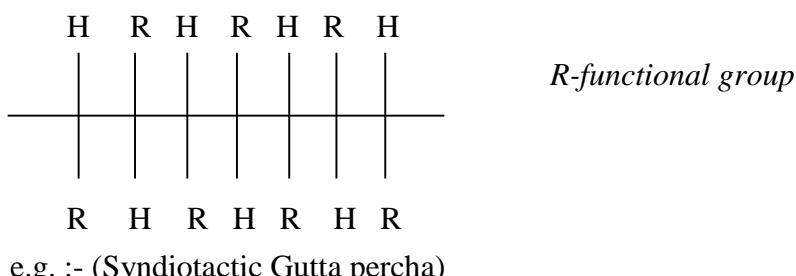


e.g. :- Polyethylene

- ii) **Actactic Polymers** : When the functional groups are arranged *randomly around the main chain*, is called as Atactic polymers.



- iii) **Syndiotactic polymers:** When the functional groups are arranged in an *alternating fashion* in the polymer chain is called as syndiotactic polymers.



6. Crystallinity:

The extent to which polymer molecules are arranged in an ordered pattern is known as Crystallinity. On the basis of arrangement of molecules in the polymers, polymers are classified as,

- a) Crystalline polymers & amorphous polymers.
- a) **Crystalline polymers:** These polymers are hard, rigid, strong, brittle and have sharp melting points.
They have high molecular weight, high tensile strength and mechanical strength.
- b) **Amorphous Polymers :** These polymers are soft, flexible and mechanically weak.
They have low softening temperature.

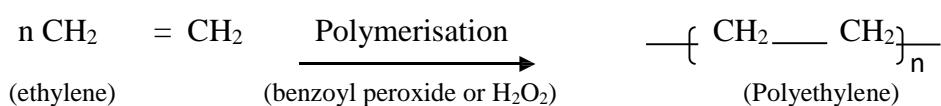
7. Polymerization : Definition:

Union of two or more simpler & smaller molecules of similar or different types with or without elimination of small molecules such as H_2O , HCl etc. resulting in the formation of new C - C linkages.

• Polymerization is of two types.

- a) **Addition or chain Polymerization :** This is the polymerization reaction in which polymer is formed from the identical monomers without the elimination of small molecules such as H_2O , HCl etc. Polymers formed by addition polymerization reaction are called **addition or chain polymers**.

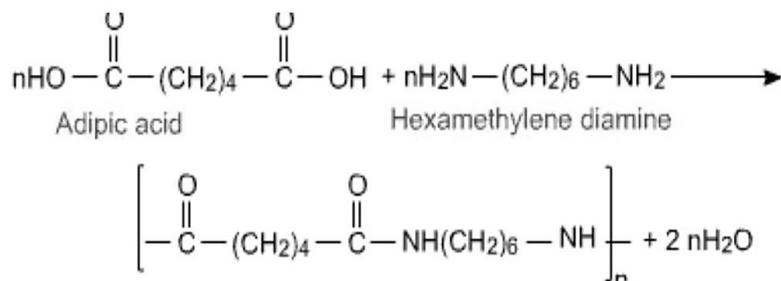
e.g. Formation of Polyethylene form ethylene monomers.



Other examples are : Polyvinyl chloride, Polypropylene, Polymethylmethacrylate etc.

- b) **Condensation or step polymerization :** This is the polymerization reaction in which polymer is formed from the two different monomers with the elimination of small molecules such as H_2O , HCl etc. Polymers formed by condensation polymerization reaction are called **condensation or Step polymers**.

e.g. Preparation of Nylon 6:6 form Hexamethylene diamine and adipic acid.



Other examples are : Phenol formaldehyde, Melamine formaldehyde, Urea formaldehyde, Epoxy resin , Teflon, Nylon 6:10 etc.

- **Difference between addition and condensation polymerization.**

Addition polymerization		Condensation polymerization	
1	It is fast and exothermic reaction.	1	It is slow and endothermic reaction
2	Byproducts are not formed	2	Byproducts are formed.
3	Polymer is an exact multiple of monomer	3	Polymer is not an exact multiple of monomer.
4	End groups are inactive or dead	4	End groups are always active.
5	Catalyst is needed for polymerization reaction	5	Catalyst is not needed for polymerization reaction
6	It involves three different steps :- Initiation, propagation & termination	6	It involves no initiation, propagation and termination

Glass Transition Temperature (T_g) :

The temperature below which the polymer becomes hard, brittle and glassy above which it is softer and flexible is known as glass transition temperature.

- **Definition :**

The hard and brittle state is the glassy state and soft flexible state is the viscoelastic state. If the viscoelastic state of polymer is heated further, the polymer becomes a viscous liquid and can flow. This state is known as viscofluid state.



1. Below T_g molecules don't have movements within the polymer chain.
2. Above T_g molecules move locally therefore they have flexibility or stress transfer property.
3. Above T_m (melting temperature) molecules acquire kinetic energy and moves from one position to another position therefore they have flexibility or stress transfer property.

Factors affecting T_g Value :

- a) **Crystallinity** : Higher the Crystallinity , higher is the T_g value.
- b) **Molecular weight** : Higher the molecular weight, greater is the T_g value.
- c) **Side groups on chain** : Presence of bulky groups on polymer chain increases the T_g value.
- d) **Cross linking of polymer Chains** : Higher the cross linking of polymer chains greater is the T_g value.
- e) **Plasticizer effect** : Addition of plasticizer of polymer decreases the T_g value.
- f) **Coiled polymer chains** :e.g Rubber . Polymer with spring like structure having lower T_g value.
- g) **Force of attraction between chains** :Polymers having stronger force of intermolecular attraction have greater T_g value.

Few of the polymers are given along with their T_g values.

Polymer	T _g °C	T _m °C
Polyethylene	-125	115
Polypropylene	-18	175
Polystyrene	100	240
Polyvinyl Chloride	80	212
Polyacrylonitrile	97	241

Plastics :

The word plastic is derived from the Greek word ‘Plastikos’. Plastikos means fit for moulding. Plastic has plasticity property. Plasticity is the property by virtue of which material undergoes permanent deformation when it is subjected to heavy stress or pressure.

Characteristic Properties of Plastic :

- 1) Plastic is resistant to corrosion
- 2) Plastic is resistant to atmospheric O₂, O₃ etc.
- 3) Bad conductor of heat and electricity
- 4) Resistant to acid, alkalis and solvents
- 5) Resistant to Oil
- 6) Plastic increases the decorative value
- 7) Plastics are 4 to 6 times lighter than metals
- 8) Plastics have excellent mechanical strength
- 9) They have high refractive index.
- 10) They have low coefficient of expansion
- 11) Can be moulded, drilled and mechanized
- 12) Can not attacked by moths, fungi, insects and vermin
- 13) Specific gravity of plastic lies from 1 to 2.4
- 14) On the basis of thermal behavior the polymers are classified into thermosoftening and thermosetting plastics.

Difference between Thermosetting and Thermosoftening Plastic :

Thermo softening plastic/Thermoplasts		Thermosetting plastic	
a	These polymers are formed by addition polymerization	a	These polymers are formed by condensation polymerization
b	They consists of long chain polymers with negligible cross links. M- M- M- M- M- M-	b	They have three dimensional structure -M- M- M- M- M- M- -M- M- M- M- M- M- -M- M- M- M- M- M- -M- M- M- M- M- M-
c	They can be softened on heating	c	They cannot be softened on heating.
d	They can be reshaped and reused	d	They cannot be reshaped and reused.
e	They are soft and weak	e	They are hard and brittle
f	They can be reclaimed from the waste	f	They cannot be reclaimed form the waste.
g	They are soluble in organic solvents	g	They are insoluble in organic solvents.
h	e.g. polyethylene, PVC, polypropylene, PMMA etc	h	e.g. Bakelite, Melamine formaldehyde, urea formaldehyde, epoxy resin etc.

Polymerization Mechanism :

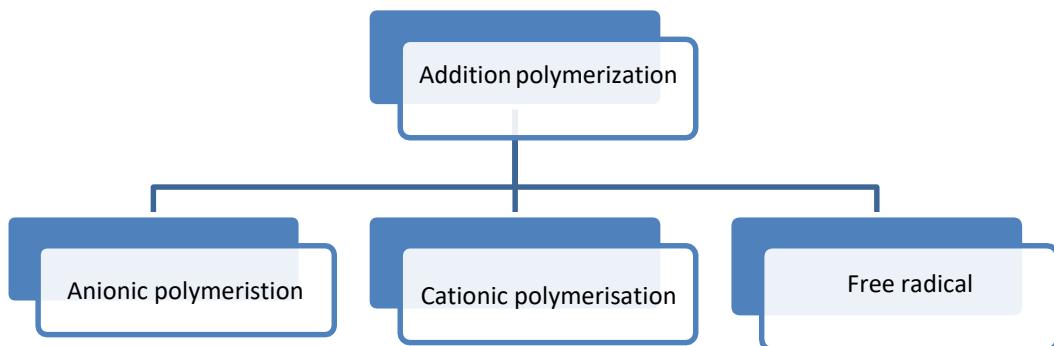
Actually there are three different types of polymerization reactions, by using which we can prepare the various types of polymers.

- 1) Addition or chain polymerization
- 2) Condensation or step polymerization
- 3) Ring opening polymerization

1. Addition or chain polymerisation mechanism:

Characteristic properties of Addition or chain polymerisation reaction :

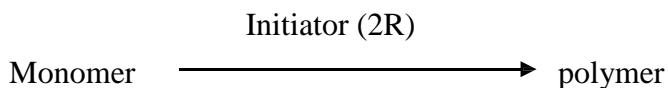
- a) It is fast and exothermic reaction.
- b) Byproducts are not formed
- c) Polymer is an exact multiple of monomer
- d) End groups are inactive or dead
- e) Catalyst is needed for polymerization reaction
- f) It involves three different steps :- Initiation, propagation & termination



- Free radical addition polymerization mechanism :

Formation of polymer is takes place in the presence of free radical. *Any molecule containing one or more unpaired electrons in its outermost orbital is called free radical. These molecules are chemically reactive and are highly unstable. Free radicals are generally represented by superscript dot.*

In free radical addition polymerization mechanism,



1. Initiation :

First of all the Initiator undergoes decomposition either in the presence of light , heat, pressure or catalyst and forms initiator free radicals. Initiator free radical then attacks the double bond of the monomer to form monomer free radical.

2. Propagation :

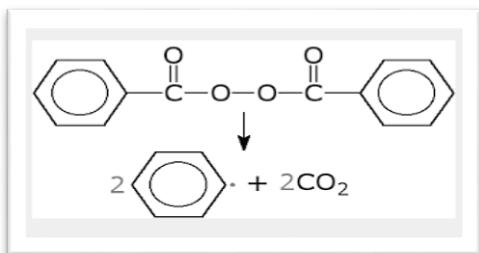
(Successive addition of monomer to the system): Due to the addition of monomers to the system a long chain of polymer is formed.

3. Termination:

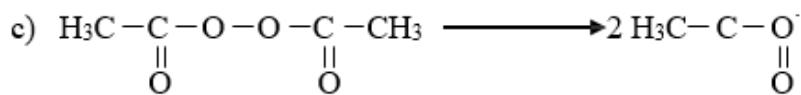
Finally the long chain of polymer is being terminated by using the various methods.

- **Decomposition of Initiators**

- a) Benzoyl peroxide

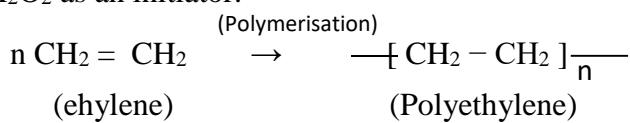


(Hydrogen Peroxide)

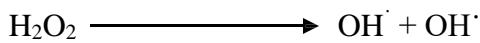


(Acetone Peroxide)

- Let us see the formation of polyethylene from ethylene monomers by using H_2O_2 as an initiator.

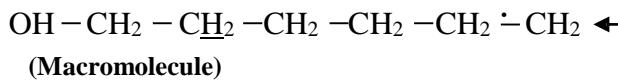
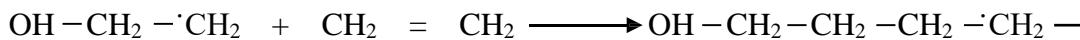


i. Initiation:



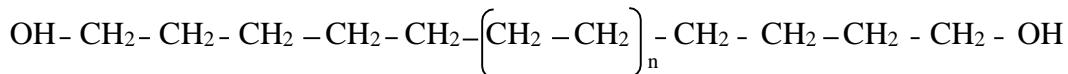
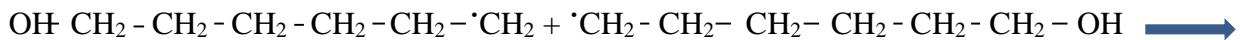
(Monomer free radical)

ii. **Propagation**(Successive addition of monomer to the system):

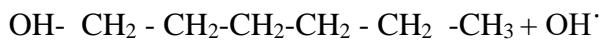
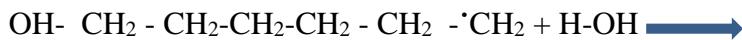


iii. **Termination :**

a) **Termination of chain by combination of monomer free radical**



b) **Termination of chain by adding water**



[Unlike polyethylene, *polypropylene*, *polyvinyl chloride*, *polystyrene* can be prepared by using different type of initiators.]

Conjugated polymers-factors influencing charge transport

Conjugated polymers are a class of materials known for their unique electronic properties, making them useful in various applications, including organic electronics and photovoltaics.

- **Factors influencing charge transport in conjugated polymers:**

- 1. Conjugation Length:**

Longer chains of conjugated units typically enhance charge transport. This extended conjugation allows for more delocalized π -electron systems which promote efficient electron or hole mobility.

- 2. Crystal Structure:**

The arrangement of polymer chains in a crystalline structure can facilitate charge transport. Crystalline regions provide well-defined pathways for charge carriers, reducing scattering and enhancing mobility.

- 3. Doping:**

Doping with electron-rich (n-doping) or electron-deficient (p-doping) molecules can significantly impact charge transport by introducing extra charge carriers or creating charge traps. The choice of dopant and doping level can tune the material's conductivity.

- 4. Temperature:**

Charge mobility in conjugated polymers is temperature-dependent. Typically, higher temperatures increase mobility by providing more thermal energy to overcome energy barriers.

- 5. Polymer Morphology:**

The organization of polymer chains, such as the degree of order or disorder in the material, can influence charge transport. Well-ordered structures often lead to higher mobility.

6. Defects and Impurities:

The presence of defects or impurities within the polymer structure can hinder charge transport by trapping charge carriers or disrupting the conjugation pathway.

7. Dielectric Environment:

The dielectric constant of the surrounding environment can impact charge transport. Higher dielectric constants tend to reduce the Coulombic interactions between charge carriers, potentially improving mobility.

8. Chemical Structure:

The specific chemical structure of the conjugated polymer plays a crucial role. The choice of monomers, side chains, and substituents can affect the bandgap, energy levels, and overall charge transport properties.

9. Oxidation and Aging:

Conjugated polymers are sensitive to oxidation and aging, which can degrade their charge transport properties over time.

10. Device Architecture:

The design of the device in which the conjugated polymer is used also matters. For example, the choice of electrodes and interfaces can affect charge injection and extraction processes. Understanding and optimizing these factors are essential for tailoring the charge transport properties of conjugated polymers for specific applications, such as organic solar cells, organic light-emitting diodes (OLEDs), and organic field-effect transistors (OFETs).

Structural features of Conjugated polymers

Conjugated polymers are a unique class of organic materials with specific structural features that give rise to their exceptional electronic and optical properties.

Here are some key structural features of conjugated polymers.

1. Conjugation:

Conjugated polymers are characterized by a series of alternating single and double bonds along the polymer backbone. This delocalized π -electron system allows for the efficient movement of charge carriers, resulting in semiconducting or conducting behavior.

2. Polymeric Backbone:

Conjugated polymers consist of a long, repeating chain of monomer units linked together through covalent bonds. The structure of the polymer backbone can vary depending on the specific polymer, but it typically contains alternating single and double bonds.

3. Aromatic Rings:

Many conjugated polymers incorporate aromatic rings (such as benzene or thiophene rings) as part of their monomer units. These rings contribute to the conjugation and stability of the π -electron system.

4. Side Chains:

Conjugated polymers often have side chains or substituents attached to the polymer backbone. These side chains can influence the solubility, processability, and physical properties of the polymer. They can also affect the polymer's ability to form ordered structures.

5. Heteroatoms:

Some conjugated polymers contain heteroatoms (such as oxygen, sulfur, or nitrogen) within their monomer units. These heteroatoms can modify the electronic properties of the polymer and introduce new energy levels in the electronic band structure.

6. Regioregularity:

The arrangement of monomer units along the polymer backbone can be either regular (head-to-tail, known as 1,2-addition) or irregular (head-to-head or tail-to-tail, known as 1,4-addition). Regioregularity can significantly impact the polymer's electronic properties and charge transport behavior.

7. Polydispersity:

The distribution of chain lengths in a conjugated polymer sample can vary, leading to polydispersity. Narrower polydispersity can result in more consistent properties and improved performance in electronic devices.

8. Conformational Flexibility:

Conjugated polymers often exhibit some degree of conformational flexibility, allowing them to adopt different conformations in solution or in solid-state films. This flexibility can influence the packing and ordering of polymer chains.

9. Planarity:

To maximize conjugation, many conjugated polymers adopt a planar or nearly planar conformation. This planarity is essential for efficient charge carrier transport along the polymer backbone. These structural features collectively determine the electronic band structure, optical absorption, charge mobility, and other properties of conjugated polymers. Tailoring these features through chemical design and synthesis is essential for optimizing the performance of conjugated polymers in various applications, such as organic electronics, photovoltaics, and light-emitting devices.

• Molecular weight of conjugated polymers

The molecular weight of conjugated polymers can vary widely depending on the specific polymer and its intended application. Conjugated polymers are typically characterized by their degree of polymerization, which refers to the number of repeating monomer units in the polymer chain. The molecular weight of a conjugated polymer can be calculated by multiplying the degree of polymerization (n) by the molecular weight of a single monomer unit.

The formula for calculating the molecular weight (M_w) of a conjugated polymer is as follows:

$$M_w = n * M_{\text{monomer}}$$

Where:

M_w is the molecular weight of the polymer.

n is the degree of polymerization, indicating the number of monomer units in the polymer chain.

M_{monomer} is the molecular weight of a single monomer unit.

The molecular weight of the monomer unit will depend on the specific chemistry of the conjugated polymer.

For example, in the case of polythiophene, the molecular weight of the monomer unit would be the sum of the atomic weights of the individual atoms in the repeating thiophene ring.

It's important to note that the molecular weight of conjugated polymers can vary significantly depending on the synthesis method, reaction conditions, and the desired properties of the material.

In some cases, researchers may target specific molecular weight ranges to optimize the performance of the polymer in electronic devices or other applications.

Crystalline /Amorphous nature of polymers :

Polymers can exist in both crystalline and amorphous forms, and the nature of a polymer's structure is influenced by factors such as its chemical composition, processing conditions, and cooling rate.

Crystalline Polymers:

1. Ordered Structure:

Crystalline polymers have a highly ordered molecular structure. The polymer chains align in a regular, repeating pattern, forming well-defined crystalline regions.

2. Sharp Melting Point:

Crystalline polymers typically exhibit a sharp and distinct melting point because the ordered arrangement of molecules breaks down when the polymer transitions from the solid to the liquid state.

3. Higher Density:

Due to their close packing and ordered structure, crystalline polymers tend to have higher densities compared to amorphous polymers of the same chemical composition.

4. Improved Mechanical Properties:

The ordered structure in crystalline polymers contributes to improved mechanical properties, such as stiffness, strength, and durability. This makes them suitable for applications where structural integrity is critical.

5. Transparency:

Some crystalline polymers can be transparent if the size of the crystalline regions is smaller than the wavelength of visible light.

Amorphous Polymers:

1. Random Structure:

Amorphous polymers lack long-range molecular order. The polymer chains are tangled and have a random arrangement, resulting in an absence of well-defined crystalline regions.

2. Glass Transition:

Instead of a sharp melting point, amorphous polymers undergo a glass transition when heated. At this transition temperature (T_g), the polymer becomes rubbery and transitions from a glassy to a more flexible state.

3. Lower Density:

Amorphous polymers generally have lower densities than crystalline polymers with the same chemical composition because of their less dense, disordered structure.

4. Improved Transparency:

Many amorphous polymers are transparent due to the absence of large, ordered crystalline regions. This transparency makes them suitable for applications like clear plastics and packaging materials.

5. Toughness:

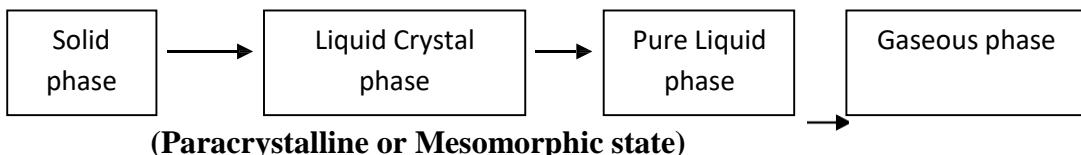
Amorphous polymers often exhibit excellent toughness and impact resistance, making them valuable in applications requiring flexibility and durability.

It's important to note that most polymers fall somewhere on a spectrum between completely crystalline and completely amorphous. The degree of crystallinity or amorphousness can be controlled through processing techniques, such as cooling rate during solidification or annealing, allowing for the tailoring of polymer properties to meet specific application requirements.

Liquid crystalline polymers:

- It is liquid crystal polymer.

As we know that there are four state of matters : Solid ,liquid, gaseous and plasma.

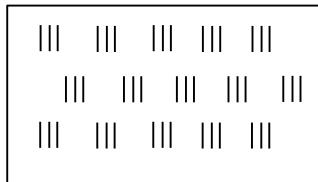


e.g :p-Azoxyaniline forms liquid crystal phase at 50°C and gets converted into pure liquid at 85°C .

Generally we says that when the solid phase is heated it gets directly converted into pure liquid phase but fact is that prior getting the pure liquid phase we get the liquid crystals. This is observed not only in solids but also observed in polymers that's why it is known as liquid Crystal polymers. This liquid crystal phase is known as *Paracrystalline or Mesomorphic state*. In this state no. of molecules are present which are thin and long.

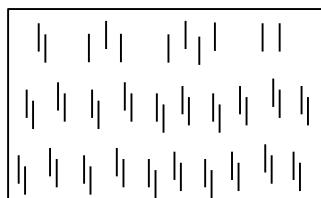
On the basis of the **arrangement of molecules** present in the liquid crystal polymer, they are classified as

1. Smectic liquid crystal polymer:



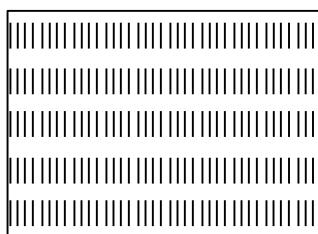
Oriented, parallel with periodicity but no lateral order.

2. Nematic liquid crystal polymer :



Oriented, parallel but no periodicity and no lateral order.

3. Cholesteric liquid crystal polymers



Molecules with orientation and periodicity in planes.

Polymers which have tendency to align their chains parallel over a long distance, prior to the crystallization from their melt or solution are called **liquid crystal polymers**. Thin and long molecules are present in the liquid crystal polymers.

On the basis of formation the liquid crystals are classified as :

a) **Lyotropic liquid crystal polymer :**

Polymers which have tendency to align their chains parallel over a long distance prior to the crystallization from their **solution** are called lyotropic liquid crystal polymers. e.g. : **Kevlar**.

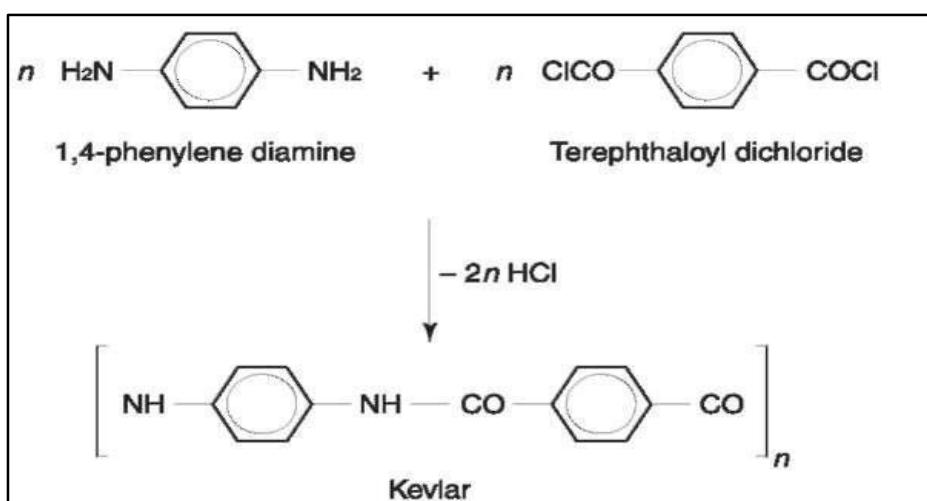
b) **Thermo tropic liquid crystal polymer :**

Polymers which have tendency to align their chain parallel over a long distance prior to the crystallization from their **melt** are called thermo tropic liquid crystal polymers.

e.g. :- Victra, Victex, xyder etc.

Preparation of KEVLAR :

It is prepared by treating terephthalic acid dichloride with 1, 4 diaminobenzene.



Properties :

1. Exceptionally strong (5 times stronger than steel)
2. It is very tough
3. It is thermally stable
4. It has high melting point, but can be easily moulded.
5. It has very high tensile strength.
6. High crystallinity
7. Have higher Tg value
8. Light in weight.

Applications :

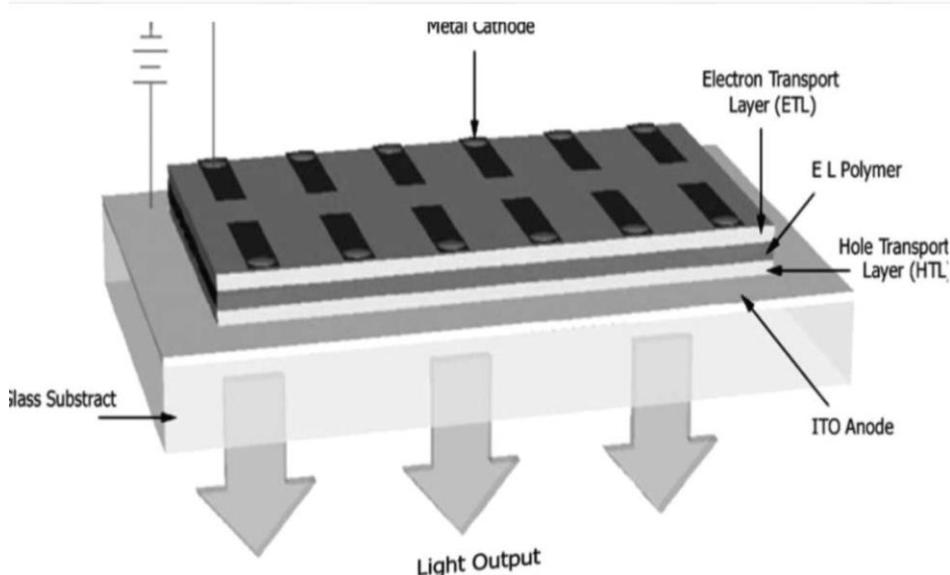
1. Used for car parts
2. Used for ropes and cables.
3. Used for making helmets
4. Used for optical fibers in landline communication
5. Used for puncture resistant tyres.

Electroluminescent Polymer :

Different types of organic polymeric materials act as self emitting device of high brightness, high efficiency, high speed response etc.

The material which shows **electroluminescence**, is called as *electroluminescent material*. The property in which a material produces bright light of different colors when stimulated electronically is known as electroluminescence.

Construction and Working :



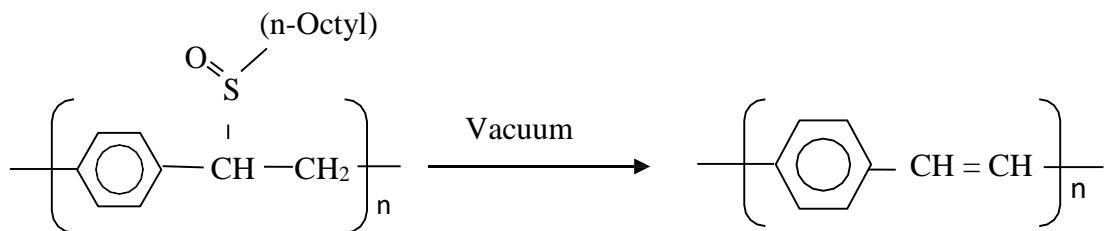
The organic electroluminescent device consists of a transparent anode, hole transport layer , emitter layer of organic polymeric material and a cathode which is made up of either from A1 or Mg alloy stacked upon a glass support.

During its working anode injects a hole towards hole transport layer and an electron is injected by cathode layer into the emitter layer. Then the hole and electron recombine in the emitter layer to excite the emitter layer which results in emission of light, during the return of excited electrons to ground state.

e.g. :- Poly (paraphenylene vinylene) i.e. PPV

PPV is used as mixture with (6, 6) phenyl C₆₀ butyric acid methyl ester (PCBM) for applications.

PPV is prepared by heating the polymer poly (α -n-Octyl sulphanyl paraphenylene ethylene) in vacuum. Elimination of n-Octylthiol introduces the double bonds in the chain.



Properties :

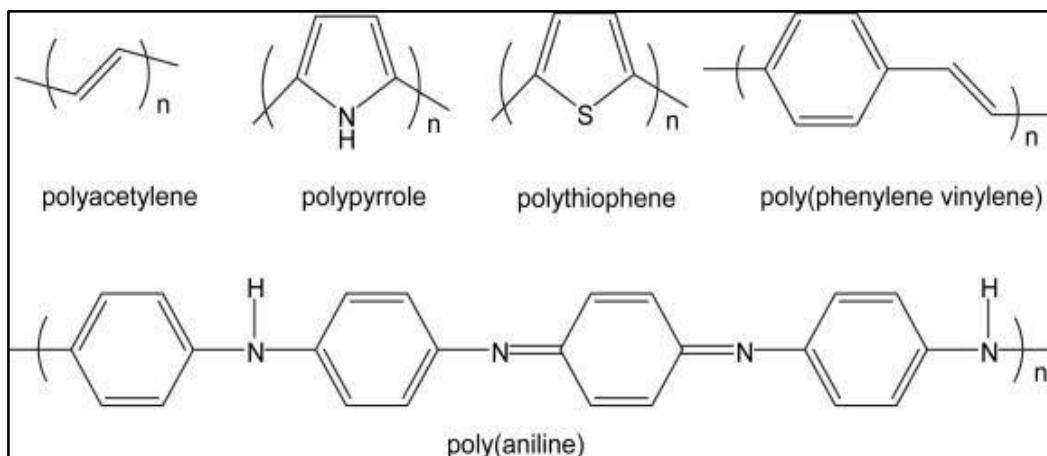
1. They are thin, flexible and light weight

2. Highly resistant to aging and atmospheric effects.
3. Perform well under humid conditions.
4. Generate low heat during its working
5. Resistant to heat, impact and vibration
6. Lower power consumption
7. It has long life
8. It gives green yellow fluorescence when an electric field is applied.
9. Conductivity of electroluminescent material is low (10^{-13} s/cm) Siemen/cm.
10. It is diamagnetic material.

Applications :

1. Used in electroluminescent night lamp.
2. Used in flat panel displays (mobile phone displays, computer screen, television screen etc.)
3. Used for theatre and assembly hall decoration.
4. Also used in photo voltaic cells
5. Light stripes are used for decorating buildings.

Conducting Polymer



CONDUCTING POLYMER Until 1960, all organic polymers were used in electrical, electronic and other applications as insulations.

The idea that polymers can also conduct electricity as good as metal was discovered accidentally at the plastic research laboratory of BASF, Germany in 1977. A chemist by the name shirakawa, accidentally added a catalyst 1000 times more than the required amount during the polymerization of acetylene, which resulted in a conducting polyacetylene.

- **There are two different types of conducting polymers.**

- a) **Extrinsically conducting polymers :**

An extrinsically conducting polymer materials are prepared by mixing conducting fillers like metal fibers, metal oxides, carbon black with insulating polymers. These are also called conductive element filled polymers.

b) Intrinsically conducting polymers :

These are the polymeric materials which can conduct electricity by their own.

Most of the polymers do not conduct electricity because of non-availability of free electrons, but the polymers having conjugation (Alternate single and double bonds) are capable of conducting electricity due to **delocalized or mobile or non-stationary** or π electrons. Presence of aromatic rings in the chain enhances conductivity.

Doping of Polymers :-

According to Heeger-Mac, conductivity of polymer chain can be increased by doping. Polymer chain carries resonating charge by doping.

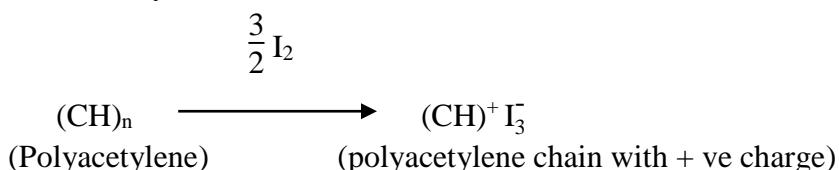
Doping are of three types:

a) Oxidative or p-doping :

In p-type of doping oxidizing agents such as I_2 vapors, I_2 dissolved in CCl_4 , $HClO_4$, Br_2 , $FeCl_3$, PF_6 , AsF_5 are used. e.g. Polyacetylene.

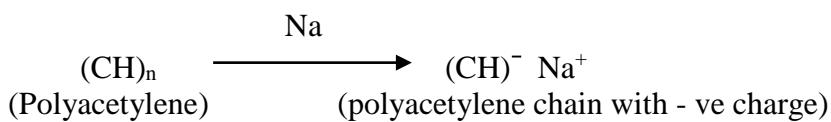
When the oxidative dopant such as iodine is added to takes away an electron from the π backbone of the polyacetylene chain and creates a positive center (hole) on one of the carbon atoms. The other π electrons resides other carbon making it a radical.

The radical ion formed is called polaron. A dipolaron is formed on further oxidation. Then these radicals migrate and combines to establish a backbone double bond. As the two electrons are removed, the chain will have two positive centers (holes). The chain as a whole is neutral, but holes are mobile and when a potential is applied they migrate from one carbon to another and account for conductivity.

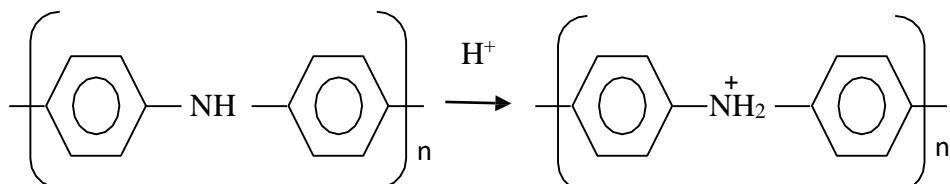


b) Reductive or n-doping:

In this method the reducing agents such as Na & Li metal, $FeCl_2$, sodium naphthalide are used as dopants.



c) A polymer like polyaniline can be H^+ doped with acid solution.



Properties :

1. They are light in weight
2. They are easy to fabricate
3. They are flexible
4. They are insoluble in solvents
5. They are non toxic
6. High manufacturing cost

Applications :

1. Used as electrode material for rechargeable batteries.
2. They are used in light emitting diodes.
3. Used as conductive track on printed circuit boards (especially Polyaniline)
4. Used as humidity sensors, gas sensors, radiation sensors etc.
5. Used as electro catalytic material in fuel cells.
6. Used as membrane for gas separation.
7. Also used in solar cells transistors, super capacitors

Electroluminescence Electroluminescence is a phenomenon in which a material emits light when an electric current passes through it. It's the underlying principle behind various technologies, including LED (Light Emitting Diode) displays and OLED (Organic Light Emitting Diode) screens.

Electroluminescent materials are used in a wide range of applications due to their energy efficiency and versatility in producing different colors of light.

OLED materials :

OLED (Organic Light Emitting Diode) displays rely on organic materials to emit light. There are several key components in an OLED display:

• Organic Electroluminescent Material:

These are organic compounds that emit light when an electric current is applied. OLEDs use various types of organic materials, including small organic molecules and polymers. Commonly used materials include small molecules like tris (8-hydroxyquinoline) aluminum (Alq_3) and polymeric materials like poly(p-phenylene vinylene) (PPV).

• Substrate:

The substrate is typically made of glass or flexible plastic. It provides structural support and can be transparent to allow light to pass through.

• Anode:

The anode (anode electrode) is a transparent conductor, often made of indium tin oxide (ITO), which is used to inject positive charge carriers (holes) into the organic layer.

• Cathode:

The cathode (cathode electrode) is responsible for injecting negative charge carriers (electrons) into the organic layer. Materials like aluminum and calcium are commonly used for this purpose.

• Emissive Layer:

This layer contains the organic electroluminescent material, which emits light when electrons and holes recombine within it. There are different types of emissive layers, depending on the specific OLED design.

- **Electron Transport Layer (ETL) and Hole Transport Layer (HTL):**

These layers facilitate the movement of electrons and holes, respectively, towards the emissive layer. Common materials for ETL include materials like lithium fluoride (LiF) and for HTL, materials like N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine (NPB).

- **Encapsulation Layer:**

This layer is crucial for protecting the organic materials from environmental factors like moisture and oxygen, which can degrade OLED performance over time.

OLED displays can be divided into two main categories: small molecule OLEDs (SMOLEDs) and polymer OLEDs (PLEDs), depending on the type of organic material used. Each has its advantages and limitations, making them suitable for different applications.

Charge transfer complexes

Charge transfer complexes (CTCs) are chemical compounds or molecular entities formed when electrons are transferred between two or more interacting molecules or molecular groups. This transfer of electrons typically involves one molecule donating electrons (electron donor) and another molecule accepting them (electron acceptor). CTCs often result in distinct spectral and chemical properties due to the altered electronic structure.

Charge transfer complexes:

- **Electron Donor and Acceptor:**

In a CTC, there is usually a molecule with electron-rich regions (donor) and another molecule with electron-deficient regions (acceptor). The transfer of electrons occurs between these regions.

- **Spectral Properties:**

CTCs can have unique absorption and emission spectra compared to their individual components. This can result in the appearance of new colors or changes in the absorption characteristics.

- **Stabilization:**

The formation of CTCs can lead to increased stability for the involved molecules. This stabilization can impact the reactivity and chemical behavior of the compounds.

- **Applications:**

Charge transfer complexes find applications in various fields, including chemistry, physics, and materials science. They are often used in the design of sensors, organic semiconductors, and photovoltaic devices.

- **Examples:**

A classic example of a charge transfer complex is the interaction between iodine (electron acceptor) and starch (electron donor) in the iodine clock reaction, where the formation of a blue-black complex signifies the completion of the reaction.

- **Supramolecular Chemistry:**

CTCs are an essential aspect of supramolecular chemistry, where non-covalent interactions between molecules play a central role in the design of functional materials and molecular assemblies.

The study and understanding of charge transfer complexes are significant in the development of new materials, chemical reactions, and technologies across various scientific disciplines.

- **Metal chelates**

Metal chelates are chemical compounds formed by the binding of a metal ion to a chelating agent or ligand. The term "chelate" comes from the Greek word "chele," which means "claw," reflecting the

way these ligands wrap around and tightly bind metal ions, similar to the grasp of a claw.

- **Chelating Agents:**

Chelating agents are organic molecules or ligands with multiple coordination sites, typically oxygen, nitrogen, or sulfur atoms, capable of forming coordinate bonds with metal ions. Common chelating agents include ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and 1,10-phenanthroline.

- **Coordination Bonds:**

In a metal chelate complex, the metal ion is bound to the chelating agent through coordinate covalent bonds. The ligand forms a ring-like structure around the metal ion, enhancing the stability of the complex.

- **Stability:**

Chelation significantly enhances the stability of metal ions in solution. This property is essential in various applications, such as metal ion extraction, water treatment, and medical chelation therapy.

- **Applications:**

Metal chelates have a wide range of applications, including:

1. In analytical chemistry for metal ion detection and quantification.
2. In agriculture as micronutrient fertilizers (e.g., iron chelates) to improve nutrient uptake by plants.
3. In medicine for chelation therapy to remove toxic heavy metals from the body.
4. In industry for metal extraction and purification processes.
5. In catalysis and coordination chemistry for the design of novel catalysts and materials.

- **Color and Properties:**

Some metal chelates exhibit distinctive colors due to electronic transitions within the complex. For example, copper(II) complexes with certain ligands can appear blue or green.

- **Biological Importance:**

Metal chelation is critical in biochemistry and plays a role in various biological processes. For instance, metalloenzymes often use metal chelates as cofactors for catalytic activities.

Overall, metal chelates are essential compounds with diverse applications in chemistry, industry, agriculture, and medicine. They are valued for their ability to stabilize metal ions and control their reactivity in various chemical and biological contexts.

- **Polycyclic aromatic oligomers**

Polycyclic aromatic oligomers (PAOs) are a class of chemical compounds that consist of fused aromatic rings in a cyclic or polycyclic structure. Unlike larger polymers, oligomers are composed of a relatively small number of repeating units, typically fewer than 10 monomer units. PAOs are derived from aromatic hydrocarbons and are known for their unique electronic, optical, and chemical properties.

- **Polycyclic aromatic oligomers:**

- 1. **Aromatic Rings:**

PAOs are composed of aromatic rings, which are planar and contain alternating single and double carbon-carbon bonds. These rings are often derived from benzene or other similar aromatic compounds.

2. Conjugation:

PAOs have extensive conjugated pi-electron systems due to the fused aromatic rings. This conjugation imparts distinctive electronic and optical properties, including absorption and emission of light in the visible or UV spectrum.

3. Size and Structure:

PAOs can vary in size and complexity, with a defined number of aromatic rings in their structure. Examples include naphthalene (two fused benzene rings), anthracene (three fused benzene rings), and pentacene (five fused benzene rings).

• Applications:

PAOs have applications in organic electronics, where their semiconducting properties make them useful in organic light-emitting diodes (OLEDs), organic photovoltaics (solar cells), and organic field-effect transistors (OFETs). They are also studied for their potential in molecular electronics and as model compounds for understanding larger polycyclic aromatic hydrocarbons (PAHs).

• Synthesis:

PAOs can be synthesized through various organic chemistry methods, including cyclization reactions of aromatic precursors or stepwise coupling of smaller aromatic molecules.

• Properties:

The properties of PAOs, such as their electronic bandgap and charge transport characteristics, can be tuned by modifying their chemical structure through functionalization or by altering the size of the oligomer.

• Research Interest:

PAOs are of interest in materials science and condensed matter physics due to their unique properties and potential for use in next-generation electronic devices.

Polycyclic aromatic oligomers serve as important building blocks for the development of new materials and technologies in the field of organic electronics and have garnered significant attention in both academic and industrial research.

Liquid Crystal Polymer:

LCP often stands for Liquid Crystal Polymer, which is a type of highly crystalline thermoplastic material. LCPs have unique properties, including high-temperature resistance, chemical resistance, and excellent electrical insulating properties. They are commonly used in the manufacturing of high-performance electronic components, connectors, and packaging.

Classification of LCP

In the context of "LCP" referring to Liquid Crystal Polymers, these materials can be classified based on their molecular structure, properties, and applications. Here's a classification of LCPs

Based on Molecular Structure:

1. **Main-Chain LCPs:** These LCPs have liquid crystal units forming the backbone or main chain of the polymer. Examples include polyesters and polyimides with liquid crystal segments in the polymer chain.
2. **Side-Chain LCPs:** In these polymers, liquid crystal moieties are attached as side chains to a polymer backbone. This configuration often provides more flexibility in tuning properties.

Based on Properties:

1. **Thermotropic LCPs:** These LCPs exhibit liquid crystal behavior as a function of temperature. They transition from a crystalline solid to a liquid crystalline phase within a specific temperature range.
2. **Lyotropic LCPs:** These LCPs form liquid crystal structures in solution, typically when dissolved in certain solvents. The liquid crystal behavior is concentration-dependent.

Based on Applications:

1. **Electronics and Electrical Components:** LCPs are used in the manufacturing of high-frequency connectors, circuit boards, and electronic components due to their excellent electrical properties and dimensional stability.
2. **Packaging Materials:** LCPs find applications in the packaging industry, especially for microwaveable food containers, as they can withstand high temperatures.
3. **Automotive:** LCPs are used in automotive components such as sensors, connectors, and engine parts due to their resistance to heat and chemicals.
4. **Medical Devices:** LCPs are used in medical devices and equipment due to their biocompatibility and resistance to sterilization methods.
5. **Aerospace:** LCPs are employed in the aerospace industry for lightweight, high-performance applications such as aircraft components.
6. **Consumer Electronics:** LCPs are used in smartphones, laptops, and other consumer electronics for their thermal stability and dimensional accuracy.

Based on Chemical Composition:

Different LCPs can have varying chemical compositions, which affect their properties and applications. Common LCPs include Vectra, Xydar, and Sumikasuper.

It's important to note that LCPs are known for their anisotropic properties, meaning their properties can vary depending on the direction of measurement. This anisotropy is a result of their liquid crystalline structure, making them valuable materials in a wide range of industries and applications.

Chemical Constitution of LCP

The chemical constitution of Liquid Crystal Polymers (LCPs) can vary, but they generally share some common characteristics in their molecular structure. LCPs are typically composed of repeating units that contain rigid, planar, and aromatic segments connected by flexible or aliphatic linkers. This unique combination of rigid and flexible components contributes to their liquid crystalline behavior and desirable properties. Here's an overview of the common features in the chemical constitution of LCPs:

1. Aromatic Rings:

LCPs often contain aromatic rings, such as benzene or naphthalene rings, in their repeating units. These aromatic rings contribute to the rigidity of the polymer chain and promote pi-electron delocalization.

2. Rigid and Flexible Segments:

LCPs have both rigid and flexible segments within their molecular structure. The rigid segments, typically aromatic rings, provide the liquid crystalline behavior, while the flexible segments, often composed of aliphatic or ether linkers, allow for flexibility and movement within the polymer chain.

3. Conjugated Pi-Electron System:

Due to the presence of aromatic rings, LCPs feature a conjugated pi-electron system along the polymer

chain. This system is responsible for their unique electronic and optical properties.

4. Functional Groups:

Depending on the specific LCP, functional groups like ester, amide, or imide groups can be incorporated into the repeating units. These functional groups can affect the LCP's properties and reactivity.

5. Side Chains:

Some LCPs have side chains attached to the main polymer backbone. These side chains can influence the solubility, processability, and other properties of the LCP.

6. Stereochemistry:

The arrangement of atoms within the repeating units can also vary, affecting the LCP's properties. Isomeric forms of LCPs may exist with different spatial arrangements of atoms.

7. Liquid Crystalline Phases:

LCPs exhibit different liquid crystalline phases, such as nematic, smectic, or cholesteric, depending on the specific molecular structure and environmental conditions (e.g., temperature and pressure).

8. Polymerization Methods:

LCPs can be synthesized using various polymerization methods, including step-growth polymerization or chain-growth polymerization, depending on the desired properties and application. It's important to note that the precise chemical constitution of LCPs can vary widely among different types and grades of LCPs. The specific chemical structure of an LCP will determine its properties, including its thermal stability, mechanical strength, electrical conductivity, and more. Manufacturers often tailor LCP formulations to meet specific application requirements.

9. Stability and applications of LCP

Liquid Crystal Polymers (LCPs) are known for their unique combination of properties, making them suitable for various applications. Their stability and applications are influenced by their chemical structure, which includes rigid aromatic segments and flexible linkers. Here's a look at the stability and some key applications of LCPs:

Stability:

- **Thermal Stability:**

LCPs exhibit excellent thermal stability, with high glass transition temperatures (T_g) often exceeding 200°C. This property makes them resistant to heat and thermal degradation, which is particularly valuable in high-temperature applications.

- **Chemical Resistance:**

LCPs are resistant to many chemicals, including acids, bases, and solvents. This chemical resistance allows them to maintain their structural integrity when exposed to harsh environments.

- **Dimensional Stability:**

LCPs have low coefficients of thermal expansion (CTEs), meaning they undergo minimal dimensional changes with temperature fluctuations. This makes them suitable for applications requiring precise dimensions over a wide temperature range.

- **Electrical Insulation:**

LCPs possess excellent electrical insulating properties, making them valuable in electronics and electrical components where electrical insulation and dimensional stability are critical.

Applications:

- **Electronics and Electrical Components:**

LCPs are widely used in the electronics industry for applications like high-frequency connectors, printed circuit boards (PCBs), and insulating materials. Their excellent electrical properties, including low dielectric constants and low dissipation factors, make them ideal for high-speed data transmission.

- **Aerospace:**

LCPs find applications in the aerospace sector, where their thermal stability and lightweight properties are valuable for components like aircraft connectors, sensor housings, and insulation.

- **Automotive:**

LCPs are used in the automotive industry for engine components, connectors, and sensors. Their resistance to high temperatures and chemicals is beneficial in engine compartments.

- **Medical Devices:**

LCPs are employed in the manufacture of medical devices due to their biocompatibility, chemical resistance, and dimensional stability. They are used in applications like surgical instruments, diagnostic equipment, and medical connectors.

- **Packaging Materials:**

LCPs are used in the packaging industry, particularly for microwavable food containers and packaging that requires both heat resistance and barrier properties.

- **Consumer Electronics:**

LCPs are utilized in consumer electronics, such as smartphones, laptops, and wearable devices, for their thermal stability, dimensional accuracy, and suitability for miniaturization.

- **Industrial Equipment:**

LCPs are applied in various industrial equipment where heat resistance, chemical resistance, and electrical insulation are required.

- **Sensors and MEMS Devices:**

LCPs are used in microelectromechanical systems (MEMS) and sensors due to their ability to maintain precise dimensions in changing temperatures.

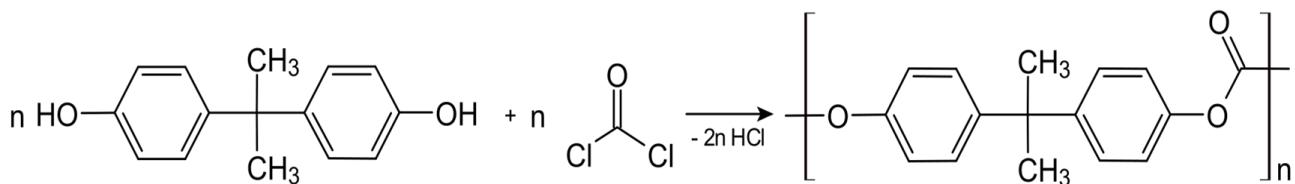
LCPs' unique combination of properties, including thermal stability, chemical resistance, and electrical performance, makes them valuable in a wide range of industries and applications, particularly in fields requiring high-performance materials that can withstand challenging environments.

Polycarbonates:

Polycarbonates (PC) are a group of thermoplastic polymers containing carbonate groups in their chemical structures. Polycarbonates used in engineering are strong, tough materials, and some grades are optically transparent. They are easily worked, molded, and thermoformed. Because of these properties, polycarbonates find many applications.

The main polycarbonate material is produced by the reaction of bisphenol A (BPA) and phosgene COCl

The overall reaction can be written as follows:



Properties

1. Polycarbonate is a durable material.
2. Although it has high impact-resistance, it has low scratch-resistance.
3. Therefore, a hard coating is applied to polycarbonate eyewear lenses and polycarbonate exterior automotive components. Polycarbonate is stronger and will hold up longer to extreme temperature.
4. Thermally processed material is usually totally amorphous and as a result is highly transparent to visible light, with better light transmission than many kinds of glass.
5. Polycarbonate has a glass transition temperature of about 147 °C (297 °F), so it softens gradually above this point and flows above about 155 °C (311 °F). Tools must be held at high temperatures, generally above 80 °C (176 °F) to make strain-free and stress-free products.
6. Low molecular mass grades are easier to mold than higher grades, but their strength is lower as a result.
7. The toughest grades have the highest molecular mass, but are more difficult to process.
8. Unlike most thermoplastics, polycarbonate can undergo large plastic deformations without cracking or breaking.
9. Even for sharp angle bends with a tight radius, heating may not be necessary. This makes it valuable in prototyping applications where transparent or electrically non-conductive parts are needed, which cannot be made from sheet metal. PMMA/Acrylic, which is similar in appearance to polycarbonate, is brittle and cannot be bent at room temperature.

Applications

1. Electronic components

Polycarbonate is mainly used for electronic applications that capitalize on its collective safety features. A good electrical insulator with heat-resistant and flame-retardant properties, it is used in products associated with electrical and telecommunications hardware.

It can serve as a dielectric in high-stability capacitors.

2. Construction materials

Polycarbonate sheeting in a greenhouse

The second largest consumer of polycarbonates is the construction industry, e.g. for domelights, flat or curved glazing, roofing sheets and sound walls. Polycarbonates are used to create materials used in buildings that must be durable but light.

3. 3 D Printing

Polycarbonates are used extensively in 3D FDM printing, producing durable strong plastic products with a high melting point. 3D printing using polycarbonates is common in the professional community.

4. Data storage

CDs and DVDs

A major polycarbonate market is the production of compact discs, DVDs, and Blu-ray discs. These discs are produced by injection-molding polycarbonate into a mold cavity that has on one side a metal stamper containing a negative image of the disc data, while the other mold side is a mirrored surface. Typical products of sheet/film production include applications in advertisement (signs, displays, poster protection).

5. Mobile phones

Some smartphone manufacturers use polycarbonate

QUESTIONS

- Q.1.** What is polymerization ? What are the types of polymerization ? (3M)
- Q.2** Distinguish between addition and condensation polymerization. (3M)
- Q.3** What is glass transition Temperature ? What are the factors affecting the glass transition temperature. (5M)
- Q.4** Define the term Plastic. Give the general properties of the plastic. (5M)
- Q.5** What are the characteristic properties of Addition polymerization.? (5M)
- Q.6** Explain addition polymerization on the basis of Free-radical reaction mechanism with suitable example. (5 M)
- Q.7** What are the characteristic properties of Condensation or Step polymerization.? Give any one example of the polymer which is formed by Condensation polymerization. (3M)
- Q.8** Distinguish between Thermosetting and Thermosoftening Plastic. (3 M)
- Q.9** Give the preparation, properties and applications of Kevlar (3M)
- Q.10** What are Plastics ? Discuss various compounding of plastics. (5M)
- Q.11** How polyparaphynylene vinylene (PPV) is prepared? Give its Properties and applications. (3M)
- Q.12** Give the preparation, properties and applications of Polycarbonates. (5M)



Engineering Materials

CONTENT: Nanomaterials - Molecular electronics - fullerenes, carbon nanotubes – structure, synthesis, properties and applications.

Electrochemistry: Electrolytic & Conductance, types of conductance, conductometric titration, Electrode potential, Electromotive force, types of electrodes- Calomel, Quinhydrone, Glass electrode.

Thermal Analysis: Principle block diagram of thermo gravimetric analysis (TGA) & analysis of Calcium oxalate. Principle block diagram of Differential scanning calorimetry.

Nanomaterials-Molecular Electronics

Nanomaterials:

These are materials with structures or properties at the nanoscale, typically ranging from 1 to 100 nanometers. They exhibit unique characteristics due to their small size, which can be different from bulk materials. Examples include nanoparticles, nanotubes, and nanowires.

Molecular Electronics:

This is a branch of nanotechnology that explores the use of individual molecules as electronic components. It's an area with great potential for creating smaller, faster, and more efficient electronic devices. The aim is to utilize the properties of individual molecules, like their electronic states or conductance, for building circuits and devices.

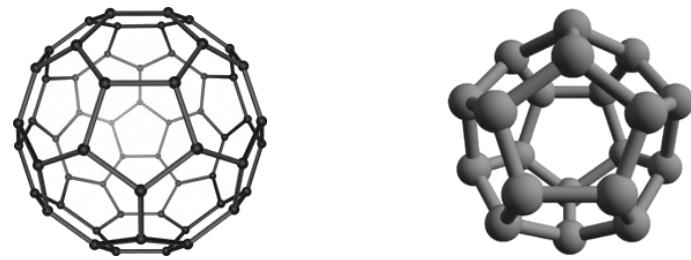
Fullerenes:

These are a class of molecules composed entirely of carbon, taking the form of hollow spheres, ellipsoids, or tubes. The most well-known fullerene is Buckminsterfullerene, commonly referred to as "buckyballs", which has a soccer ball-like structure. Fullerenes have unique electronic and structural properties that make them interesting for various applications, including drug delivery systems, superconductors, and nanotube production.

Fullerenes are a fascinating class of molecules composed entirely of carbon. They were first discovered in 1985 by a team of scientists led by Sir Harry Kroto, Robert Curl, and Richard Smalley, which earned them the Nobel Prize in Chemistry in 1996. The most well-known and studied fullerene is Buckminsterfullerene, often referred to as "buckyball" due to its soccer ball-like structure.

- **Structure:**

Buckminsterfullerene is the smallest fullerene molecule containing pentagonal and hexagonal rings in which no two pentagons share an edge . It is also most common in terms of natural occurrence, as it can often be found in soot.



The empirical formula of buckminsterfullerene is C_{60} and its structure is a truncated icosahedron, which resembles an association football ball of the type made of twenty hexagons and twelve pentagons, with a carbon atom at the vertices of each polygon and a bond along each polygon edge.

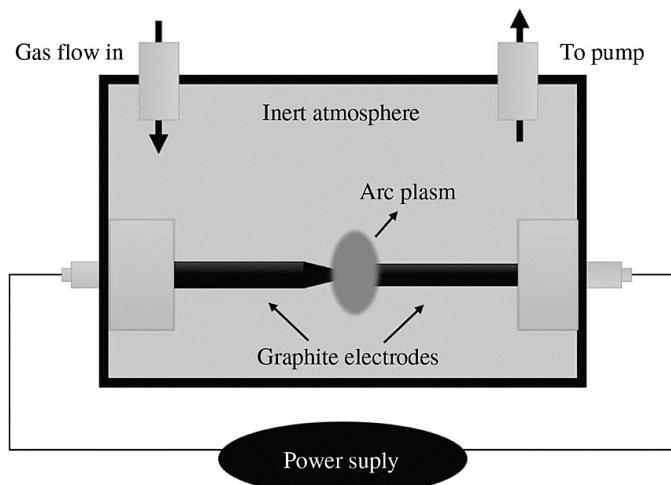
The van der Waals diameter of a buckminsterfullerene molecule is about 1.1 nanometers (nm). The nucleus to nucleus diameter of a buckminsterfullerene molecule is about 0.71 nm.

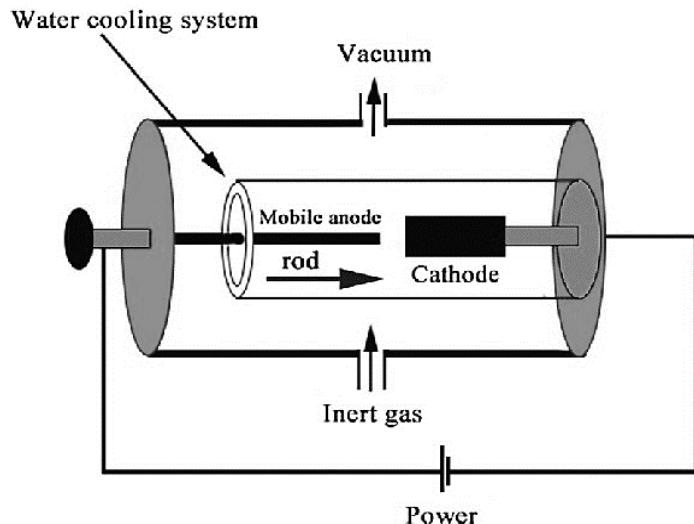
The buckminsterfullerene molecule has two bond lengths. The 6:6 ring bonds (between two hexagons) can be considered "double bonds" and are shorter than the 6:5 bonds (between a hexagon and a pentagon). Its average bond length is 1.4 Å.

Synthesis Of Fullerenes :

Arc Discharge Method-

1. This is a pulsed arc discharge method of synthesis operated at high temperature.
2. Parts of the apparatus are furnace for heating purpose, a tube made up of quartz, electrodes of carbon, a trap which is water cooled and a high voltage pulsed power input.
3. For annealing process of carbon clusters, a buffer gas is allowed to pass through the quartz tube.
4. The tube temperature is between 25 and 1000°C.
5. The flow rate of the buffer gas is maintained at $300 \text{ cm}^3/\text{s}$. Pressure of the buffer gas is maintained at 500 Torr.
6. The input power supply provides pulsated high voltage of 1.1 kV, 22 A and 50–300 sec duration.
7. By this method, electrode at negative terminal is consumed. Then the carbon after condensation is annealed to form fullerenes.
8. The fullerene and other carbon particles are then collected on the water cooled trap. 9. Analysis of fullerenes is done by high performance liquid chromatography (HPLC). The present HPLC system can detect fullerenes at low concentrations.





Properties:

1. Electrical Properties:

Fullerenes can conduct electricity, but their conductivity can be modified by doping or altering their structure.

2. Stability:

They are stable molecules and are not easily degraded under normal conditions.

3. Reactivity:

Fullerenes can undergo various chemical reactions, allowing for functionalization with other molecules or atoms. This property makes them versatile for a wide range of applications.

Applications of Fullerene:

1. Medical Applications:

Fullerenes show promise in drug delivery systems due to their ability to encapsulate other molecules. They can potentially be used for targeted drug delivery in treatments for cancer and other diseases.

2. Material Science:

Fullerenes are used in the development of novel materials, including superconductors and high-strength materials.

3. Nanotechnology:

They serve as building blocks for the creation of more complex nanostructures, including carbon nanotubes and graphene.

Overall, fullerenes represent a remarkable class of molecules with a wide array of potential applications, and ongoing research in this area is driving innovations in various fields of science and technology.

Carbon nanotubes

Carbon nanotubes (CNTs) are another remarkable form of carbon allotropes, much like fullerenes. They were discovered in 1991 by Sumio Iijima, which also sparked significant interest and research in the field of nanotechnology. Carbon nanotubes are cylindrical structures composed entirely of carbon atoms arranged in a hexagonal lattice, akin to a rolled-up sheet of graphene. This remarkable structure is what makes carbon nanotubes so versatile and desirable for a wide range of applications in fields like materials science, electronics, aerospace, medicine, and more.

Production Methods:**1. Chemical Vapor Deposition (CVD):**

This is a common method for producing carbon nanotubes. It involves the decomposition of carbon-containing gases on a substrate in the presence of a catalyst.

2. Arc Discharge:

This method involves the evaporation of graphite in a high-temperature arc, leading to the formation of carbon nanotubes.

Structure:

Carbon nanotubes are cylindrical fullerenes. These tubes of carbon are usually only a few nanometres wide, but they can range from less than a micrometer to several millimeters in length. They often have closed ends, but can be open-ended as well. There are also cases in which the tube reduces in diameter before closing off.

There are two main types of carbon nanotubes based on their structure

- **Single-Walled Nanotubes (SWNTs):**

These consist of a single layer of carbon atoms rolled into a seamless cylinder. SWNTs can have varying diameters and lengths. These consist of a single layer of carbon atoms arranged in a cylindrical tube.

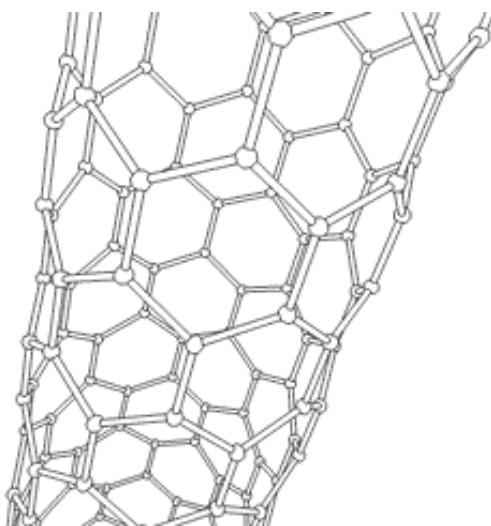
They can have varying diameters, ranging from about 0.4 nanometers to several nanometers. The diameter-to-length ratio of SWNTs can be incredibly high, sometimes reaching over a thousand.

- **Multi-Walled Nanotubes (MWNTs):**

These are composed of multiple layers of carbon sheets arranged concentrically. They resemble a series of tubes nested within each other. These are composed of multiple layers of carbon sheets arranged concentrically, similar to the layers of an onion.

MWNTs can have two or more walls, with the number of walls varying depending on the specific nanotube.

Both SWNTs and MWNTs exhibit extraordinary mechanical, electrical, and thermal properties due to their unique structure. The seamless arrangement of carbon atoms results in high tensile strength, efficient electrical conductivity, and excellent thermal conductivity.



Properties:

Their unique molecular structure results in extraordinary macroscopic properties, including

1. high tensile strength,
2. high electrical conductivity,
3. high ductility,
4. high heat conductivity,
5. relative chemical inactivity, they are resistant to most chemical reactions.
6. Low Density: They are extremely lightweight despite their strength.
7. they are very stiff
8. Lightweight: carbon nanotubes are incredibly lightweight

Applications:

1. One proposed use of carbon nanotubes is in paper batteries, developed in 2007.
2. Another highly speculative proposed use in the field of space technologies is to produce high-tensile carbon cables required by a space elevator
3. CNTs are used to reinforce materials like polymers, ceramics, and metals, leading to enhanced mechanical and electrical properties.
4. **Electronics:** They are employed in various electronic components, such as transistors, sensors, and conductive films.
5. **Energy Storage:** Carbon nanotubes have been investigated for use in batteries, supercapacitors, and fuel cells.
6. **Medical Applications:** They hold promise in drug delivery, imaging, and as scaffolds for tissue engineering.
7. **Nanotechnology Research:** Carbon nanotubes serve as a foundation for building other nanoscale structures and devices.
8. CNTs are used in transistors, interconnects, and other electronic components
9. **Transparent conductive films** made from CNTs find applications in touch screens, displays, solar cells, and other electronic devices.
10. CNTs are employed in water purification and environmental cleanup processes due to their ability to adsorb contaminants and toxins.
11. CNTs are used in the production of sports equipment like tennis rackets and bicycles, where the combination of strength and light weight is crucial.
12. **Aerospace Engineering:** CNT-reinforced composites are used to construct lightweight yet strong components in aircraft and spacecraft, contributing to improved fuel efficiency and performance.

Carbon nanotubes continue to be a subject of extensive research due to their unique properties and potential for a wide range of applications across various industries. They represent a significant advancement in materials science and nanotechnology.

The exceptional properties of carbon nanotubes have led to extensive research and exploration of applications in fields such as materials science, electronics, energy storage, aerospace, medicine, and environmental engineering, among others. However, it's important to note that while carbon nanotubes hold great promise, challenges like large-scale production, purification, and toxicity concerns in certain forms remain areas of active research and development.

Electrochemistry :

Electrochemistry is a branch of chemistry that deals with the study of chemical reactions involving the transfer of electrons between species. It encompasses both the spontaneous processes that generate electric current through chemical reactions (galvanic or voltaic cells) and the non-spontaneous processes that use electric current to drive chemical reactions (electrolysis).

Some key concepts in electrochemistry:

- **Redox Reactions:**

Electrochemistry revolves around redox (reduction-oxidation) reactions, where one chemical species loses electrons (oxidation) and another gains electrons (reduction).

- **Electrochemical Cells:**

These are systems that convert chemical energy into electrical energy or vice versa. There are two main types:

1. **Galvanic (Voltaic) Cells:**

Spontaneous reactions produce electric current.

2. **Electrolytic Cells:**

Non-spontaneous reactions require an external power source to drive the reaction.

3. **Electrodes:**

Electrodes are conductive materials (often metals or graphite) where electron transfer takes place. There are two types:

4. **Anode:**

The electrode where oxidation occurs (loses electrons).

5. **Cathode:**

The electrode where reduction occurs (gains electrons).

6. **Electrolyte:**

This is a solution or medium that allows ions to move and complete the circuit in an electrochemical cell. It contains the species involved in the redox reactions.

7. **Cell Potential (Electromotive Force):**

The voltage or electric potential difference between the two electrodes in a cell. It's a measure of the cell's ability to drive electrons through an external circuit.

8. **Faraday's Laws of Electrolysis:**

These laws describe the relationship between the amount of substance deposited or liberated at an electrode and the quantity of charge passed through the electrolyte.

9. **Nernst Equation:**

It relates the cell potential to the activities (concentrations) of the species involved in the redox reaction. It allows us to predict the cell potential under non-standard conditions.

10. **Applications:**

a) **Batteries and Fuel Cells:** These are common electrochemical devices used for energy storage and conversion.

b) **Electroplating:** Used to apply a thin layer of metal onto a surface for decorative or protective purposes.

- c) **Corrosion Protection:** Understanding electrochemical reactions is crucial in designing materials that resist corrosion.
- d) **Electrolysis for Industrial Processes:** For example, in the production of aluminum, chlorine, and hydrogen.
- e) **Electrochemical Sensors and Biosensors:** These devices use electrochemical principles to measure the concentration of specific substances, like pH, glucose, or certain ions.
- f) **Environmental Applications:** Electrochemical methods are used in wastewater treatment, pollutant detection, and in the removal of contaminants from water.
- g) **Materials Science:** Electrochemical techniques are used to study and control properties of materials, such as corrosion resistance, conductivity, and catalytic activity.

Overall, electrochemistry plays a crucial role in various industries and scientific fields, including energy production and storage, environmental protection, materials science, and analytical chemistry. It forms the foundation for many technological advancements and innovations.

Electrochemistry-Electrolytic Conductance

Electrolytic conductance is a fundamental concept in electrochemistry that refers to the **ability of a substance to conduct electric current when dissolved in a solvent**. It's a crucial aspect of electrolysis, a process in which an electric current drives a non-spontaneous chemical reaction.

Some key points about electrolytic conductance:

- **Electrolytes:**
Substances that conduct electricity when dissolved in a solvent are called electrolytes. They can be ionic compounds, acids, or bases.
- **Ions in Solution:**
When an electrolyte dissolves in a solvent (usually water), it dissociates into ions. These ions are charged particles that can move freely within the solution.
- **Electrolytic Conductance Mechanism:**
Electric current is carried in a solution by the movement of ions. Positively charged cations migrate towards the cathode (negative electrode), while negatively charged anions migrate towards the anode (positive electrode).
- **Conductivity:**
The measure of a solution's ability to conduct electricity is called its conductivity. It is often represented by the symbol κ (kappa) and is measured in siemens per meter (S/m) or mho per centimeter (mho/cm).
- **Specific Conductance (or Specific Conductivity):**
This is a measure of the conductivity of a solution, taking into account the dimensions of the cell used for the measurement. It is often represented by κ_s or σ (sigma) and is expressed in S/cm.

Factors Affecting Conductance:

The conductance of a solution depends on factors like the concentration of ions, their mobility, and the temperature of the solution. Higher concentrations of ions and higher ion mobility lead to greater conductance.

Kohlrausch's Law:

This law states that the equivalent conductance of an electrolyte at infinite dilution (when the

concentration approaches zero) is the sum of the equivalent conductances of its individual ions.

Molar Conductivity:

This is the conductivity of a solution containing one mole of the electrolyte. It is represented by Λ (lambda) and is expressed in $S\ m^2/mol$.

Applications:

Electrolytic conductance is a critical factor in various industries, including chemical manufacturing, electroplating, metal refining, and wastewater treatment. It's also important in the operation of batteries and fuel cells.

- **Measurement Techniques:**

Conductivity of a solution can be measured using a conductance cell or conductivity meter, which applies a voltage and measures the resulting current.

Understanding electrolytic conductance is crucial for designing and optimizing electrochemical processes and for controlling the behavior of electrolytes in a wide range of industrial applications.

Types of Conductance

Conductance refers to the ability of a material to conduct electric current. There are several types of conductance, each with its own characteristics and applications:

1. **Electrical Conductance:**

This is the ability of a material to conduct electric current. Metals, for example, have high electrical conductance due to the presence of free electrons that can move easily through the material.

2. **Thermal Conductance:**

This type of conductance measures a material's ability to conduct heat. Materials with high thermal conductance allow heat to pass through them efficiently. Metals, particularly metals like copper and aluminum, are good thermal conductors.

3. **Ionic Conductance:**

Ionic conductance refers to the ability of ions to carry an electric current through a solution or a molten salt. It's important in electrolysis and the operation of batteries and fuel cells.

4. **Electronic Conductance:**

Electronic conductance specifically pertains to the movement of electrons in a material. It's the type of conductance that's responsible for the flow of electric current in metals.

5. **Acoustic Conductance:**

This type of conductance measures the ability of a material to transmit sound waves. Materials with high acoustic conductance efficiently transmit sound, whereas insulating materials dampen sound transmission.

6. **Thermoelectric Conductance:**

This is the ability of a material to convert a temperature gradient into an electric voltage. It's crucial in thermoelectric devices, which can generate electricity from a temperature difference.

7. **Superionic Conductance:**

Superionic conductors are materials that can conduct ions at a high rate, often at elevated temperatures. They find applications in solid-state batteries and fuel cells.

8. Electronic Band Conductance:

In solid-state physics, the concept of electronic bands refers to the allowed ranges of energy levels that electrons can occupy in a crystal lattice. Materials with a partially filled band can conduct electricity, while those with completely filled bands are insulators.

9. Photoconductive Conductance:

This is the ability of a material to conduct electricity when exposed to light. Photoconductors are used in devices like photodiodes and phototransistors.

10. Gas Conductance:

This refers to the ability of a gas to conduct electricity under specific conditions, such as in plasmas or at very high pressures.

Understanding these different types of conductance is crucial in various fields of science and engineering, as it allows for the selection of materials and the design of systems with specific electrical, thermal, or ionic properties to suit particular applications.

Conductometric Titration

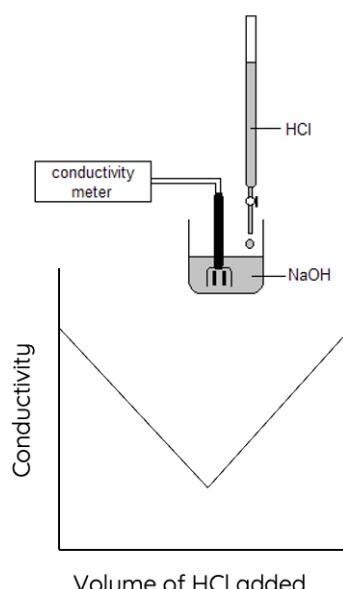
Conductometric titration is a technique used in analytical chemistry to determine the endpoint of a chemical reaction between a titrant (a solution of known concentration) and an analyte (the substance being analyzed) by monitoring changes in electrical conductivity.

Principle:

The basis of conductometric titration lies in the fact that the conductance (or conductivity) of a solution depends on the concentration of ions present. As the reaction proceeds, the concentration of ions in the solution changes, affecting its conductivity.

Setup:

A conductometric cell is used, consisting of two electrodes immersed in the solution being titrated. These electrodes are connected to a conductivity meter.

**Procedure:**

1. The titrant is added incrementally to the analyte solution while monitoring the change in conductivity. Initially, the conductivity will be low due to the low concentration of ions.

2. As the titration progresses, the conductivity will change. Near the equivalence point there will be a sudden change in conductivity.
3. The point at which this rapid change occurs is the endpoint of the titration.
4. Endpoint Detection: Endpoint detection can be automated using a titrator equipped with a conductivity sensor. Alternatively, it can be done manually by observing the conductivity readings

Applications:

Conductometric titration is particularly useful for titrations involving strong acids and bases or reactions that produce ions in solution. It's commonly used in determining concentrations of acids, bases, and salts.

Advantages:

Conductometric titration is relatively fast and precise. It doesn't require the use of indicators, making it suitable for reactions without a noticeable color change.

Limitations:

Conductometric titration may not be suitable for reactions involving weak acids or bases with low ionic conductivity. Additionally, it requires specialized equipment.

Examples:

Determining the concentration of hydrochloric acid using a sodium hydroxide solution. Conductometric titration is a valuable technique in analytical chemistry, providing an accurate and reliable method for determining concentrations of various substances in solution. It's widely used in laboratories for quality control and research purposes.

Electrode Potential

In electrochemistry, **electrode potential** is the voltage of a galvanic cell built from a standard reference electrode and another electrode to be characterized.

Electromotive Force :

Electromotive force (EMF) is a term used in engineering to describe the electrical potential difference or voltage provided by a source such as a battery or a generator.

It's the force or energy per unit charge that drives the flow of electric current in a circuit.

- **Symbol:**

EMF is denoted by the symbol "E" and is measured in volts (V).

Sources:

1. **Batteries:**

Chemical reactions in a battery create an EMF, providing a potential difference that can drive electrons through a circuit.

2. **Generators:**

Devices that convert mechanical energy into electrical energy also generate an EMF.

EMF determines the direction of electron flow in a circuit. Electrons flow from the negative terminal (lower potential) to the positive terminal (higher potential).

Units:

The SI unit for EMF is the volt (V), which is equivalent to one joule per coulomb ($1\text{ V} = 1\text{ J/C}$).

Types of Electrodes

Electrodes are crucial components in various electrochemical processes, including electrolysis, electroplating, batteries, and sensors. They facilitate the transfer of electrons into or out of a solution. There are several types of electrodes, each designed for specific applications.

Here are some common types:

- **Inert Electrodes:**

These electrodes are made of materials that do not react with the substances in the solution. Common examples include platinum, gold, and graphite electrodes. Inert electrodes are used in processes where the electrode material should not participate in the chemical reaction.

- **Active Electrodes:**

Active electrodes are made of materials that can participate in the chemical reaction. For example, in the extraction of metals from ores, the electrode itself may be involved in the reduction or oxidation process.

- **Reference Electrodes:**

These electrodes are used to establish a known electrical potential in an electrochemical cell. They are crucial for measuring and controlling the electrochemical potential of the working electrode. Examples include the Standard Hydrogen Electrode, Calomel Electrode

Calomel Electrode- Construction and Working

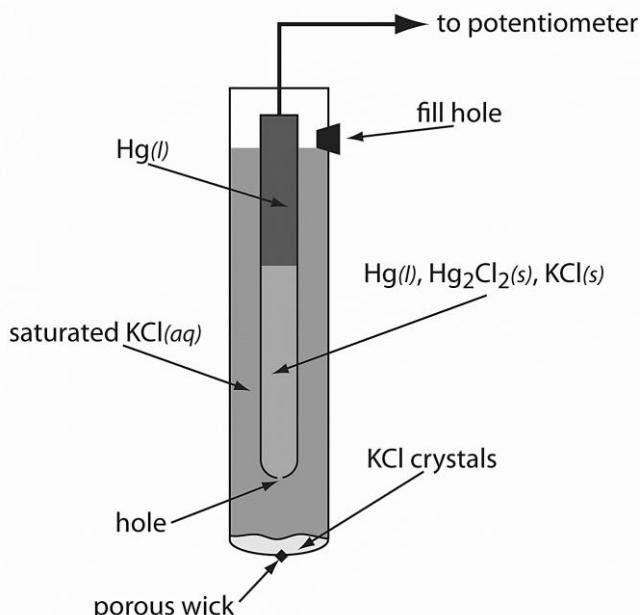
Construction:

The calomel electrode is the mercury-mercurous chloride electrode.

It consists of a glass vessel having a bent side tube.

Pure mercury is placed at the bottom of the tube, which is covered with a paste of mercury-mercurous chloride ($Hg + Hg_2Cl_2$) that is calomel.

The remaining portion of the cell is filled with a solution of normal (1 N) or saturated KCl (Potassium chloride).



A platinum wire sealed into a glass tube is dipped into a mercury layer and is used to provide external electrical contact.

The side tube is used for making electrical contact with a salt bridge.

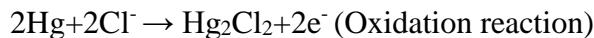
The calomel electrode can act as an anode or cathode depending on the nature of another electrode of the cell.

Working:

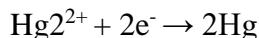
- Reaction at the anode:**



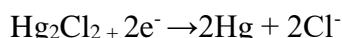
- Overall reaction:**



- Reaction at the cathode:**



- Overall reaction:**



Applications of Calomel Electrode in Engineering

The calomel electrode is commonly used in various electrochemical studies, including

1. pH measurements,
2. corrosion studies
3. other analytical techniques.
4. **Corrosion Studies:** Calomel electrodes are employed in studies related to corrosion and material degradation.
5. **Electroplating and Coatings:** In industries where precise control of plating and coating processes is crucial, calomel electrodes are used to monitor and optimize electrochemical reactions. This ensures uniform and high-quality coatings on metal surfaces.

Limitations :

The potential for mercury contamination and the inability to be used in environments where mercury contamination is a concern. As a result, alternative reference electrodes like the silver/silver chloride electrode have gained popularity in certain applications.

Quin Hydron Electrode Construction and Working

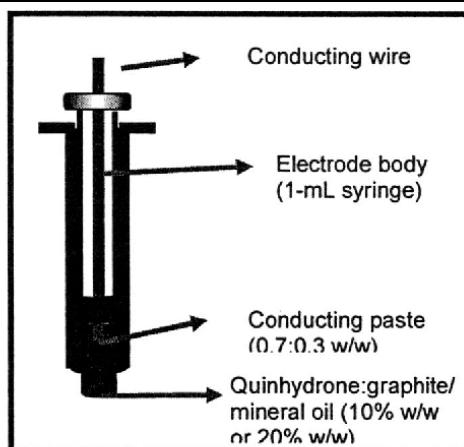
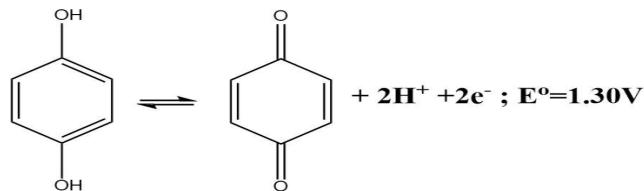


Figure 1: Diagram of the Quinhydrone electrode.

Contains a solution of Quinones and Hydroquinones prepared from Quinhydrone



The Quinhydrone electrode consists of Pt wire immersed into a solution of saturated Quinhydrone, which is sparingly soluble in water & is formed by the combination of equimolar mixture of Quinone (Q) and hydroquinone (QH_2).

It is represented as Pt, Q, QH_2 ; $\text{H}^+(\text{aq})$ & is reversible with respect to H^+ ions

It will either acts as anode or cathode depending on the other electrode connected to it. If it acts as cathode, then the electrode reaction is $\text{Q} + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{QH}_2$

The potential of Quinhydrone Electrode depends upon the PH of the electrolyte solution with which it is in contact.

Determination of pH using Quinhydrone electrode:

For determining the pH of a solution, the Quinhydrone electrode is connected to saturated calomel electrode & the emf of the cell produced is determined potentiometrically. The Quinhydrone electrode acts as cathode ($E^\circ = +0.6994$ v), While the SCE acts as anode ($E^\circ = + 0.2422$ v).

$$\text{pH} = (\mathbf{0.4572 V} - \mathbf{E_{cell}}) / \mathbf{0.0591}$$

- **Advantages:**

1. It is very useful for Acid – Base titrations.
2. Equilibrium is rapidly attained
3. It can be used in presence of ions of Many metals (Zn,Pb,Cu,Sn,Ni etc) which affect hydrogen electrode
4. It has low internal resistance
5. It is simple & free of errors due to the presence of Non – reducing gases or salts.
6. Very small quantities of solution are sufficient for the measurement.

- **Disadvantages:**

1. It cannot be used in solutions of $\text{pH} > 8$, since Hydroquinone ionizes as it is a weak dibasic acid ($\text{QH}_2 \rightarrow \text{Q}^{2-} + 2\text{H}^+$)
2. It is also oxidized by atmospheric oxygen
3. It cannot be used in solutions containing Redox systems, which would react with either Q or QH_2 .
4. It is not stable for a long time (above 30°C)

Applications of Quinhydrone electrode in Engineering

1. **Corrosion Studies:**

Quinhydrone electrodes can be used in studies related to corrosion and material degradation.\

2. **Battery Research:**

In research and development related to batteries and energy storage systems, quinhydrone electrodes might be used for assessing the electrochemical properties of electrolytes and electrode materials.

3. Electrochemical Sensors:

Quinhydrone electrodes could find applications in specialized electrochemical sensors, particularly those designed for non-aqueous or corrosive environments.

4. Electroplating and Coatings:

In industries where precise control of plating and coating processes is critical, quinhydrone electrodes might be used for monitoring and optimizing electrochemical reactions..

5. Fuel Cell Research:

Researchers studying non-aqueous electrolytes and redox reactions in fuel cells might find applications for quinhydrone electrodes in their investigations.

6. In engineering applications where non-aqueous electrolytes are used, such as in some industrial processes, quinhydrone electrodes can be used for electrochemical characterization and control.

Glass Electrode-Construction and working

GLASS ELECTRODE –It is usually employed for pH measurement.

- **Construction:**

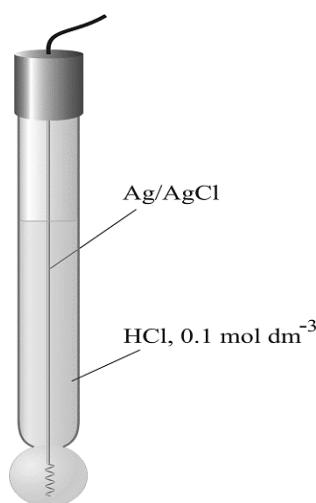
It consists of glass bulb made up of special type of glass called Corning glass (22% Na₂O, 6% CaO, and 72% SiO₂).

It has low melting point and high electrical conductivity.

The glass bulb is filled with 0.1 M HCl solution.

A silver wire coated with AgCl is immersed in it.

Ag/AgCl act as internal reference electrode.

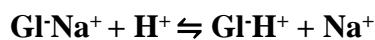


Glass electrode is represented as **Ag | AgCl (s) | HCl (0.1M) | glass**

- **Working :**

When glass electrode is dipped in the solution whose pH is to be determined there develops a potential difference between two surfaces of membrane then the potential difference developed is proportional to the difference in pH of the two solutions.

Glass membrane functions as ion exchange resin and an equilibrium is set up between Na⁺ ions of glass & H⁺ ions of solution.



The electrode potential of glass electrode can be represented by

$$EG = EG^0 - 0.0591 \text{ pH}$$

- **Determination of pH**

For the determination of pH of solution, glass electrode is coupled with saturated calomel electrode and is placed in the solution, whose pH is to be determined and E_{cell} is measured.

The cell is represented as



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

Or

$$E_{right} - E_{left} = E_{ref} - EG$$

(where E_{ref} = Saturated calomel electrode = 0.2422 V)

$$= E_{ref} - ({}^0 - 0.0591 \text{ pH})$$

$$= E_{ref} - EG^0 + 0.0591 \text{ pH}$$

$$pH = E_{cell} - E_{ref} + EG^0 / 0.0591$$

- **Advantages :**

1. Glass electrode is simple & easy to operate
2. Equilibrium is rapidly attained,
3. The results are accurate and is not easily poisoned,
4. It can be used in coloured, turbid or in colloidal solutions,
5. It can be used both in alkaline and oxidizing solutions.

- **Limitations :**

1. As the resistance of glass electrode is high, potentiometers containing vacuum tubes are required (Electronic potentiometers).
2. It is used up to a pH range of 0-10. Special glasses can be used to measure up to 12. If $pH > 12$, glass is attacked by an alkaline solution.
3. It only compares pH values

Applications of Glass electrode in Engineering

1. Water Treatment and Quality Control:

Engineers use glass electrodes to monitor and control the pH levels in water treatment processes. This is crucial for ensuring that water is safe for consumption and meets regulatory standards.

2. Chemical Process Engineering:

Glass electrodes are employed in chemical industries to monitor and control pH levels in various processes, such as chemical reactions, neutralizations, and precipitation reactions.

3. Wastewater Treatment:

Glass electrodes play a vital role in wastewater treatment plants, where they are used to monitor and adjust pH levels to optimize treatment processes and meet discharge regulations.

4. Food and Beverage Industry:

Engineers in the food and beverage industry use glass electrodes to control the pH levels in various stages of production, including fermentation, pasteurization, and packaging. This ensures product quality and safety.

5. Bioprocessing and Biotechnology:

Glass electrodes are utilized in bioprocessing applications, such as bioreactors and fermentation processes, where precise control of pH levels is crucial for the growth of microorganisms or cell cultures.

6. Environmental Engineering:

In environmental engineering projects, glass electrodes are used to monitor pH levels in natural water bodies, such as rivers, lakes, and oceans. This information is essential for assessing water quality and its impact on aquatic ecosystems.

7. Electroplating and Surface Finishing:

Glass electrodes are employed to control pH levels in electroplating baths. Maintaining the proper pH is crucial for achieving uniform and high-quality metal coatings.

8. Boiler Water Treatment:

In power plants and steam generation facilities, engineers use glass electrodes to monitor and control the pH levels in boiler water to prevent corrosion and ensure efficient heat transfer.

9. Engineers in the paper and pulp industry use glass electrodes to control the pH levels in various stages of the papermaking process, which helps maintain product quality and production efficiency.

Thermal Analysis

Thermal gravimetric analysis (TGA) is a thermal characterization method that measures the mass of a sample over time as the temperature increases at a determined rate.

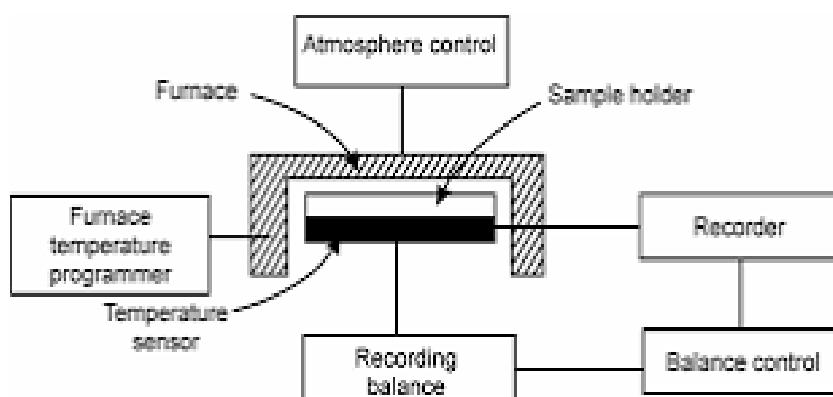
The main use is to detect chemical based changes that include decompositions of volatiles, solid-gas reactions and chemisorption's based on temperature.

The instrumentation itself is rather basic and is called a Thermogravimetric Analyzer.

It is equipped with a furnace that has a precision balance with a sample pan and programable control for temperature that enables precision heating ramps. The temperature is normally increased at a constant rate to induce the thermal reactions. The atmosphere within the furnace can be changed based on the experimental conditions required for testing. The input gas into the furnace can be ambient air, Nitrogen or gases that provide an oxidizing or reducing environment to determine how the reaction of the samples changes.

Block diagram of Thermogravimetric Analysis

Thermogravimetric Analysis (TGA) is a technique used in analytical chemistry to study changes in a material's weight as a function of temperature or time, while the material is subjected to a controlled atmosphere. Here is a simplified block diagram of a typical TGA system:



1. Sample Pan and Furnace:

Sample Pan: This is where the sample material is placed. It's typically made of a material like alumina, which is inert and can withstand high temperatures.

Furnace: The furnace provides controlled heating to the sample pan. It's equipped with a heating element, temperature controller, and thermocouple for temperature measurement.

2. Balance (Gravimetric Measurement):

A precision balance is used to measure the weight of the sample throughout the analysis. This is the "gravimetric" aspect of the analysis.

3. Gas Flow System:

The TGA may be equipped with a gas flow system to control the atmosphere around the sample. It can include components like gas cylinders, flow controllers, and a gas delivery system.

4. Gas Controller :

This component regulates the flow of gases into the chamber. It may allow for the use of different gases or mixtures, depending on the experimental requirements.

5. Evolved Gas Analysis (Optional):

Some advanced TGA systems may include a provision for analyzing gases evolved from the sample during heating. This can involve components like a mass spectrometer or a Fourier-transform infrared (FTIR) spectrometer.

6. Computer and Data Acquisition System:

A computer is used to control the TGA system, record data, and perform analysis. Specialized software is used to monitor the balance reading, control temperature, and process data.

7. User Interface:

This is the interface where the operator sets experimental parameters, such as heating rate, temperature range, gas atmosphere, and any additional analysis parameters.

8. Data Display and Analysis:

The system displays real-time data, such as weight change vs. temperature or time. It also allows the user to analyze the data after the experiment is complete.

9. Safety Systems:

Safety features like alarms for high temperatures or gas pressure may be integrated to ensure the safety of the system and operator.

10. Sample Holder and Clamps:

These components secure the sample pan in place and ensure that it's properly positioned for accurate measurements.

TGA analysis of calcium oxalate

Thermogravimetric Analysis (TGA) of calcium oxalate involves subjecting a sample of calcium oxalate to controlled heating in order to observe changes in its weight as a function of temperature. This can provide valuable information about its thermal stability, decomposition characteristics, and associated phase transitions.

• Sample Preparation:

A small amount of calcium oxalate sample is accurately weighed and placed in the sample pan of the TGA instrument. The sample pan is usually made of an inert material like alumina.

- **Initial Weight Measurement:**

The initial weight of the sample is recorded. This serves as the baseline reference for the analysis.

- **Heating Ramp:**

The TGA instrument is programmed to ramp up the temperature at a controlled rate. The rate of heating can vary depending on the specific objectives of the analysis.

- **Weight Change:**

As the temperature increases, the calcium oxalate sample may undergo various thermal events, such as dehydration, decomposition, or phase transitions. These processes can result in a loss of weight, which is recorded by the TGA instrument.

- **TG Curve:**

The TGA instrument generates a thermogravimetric (TG) curve, which plots the percentage weight change of the sample against the temperature or time.

- **DTG Curve (Optional):**

Some TGA instruments are equipped with a differential thermogravimetric (DTG) analysis feature, which provides the rate of weight change with respect to temperature. This can help identify specific thermal events.

- **Interpretation:**

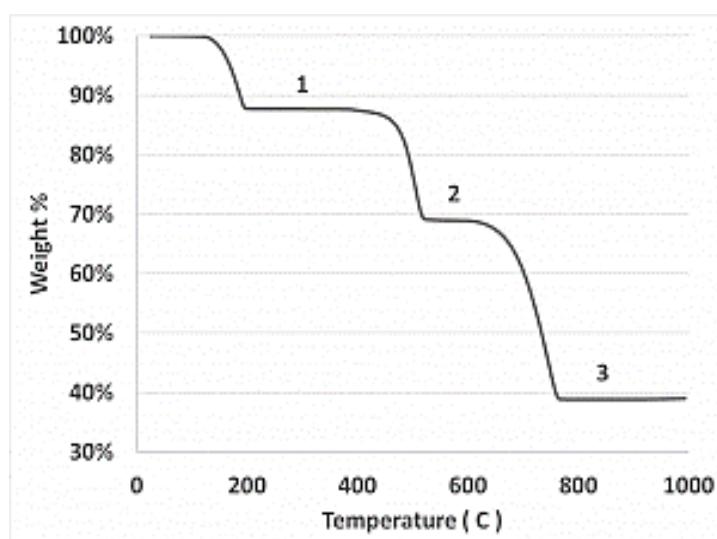
Based on the TG and DTG curves, you can identify specific temperature ranges or events associated with processes like dehydration, decomposition, phase transitions, or other thermal reactions.

- **Peak Identification:**

Peaks or inflection points on the TG or DTG curves correspond to specific thermal events. These can be used to identify the temperatures at which significant changes in the sample occur.

- **End of Analysis:**

The analysis concludes once the desired temperature range has been covered or when no further significant weight change is observed.

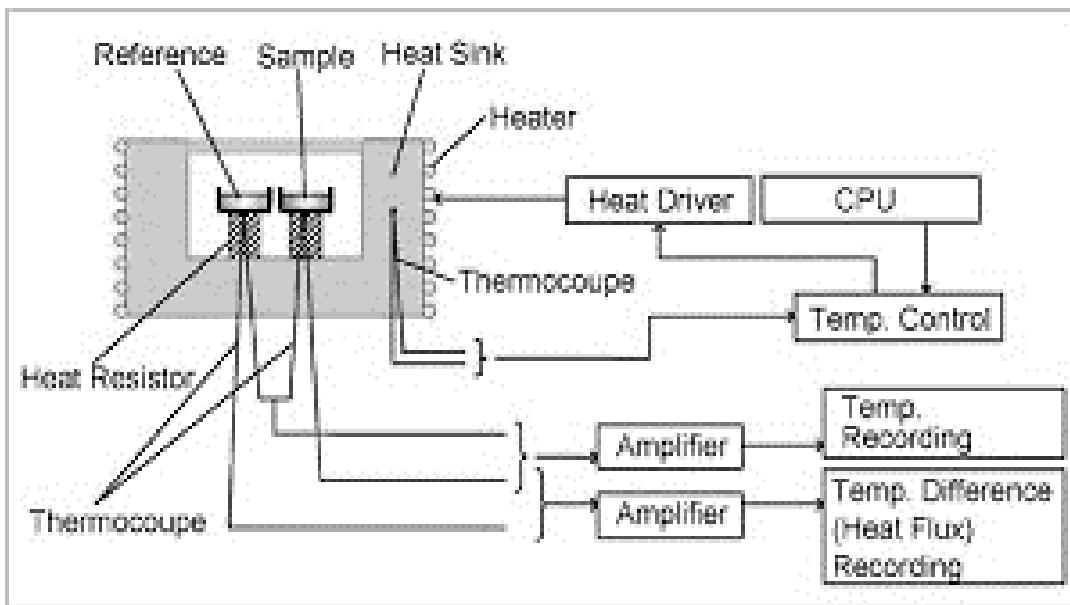


The information obtained from a TGA analysis of calcium oxalate can be used to understand its thermal behavior, estimate decomposition temperatures, and provide insights into its stability under different environmental conditions. This data is valuable in various fields, including materials science, pharmaceuticals, chemistry, and environmental science.

Principle Block Diagram of Differential scanning calorimetry

Differential Scanning Calorimetry (DSC) is a technique used to measure the heat flow associated with a sample as it is subjected to controlled heating or cooling.

Here's a simplified block diagram illustrating the principle components of a DSC instrument:



- **Heat Flux DSCs :**

A technique in which the temperature of the sample unit, formed by a sample and reference material, is varied in a specified program, and the temperature difference between the sample and the reference material is measured as a function of temperature.

- **Power Compensation DSC**

A technique in which difference of thermal energy that is applied to the sample and the reference material per unit of time is measured as a function of the temperature to equalize their temperature, while temperature of the sample unit, formed by the sample and reference material, is varied in a specified program SC is a commercially available instrument which has two (2) types: Heat Flux Type and Power Compensation Type.

Above Figure shows the block diagram of Heat Flux DSC as an example.

Heat Flux DSC comprises the sample and reference holder, the heat resistor, the heat sink, and the heater.

Heat of heater is supplied into the sample and the reference through heat sink and heat resistor.

Heat flow is proportional to the heat difference of heat sink and holders. Heat sink has the enough heat capacity compared to the sample.

In case the sample occurs endothermic or exothermic phenomena such as transition and reaction, this endothermic or exothermic phenomena is compensated by heat sink.

Thus the temperature difference between the sample and the reference is kept constant. The difference the amount of heat supplied to the sample and the reference is proportional to the temperature difference of both holders.

By calibrating the standard material, the unknown sample quantitative measurement is achievable.

DSC enables the measurements of the transition such as the glass transition, melting, and crystallization.

Furthermore, the chemical reaction such as thermal curing, heat history, specific heat capacity, and purity analysis are also measurable.

Recently, with the development of the highly-functional polymeric material, these thermal properties analysis needs are increasing dramatically.

DTA and DSC detect the temperature differences between the sample and the reference; however, DSC can perform the quantitative measurement of the amount of heat on top.

1. Sample Compartment:

This is where the sample to be analyzed is placed. It's typically a small chamber or well designed to hold a precise amount of sample material.

2. Reference Compartment:

A similar compartment is present, which holds a reference material. This reference material should have well-known thermal properties and is used as a baseline for comparison.

3. Heating Element and Cooling System:

A heating element is used to control the temperature of both the sample and reference compartments. A cooling system may also be included to enable controlled cooling experiments.

4. Thermocouples:

Each compartment is equipped with a thermocouple. These sensors measure the temperature of the sample and reference materials.

5. Differential Temperature Measurement:

The temperature difference (ΔT) between the sample and reference compartments is continuously monitored. This allows the instrument to detect any heat flow associated with the sample.

6. Feedback Loop and Control System:

The temperature control system maintains a constant temperature difference (ΔT) between the sample and reference compartments. It adjusts the heating power based on the thermocouple readings.

7. Data Acquisition System :

A data acquisition system collects temperature data from the thermocouples. It records the temperature difference over time.

8. Computer and Software:

A computer is used to control the DSC instrument, record data, and perform analysis. Specialized software is used to process and analyze the collected data.

9. User Interface

This is where the operator sets experimental parameters, such as heating rate, temperature range, and any additional analysis parameters.

10. Heat Flux Sensor (Optional):

Some advanced DSC systems include a heat flux sensor to directly measure the heat flow. This provides additional information for detailed analysis.

11. Calorimeter Cell:

The sample and reference compartments are usually separated by a calorimeter cell. This prevents any direct contact between the sample and reference materials.

12. Data Display and Analysis:

The system displays real-time data, such as heat flow vs. temperature or time. It also allows the user to analyze the data after the experiment is complete.

Differential scanning calorimetry in details :

Differential Scanning Calorimetry (DSC) is an analytical technique used to measure the heat flow associated with a sample as it is subjected to controlled heating or cooling. It provides valuable information about the thermal properties of materials, including phase transitions, enthalpy changes, and heat capacity.

- **Key details of how DSC works:**

1. Principle:

DSC operates on the principle that different phases or chemical reactions within a sample absorb or release heat in a manner that is detectable. The instrument measures the temperature difference between a sample and a reference material while both are subjected to a controlled thermal program.

2. Instrumentation:

Sample Holder: A small amount of the sample material is placed in a sample pan. The pan is typically made of a material like aluminum, which is thermally conductive and inert.

Reference Material: An identical empty pan (or a pan filled with an inert material) is used as a reference. This provides a baseline for comparison.

Thermocouples: Each pan is equipped with a thermocouple, which measures the temperature.

Furnace and Temperature Controller: The furnace provides controlled heating or cooling to both the sample and reference pans. The temperature controller regulates the temperature program.

Data Acquisition System: This system records the temperature difference (ΔT) between the sample and reference, typically at a high frequency.

Calorimeter Cell: This is a sealed compartment that separates the sample and reference pans. It prevents any direct contact between the materials.

3. Experimental Procedure:

Baseline Measurement: The DSC is calibrated by running a reference pan through the same temperature program. This establishes the baseline for heat flow measurements.

Heating or Cooling Program: The temperature of the sample and reference pans is controlled by the furnace according to a predefined heating or cooling program. This program can vary widely depending on the specific experiment.

Heat Flow Measurement: As the sample undergoes phase transitions or chemical reactions, it either absorbs or releases heat. This results in a temperature difference (ΔT) between the sample and reference pans, which is recorded by the thermocouples.

4. Data Analysis:

DSC Curve: The output of a DSC experiment is a plot of heat flow (measured in mW) against temperature (usually in degrees Celsius). Peaks or valleys in the curve represent endothermic (heat-absorbing) or exothermic (heat-releasing) processes.

Enthalpy Change: The area under the peaks or valleys in the DSC curve corresponds to the enthalpy change (ΔH) associated with a particular process.

5. Applications:

Phase Transitions: DSC is used to study phase transitions such as melting, crystallization, glass transitions, and more.

Reaction Kinetics: It can be used to determine the activation energy and kinetics of chemical reactions.

Polymer Characterization: DSC is widely used in the study of polymers to analyze properties like glass transition temperature, melting point, and crystallinity.

Pharmaceuticals: In drug development, DSC is used to study drug stability, compatibility, and formulation.

Materials Science: It's used to analyze a wide range of materials including metals, alloys, ceramics, and composites.

DSC is a versatile technique used in various fields including chemistry, material science, pharmaceuticals, food science, and more. It provides crucial information for understanding the thermal behavior and stability of materials.

Differential Scanning Calorimetry (DSC in Engineering Applications)

Differential Scanning Calorimetry (DSC) finds several important applications in engineering across various disciplines. Here are some notable examples:

1. Material Characterization:

DSC is extensively used in engineering to analyze the thermal properties of materials. This includes phase transitions, melting points, crystallization, glass transitions, and more. Engineers use this information to select materials for specific applications and to understand how they will behave under different temperature conditions.

2. Polymer Engineering:

In polymer engineering, DSC is a crucial tool. It's used to study the thermal behavior of polymers, including glass transition temperatures, melting points, crystallinity, and cure kinetics. This information is vital for designing and processing polymer materials.

Pharmaceuticals and Drug Development:

DSC is employed in pharmaceutical engineering for drug development and formulation. It's used to assess the stability of drugs, study interactions between drug substances and excipients, and optimize drug formulations for stability and efficacy.

3. Metallurgical Engineering:

DSC is used in metallurgical engineering to investigate phase transformations, eutectic reactions, and other thermal events in metallic alloys. This information is crucial for designing and processing alloys for specific applications.

4. Electronic Components and Devices:

Engineers in electronics often use DSC to study the thermal behavior of materials used in electronic components. This includes semiconductors, dielectrics, and other materials subjected to various thermal conditions.

5. Aerospace Engineering:

In aerospace engineering, DSC is used to study the thermal behavior of materials used in aircraft components. This includes metals, composites, and coatings subjected to conditions such as high temperatures during re-entry or extreme cold in outer space.

6. Food Engineering:

DSC is used in food engineering to study the thermal properties of food ingredients, formulations, and processing conditions. This information is crucial for designing food processing operations and ensuring product quality and safety.

7. Chemical Process Engineering:

Engineers in chemical processing industries use DSC to study the thermal behavior of chemicals and reactants under different conditions. This information is used in the design and optimization of chemical processes.

8. Automotive Engineering:

DSC is used in automotive engineering to study the thermal behavior of materials used in vehicle components, such as engine parts, exhaust systems, and interior components.

9. Construction Materials Engineering:

Engineers involved in construction materials use DSC to study the thermal properties of materials like concrete, asphalt, and other construction materials. This information is crucial for understanding how these materials will perform under different temperature conditions.

Overall, DSC is a versatile technique that provides valuable information about the thermal behavior of materials, which is critical in the design, development, and processing of various engineering products and systems.



Energy Generation

CONTENT: Fuels: GCV, NCV, Solid fuels; Proximate & Ultimate Analysis, Bomb calorimeter. Liquid fuels. Octane & Cetane number, Gaseous fuel - CNG, LPG, Alternate Fuels: H₂ as a future Fuel, Biodiesel, Ethanol, Methanol

Fuels are things that burn to give heat. They can be natural, like coal, or made by people. Long ago, coal was the main material used to make things like benzene and methane. Now, we also use gases from processing oil to make products. Wood and waste are used to make cellulose, alcohol, and more.

People now use natural gas or oil in their homes, not just wood. Coal and oil are used to make steam for big power systems. These are called fossil fuels.

Definition:

Fuel is anything that gives heat when burned, like wood or oil.

Classification:

Fuels can be solid, liquid, or gas. They can also be natural or made by people.

Solid fuels: like coal

Liquid fuels: like crude oil

Gaseous fuels: like natural gas

Characteristics of good fuel:

1. **Calorific Value:** A good fuel gives a lot of heat.
2. **Moderate Ignition Temperature:** It should start burning at the right temperature.
3. **Moderate Velocity of Combustion:** It should burn at the right speed.
4. **Low Moisture Content:** It should not have much water because water reduces its heat.
5. **Low Non-Combustible Matter:** It should not have a lot of stuff left after burning.
6. **Safe Products of Combustion:** Burning should not make harmful gases.
7. **Low Cost:** It should be cheap.
8. **Easy to Transport:** It should be easy to move around.
9. **Efficient Burning:** It should burn well without making a lot of smoke.
10. **Controllable Burning:** We should be able to control how it burns.

Calorific Value:

The main thing about fuel is its calorific value.

- **What is calorific value?**

It's the total heat released when a certain amount of fuel is completely burned in the air.

Units of Calorific Value:

1. **Calorie:** Amount of heat required to raise the temperature of 1 gram of water by one degree Celsius (15-16°C).
2. **Kilocalorie:** Amount of heat required to raise the temperature of 1 kilogram of water by one degree Celsius (15-16°C).
3. **B.T.U. (British Thermal Unit):** Amount of heat required to raise the temperature of 1 pound of water by one degree Fahrenheit (60-61°F).
4. **Centigrade Heat Unit (C.H.U.):** Amount of heat required to raise the temperature of 1 pound of water by one degree Celsius (15-16°C).

Calorific Values:

Higher or Gross Calorific Value (HCV or GCV):

- **Definition:**

The total heat produced when one unit (weight or volume) of fuel burns completely, and the products of combustion are cooled to room temperature.

- **Explanation:**

When fuels contain hydrogen, it's converted into steam during combustion. If the combustion products are condensed to room temperature, the latent heat of steam is included in the measured heat, making it the 'Higher or Gross Calorific Value.'

Net or Lower Calorific Value (NCV or LCV):

- **Definition:**

The net heat produced when a unit mass or volume of fuel burns completely in the air, and the products of combustion are allowed to escape.

- **Explanation:**

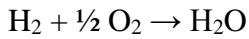
In practical scenarios, water vapor and moisture in the fuel don't condense and escape with hot gases. This results in less available heat. Net or Lower Calorific Value is calculated by subtracting the latent heat of water vapor formed from the Gross Calorific Value (GCV).

- **Formula:**

$$\text{NCV} = \text{GCV} - \text{Latent heat of water vapor formed.}$$

Combustion of Hydrogen in Fuel:

During the burning of solid or liquid fuel, the hydrogen in it combines with oxygen from the air to form water. The chemical reaction is written as:



This can be expressed in parts by weight as:

$$(2 \text{ parts}) \rightarrow (18 \text{ parts})$$

or

$$(1 \text{ part}) \rightarrow (9 \text{ parts})$$

Since 1 part by weight of hydrogen gives 9 parts by weight of water, the Net Calorific Value (NCV) can be calculated using the formula:

$$\text{NCV} = \text{GCV} - 0.09H \times \text{Latent heat of steam}$$

Given that the latent heat of steam is 587 cal/gm or 2.45 MJ/kg, the formula becomes:

$$\begin{aligned} \text{NCV} &= \text{GCV} - 0.09H \times 587 \text{ cal/gm (or kcal/kg)} \\ &= \text{GCV} - 0.09H \times 2.45 \text{ MJ/kg} \end{aligned}$$

Solid Fuels:

Solid fuels are made mostly of carbon and hydrogen, with varying amounts of oxygen, nitrogen, sulfur, and other volatile substances.

Natural Solid Fuel:

- **Coal:**

It's a significant natural solid fuel formed from the alteration of plant material like plants, subjected to conditions of high temperature, pressure, bacterial action, and absence of oxygen.

- **Classification of Coal:**

Coal is categorized based on its rank or the degree of transformation from the parent material (like wood).

Wood → Peat → Lignite → Bituminous Coal → Anthracite Coal

Transformation of Wood to Anthracite results in:

- Increased carbon content, hardness, and calorific value.
- Decreased moisture content, oxygen, volatile matter, nitrogen, hydrogen, sulfur, ash, etc.

To evaluate coal quality, two types of analyses are conducted:

- Proximate Analysis&
- Ultimate Analysis

- a) **Proximate Analysis:**

Involves determining the percentages of moisture, volatile matter, ash, and fixed carbon.

- 1. **% of Moisture:**

A finely powdered air-dried coal sample is heated in an electric hot air oven at 105-110°C for 1 hour. The loss in weight gives the percentage of moisture.

Formula: % of Moisture = $\frac{\text{Loss in weight}}{\text{Weight of coal}} \times 100$

Weight of coal

- 2. **% of Volatile Matter:** The same coal sample is heated in a muffle furnace at $925 \pm 20^\circ\text{C}$ for 7 minutes. The loss in weight provides the percentage of volatile matter.

Formula: % of Volatile Matter = $\frac{\text{Loss in weight}}{\text{Weight of coal}} \times 100$

Weight of coal

- 3. **% of Ash:** The coal sample is heated in a muffle furnace at $700 \pm 50^\circ\text{C}$ for half an hour. The loss in weight gives the percentage of ash.

The formula for calculating the percentage of ash is:

$$\% \text{ of Ash} = \frac{\text{Weight of Residue (Ash)} \times 100}{\text{Weight of Coal}}$$

- 4. **% of Fixed Carbon:**

Formula: % of Fixed Carbon = $100 - \% [\text{moisture} + \text{ash} + \text{volatile matter}]$

Gross Calorific Value (GCV) Determination:

Goutel Formula: GCV = 82 FC + aVm (cal/gm)

FC: % of fixed carbon

Vm: % of volatile matter

'a' is an empirical constant, its value depends on the percentage of volatile matter in the fuel sample.

Significance of Proximate Analysis:

1. Moisture lowers the energy in fuel. Good fuel needs less moisture for higher energy output.
2. **Volatile Matter:** Volatile matter decreases fuel energy and creates pollution. Quality fuel has less volatile matter for cleaner use.
3. **Ash:** Ash lowers coal energy and can disrupt burning. Good fuel should have minimal ash content.
4. **Fixed Carbon:** More fixed carbon means better fuel quality, with higher energy and efficiency.

Numerical on Proximate analysis

1. Accurately weighed 2.5 gm of a sample of coal was heated in a silica crucible for 1 hour at 110°C and the residue obtained is weighed as 2.42 gm. This residue was heated strongly for 7 minutes at $950 \pm 20^{\circ}\text{C}$ covered with a vented lid. The residue weighed as 1.55 gm and was further heated uncovered until a constant weight of 0.25 gm was obtained. Calculate the % of Proximate analysis.

Solution :

- a) Weight of coal sample = 2.5 gm
- b) Weight of coal sample after heating at 110°C = 2.42 gm
- c) Amount of Moisture = $2.5 - 2.42 = 0.08$ gm
- d) Weight of volatile Matter = $2.42 - 1.55 = 0.87$ gm
- e) Weight of Ash = Weight of residue = 0.25 gm

$$\begin{aligned}\% \text{ of Moisture} &= \frac{\text{Loss in weight}}{\text{Weight of coal}} \times 100 \\ &= \frac{0.08}{2.5} \times 100 = 3.2\end{aligned}$$

$$\begin{aligned}\% \text{ of Volatile Matter} &= \frac{\text{Loss in weight}}{\text{Weight of coal}} \times 100 \\ &= \frac{0.87}{2.5} \times 100 \\ &= 34.8\end{aligned}$$

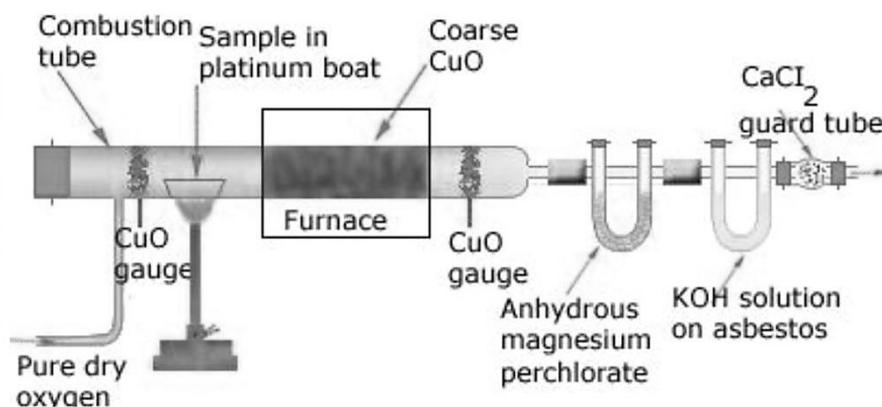
$$\begin{aligned}\% \text{ of Ash} &= \frac{\text{Weight of Residue (Ash)}}{\text{Weight of Coal}} \times 100 \\ &= \frac{0.25}{2.5} \times 100 \\ &= 10\end{aligned}$$

$$\begin{aligned}\% \text{ of Fixed carbon} &= 100 - \% [\text{Moisture} + \text{Volatile matter} + \text{Ash}] \\ &= 100 - \% [3.2 + 34.8 + 10] \\ &= 100 - 48 \\ &= 52\end{aligned}$$

Ultimate Analysis

Ultimate analysis involves the determination of % of C, H, N, S, ash and oxygen

1. Determination of Percentage of Carbon.



A known amount of dry coal is burned with oxygen at 1290°C , forming CO_2 and H_2O through oxidation of carbon and hydrogen:

- $\text{C} + \text{O}_2 \rightarrow \text{CO}_2$, $2\text{KOH} + \text{CO}_2 \rightarrow \text{K}_2\text{CO}_3 + \text{H}_2\text{O}$
- $\text{H}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{O}$, $7 \text{H}_2\text{O} + \text{CaCl}_2 \rightarrow \text{CaCl}_2 \cdot 7\text{H}_2\text{O}$

The combustion products pass through a water-absorbing unit with Mg perchlorate or CaCl_2 , and a CO_2 -absorbing unit with soda lime or KOH. The weight gain in these units corresponds to the weight of H_2O and CO_2 from carbon and hydrogen combustion.

$$\% \text{ of carbon} = \frac{12 \times \text{Increase in weight of KOH/sodalime tube}}{44 \times \text{weight of coal sample}} \times 100$$

$$\% \text{ of hydrogen} = \frac{2 \times \text{Increase in weight of Mg-Perchlorate tube}}{18 \times \text{weight of coal sample}} \times 100$$

2. Determination of Nitrogen by Kjeldahl's method

To find the percentage of Nitrogen in a coal sample using Kjeldahl's method, follow these steps:

- Take 1 gram of precisely weighed powdered coal.
- Heat it with concentrated H_2SO_4 and K_2SO_4 catalyst in a Kjeldahl's flask.
- When the solution clears, add excess NaOH solution.
- Distill and capture the liberated ammonia in a known acid solution.
- Determine the unused acid through back titration with standard NaOH solution.
- Calculate the percentage of Nitrogen from the volume of acid used.

• Chemical Reactions:

- $2\text{N} + 6\text{H} + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4$
- $(\text{NH}_4)_2\text{SO}_4 + 2\text{NaOH} \rightarrow 2\text{NH}_3 \uparrow + \text{Na}_2\text{SO}_4 + 2\text{H}_2\text{O}$
- $2\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_4)_2\text{SO}_4$

Percentage of Nitrogen (% of N) can be calculated using formula:

$$= \frac{[(\text{Volume of acid used}) - (\text{Blank titration reading})] \times \text{Normality of acid} \times 1.4}{\text{Weight of coal sample taken}}$$

3. Determination of sulfur using the ESCHKA method

In this method, follow these steps:

1. Burn a known quantity of coal completely in a Bomb calorimeter with oxygen.
2. During combustion, sulfur in the coal is oxidized to sulfate.
3. Treat the sulfate formed with BaCl₂ solution to produce BaSO₄.
4. Filter, wash, and heat the precipitate until a constant weight is obtained.
5. Calculate the percentage of sulfur using the formula:

$$\% \text{ of Sulfur} = \frac{32 \times \text{weight of BaSO}_4}{233 \times \text{weight of coal sample}} \times 100$$

4. Ash Determination: % of Ash:

The coal sample is heated in a muffle furnace at 700 ± 50°C for half an hour. The loss in weight gives the percentage of ash.

The formula for calculating the percentage of ash is:

$$\% \text{ of Ash} = \frac{\text{Weight of Residue (Ash)}}{\text{Weight of Coal}} \times 100$$

5. Percentage of Oxygen:

Calculate theoretically by subtracting the percentages of C,H,N, S, and ash from 100.

$$\% \text{ of oxygen} = 100 - \% [\text{C} + \text{H} + \text{S} + \text{N} + \text{Ash}]$$

Numericals on Ultimate analysis.

- 1) 0.250 gm of coal sample was burnt in a stream of oxygen at 1290°C in a combustion tube. There was increase in weight of Mg-Perchlorate tube by 0.025 gm and that of sodalime unit by 0.800 gm after combustion. Find out % of C & H in coal sample.

Solution :

$$\begin{aligned} \% \text{ of carbon} &= \frac{12 \times \text{Increase in weight of KOH/sodalime tube}}{44 \times \text{weight of coal sample}} \times 100 \\ &= \frac{12 \times 0.800}{44 \times 0.250} \times 100 \\ &= 87.264 \% \end{aligned}$$

$$\begin{aligned} \% \text{ of hydrogen} &= \frac{2 \times \text{Increase in weight of Mg-Perchlorate tube}}{18 \times \text{weight of coal sample}} \times 100 \\ &= \frac{2 \times 0.025}{18 \times 0.250} \times 100 \\ &= 1.11 \% \end{aligned}$$

2. 1.0 gm of coal sample was burnt in a current of pure oxygen. CO₂ was absorbed in KOH and water vapor in CaCl₂. The increase in weight of KOH and CaCl₂ was 3.157 and 0.504 gm respectively. Determine the % of carbon and hydrogen in fuel sample.

Solution :

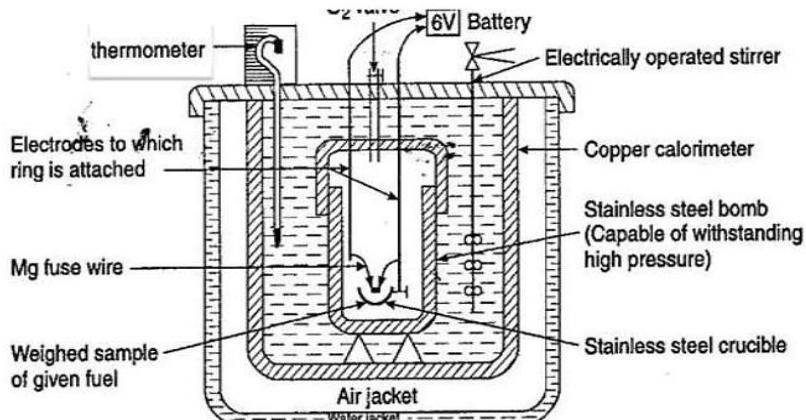
$$\% \text{ of carbon} = \frac{12 \times \text{Increase in weight of KOH}}{44 \times \text{weight of coal sample}} \times 100$$

$$\begin{aligned}
 &= \frac{12 \times 3.157}{44 \times 1} \times 100 \\
 &= 86.09\% \\
 \% \text{ of hydrogen} &= \frac{2 \times \text{Increase in weight of } \text{CaCl}_2}{18 \times \text{weight of coal sample}} \times 100 \\
 &= \frac{2 \times 0.504}{18 \times 1} \times 100 = 5.59\%
 \end{aligned}$$

Bomb Calorimeter

Principle:

The total heat produced by the combustion of fuel is absorbed by a known weight of water in a copper calorimeter. The calorific value can be calculated from the rise in temperature of the water.



Construction:

1. Bomb Calorimeter consists of a cylindrical stainless steel vessel called the Bomb for fuel combustion.
2. The bomb has a tightly screwable lid for a gas-tight seal, having two electrodes and an oxygen inlet valve.
3. One electrode has a ring for supporting a crucible, and the bomb is placed in a copper calorimeter with air and water jackets.
4. The copper calorimeter includes an electric stirrer and a Beckman's thermometer for precise temperature measurement.

Working:

1. Take a known mass (approximately 0.5 to 1 gm) of the provided fuel in a clean silica crucible.
2. Support the crucible over the ring and stretch a fine Mg-wire across the electrodes, ensuring contact with the fuel sample.
3. Tighten the bomb lid securely and fill the bomb with oxygen, maintaining a pressure of 25 atmospheres.
4. Lower the bomb into the copper calorimeter, which holds a known mass of water. Begin stirring and note the initial temperature of the water.
5. Connect the electrodes to a 6-volt battery, completing the circuit. The fuel ignites, releasing heat. Continuously stir the water and record the highest temperature reached.

Let, x = Mass of fuel sample taken in crucible

W = Mass of water in copper calorimeter

ω = Water equivalent in grams of calorimeter, stirrer, thermometer, Bomb etc.

t_1 = Initial temperature of water

t_2 = Final temperature of water

θ = Higher or Gross calorific value

Heat liberated by fuel = Heat absorbed by water + Heat absorbed by apparatus

$$\theta \times x = W (t_2 - t_1) + \omega (t_2 - t_1)$$

$$\theta = \frac{W (t_2 - t_1) + \omega (t_2 - t_1)}{x}$$

NCV = GCV - $0.09 \times H \times$ latent heat of water vapor formed

Corrections:

i. **Fuse Wire Correction: (t_f)**

The heat produced by the fuse wire during combustion is included in the measured heat. The actual heat needs to be subtracted from the measured heat.

ii. **Acid Corrections (t_A):**

Sulfur (S) and Nitrogen (N) in the fuel get oxidized during combustion, forming H_2SO_4 and HNO_3 under high pressure and temperature.

The measured heat includes the heat released during acid formation.

Corrections are made by analyzing acids from bomb washings through titration.

Correction for 1 mg of S is 2.25 cal, and for 1 ml of 0.1N HNO_3 formed is 1.43 cal.

iii. **Cotton Thread Correction (t_t):**

Heat produced by the cotton thread (attached to the fine Mg-wire) is included in the measured heat.

The heat from the cotton thread must be subtracted from the measured heat.

iv. **Cooling Correction (t_c):**

The time taken to cool the water in the calorimeter from the maximum temperature to room temperature is noted.

Cooling correction is calculated from the rate of cooling (dt_0 /minute) and the time taken for cooling (t minutes).

The cooling correction ($dt \times t$) is added to the rise in temperature.

$$\theta = \frac{(W+w) (t_2-t_1+t_c) (t_a+t_t+t_f)}{X} \text{ Cal/gm or Kcal}$$

Octane and cetane No. of Fuel

Vibrations along with sound are known as 'Knocking' .

Octane and Cetane numbers are used to measure the quality of fuel for engines.

When an engine makes knocking sounds, it's not good because:

1. It makes the machine less efficient.
2. It shortens the machine's lifespan.
3. It increases maintenance costs and noise pollution.

Good fuel should prevent knocking. In petrol engines, knocking happens due to fast combustion,

while in diesel engines, it's because of delayed combustion. This depends on the fuel's nature, combustion method, and compression ratio.

Petrol engines are rated by their octane number, while diesel engines are rated by their cetane number.

Octane number: It measures how resistant petrol is to knocking. It's determined by comparing petrol's combustion to two standard fuels: n-heptane and iso-octane, which have different properties.

- **Definition Of Octane no:**

Percentage by volume of Iso-Octane and n-heptane mixture, which matches with the fuel under test in knocking characteristics.

To determine the octane number of a fuel, it's tested in a petrol engine where combustion is initiated by an electrical spark. If the fuel burns too quickly, it creates high pressure in the combustion chamber, leading to vibrations and knocking sounds. This knocking reduces engine efficiency, shortens its lifespan, and increases maintenance costs and noise pollution. To measure the octane number, the fuel being tested is compared to two standard fuels: n-heptane and iso-octane, each with different properties.

The octane number of a fuel is determined by comparing its knocking behavior to a mixture of two hydrocarbons: iso-octane and n-heptane, blended in various proportions from 0% to 100%. This creates a range of fuels with octane numbers from 0 to 100. For example, if a fuel has an octane number of 80, it means its knocking matches a mixture containing 80% iso-octane and 20% n-heptane.

The higher the octane number, the less tendency the fuel has to knock, indicating better fuel quality.

To improve a fuel's octane number, additives can be used. These include:

1. Tetraethyl lead (at a concentration of 0.5 ml per liter)
2. Branched chain alkanes
3. BTX (benzene, toluene, xylene)
4. MTBE (methyl t-butyl ether or ethyl t-butyl ether)

These additives help slow down the combustion process and reduce knocking in the engine, improving fuel performance and efficiency.

Octane No of petrol should be at least 85 for motor cycles and cars. For Aeroplane and Helicopter it should be above 100.

Relationship between Organic structure and Octane No of Fuel (Hydrocarbons)

Aromatics > *cycloalkane* > alkene > branched alkane > straight chain alkane

Cetane number:

The cetane number of diesel is a measure of its tendency to cause knocking in a diesel engine. Knocking in diesel engines happens because of a delay in the combustion or oxidation of the fuel. In diesel engines, fuel is injected into the combustion chamber, and it's essential for the fuel to ignite quickly without any delay.

To determine the cetane number of diesel fuel being tested, two standard fuels are used: cetane (n-hexadecane) and alpha-methylnaphthalene. The cetane number is determined by comparing the ignition characteristics of the test fuel with these standard fuels.

A higher cetane number indicates that the fuel ignites more readily, resulting in better performance and efficiency in diesel engines.

If we mix the two hydrocarbons, cetane (n-hexadecane) and alpha-methylnaphthalene, in various

proportions, we can create a range of fuels with cetane numbers from 0 to 100. These mixtures help us determine the cetane number of a diesel fuel being tested. By comparing the fuel's knocking behavior with the knocking properties of these mixtures, we can accurately assign it a cetane number. A higher cetane number indicates that the fuel ignites more readily, leading to better engine performance and efficiency in diesel engines.

- **Definition Of Cetane no:**

Percentage by volume of Cetane and α-methyl naphthalene mixture, which matches with the fuel under test in knocking characteristics.

e.g : A fuel is said to have an Cetane No 70, When the knocking property of the fuel matches with the knocking property of the mixture which contains 70 % cetane and 30 % α-methyl naphthalene.

Hence higher the Cetane no of fuel, lesser will be its knocking tendency and better is the quality of fuel.

How to improve the Cetane No of Fuel : Cetane No of petrol can be increased by by the addition of additives containing

- i) Ethyl nitrite
- ii) Ethyl nitrate
- iii) Isoamyl-nitrate,
- iv) Acetone peroxide etc.

Relationship between Organic structure and Cetane No of Fuel (Hydrocarbons)

n – alkanes > cycloalkanes > alkenes > branched alkanes > aromatics

High Speed diesel engine is having the cetane No = 45

Medium Speed diesel engine is having the cetane No = 35

Low Speed diesel engine is having the cetane No = 25

CNG :

Compressed Natural Gas (CNG) is natural gas compressed under high pressure. It's mainly methane, with small amounts of other gases like ethane, propane, butane, and pentane.

- **Properties:**

1. CNG is cleaner than petrol and diesel, emitting less CO, ozone, and hydrocarbons during combustion.
2. It doesn't produce sulfur or nitrogen gases during combustion.
3. No carbon particles are emitted.
4. It's cheaper than petrol and diesel.
5. The ignition temperature of CNG is 55°C.
6. CNG is a better fuel for automobiles than petrol or diesel.
7. It needs more air for ignition.

- **Uses:**

CNG is widely used in Delhi for buses, taxis, and autos due to its affordability, cleanliness, and low environmental impact.

Liquefied Petroleum Gas (LPG):

It is a by-product of heavy oil cracking or natural gas processing. It's treated to remove impurities and odorized for safety. LPG is stored under pressure in containers like Indane or Bharat gas. Its calorific value is around 27,800 kcal/m³.

LPG consists mainly of n-butane, isobutane, butylenes, and propane, with small amounts of propylene and ethane.

- **Average composition:**

n-Butane: 38.5%

Iso Butane: 37.0%

Propane: 24.5%

- **Properties of LPG:**

1. Burns Easily: LPG catches fire quickly.
2. Smells: It has a strong smell added to help detect leaks.
3. Stored Under Pressure: LPG is kept in containers under pressure.
4. Flexible: It can turn from liquid to gas easily.
5. Burns Cleanly: LPG produces fewer dirty gases when burned.

- **Uses of LPG:**

1. Cooking: Used in kitchens for cooking food.
2. Heating: Used to warm homes and buildings.
3. Industries: Used in factories for tasks like welding.
4. Cars: Some vehicles run on LPG instead of petrol.
5. Electricity: LPG generators make electricity

Introduction to Alternate Fuels:

Alternate fuels are unconventional and eco-friendly options for powering vehicles and machinery. Examples include alcohol fuel, vegetable oil, biodiesel, and natural gas (CNG).

Hydrogen as a Future Fuel:

Hydrogen is seen as a promising low-carbon energy source with the potential to reduce greenhouse gas emissions. Despite being discovered in 1766, its widespread use is limited due to concerns about safety and cost.

- **Advantages of Using Hydrogen as a Transportation Fuel:**

1. High energy yield
2. Abundant element
3. Produced from various energy sources
4. Wide flammability range
5. Versatility

- **Disadvantages of Using Hydrogen as a Transportation Fuel:**

1. Low density requiring large storage areas
2. Not found free in nature
3. Expensive to produce currently
4. Requires careful handling due to low ignition energy

Production of Hydrogen:

Several methods are used to produce hydrogen:

1. Steam reforming of methane gas: Most common method but produces CO₂ emissions.
2. Hydrogen from coal (Gasification): Utilizes coal resources but also produces CO₂ emissions.
3. Electrolysis of water: Not widely used due to the cost of electricity.
4. Solar-Hydrogen system: Still expensive due to the cost of renewable energy sources.

- **Advantages and Disadvantages of Production Methods:**

1. Steam reforming: Economical but uses nonrenewable resources and emits CO₂.
2. Gasification: Utilizes inexpensive coal resources but also produces CO₂ emissions.
3. Electrolysis of water: Depends on electricity source and may require more energy input than released.
4. Solar system: Environmentally friendly but expensive.

Storage of Hydrogen:

Various methods exist for storing hydrogen:

- Compressed gas: Reliable but costly with potential safety risks.
- Liquid: High density but requires low temperatures and poses safety risks.
- Metal Hydride: Safe and efficient but expensive and heavy.
- Each storage form has its advantages and disadvantages, impacting its feasibility for widespread use.

Biofuels:

Biofuels are substitutes for fossil fuels made from agricultural crops and biomass sources. They're produced from organic matter over short periods, like days or months, and are seen as an alternative energy source.

Importance:

1. Ensuring Energy Security: With rising oil prices, biofuels offer an alternative energy source.
2. Reducing Greenhouse Gas Emissions: Biofuels help decrease emissions, contributing to environmental protection.
3. Promoting Rural Development: Biofuel production supports rural economies and communities.
4. Biofuels are liquid fuels derived from plants or animal waste, contributing to a cleaner environment by regulating carbon dioxide levels and reducing global warming.

Significance of Biofuels:

1. **Cost-Effective:** Biofuels can be cheaper than gasoline and other fossil fuels.
2. **Versatile Sources:** They can be made from various materials like crop waste and manure, promoting efficient recycling.
3. **Renewable:** Biofuels are renewable as new crops are grown and waste is collected.
4. **Job Creation:** Biofuel production creates employment opportunities, especially in rural areas.
5. **Reduced Emissions:** When burned, biofuels produce fewer carbon emissions, improving air quality and lowering pollution levels.

First Generation Biofuel - Bioethanol:

Bioethanol is an alcohol produced by fermenting starch from basic feedstocks, mainly sugar or starch crops like corn or sugarcane. It's used as a substitute for petrol in road transport vehicles and is more environmentally friendly with low toxicity levels.

- **Production of Bioethanol:**

Bioethanol is produced through fermentation of starch from crops like corn or sugarcane.

- **Applications of Bioethanol:**

1. Vehicular fuel to replace gasoline.
2. Power generation through thermal combustion.
3. Fuel for fuel cells through thermochemical reaction.
4. Blending with gasoline for cost-effective use.

- **Advantages of Bioethanol:**

1. Renewable energy resource and alternative fuel.
2. Clean burning with complete combustion.
3. Reduces greenhouse gas emissions.
4. Easily biodegradable in case of spills.
5. Can be produced from various plants containing sugar and starch.
6. High octane number increases engine compression ratio for better thermal efficiency.

- **Disadvantages of Bioethanol:**

1. Less efficient than petroleum.
2. Start-up issues in cold temperatures.
3. Requires large land areas for crop cultivation, leading to habitat destruction.
4. Competition with food crops may raise food prices.
5. Bioethanol production releases significant carbon dioxide emissions.

Numerical- NCV

1. Calculate LCV of a fuel which has 8% hydrogen and HCV as 6500 cal/gm. Given that latent heat of steam = 580 cal/gm.

Solution :-

$$\text{LCV} = \text{GCV} - 0.09 \text{ H} \times \text{Latent heat of condensation of steam.}$$

$$\% \text{ of H} = 8$$

$$\begin{aligned}\text{LCV} &= \text{GCV} - 0.09 \times 8 \times 580 \\ &= 6500 - 0.09 \times 8 \times 580 \\ &= 6500 - 417.6 \\ &= 6082.4 \text{ cal/gm}\end{aligned}$$

Questions

1. What is the definition of fuel, and how are fuels classified?
2. What is calorific value, and what are its types?
3. Can you explain the principle, construction, and working of a Bomb Calorimeter with a diagram?
4. How is the calorific value of a solid and liquid fuel sample determined using a Bomb Calorimeter?
5. Explain the process and significance of Proximate Analysis of coal.
6. How is the percentage of carbon and hydrogen determined from a coal sample?
7. What is knocking, and how is the octane number of petrol/gasoline determined?
8. What is knocking, and how is the cetane number of diesel determined?
9. Explain hydrogen as a future fuel
10. Explain Biofuels.
11. Write a note on Biodiesel.
12. Write a note on Bioethanol.
13. Write properties and uses of CNG and LPG fuels.

