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1)⇐The property of water to form an insoluble curd with soap instead of lather (foam). ⇐A water sample's ability to consume soap, or precipitate soap as a characteristic property.

Causes of Hardness

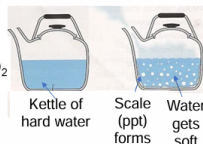
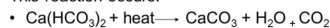
Hard water contains more number of salts like CaCl_2 , MgCl_2 , CaSO_4 and MgSO_4 etc.

Type of hardness

Temporary hardness

- It is caused by the presence of dissolved bicarbonate of calcium (Ca), magnesium (Mg), and the carbonate of iron (Fe).
- Dissolved bicarbonates destroyed by boiling of water, when bicarbonates are decomposed yielding insoluble carbonates.

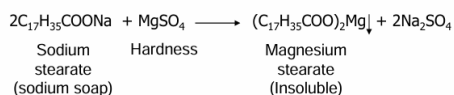
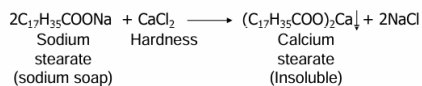
This reaction occurs:



Almost insoluble Ca/MgCO_3 are formed and are deposited as a scale at the bottom of the vessel, while carbon dioxide escapes.

Permanent hardness

- It is due to chlorides and sulphates of calcium and magnesium.
- This type of hardness cannot be removed by simple boiling.
- It is removed by ion exchange, zeolite process etc.



Numerical problems based on hardness calculation

CaCO₃ equivalent hardness

$$\text{Calcium carbonate equivalent} = \frac{\text{Mass of hardness producing substance} \times \text{Molecular weight of CaCO}_3}{\text{Molecular weight of hardness producing substances}}$$

Problem 1

Calculate the calcium carbonate equivalent hardness of a water sample containing 204 mg of CaSO₄ per liter

Solution :

$$\begin{array}{lcl} \text{Calcium carbonate} & = & \frac{204 \times 100}{136} = 150 \text{ mg of CaCO}_3/\text{L} \\ \text{equivalent hardness} & & = 150 \text{ ppm} \end{array}$$

Note : Mol. Weight of CaCO₃ = 100
Mol. Weight of CaSO₄ = 136

Water sample from an industry in Vijawada had the following data
Mg(HCO₃)₂ = 16.8mg/L, MgCl₂ = 19 mg/L, CaCO₃ = 20 ppm, MgSO₄ = 24.0mg/L and KOH = 1 ppm.

Calculate the temporary, permanent and total hardness of the water sample.

Solution Step 1: Conversion in to CaCO₃ equivalent

Constituent present	Quantity (mg/L)	Conversion factor	Hardness
Mg(HCO ₃) ₂	16.8	100/146	16.8 * 100/146 = 11.5ppm
MgCl ₂	19.0	100/95	19.0 * 100/95 = 20ppm
CaCO ₃	20	100/100	20.0 * 100/100 = 20 ppm
MgSO ₄	24.0	100/120	24.0 * 100/120 = 20 ppm

Calculation

$$\text{Temp. Hardness} = 31.5 \text{ ppm} \quad \text{P. Hardness} = 40 \text{ ppm}$$

$$\text{Tot. Hardness} = 71.5 \text{ ppm}$$

Advantages of Hard Water	Disadvantages of Hard Water
1. Ca for healthy teeth and bones 	1. Limescale -blocks pipes and leaves a scale on kettles.  
2. Good for Brewing 	2. Wastes soap 
3. Tastes better 	3. Scum produced with soap 

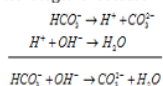
Draw backs (or) Disadvantages of Hard Water

Domestic Use	Industrial Use
1. Washing 2. Bathing 3. Drinking 4. Cooking	1. Textile Industry 2. Sugar Industry 3. Dyeing Industry 4. Paper Industry 5. Pharmaceutical Industry 6. In Steam generation in Boilers
The sticky precipitate adheres on the fabric/cloth and gives spots & streaks. Fe salts stain the cloths.	
Produces sticky scum on the bathtub and the body	
Bad to the digestive system and calcium oxalate formation is possible in urinary tracts	
Requires more fuel and time. Certain food don't cook soft and also gives unpleasant taste	

4)Determination of alkalinity

ALKALINITY OF WATER

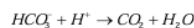
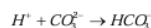
- ✓ Alkalinity of water is mainly due to the presence of anions like CO_3^{2-} , HCO_3^- , and OH^- .
- ✓ The estimation of alkalinity in water is done by titrating water sample against standard acid using phenolphthalein and methyl orange as indicators.
- ✓ In this titration, two indicators are used as the different anions give end points at different PH values.
- ✓ Out of the three anions CO_3^{2-} , HCO_3^- , and OH^- , any two of them can exist in water together.
- ✓ (CO_3^{2-} , HCO_3^-) and (CO_3^{2-} , OH^-)
- ✓ HCO_3^- and OH^- cannot be present together because H^+ ion of HCO_3^- neutralizes OH^- .



Experimental Procedure:

- A known volume of water sample is taken into a conical flask and adds two drops of phenolphthalein indicator.
- The colour will become pink (due to pH>10). This solution is titrated against HCl solution until pink colour disappears. This end point is termed as P.
- Now add two drops of methyl orange indicator to the same water (pH falls below 7) and titrate with HCl. At the end point, pink colour reappears. This end point is taken as M.

Reactions:



Calculations:

Phenolphthalein alkalinity in terms of CaCO_3 is calculated by using the formula

$$\frac{\text{P} \times \text{Molarity of HCl} \times 50 \times 1000}{\text{Volume of water sample}} \text{ ppm}$$

Methyl Orange alkalinity in terms of CaCO_3 is calculated by using the formula

$$\frac{\text{M} \times \text{Molarity of HCl} \times 50 \times 1000}{\text{Volume of water sample}} \text{ ppm}$$

Conclusions:

Burette reading	OH^- alkalinity	CO_3^{2-} alkalinity	HCO_3^- alkalinity
P = 0	-	-	M
P = M	P	-	-
P = $\frac{1}{2}$ M	-	2P	-
P < $\frac{1}{2}$ M	-	2P	M - 2P
P > $\frac{1}{2}$ M	2P - M	2(M - P)	-

Softening of hard water-External treatment

1. Lime soda process

- It is a process in which Lime (Ca(OH)_2) and soda (Na_2CO_3) are added to the hard water to convert the soluble calcium and magnesium salts **to insoluble compounds** by a chemical reaction.
- CaCO_3 and Mg(OH)_2 so precipitated are **filtered off and removed** easily.

It is further divided in to two types

1. Cold lime soda process

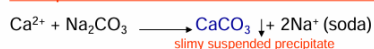
2. Hot lime soda process

1. Lime soda process

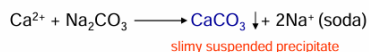
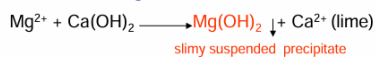
I. Cold lime soda process

- In this process a calculated quantity of Ca(OH)_2 (lime) and Na_2CO_3 (soda) are mixed with water at room temperature and added to the hard water.
- Following reactions takes place depending on the nature of hardness.

If it is permanent hardness and due to calcium salt



If it is due to Magnesium salt



1. Lime soda process

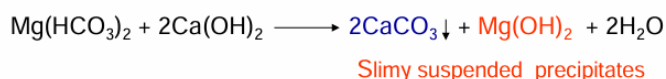
I. Cold lime soda process

Step 1

If it is Temporary hardness and due to calcium salt



If it is due to Magnesium salt

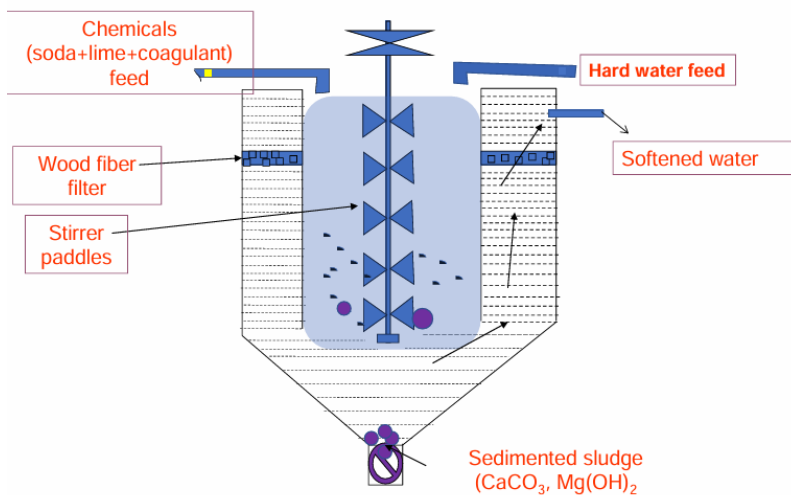


1. Lime soda process I. Cold lime soda process

Step 2

- Precipitates CaCO_3 and $\text{Mg}(\text{OH})_2$ are very fine and forms sludge like precipitates in the boiler water.
- Which are difficult to remove because it does not settle easily making it difficult to filter and the removal process. Finally reduces the efficiency of the boiler.
- Thus, it is essential to add small amount of coagulant (such as Alum, Aluminum sulfate, sodium aluminate etc.) which hydrolyses to flocculent precipitate of $\text{Al}(\text{OH})_3$ which entraps the fine precipitates.

Continuous cold lime soda softener



2. Hot lime soda Process

In this process a calculated quantity of Ca(OH)_2 (lime) and Na_2CO_3 (soda) are mixed with hot water at a temperature range of 80 to 150°C and added to the hard water. The following reactions takes place depending on the nature of hardness

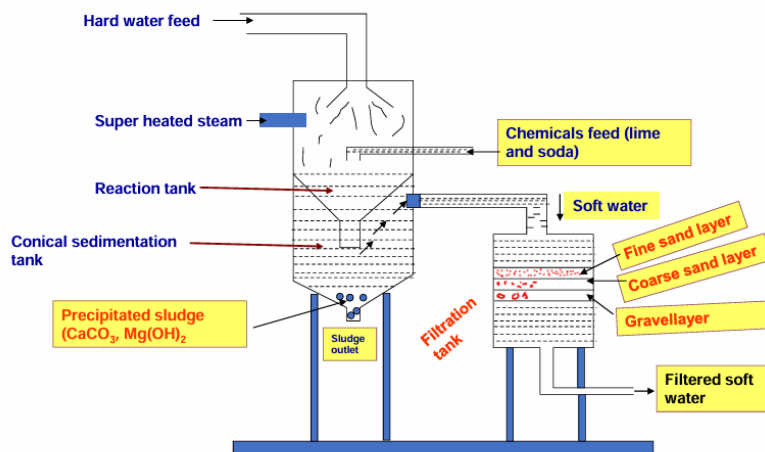
Advantages of Hot Lime Soda Process

1. Reaction between hardness producing substance and lime soda proceeds at a faster rate.
2. Precipitates and sludges formed are settled at the bottom easily and hence No coagulants are required
3. Dissolved gases (CO_2 escapes) and the water becomes free from dissolved gases
4. It produces soft water with the residual hardness of 15-30ppm in contrast to the cold lime soda process which produces soft water with 50-60ppm of residual hardness

Hot lime soda Plant consists of three parts

1. **Reaction tank**: water, chemicals and steam are mixed
2. **Conical sedimentation tank**: sludge settles down
3. **Sand filter**: complete removal of sludge from the soft water is ensured

Continuous Hot Lime soda Process



Advantages of Lime soda process

1. It is very economical compared to other methods
2. Iron and manganese salts are also removed by this process
3. It increases the pH of the softened water hence corrosion is minimized also pathogenic bacteria

Disadvantages of Lime soda process

1. Disposal of large amount of sludge (insoluble precipitates) poses a problem
2. This can remove hardness to the extent of 15ppm which is not good for boilers

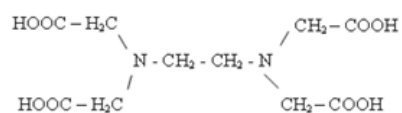
6)Complexometric titration method or EDTA method - principle, procedure, uses.

DETERMINATION OF HARDNESS OF WATER BY EDTA METHOD

- ✦ EDTA method is the most common and accurate method of determination of hardness of water.
- ✦ This method is called complexometric method.

Principle:

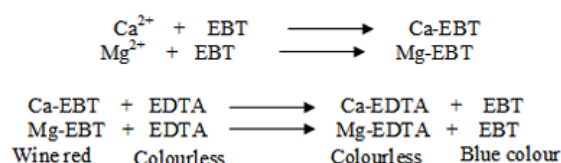
- ✓ EDTA acts as complexing agent or chelating agent.
- ✓ It forms complexes with various metal ions present in water.
- ✓ From the amount of the EDTA consumed during complex formation, the hardness of the water sample can be calculated.
- ✓ Structural formula of EDTA, ethylene diamine tetra acetic acid is



Theory:

- Water is colourless and EDTA is also colourless.

- So in order to know the formation of the complexes Eriochrome black-T indicator is used along with EDTA.
- Eriochrome black-T (EBT) is first added to water, then it forms wine red colour complex with the metal ions present in water.
- This complex is less stable.
- After the addition of EDTA, EDTA is added.
- EDTA forms stable complex with the metal ions and EBT is released which has blue colour.
- EDTA replaces EBT from the complex.



Solutions required:

- * Standard EDTA solution, Water sample, Eriochrome black- T indicator and ammonia – ammonium chloride buffer solution ($\text{NH}_4\text{Cl} + \text{NH}_4\text{OH}$, $\text{pH} = 10$)
- * To maintain $\text{pH} 10$, buffer solution is used. Instead of EDTA solution, Na_2EDTA is used because it is more soluble.

Procedure:

- ☞ Burette is filled with standard EDTA solution.
- ☞ Pipette out 10ml of the water sample into a conical flask. Add 2ml of ammonia-ammonium chloride buffer solution and 2 or 3 drops of **Eriochrome black-T indicator**.
- ☞ Now the solution is wine red in color.
- ☞ Titrate this solution with standard EDTA solution from a burette until the color changes from **wine red to blue**.
- ☞ Repeat the titration until the concurrent value is obtained.

Total hardness of water sample can be calculates as follows

$$\text{Total Hardness} = \frac{\text{Volume of EDTA} \times \text{Molarity of EDTA} \times 100 \times 1000}{\text{Volume of water sample}} \text{ mg of CaCO}_3/\text{L or ppm}$$

Uses

Complexometric titrations are used in many applications, including:

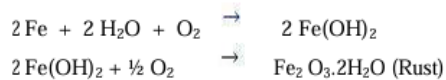
- Determining metal ion concentrations in environmental samples, such as water and soil
- ☑ ☑ Analyzing trace metal ions in pharmaceuticals
- ☑ ☑ Quality control in the production of food and beverages
- ☑ ☑ Monitoring heavy metal pollution in industrial effluents
- ☑ ☑ Research in analytical chemistry and metallurgy

7) Boiler corrosion- reason, chemical reactions, disadvantages, treatment methods

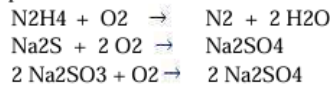
BOILER CORROSION

Boiler corrosion is the decay or loss of the boiler body material by the chemical or electrochemical reactions. Corrosion in boilers is due to the presence of dissolved oxygen, carbon dioxide and mineral acids in the feed water.

Dissolved oxygen: Usually natural water contains 8 ppm of dissolved oxygen. At high temperatures dissolved oxygen comes out of the water and they attack the iron of the boiler as



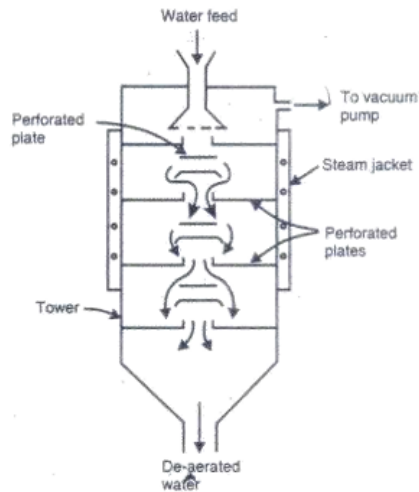
Dissolved oxygen can be removed by adding chemicals like hydrazine, sodium sulphite or sodium sulphide.



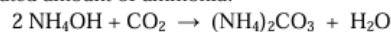
Also, dissolved oxygen can be removed along with CO_2 and other gases, if any by mechanical deaeration process.

Dissolved CO_2 : If carbon dioxide is already present in water or introduced by the decomposition of bicarbonates [$\text{Ca}(\text{HCO}_3)_2 \rightarrow \text{CaCO}_3 \downarrow + \text{H}_2\text{O} + \text{CO}_2 \uparrow$] present in water has slow corrosive effect on boiler material.

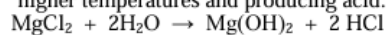
- a) By mechanical deaeration process: A deaerator is a device that is widely used for the removal of air and other dissolved gases from the feed water to steam generating boilers. Most deaerators are designed to remove oxygen down to levels of 7 ppb by weight (0.005 cm^3 per liter or less). There are many different horizontal and vertical designs available from a number of manufacturers, and the actual construction details will vary from one manufacturer to another. So by increasing temperature, decreasing pressure and exposing large surface area of water much of the dissolved gases are driven out of water.



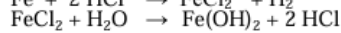
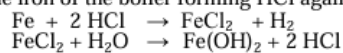
b) By using calculated amount of ammonia:



Acids producing salts: If MgCl_2 is present in feed water it undergoes hydrolysis at higher temperatures and producing acid.



Acid attacks the iron of the boiler forming HCl again and again.



And corrosion continues in a chain like reaction. So even small quantities of salt causes severe corrosion of the boiler.

Disadvantages:

- Shortening of boiler life
- Leakages of joints and reverts, increased cost of repairs and maintenance.

9)> Differences between foaming and priming in boilers



Foaming



Normal bubble

Foaming
It is the production of continuous foam or hard bubblers in boilers. Foaming is due to the presence of substance like oil in boiling water.



Priming



Carry over bubble

Priming
It is the process in which some particles in water are carried along with the steam. Resulting process is called as wet steam or carry over. Process of formation of wet steam in boilers is called as priming.

Causes of Priming •

Very high level of water • Uneven heating • Presence of large quantity of dissolved salts, organic matter, alkalies and suspended matter etc. • Improper design of the boiler. • High steam velocity

Prevention of Priming • Maintaining proper water level in the boiler. • Removing dissolved salts and oily matter. • Avoiding sudden changes in temperature. • Proper design of the boiler.

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Differentiate between Sludge & Scale

Sludge		Scale	
1	Due to heating, the salt containing water will get concentrated and changes into loose and slimy precipitates called sludge.	1	When these precipitates becomes hard and adherent called scales.
2	Sludge is not harmful for boiler.	2	Scales is harmful for boiler.
3	Sludge can be removed from the bottom of the boiler time to time.	3	Scale can be removed by either external or internal treatment or hammering.
4	Sludge doesn't cause clogging and corrosion.	4	Scale causes clogging and corrosion.
5	Sludge increases the discarding cost of waste.	5	Scale increases the maintenance and operation cost.

Differentiate between Priming & Foaming

Priming		Foaming	
1	When boiler is producing steam very rapidly some particles of the water carried along with the steam. This process of "Wet Steam" formation is called priming.	1	Foaming is the persistent formation of bubbles or foam in the boiler.
2	Priming is caused by dissolved salts, high steam velocity, sudden heating, improper design etc.	2	Foaming is caused by the presence of oily substances in water.
3	Priming can be prevented by improving the boiler design, adding mechanical purifier, maintaining low water level and decreasing the salt concentration.	3	Priming can be prevented by addition of anti-foaming agents such as castor oil, Gallic acid, Tannic acid, sodium aluminate etc.
4	Priming reduces the boiler efficiency, life of machinery parts.	4	Foaming reduces the boiler efficiency and damages machinery parts.
5	Due to priming one can't judge the water level properly.	5	Due to foaming boiler pressure can't be maintained and water level also can't be judged.

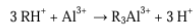
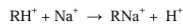
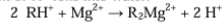
10)

ION EXCHANGE PROCESS (OR) DEIONISATION PROCESS

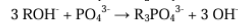
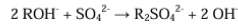
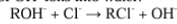
The ion exchange resins are long chain organic polymers with micro porous structure and the functional groups attached to the resins are responsible for the exchanging properties.
 Cation exchange resins: It is a styrene – divinyl benzene copolymer which on sulphonation or carboxylation becomes capable to exchange the H^+ ions with cations present in water.

Anion exchange resins: It is styrene – divinyl benzene copolymer which contains quaternary ammonium or quaternary phosphonium groups as an integral part of the resin. This on treatment with dil. NaOH becomes capable to exchange OH^- ions with anions present in water.

Process: First hard water is allowed to pass through cation exchange resin which takes up all the cations (such as Ca^{2+} , Mg^{2+} , Al^{3+} , etc...) and releases equivalent amount of H^+ ions into water.

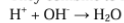


Then water containing anions and H^+ ions is allowed to pass through anion exchange resin which removes all the anions (such as Cl^- , SO_4^{2-} , CO_3^{2-} , etc...) and releases equivalent amount of OH^- ions into water.



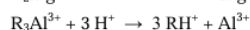
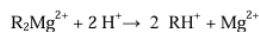
The water coming out of the anion exchange resin contains H^+ and OH^- ions.

They combine to form water.

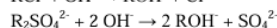
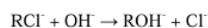


Ion free water is known as demineralised water or deionised water.

Regeneration: Once the cation exchanger resin and anion exchange resin to exchange cations and anions are lost then the resins are said to be exhausted. The exhausted cations exchange resin is regenerated by passing dil. HCl solution through it.



The exhausted anion exchange resin can be regenerated by passing dil. NaOH solution through it.



The regenerated resins can be used again.

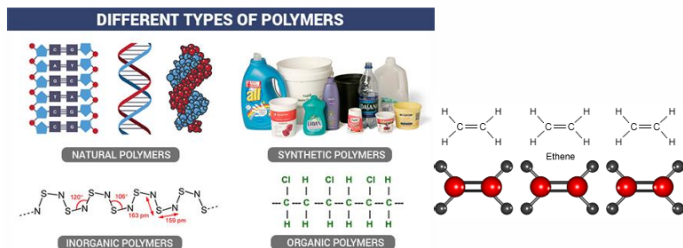
11) Classification of polymers based on their source of origin with examples.

The term **polymer** refers to chemical compounds consisting of large molecules/macromolecules which are **constructed** from **repeating subunits** that are linked by numerous intertwined links.

There are two types of polymers.

Natural Polymers: Wool, cotton, DNA, proteins.

Synthetic polymers : Teflon, Polyethylene, Nylon, polyester.



Natural polymers

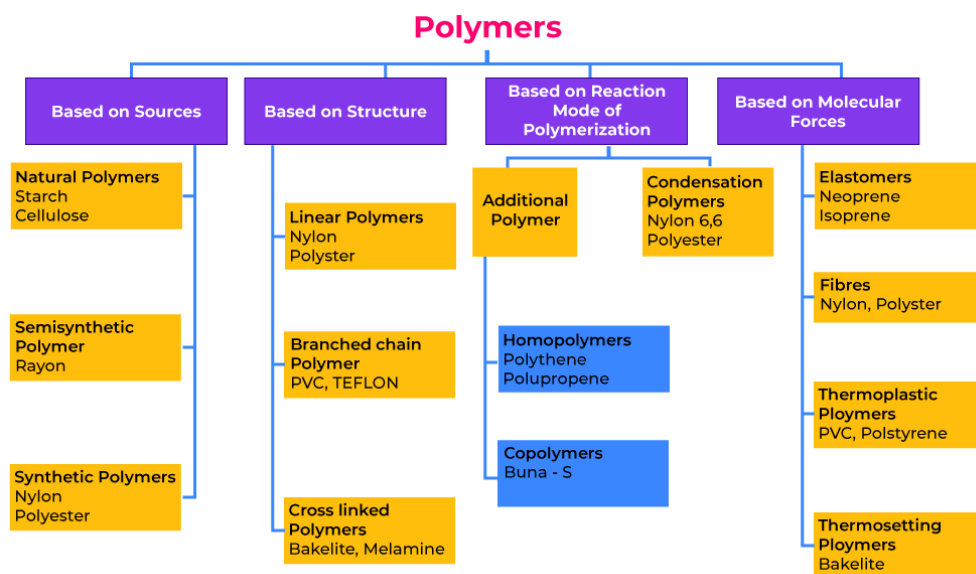
These polymers are found in nature, such as in plants and animals. Examples include cellulose, starch, rubber, proteins, and nucleic acids. Natural polymers are usually biodegradable and more environmentally friendly than synthetic polymers.

📌 Synthetic polymers

These polymers are created artificially in laboratories using chemical substances. Examples include nylon, polyethylene, polyester, Teflon, and epoxy. Synthetic polymers are more stable and less expensive than natural polymers.

📌 Semi-synthetic polymers

These polymers are made by modifying the properties of natural polymers through chemical treatment. Examples include rayon, cellulose nitrate, acetate rayon, viscose rayon, and cuprammonium silk. Nylon is an example of a semi-synthetic polymer because it is made from both coal and water.



12) Differences between addition polymerization and condensation polymerization with examples

Addition Polymerisation	Condensation Polymerisation
1. Polymer is formed by addition of monomers with out elimination of small molecules.	1. Polymer is formed by two or more monomers by the elimination of small molecules.
2. No by-products are formed.	2. By products are formed.
3. Homo chain polymers, generally thermo plastic is obtained.	3. Hetero chain polymer either thermo plastic or thermo setting can be obtained.
4. Proceeds by chain growth mechanism.	4. Proceeds by step growth mechanism.
5. Weight of polymer is identical with sum of the monomers.	5. Weight of polymer is not identical with sum of the monomers.
$n \begin{array}{c} \text{H} & & \text{H} \\ & \backslash & / \\ & \text{C} = \text{C} \\ & / & \backslash \\ \text{H} & & \text{H} \end{array} \longrightarrow \left(\begin{array}{c} \text{H} & \text{H} \\ & \\ -\text{C} & - & \text{C}- \\ & \\ \text{H} & \text{H} \end{array} \right)_n$ <p>ethylene polyethylene</p>	$n \begin{array}{c} \text{O} & & \text{OH} \\ & & \\ \text{HO}-\text{C} & - & \text{C}-\text{OH} \\ & & \\ \text{HO} & & \text{OH} \end{array} + n \text{OH}-\text{CH}_2-\text{CH}_2-\text{OH} \longrightarrow \left[\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{C}_6\text{H}_4-\text{CO} \right]_n$ <p>Terephthalic acid Ethylene glycol Terylene</p>

Here are some examples of addition and condensation polymers:

- Addition polymers**

These polymers are made from monomers with double or triple bonds. Examples include:

- Polyethylene: Made from ethylene monomers at high pressure and temperature

☐ ☐ Polystyrene: Made from styrene through a free radical mechanism

☐ ☐ Polyacrylonitrile: Also known as orlon, made from acrylonitrile in the presence of a peroxide catalyst

☐ ☐ Natural rubber: Made from isoprene, which is a long chain polymer

- ☐

☐ Condensation polymers

These polymers are made from monomers with different functional groups. Examples include:

- Polyester: A condensation polymer

☐ Polyamide: Also known as nylon, a condensation polymer

☐ Polyurethane: A condensation polymer

☐ Polysiloxane: A condensation polymer

☐ Bakelite: A synthetic condensation polymer

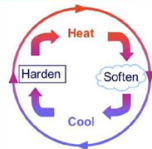
☐ Dacron: A synthetic condensation polymer

☐ Urea-formaldehyde: A synthetic condensation polymer

14) Classification of polymers based on their thermal behaviour with examples or differences between thermosetting and thermoplastics

Thermoplastic polymers

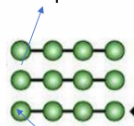
- Linear polymers with long chains that **soften on heating** and **harden on cooling** reversibly.
- These are **solid at room temperatures** and **viscous liquids** when heated. So, they are shaped by extrusion, molding or pressing.
- They can be **recycled and reused** several times by heating and cooling.
- These plastics will return to its original shape, unless damaged due to overheating or overstretching; this property is called **plastic memory**. E.g., polystyrene, polyethylene, PVC, PTFE.
- Applications: Milk jugs, soft drink bottles, etc.



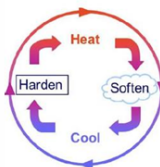
Thermoplastic polymers

- They are synthesized by **addition polymerization**
- They are straight chain or slightly branched polymers, held together by **weak van der Waal's forces of attraction**.
- Molecules of thermoplastics are **linear**, or long chains with very few entanglements.
- So, when heat is applied, molecules move apart and **disentangle**, causing them to soften, making them **malleable** to reshaping.
- On cooling, the **molecules regain their original positions**, making the plastic stiff and hard again. This process of heating and cooling can be repeated several times.
- They are generally **soluble** in **organic solvents**.

No links b/w polymers chains helps movement



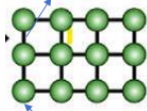
Monomers



Thermosetting polymers

- Thermosetting polymer or resins, also called thermoset, is a polymer that is **irreversibly hardened** by curing from a soft solid or viscous liquid prepolymer or resin
- Various polymer chains are **cross-linked** three dimensionally using **strong covalent bonds** or cross links.
- They are prepared by **condensation polymerization**.
- They resist heat softening and solvent attack.
- Once **set after curing**, they cannot be softened and recycled. E.g., polyester resins like fiber glass; polyurethanes: mattresses, coatings, adhesives; vulcanized rubber; bakelite: phenol-formaldehyde resin.

Links b/w polymers chains stops movement b/w them



Monomers



Thermoplastic polymers	Thermosetting polymers
Linear, long chain polymers, held together by weak van der Waal's forces	Long chain polymers that are interlinked three dimensionally by strong covalent bonds
They are formed by addition polymerization	They are formed by condensation polymerization
They are different types of thermoplastics, some rigid, and others extremely flexible, though they are malleable and flexible at high temperatures	They are rigid and non-flexible at high temperatures, and are usually brittle and strong
Soften upon heating, and harden on cooling reversibly due to the weak interlinking forces	Upon heating and cooling, they harden irreversibly, they set permanently.
Repeated heating and cooling does not affect their structure, and the changes are purely physical	Prolonged heating causes charring of polymers
Soluble in organic solvents	Insoluble in organic solvents
E.g., Polyethylene, polyvinyl chloride	E.g., Polyester resin, bakelite

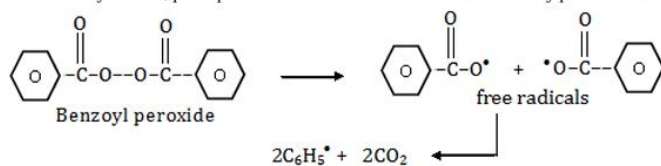
Thermo Plastics	Thermo Settings
Formed by either addition (or) condensation polymerisation.	Formed by condensation polymerisation.
They are linear (or) branched linked structures.	They are cross linked (or) three dimensional structures.
Polymers chains are held together by weak attractive forces.	Polymers chains are held together by covalent cross links.
They soften on heating and stiffen on cooling.	They don't soften on heating.
They are soluble.	They are not soluble.
They can be remoulded, reshaped and reused.	They cannot be remoulded.
They can be recycled.	They cannot be recycled.
They are tough.	They are brittle.
They have low melting points.	They have high melting points.

15) Free radical polymerization mechanism- chemical reactions and intermediates involved.

Free radical polymerization

In this type of polymerization monomer is activated to free radical by any one of the following methods.

- Photo chemical initiation:-** By exposing to sunlight free radicals are generated.
- Thermal initiation:-** By heating free radicals are generated.
- Radiation initiation:-** By exposing to α, β or γ -rays free radicals are generated.
- Chemical initiation:-** By using initiators like peroxides free radicals are generated. Benzoyl peroxide or Azo bis isobutyronitrile, persulphates etc are used as chemical initiators. They produce free radicals as



Mechanism of free radical polymerization involves three steps.

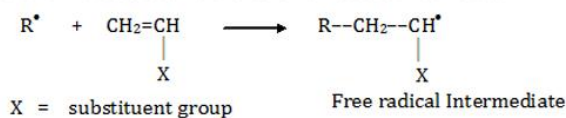
1. Chain initiation:-

It involves two steps.

- Formation of free radicals from the initiator.



- Addition of free radicals to monomer to form a free radical intermediate.



2. Chain propagation:-

Here addition of monomer molecules to the intermediate takes place one by one leads to the formation of macro-radicals.

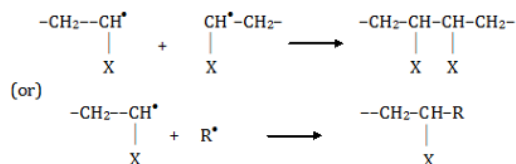


3. Chain termination:-

The growing polymer chain is terminated by many ways.

- Recombination:-**

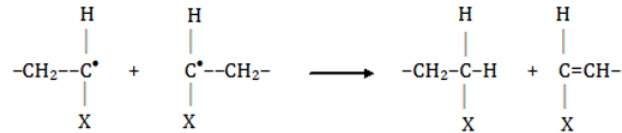
Combination of two free radicals leads to termination.



At 60°C poly styrene or Acrylonitrile chains terminate mainly by recombination.

b) Disproportionation:-

Transfer of 'H' atom from one radical to another leads to formation of two macro molecules, one of them with a double bond.

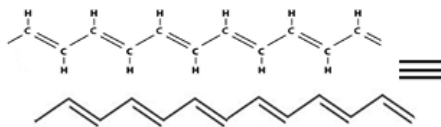


16) Differences between intrinsic and extrinsic conductivity in conducting polymers.

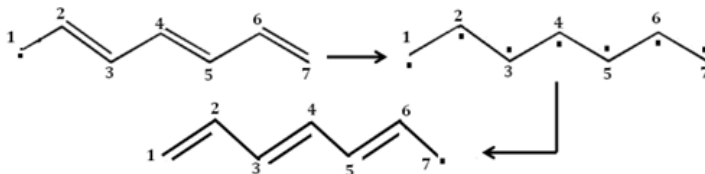
Intrinsically Conducting Polymers:

Conjugation:

- These polymers contain conjugated or delocalized π - e^- pairs in the back bone responsible for conduction.
- The orbital's of conjugated π - e^- form valency band as well as conduction band and they are extended over the entire polymer molecule.
- When current is passed electrons enter conduction band due to shifting of π - e^- .
- Ex; Conduction of poly acetylene due to conjugation.



- When current is passed into poly acetylene, the electron enters the unhybridised P-orbital of carbon atom and moves through the C - C bonds.

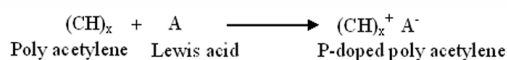


Explanation:

- When the electron enters the chain, breakage of π - bond takes place and a new π -bond is formed.
- π -bond between 2&3 is broken and a new π - bond is formed between 1&2.
- Similarly π -bond between 4&5 is broken and anew π -bond is formed between 3&4.
- π -bond between 6&7 is broken and a new π - bond is formed between 5&6.
- A long as current flows in to the polymer this process is continued and there by a conducting path is created in the polymer.

P-Doping (or) Oxidative Doping:

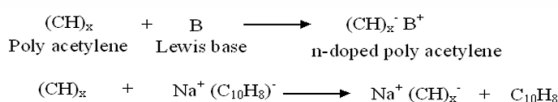
- In this method the polymer is treated with an oxidizing agent like Lewis acid which acts as a dopant.
- Examples of dopants used: FeCl_3 , I_2 etc.

**Mechanism of P-Doping:**

- During this process, oxidation of polymer takes place due to dopant and forms a cation called Polaron.
- On further oxidation of polymer results in the formation of a dication or bipolaron.

n-Doping (or) Reductive Doping:

- In this method, the polymer is treated with a reducing agent like a Lewis base which acts as a dopant.
- Ex; Sodium Naphthalide $\text{Na}^+ (\text{C}_{10}\text{H}_8)^-$

**Mechanism of n-Doping:**

- During this process, reduction of polymer takes place due to dopant and forms an anion called Polaron.
- On further reduction of polymer results in the formation of a dianion or bipolaron.

Extrinsically Conducting Polymers:

- ▲ Some of the polymers conduct electricity due to externally added ingredients to them. They are of two types.
 - Polymers with conductive elements filled

- Blended conducting polymers

Polymers with conductive elements filled:

- ◆ In these polymers, the polymer acts as a 'binder' and holds the conducting element added so that the polymer becomes a conductor.
- ◆ Examples of conductive elements are carbon black, metallic fibers, metallic oxides etc.
- ◆ Minimum concentration of conductive element to be added so that the polymer becomes a conductor is called percolation threshold.
- ◆ The conductive elements added to create a conducting path in the polymer.

Blended conducting polymers:

- ◆ These polymers are obtained by blending a conventional polymer with a conducting polymer.
- ◆ The polymer thus obtained has good chemical, physical, electrical properties and mechanical strength.
- ◆ Ex; 40% pyrrole when blended with a conventional polymer, the combination gives conducting polymer with good impact strength.

Applications of conducting polymers in biomedical devices:

- ★ Conducting polymers are used in preparation of artificial devices like Heart valves, kidneys, and lungs.
- ★ Poly methyl methacrylate is used as bone cement used for some fracture repairs.
- ★ Poly methyl methacrylate is also used for artificial teeth.
- ★ Used in preparation other medical devices include sutures, pins, screws used during surgery on bones, ankles, hands etc.
- ★ They are used to prepare contact lenses which permit O₂ to the eyes. These lenses are called rigid gas permeable lenses (RGP).

Applications of conducting polymers in electronics:

- ✎ They are used in rechargeable batteries.
- ✎ They are used in analytical sensors of p^H, O₂, NO₂, SO₂, NH₃ etc.
- ✎ Used in photo voltaic cells. Ex; Al/polymer/Au.
- ✎ Used in telecommunication systems.

Feature	Intrinsic Conductivity	Extrinsic Conductivity
Definition	Conductivity inherent to the polymer's molecular structure.	Conductivity induced by external factors such as doping.
Mechanism	Due to the presence of conjugated π -electrons in the polymer backbone.	Achieved by introducing charge carriers via doping.
Role of Doping	Not required; the polymer is inherently conductive.	Requires doping (e.g., p-type or n-type) to enhance conductivity.
Charge Carriers	Generated intrinsically by the polymer's conjugated system.	Created by the addition of dopants.
Conductivity Range	Lower compared to extrinsic; moderate intrinsic conductivity.	Higher due to the presence of additional charge carriers.
Examples	Polyaniline in its emeraldine salt form, polythiophene.	Polyaniline doped with HCl, polypyrrole doped with iodine.
Environmental Stability	Generally more stable as no external dopants are involved.	May degrade faster due to dopant instability or leaching.
Applications	Limited use in applications requiring high conductivity.	Widely used in electronic devices, sensors, and batteries.
Tuning Conductivity	Less tunable since it relies on the polymer's structure.	Highly tunable by varying the type and level of doping.

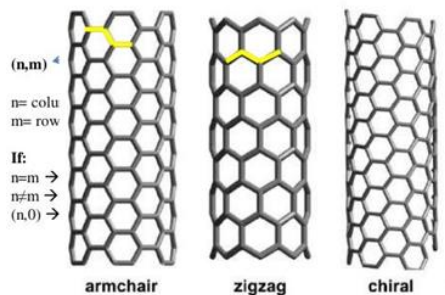
17) Classification of carbon nanotubes based on their structures

TYPES OF CARBON NANO TUBES

- Carbon nano tubes are lattice structure of carbon atom.
- Each carbon atoms are covalently bonded to each other.
- Depending upon the arrangement of carbon atoms, these are classified into two types.
 - Single walled nano tubes (SWNTs)
 - Multi walled nano tubes (MWNTs)

Single walled nano tubes (SWNTs)

- ♣ SWNT have diameter close to one nano meter
- ♣ It is obtained by wrapping graphene in to seamless cylinder.
- ♣ One atom thick layer of graphite is graphene.
- ♣ One useful application of SWNT's is in the development of first intermolecular field effect transistors (FET).
- ♣ Based on the way the graphene sheet is wrapped SWNT's are three types.
 - a) Zig – Zag
 - b) Arm Chair
 - c) Chiral



Graphene sheet consisting of pair of indices n, m

Arm chair

- If $n=m$ the nano tubes are called armchair.
- The lines of hexagons are parallel to the axis of the nano tube.

Zig – Zag

- If $m=0$ the nano tube are called zig-zag.
- The lines of carbon bonds are down the centre.

Chiral

- Remaining all are Chiral.
- It has twist or spiral around the nano tube.

Multi walled nano tube (MWNTs)

- ✍ It consists of multiple rolled layers of graphite.
- ✍ These are concentric tubes.
- ✍ The distance between two layers is 3.3 \AA .
- ✍ These are two models.
 - a) Russian doll model
 - b) Parchment model

Russian doll model

- ✍ Sheets of graphite are arranged in concentric cylinders.
- ✍ A tube is arranged inside the larger tube.

Parchment model

- ✍ A single sheet of graphite is rolled in around itself like a rolled News paper.

Feature	(SWCNTs)	(MWCNTs)
Structure	Consist of a single layer of graphene rolled into a tube.	Composed of multiple concentric graphene layers rolled into a tube.
Diameter	Small, typically 0.4–2 nm.	Larger, typically 2–100 nm.
Length	Can reach several micrometers to millimeters.	Similar or slightly shorter than SWCNTs.
Wall Thickness	Single layer of carbon atoms.	Multiple layers of carbon atoms.
Electrical Properties	Can be metallic or semiconducting based on chirality.	Generally metallic due to overlapping layers.
Mechanical Strength	Higher tensile strength due to the absence of defects in additional layers.	Slightly lower tensile strength due to interlayer defects.
Flexibility	More flexible due to their single-layer structure.	Less flexible due to the rigidity of multiple walls.
Synthesis Complexity	More challenging to synthesize and purify.	Easier to synthesize with higher yields.
Cost	Higher due to complex synthesis and purification processes.	Lower, as they are easier to produce.
Applications	Nanoelectronics, sensors, and lightweight composites.	Conductive materials, structural reinforcements, and energy storage.
Thermal Conductivity	Excellent along the tube axis, better for heat dissipation.	Good but slightly lower than SWCNTs.
Defects	Fewer defects as only a single wall exists. <div>↓</div>	More defects due to interlayer interactions and multiple walls.

19)

The coordination mechanism in the polymerization process refers to a catalytic system where a coordination complex facilitates the polymerization of monomers. This mechanism is particularly significant in olefin polymerization (e.g., ethylene, propylene). Below are the key aspects:

1. Chemical Reactions:

The polymerization involves **coordination insertion**, where monomers are added sequentially to the growing polymer chain.

• Overall Reaction:

$$n\text{CH}_2 = \text{CH}_2 \xrightarrow{\text{Catalyst}} (-\text{CH}_2 - \text{CH}_2-)_n$$

• Steps:

1. **Initiation:** The monomer coordinates with the catalyst's active center (usually a metal).

2. **Propagation:** The coordinated monomer inserts into the metal-carbon bond, elongating the chain.

3. **Termination:** The polymer chain detaches from the catalyst via chain transfer or other termination mechanisms.

2. Mechanism:

The process generally follows the Cossee-Arlman mechanism, involving the following stages:

1. Coordination:
- The π -electrons of the double bond in the monomer interact with the metal center of the catalyst.
 - Example: Ethylene coordinates to the titanium center in Ziegler-Natta catalysts.
2. Insertion:
- The monomer inserts into the metal-carbon bond of the catalyst complex via a migratory insertion mechanism.
 - The polymer chain grows in a head-to-tail fashion.
3. Chain Propagation:
- The process repeats as more monomers coordinate and insert, resulting in chain growth.
4. Termination:
- Chain transfer to monomer or solvent, or catalyst deactivation ends the polymer growth.

3. Types of Catalysts Used:

Catalyst Type	Examples	Features
Ziegler-Natta Catalysts	TiCl_4 , $\text{Al}(\text{C}_2\text{H}_5)_3$	Widely used for isotactic polypropylene and polyethylene.
Metallocene Catalysts	Cp_2ZrCl_2 , MAO	High activity and precise control over polymer microstructure.
Post-Metallocene Catalysts	Fe or Cr-based complexes	Tunable properties for specialty polymers.
Single-Site Catalysts	MAO-activated complexes	Uniform active sites, leading to high molecular weight polymers.
Phillips Catalysts	CrO_3 on SiO_2	Used for high-density polyethylene (HDPE) production.

4. Types of Polymerization Processes:

Type	Description
Homogeneous Polymerization	Catalysts are soluble in the reaction medium (e.g., metallocene catalysts).
Heterogeneous Polymerization	Catalysts are solid, and polymerization occurs on the catalyst surface (e.g., Ziegler-Natta).
Gas-Phase Polymerization	Monomers in the gaseous state interact with solid catalysts.
Slurry Polymerization	Monomers are polymerized in a non-solvent slurry system.
Solution Polymerization	Monomers and catalysts are dissolved in a solvent.

Applications:

1. Polyethylene and Polypropylene: High- and low-density variations.

2. **Rubbers and Elastomers:** Using specific catalysts for stereoregular polymers.
3. **Specialty Polymers:** Tailored properties for films, fibers, and advanced composites.

This coordination mechanism enables precise control of polymer properties such as molecular weight, branching, and stereochemistry, making it essential in industrial polymer synthesis.

22)

Role of Doping:

Doping is the process of introducing charge carriers into the polymer to enhance conductivity.

1. **Types of Doping:**
 - **p-Type Doping:** Removal of electrons (oxidation), creating positive charge carriers (holes).
 - **n-Type Doping:** Addition of electrons (reduction), creating negative charge carriers (electrons).
2. **Mechanism of Doping:**
 - Dopants interact with the polymer backbone, introducing charges.
 - **Example:** Acid doping in polyaniline (PANI) converts the insulating emeraldine base form to the conductive emeraldine salt form.
3. **Dopant Examples:**
 - **Acids (HCl, HNO₃):** Used for p-type doping of PANI.
 - **Halogens (I₂, Br₂):** Used for doping polyacetylene.
 - **Metal salts (FeCl₃):** Used for doping polypyrrole and polythiophene.
4. **Effects of Doping:**
 - Increases the number of charge carriers and their mobility.
 - Enhances electrical conductivity by several orders of magnitude.
 - Alters optical and electrochemical properties.

5. Applications of Conducting Polymers:

1. **Energy Storage:** Batteries, supercapacitors.
2. **Sensors:** Gas sensors, biosensors.
3. **Electronics:** Organic transistors, light-emitting diodes (OLEDs).
4. **Electromagnetic Shielding:** Coatings for EMI reduction.
5. **Smart Materials:** Actuators, wearable electronics.