

BATTERIES CHEMISTRY AND CORROSION

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Topic: ELECTROLYTIC CELL AND GALVANIC CELL



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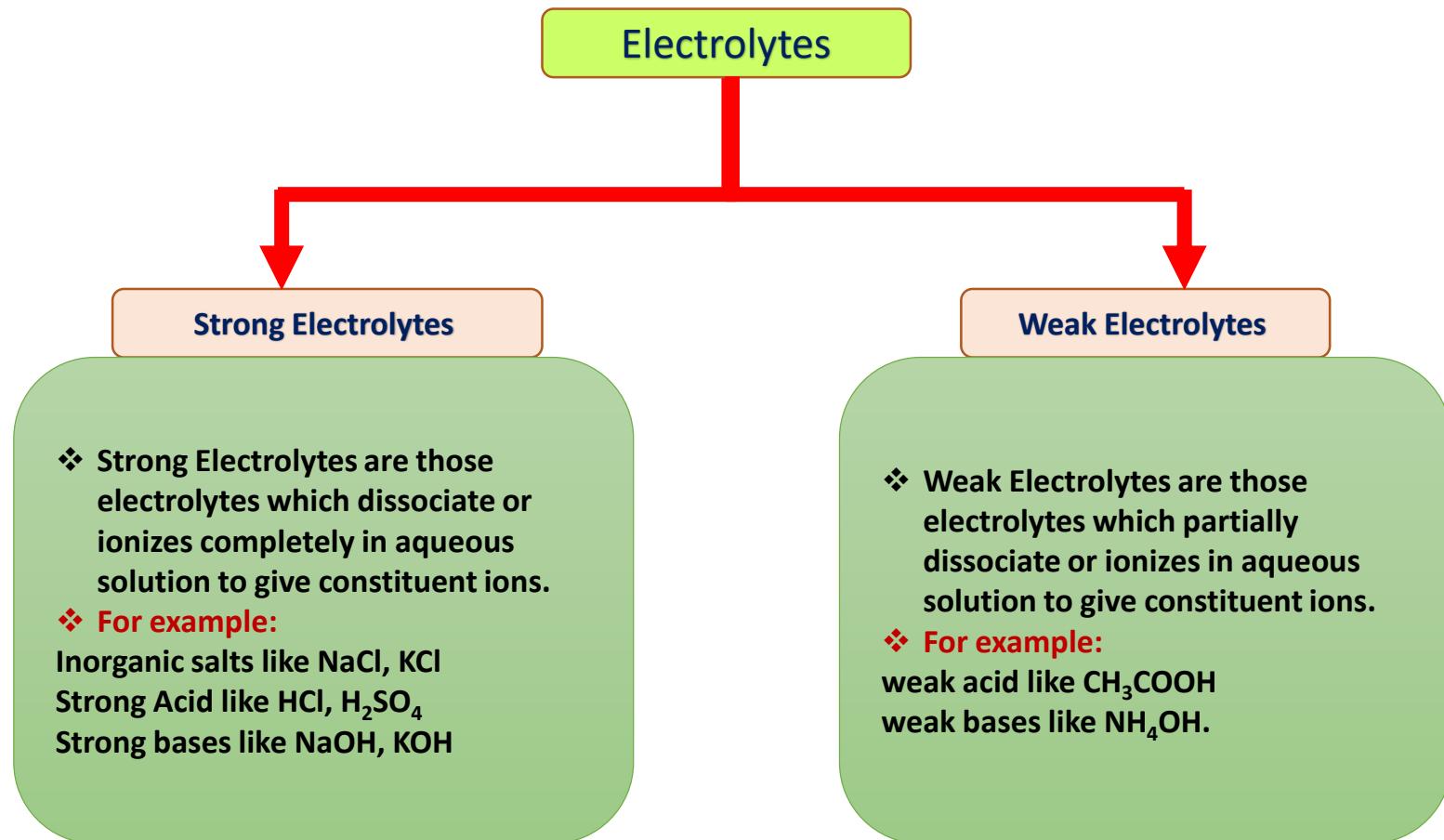
- **Electrochemistry** is a branch of physical chemistry which deals with the study of inter conversion of chemical energy into electrical energy and vice versa

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Electrolyte : Electrolyte is a substance that can conduct electricity when it dissolved in aqueous solution



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The Substances are divided into 3 types based on their capability of flow of electrons

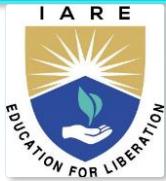
1. Conductors
2. Non-conductors (Insulators)
3. Semi conductors

Conductors: The substances which allows the electricity to pass through them are called conductors

Examples: metals, metal sulphides, acids, salt solutions etc.

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Non-Conductors: Those substances which do not allow electric current to pass through them are called non-conductors or insulators

Example: - wood, plastic, glass, rubber etc.

Semi-Conductors: The substances which partially conduct electricity are called semi-conductors

Example: Boron, Silicon, Aluminium etc.

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Electrode is a metallic rod/bar/strip which conducts electrons into and out of a solution

Anode is the electrode at which oxidation occurs. It sends electrons into the outer circuit

Cathode is the electrode at which reduction occurs. It receives electrons from the outer circuit

- When a metal rod is dipped in its salt solution (electrolyte), the metal atom tends either to lose electrons (oxidation) or to accept electrons (reduction)
- If the metal undergoes oxidation, then the positive metal ions may pass into the solution



- If the metal undergoes reduction, then the positive metal ions from the solutions may get deposited over the metal



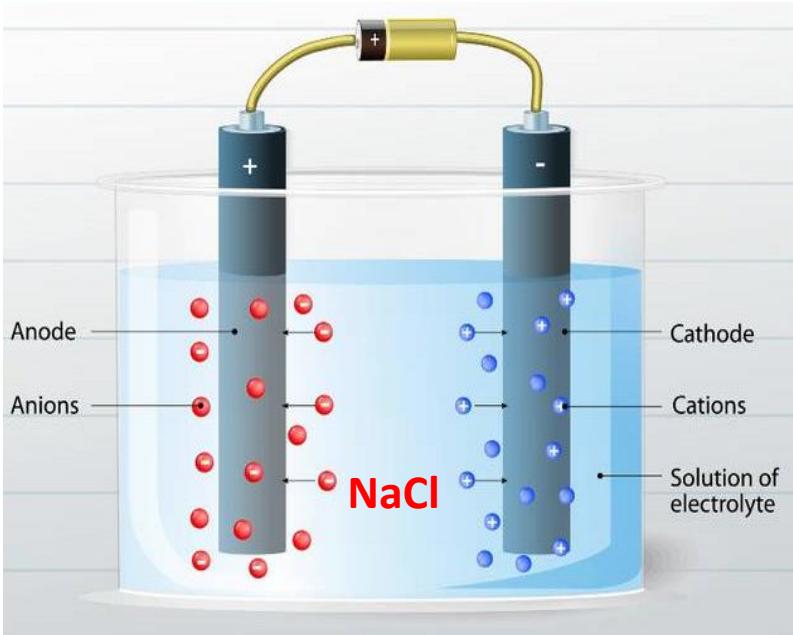
- The process of oxidation or reduction depends on the nature of the metal

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Electrolytic Cell: This device which can convert electrical energy into chemical energy



Positive electrode (anode): $2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2 \text{e}^-$

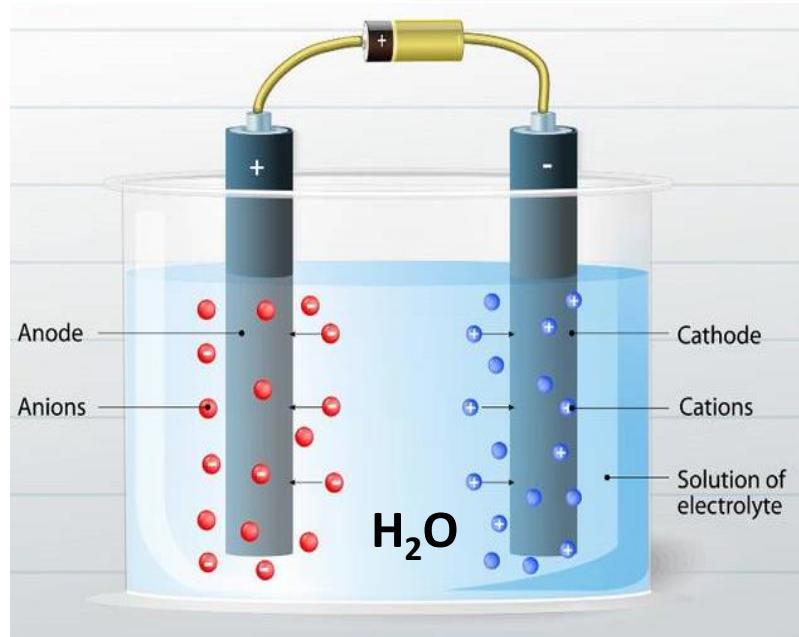
Negative electrode (cathode): $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$

Applications of electrolytic cell

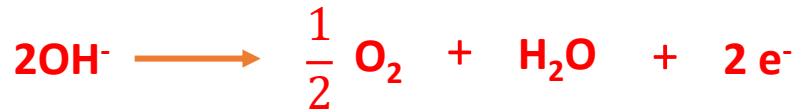
- The production of oxygen gas and hydrogen gas from water
- The extraction of aluminum from bauxite

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At Anode:



At Cathode:



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Electrochemical Cell

This device which can convert chemical energy into electrical energy

- In electrochemical cells electrons are transferred due to redox reactions are converted to electrical energy

Ex: Daniel cell

Each electrochemical cell is made up of two electrodes at one electrode electrons are evolved and at other electrode electrons are used up. Each electrode which is dipped in its salt solution is called half cell.

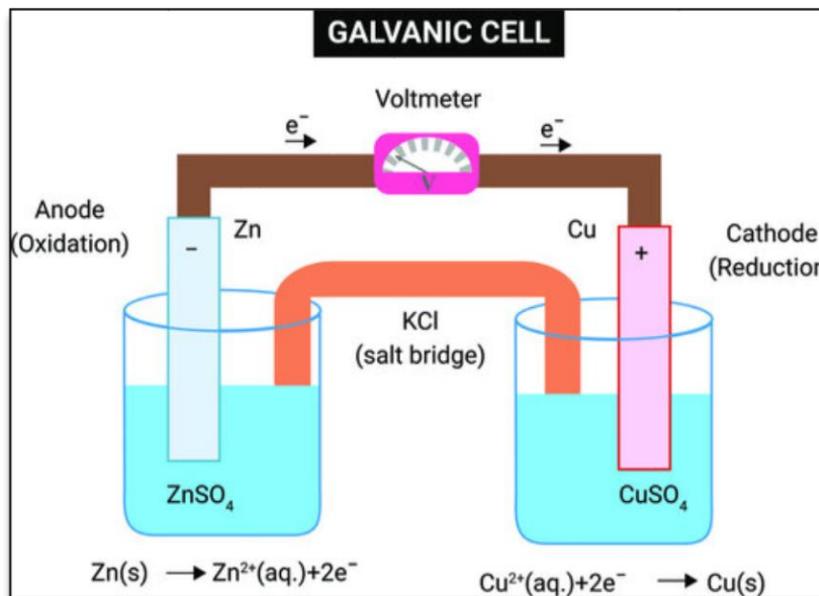
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- **Galvanic cell or Voltaic cell**

- This cell is made up of two half cells. One is oxidation or anodic half cell. The other is reduction or cathodic half-cell
- The first half cell consists of 'Zn' electrode dipped in $ZnSO_4$ solution and second half cell consists of 'Cu" electrode dipped in $CuSO_4$ solution
- Both the half cells are connected externally by metallic conductor and internally by 'salt bridge'
- Salt bridge provides electrical contact between two solutions.



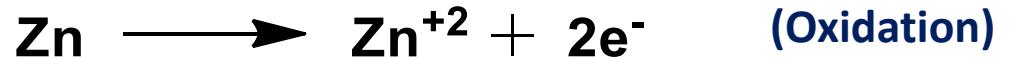
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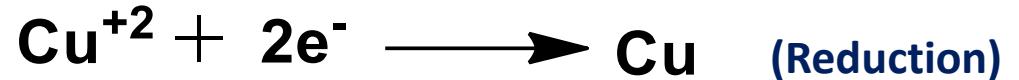


The following reactions take place in the cell

At Anode:



At Cathode



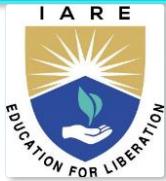
The movement of electrons from Zn to Cu produces a current in the circuit

The overall cell reaction is

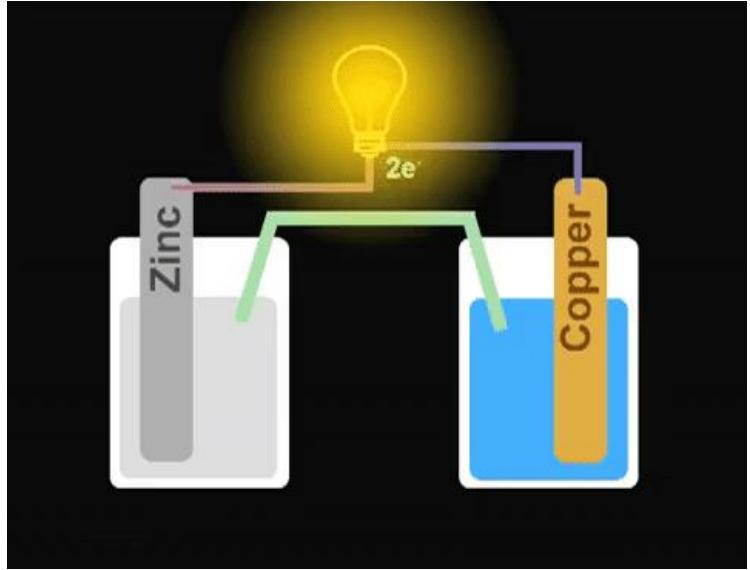


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Galvanic cell or Voltaic cell



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Function of Salt bridge

- Salt bridge is a inverted U shape glass tube containing concentrated solution of KCl or NH_4NO_3 in agar-agar gel contained porous pot
- The main function of a salt bridge is to maintain electrical neutrality within the internal circuit
- If salt bridges are absent then the reaction will likely continue, and the solution in one-half electrodes will gather a negative charge. Similarly, in the other half, electrodes will accumulate a positive charge
- This will further result in the stoppage of the reaction, and no electricity will be produced
- The salt bridge then supplies negative ions to the oxidation half-cell in order to neutralize excess of Zn^{2+} ions.
- Similarly, it supplies positive ions to the reduction half-cell in order to neutralize the excess of sulphate ions. Thus, salt bridge maintains the electrical neutrality in both the half cells

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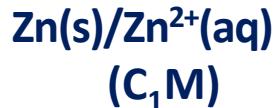
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Representation of galvanic cell

1. A galvanic cell is represented by writing the anode on the left hand side and cathode on the right hand side.
Anode // Cathode

2. The anode of the cell is represented by writing metal first and then the electrolyte (or the cation of the electrolyte) with concentrations.

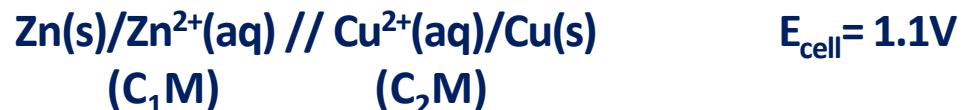


3. The cathode is represented by writing the electrolyte first with concentrations and then metal.
 $\text{Cu}^{2+}(\text{aq})/\text{Cu(s)}$
(C_2M)

4. The two half cells are separated by a salt bridge, which is indicated by two vertical lines.



5. The value of emf of a cell is written on the right of the cell diagram.



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Differences between Electrochemical cell and Electrolytic cell

Electrochemical Cell	Electrolytic Cell
Chemical energy transformed into electrical energy	Electrical energy transformed into chemical energy
An input energy is not required for the redox reaction to proceed in these cells, i.e. the nature of rxn is spontaneous	An input energy required for the redox reaction to proceed in these cells, i.e. the nature of rxn is non-spontaneous
In this cell, anode is -ve electrode and cathode is +ve electrode	In this cell, anode is +ve electrode and cathode is -ve electrode
Salt bridge is required	Salt bridge is not required

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Write cell representation for following cells



Ans: $\text{Zn}(\text{s})/\text{Zn}^{2+}(\text{aq})//\text{Cd}^{2+}(\text{aq})/\text{Cd}(\text{s})$
Anode Cathode



Ans : $\text{Ni}(\text{s})/\text{Ni}^{2+}(\text{aq})//\text{Fe}^{3+}(\text{aq})/\text{Fe}^{2+}(\text{aq})$
Anode Cathode



Ans : $\text{Cu}(\text{s})/\text{Cu}^{2+}(\text{aq})//\text{Ag}(\text{s})/\text{Ag}^{+}(\text{aq})$
Anode Cathode

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SINGLE ELECTRODE POTENTIAL

when a metal is placed in a solution of its own ions, the potential developed at the interface between electrolyte solution and metal is called single electrode potential

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Factors effects on single electrode potential

- 1.Nature of metal rod
- 2.The concentration of ions in the solution
- 3.Temperature

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Standard electrode potential

The electrode potential measured at standard conditions is called standard electrode potential.

Standard electrode potential conditions are

1M Concentration
298 K Temperature
1 atm pressure

Measurement of Single electrode potential

We are not able to measure the single electrode potential of an isolated half-cell. We can only measure electrode potential difference produced when two half-cells are connected.

In order to measure single electrode potential, it is necessary to couple an electrode with a reference or standard electrode

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- **Electromotive force or Cell potential:** The potential difference between two electrodes of a galvanic cell is called the cell potential. It is measured in Volts.
- The emf of the cell depends up on
 - i) Temperature
 - ii) Nature of reactant
 - iii) Concentration of solutions in two half cells

Mathematically

$$\text{emf or } E_{\text{cell}} = E_{\text{Reduction potential of Cathode}} - E_{\text{Reduction potential of Anode}}$$

(OR)

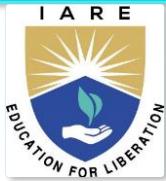
$$E_{\text{cell}} = E_{\text{Right}} - E_{\text{left}}$$

E_{Right} = reduction potential of right hand side electrode (Cathode)

E_{left} = reduction potential of left hand side electrode (Anode)

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Oxidation potential: The tendency of an electrode to lose electrons is called the oxidation potential.

Reduction potential: The tendency of an electrode to gain electrons is called the reduction potential

Reduction potential of an electrode is equal in magnitude but opposite in sign to its oxidation potential

i.e Reduction potential of electrode = - oxidation potential of that electrode

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Numerical problems on emf calculations

Example 1.

For a reaction, $2\text{Ag}^+ (\text{aq}) + \text{Cd} \rightarrow 2\text{Ag} + \text{Cd}^{+2}(\text{aq})$

The standard reduction potential given are: $\text{Ag}^+ / \text{Ag} = 0.80 \text{ volt}$, $\text{Cd}^{+2} / \text{Cd} = -0.40 \text{ volt}$, then calculate cell potential?

From the reaction, we can see that Cd losses electrons and Ag^+ gains. Hence, oxidation half cell or anode is Cd.

Using the formula,

$$\begin{aligned} E^\circ_{\text{cell}} &= E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} \\ &= 0.80 - (-0.40) \\ &= 1.20 \text{ V} \end{aligned}$$

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2. Calculate the E.M.F of voltaic cell $\text{Fe} | \text{Fe}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq}) | \text{Cu}$.

Given the standard reduction electrode potentials of iron and copper are -0.44 volt and 0.34 volt respectively.

Formula:

$$\begin{aligned}\mathbf{E_{cell}} &= \mathbf{E_{cathode}} - \mathbf{E_{anode}} \\ &= 0.34 \text{ V} - (-0.44 \text{ V}) \\ &= 0.34 \text{ V} + 0.44 \text{ V} \\ \mathbf{E_{cell}} &= 0.78 \text{ V}\end{aligned}$$

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Electrochemical series

- The electrode potentials of different electrodes can be finding using standard hydrogen electrode. The potential of hydrogen electrode is assumed as zero volts
- The arrangement of different standard reduction electrode potentials of different electrodes from highest - ve to highest +ve are called electrochemical series

Electrode	Half-cell reaction	E^0 volts (standard reduction potential)
Li^+/Li	$\text{Li}^++\text{e}^{-}\rightarrow\text{Li}$	-3.04
K^+/K	$\text{K}^++\text{e}^{-}\rightarrow\text{K}$	-2.9
Ca^{+2}/Ca	$\text{Ca}^{+2}+2\text{e}^{-}\rightarrow\text{Ca}$	-2.8
Na^+/Na	$\text{Na}^++\text{e}^{-}\rightarrow\text{Na}$	-2.7
Mg^{+2}/Mg	$\text{Mg}^{+2}+2\text{e}^{-}\rightarrow\text{Mg}$	-2.3
Zn^{+2}/Zn	$\text{Zn}^{+2}+2\text{e}^{-}\rightarrow\text{Zn}$	-0.76
Fe^{+2}/Fe	$\text{Fe}^{+2}+2\text{e}^{-}\rightarrow\text{Fe}$	-0.4
$\text{H}^+/\text{H}_2,\text{pf}$	$\text{H}^++\text{e}^{-}\rightarrow\text{H}_2$	+ 0
Cu^{+2}/Cu	$\text{Cu}^{+2}+2\text{e}^{-}\rightarrow\text{Cu}$	+0.15
Ag^+/Ag	$\text{Ag}^++\text{e}^{-}\rightarrow\text{Ag}$	+0.7
$\text{Pt},\text{Cl}_2/\text{Cl}^-$	$\text{Cl}_2+2\text{e}^{-}\rightarrow2\text{Cl}^-$	+1.3
$\text{Pt},\text{F}_2/\text{F}^-$	$\text{F}_2+2\text{e}^{-}\rightarrow2\text{F}^-$	+2.8

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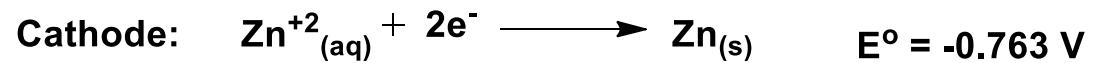
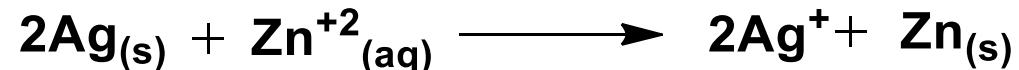
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Applications of Electrochemical series

1) Predicting feasibility of a cell reaction

- The feasibility of a redox reaction can be predicted with the help of electrochemical series
- $E^\circ_{\text{Cell}} = E^\circ_{\text{Cathode}} - E^\circ_{\text{Anode}}$
- In general, if $E^\circ_{\text{cell}} = + \text{ve}$, the reaction is feasible
- if $E^\circ_{\text{cell}} = - \text{ve}$, the reaction is not feasible
- Example 1: Predict whether reaction is feasible or not?



$$E^\circ_{\text{Cell}} = E^\circ_{\text{Cathode}} - E^\circ_{\text{Anode}}$$

$$E^\circ_{\text{Cell}} = -0.763\text{V} - 0.80\text{V}$$

$$E^\circ_{\text{Cell}} = -1.563\text{V}$$

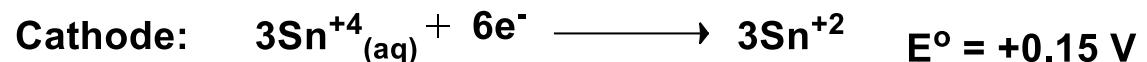
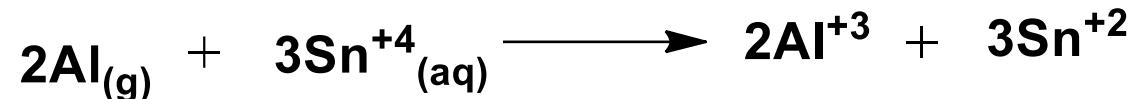
Since E°_{Cell} is negative, the given reaction is not feasible

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- Example 2: Predict whether reaction is feasible or not?



$$E^\circ_{\text{Cell}} = E^\circ_{\text{Cathode}} - E^\circ_{\text{Anode}}$$

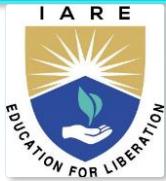
$$E^\circ_{\text{Cell}} = 0.15\text{V} - (-1.66\text{V})$$

$$E^\circ_{\text{Cell}} = 1.81\text{V}$$

Since E°_{Cell} is positive, the given reaction is feasible

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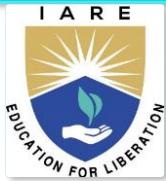


2) Reactivity of metals

- Metals are reactive if they lose electrons easily, i.e., their tendency to form cations.
- Those metals with a high negative value or smaller positive value of standard reduction potential lose electrons quickly and are highly reactive
- Group I and group II metals have high negative reduction potential, and therefore they easily dissolve in acids.

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3) Oxidizing and reducing strengths

- The electrochemical series helps identify different materials that are good reducing and oxidation agents
- All substances that appear on top of the electrochemical series act as good reducing agents
- All such substances that appear at the bottom of the electrochemical series act as good oxidizing agents

Example: Zn and Copper electrodes are connected to electrochemical cell

Zinc standard reduction electrode potential is -0.76 V,

Copper standard reduction electrode potential is +0.15 V

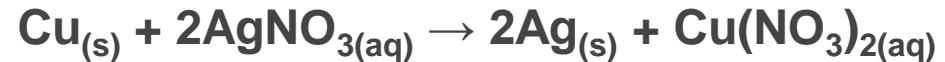
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4) Displacement reaction

- The substance with a lower standard of reduction potential will displace the metal from the salt solution with a greater value



Copper standard reduction electrode potential is +0.15 V,

Silver standard reduction electrode potential is +0.7 V

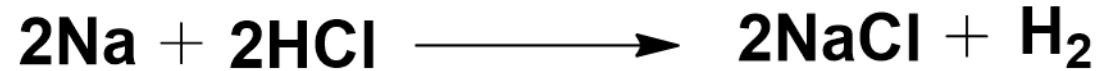
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5) Prediction of metal's ability to liberate hydrogen gas from acid

- All metals with negative electrode potential (-E) have an increased tendency to lose electrons compared to Hydrogen
- Hence, when such a substance is placed in an acid solution, it gets oxidized, and an effective reduction of H⁺ ions occurs to form hydrogen gas
- Therefore, substances having -E values have the potential to free the Hydrogen from different acids



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6) Predicting the Product of Electrolysis

- In case two or more types of ions are present in the electrolyte solution. They are liberated at the electrode according to their preference during electrolysis.
- The cations with a high value of standard reduction potential are discharged first at the cathode. Similarly, the anion with a low standard reduction potential value is liberated first at the anode.

Thus, when an aqueous solution of NaCl containing Na^+ , Cl^- , H^+ and OH^- ions is electrolyzed, the H^+ ion is preferentially deposited at the cathode (reduction) instead of Na^+ . This is because the reduction potential of hydrogen (0.00V) is higher than the reduction potential of sodium (-2.71V)

At the anode where oxidation takes place, the anion that has a lower reduction potential will be oxidized. Therefore, OH^- with a standard reduction potential of 0.40V will be oxidized in preference to Cl^- with a standard reduction potential of 1.36V.

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Battery

When two or more electrochemical cells are electrically interconnected, each of which containing two electrodes and an electrolyte is called a Battery.

Batteries are classified into a two categories depending on their recharging capabilities.

Primary Batteries: “These are non-rechargeable and are meant for single use and to be discarded after use”.

These are non-reversed, less expensive, often used in ordinary gadgets like torch lights, watches and toys.

Eg: Leclanche cell (Dry cell)

Secondary Batteries: These are rechargeable and are meant for multi cycle use. After every use the electrochemical reaction could be reversed by external application

Eg: Lead-acid cell, Ni/cd cell.

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Leclanche Cell/Dry Cell

Dry cell is a cell without fluid component

Anode: Zinc

Cathode: Graphite rod (Carbon)

Electrolyte: Moist paste of NH_4Cl and ZnCl_2

emf: 1.5V

Dry cell also called as a zinc-carbon cell.

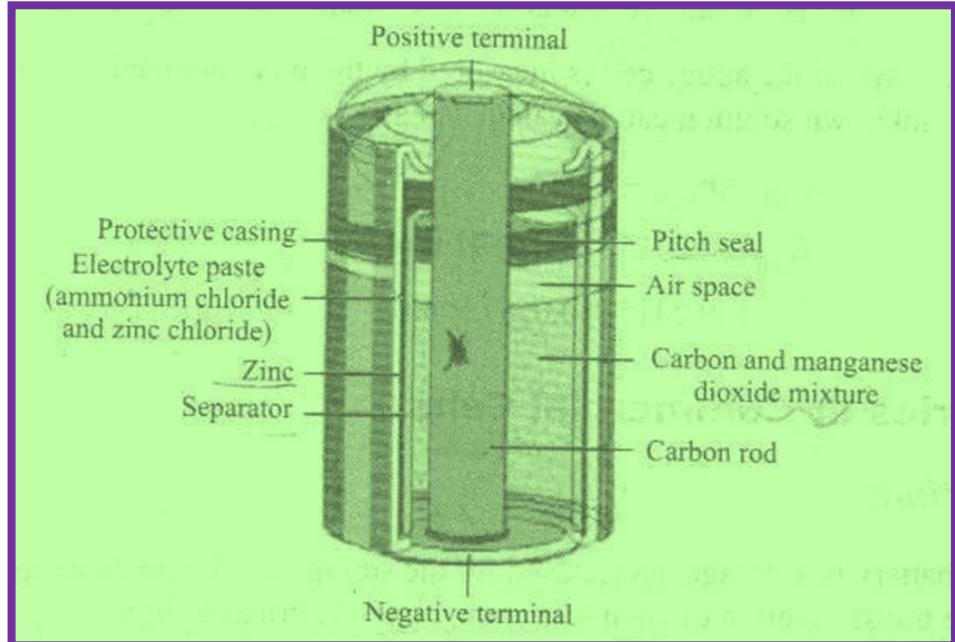


Georges Leclanché

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- ❖ Dry cell consists of a cylindrical Zinc container which acts as an anode.
- ❖ A graphite rod displaced in the center. The graphite rod does not touch the base and it acts as a cathode.
- ❖ The graphite rod is surrounded by powdered MnO_2 and carbon.
- ❖ The remaining space in between cathode and anode is filled with a paste of NH_4Cl and $ZnCl_2$.
- ❖ The graphite rod is fitted with a metal cap and the cylinder is sealed at the top with a pitch



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The reactions take place in the cell are:



Due to this reaction ammonia gas evolves and disrupts the current flow. This can be prevented by a reaction of NH_3 with Zn^{+2} to form complex.



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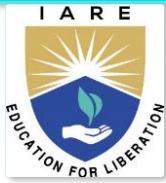


Applications

- **Toys**
- **Transistor Radio**
- **Calculator**
- **Watches**
- **Hearing Aids**

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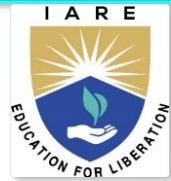
Eg: Leclanche cell (Dry cell)

Secondary Batteries: These are rechargeable and are meant for multi cycle use. After every use the electrochemical reaction could be reversed by external application

Eg: Lead-acid cell, Ni/cd cell.

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Leclanche Cell/Dry Cell

Dry cell is a cell without fluid component

Anode: Zinc

Cathode: Graphite rod (Carbon)

Electrolyte: Moist paste of NH_4Cl and ZnCl_2

emf: 1.5V

Dry cell also called as a zinc-carbon cell.



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Primary Batteries:

- These are non-rechargeable, single use and to be discarded after use
- These are non-reversed and are less expensive and are often used in ordinary gadgets like torch lights, watches and toys

Eg: Leclanche cell, Dry cell.

Secondary Batteries:

- These are rechargeable and multi cycle use
- After every use the electrochemical reaction could be reversed by external energy supply
- Eg: Lead-acid cell, Ni/cd cell

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Differences between Primary and secondary batteries:

Primary cells	Secondary cells
These are non-rechargeable and meant for a single use and to be discarded after use	These are rechargeable and meant for multi cycle use
Cell reaction is not reversible	Cell reaction can be reversed
Cannot be rechargeable	Can be rechargeable
Less expensive	Expensive
Can be used as long as the materials are active in their composition.	Can be used again and again by recharging the cell
Leclanche cell, 'Li' Cells.	Lead- acid cell and Li-ion cell

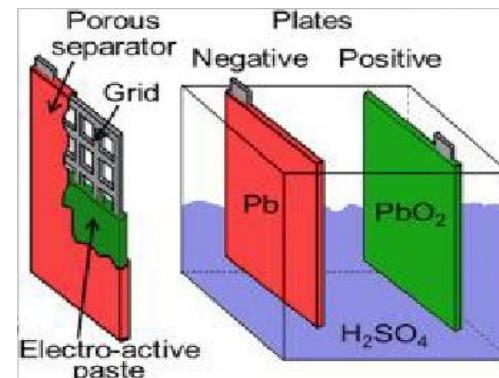
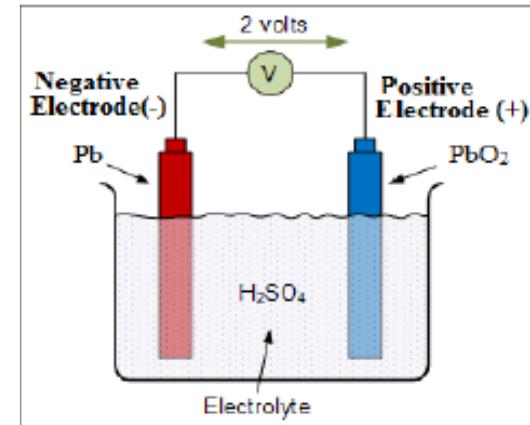
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Lead-Acid Battery

- The lead-acid battery was invented in 1859 by French physicist Gaston Planté. It is the oldest rechargeable battery and It is a secondary battery
- One electrode is Pb, the other electrode is made of lead peroxide (PbO_2)
- Number of Pb plates are connected in parallel (anode, -ve plates) and number of PbO_2 plates (cathode, +ve plates) also connected in parallel
- The Pb plates fits in between the PbO_2 plates
- These plates are separated by insulators (wood, fiber, glass, rubber)
- The entire combination is immersed in 20-21% dil H_2SO_4 .



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The main active materials required to construct a lead acid battery are

1. Lead peroxide (PbO_2) (Cathode)
2. Sponge lead (Pb) (Anode)
3. Dilute sulfuric acid (H_2SO_4)

Lead Peroxide (PbO_2)

The positive plate (Cathode) is made of lead peroxide. This is dark brown, hard and brittle substance.

Sponge Lead (Pb)

The negative plate (Anode) is made of pure lead in soft sponge condition

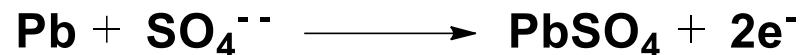
Dilute Sulfuric Acid (H_2SO_4)

Dilute sulfuric acid used for lead acid battery has a ratio of water : acid = 3:1.

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ELECTROCHEMISTRY AND CORROSION

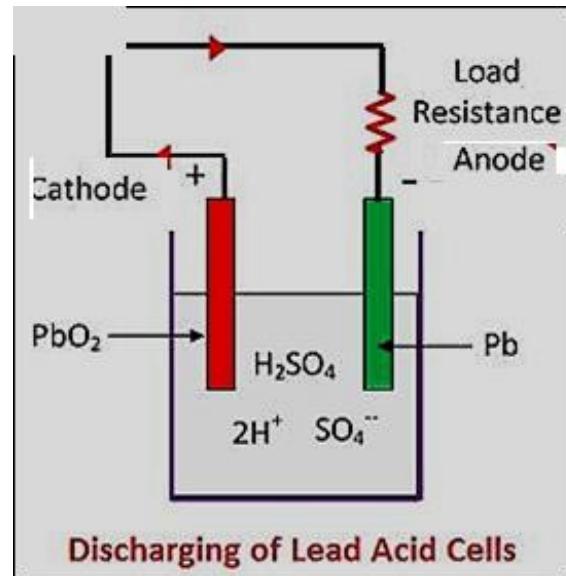
- The **lead acid storage battery** is formed by dipping lead peroxide plate and sponge lead plate in dilute sulfuric acid.
- During discharging, Lead-Acid battery acts as electrochemical cell (Voltaic cell).
- Electrochemical Reactions involved in Discharging of Lead-Acid battery**
- In diluted sulfuric acid the molecules of the acid split into positive hydrogen ions (H^+) and negative sulfate ions (SO_4^{2-}).
- At Anode



- At Cathode



- Net Reaction



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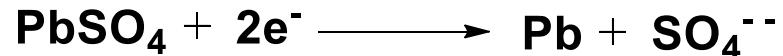
ELECTROCHEMISTRY AND CORROSION



Electrochemical Reactions involved in Charging of Lead-Acid battery

- During charging, Lead-Acid battery acts as electrolytic cell

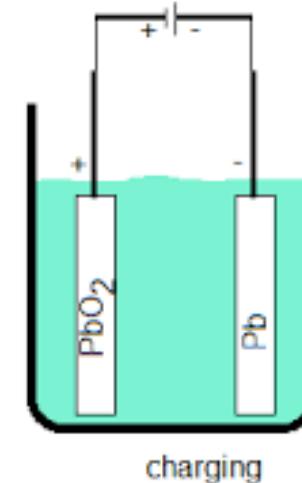
At Anode



At Cathode



Net Reaction



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ELECTROCHEMISTRY AND CORROSION



- ❑ During discharging H_2SO_4 is consumed and its concentration decreases
- ❑ During charging H_2SO_4 is regenerated and its original concentration is restored.
- ❑ Voltage of each cell is 2V. In general, lead-Acid battery consists of such 6 cells which are connected in series to get higher voltage(12V).

Discharging



Charging



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ELECTROCHEMISTRY AND CORROSION



Applications:

- Telecommunication (Telephone exchanger)
- Power stations
- Television systems
- Stand by supplies (UPS)
- Electric vehicles
- Emergency lights
- Railway mines

Advantages: Low maintenance, Low Cost.

Disadvantages: Heavy in weight, Lead is not environmentally friendly.

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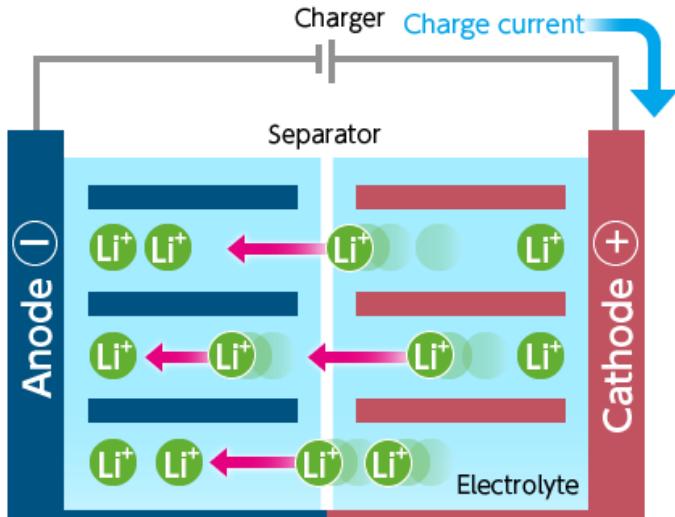
ELECTROCHEMISTRY AND CORROSION



Li-Ion battery

The main active materials required to construct Lithium Ion battery are

1. A positive electrode (Layers of lithium-metal oxide) (Cathode)
2. A negative electrode (Layers of porous carbon) (anode)
3. An electrolyte (examples organic polymers poly propylene, polyethylene))



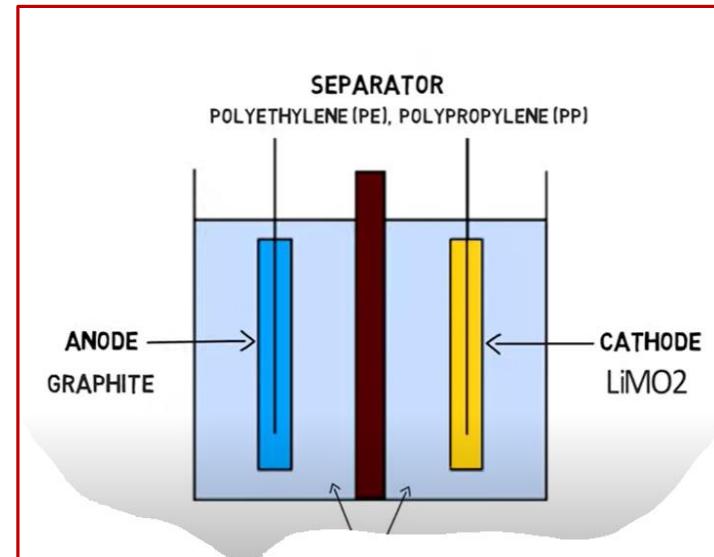
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ELECTROCHEMISTRY AND CORROSION



Construction of Lithium-Ion battery

- The positive electrode is typically made from a layers of chemical compound called lithium-cobalt oxide (LiCoO_2)
- The negative electrode is made from layers of porous carbon (C) (graphite)
- Both the electrodes are dipped in a Lithium salt electrolyte separated by a separator
- Separator is a perforated plastic and allows the Li^+ ions to pass through



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ELECTROCHEMISTRY AND CORROSION

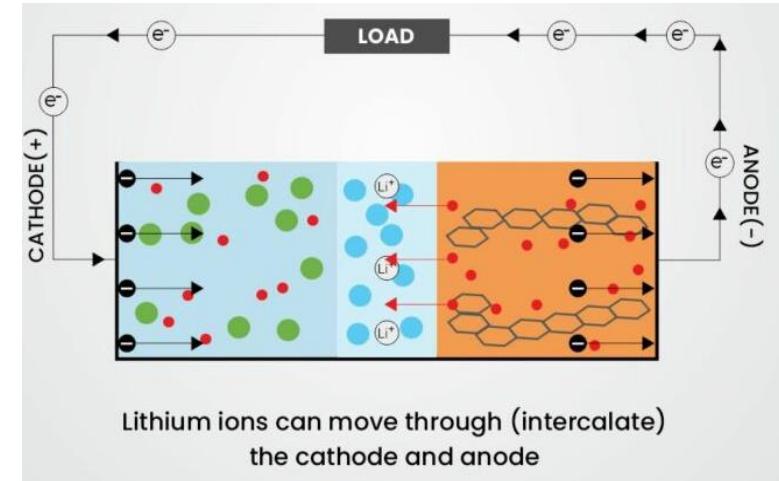


Discharging Reaction:

During discharging, the Li^+ ions flow back through the electrolyte from negative electrode to the positive electrode.

Electrons flow from the negative electrode to the positive electrode.

The Li^+ ions and electrons combine at the positive electrode and deposit there as Li.



Lithium ions can move through (intercalate)
the cathode and anode

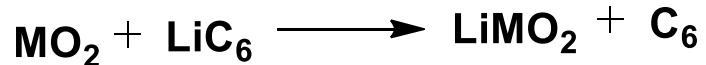
At Anode



At Cathode



Net Reaction



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ELECTROCHEMISTRY AND CORROSION



Working

Charging Reaction:

During charging, Li^+ ions flow from the positive electrode (LiCoO_2) to the negative electrode (graphite) through the electrolyte.

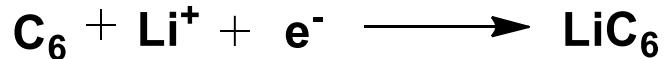
Electrons also flow from the positive electrode to the negative electrode

The electrons and Li^+ ions combine at the negative electrode and deposit there as Li

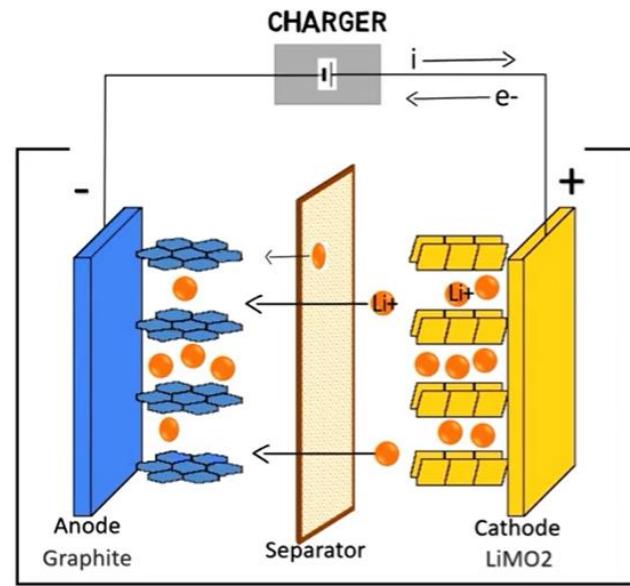
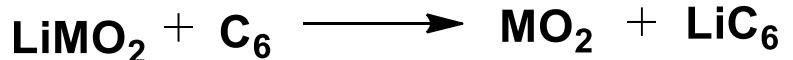
At Cathode



At Anode



Net Reaction



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ELECTROCHEMISTRY AND CORROSION



Advantages (or) Characteristics:

1. Lithium-ion batteries are high voltage and light weight batteries
2. It is smaller in size
3. It produces three times more voltage than the Ni-Cd batteries

Uses:

It is used in cell phone, note PC, portable LCD TV, semiconductor driven audio, etc.

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APPLICATIONS OF LITHIUM ION BATTERIES

1. Used for portable electronics and electric vehicles and are growing in popularity for military and aerospace applications.
2. Used in mobile phones, notebook PC's, cameras, camcorders, MP3.
3. Used in power tools such as cordless drills, sanders, saws and variety of garden equipment including whipper-snippers and hedge trimmers.
4. Secondary non-aqueous lithium batteries provide reliable backup power to load equipment in a network environment of telecommunications provider.



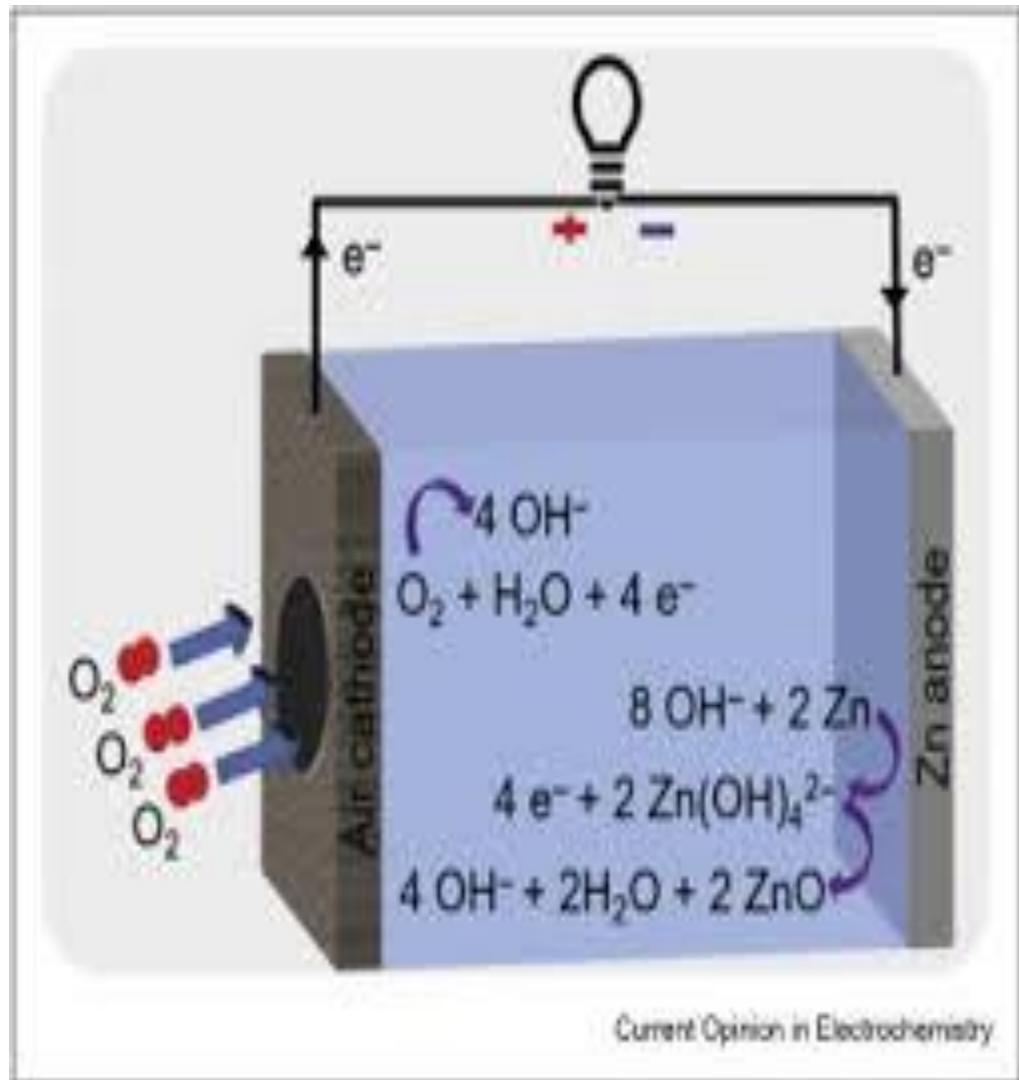
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LITHIUM -ION BATTERY

Advantages	Disadvantages
<ul style="list-style-type: none"> I. Light weight II. Have higher energy density than other rechargeable batteries III. Rate of charge loss is less IV. Have a greater number of charge and discharge cycles V. Need not be discharged completely VI. Operates at higher voltage than other rechargeable batteries 	<ul style="list-style-type: none"> I. Involves risk of bursting II. Costly compared to other batteries III. Complete discharge damage the battery IV. Extremely sensitive to high temperatures V. Very short lifespan VI. Not available in standard cells sizes

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ELECTROCHEMISTRY AND CORROSION



Zinc-air battery is primary cell and non rechargeable battery

Anode : Zn electrode

Cathode : Porous carbon electrode

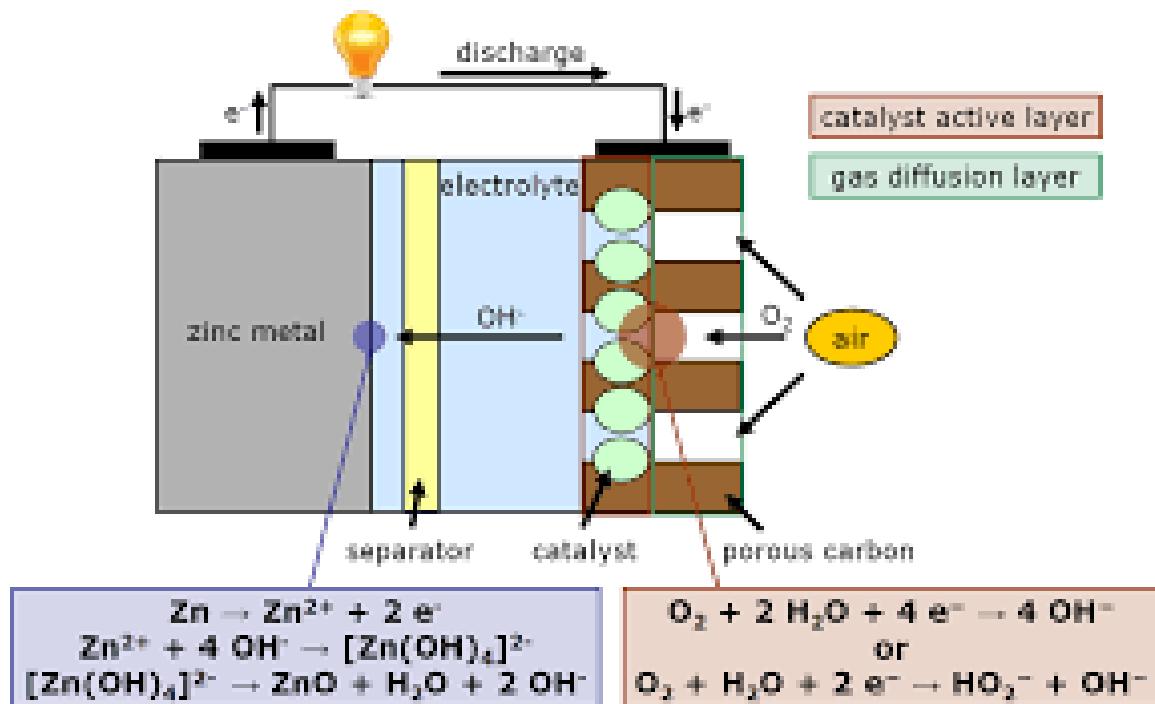
Electrolyte : Potassium Hydroxide

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Working

Zinc-air battery is represented as

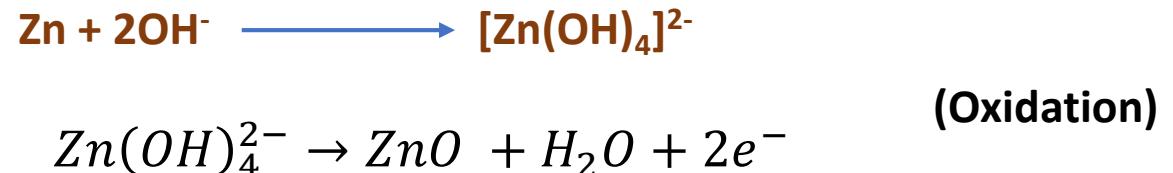
Zn/KOH//Air, C



ELECTROCHEMISTRY AND CORROSION

Cell Reactions

At Anode :



At Cathode :



Net Reaction :



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ELECTROCHEMISTRY AND CORROSION



Applications

- Hearing devices
- watches
- Mobile phones
- Military transistors and voice transmitters
- Digital cameras

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Topics:

- Corrosion definition
- Causes of corrosion
- Consequences of Corrosion
- Classifications of Corrosion
 - (i) Dry or Chemical Corrosion
 - (ii) Wet or Electrochemical Corrosion

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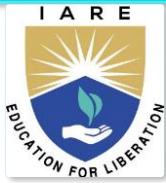
ELECTROCHEMISTRY AND CORROSION



- **Corrosion:** It is a natural process that causes the transformation of pure metals into undesirable substances when they react with substances like water or air
- The surface of almost all the metals begin to decay more or less rapidly when exposed to atmospheric gases, water or other reactive liquid medium
- The rusting of iron involves the formation of iron oxides (Fe_3O_4) via the action of atmospheric moisture and oxygen
- Formation of green film $[\text{CuCO}_3 + \text{Cu}(\text{OH})_2]$ on the surface of copper

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ELECTROCHEMISTRY AND CORROSION

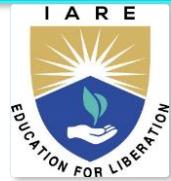


Causes of corrosion:

- The metals exist in nature in the form of their minerals or ores, in the stable combined forms as **oxides, chlorides, silicates, carbonates, sulphides** etc.
- During the extraction of metals, these ores are reduced to metallic state by supplying considerable amounts of energy.
- Hence the isolated pure metals are regarded as excited states than their corresponding ores. So metals have natural tendency to go back to their combined state (minerals/ores).
- When metal is exposed to atmospheric gases, moisture, liquids etc., and the metal surface reacts and forms more thermodynamically stabled compounds.

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ELECTROCHEMISTRY AND CORROSION



CONSEQUENCES (EFFECTS) OF CORROSION:

Consequences of corrosion cause a great loss of economy and life of machinery. The following harmful effects are specific

- ✓ Lose of efficiency
- ✓ The valuable metallic properties like conductivity, malleability, ductility etc. are lost due to corrosion.
- ✓ Life span and efficiency of metallic parts of machinery and fabrications is reduced.
- ✓ Contamination of product
- ✓ Lose of valuable materials such as blockage of pipes, mechanical damage of underground water pipes
- ✓ Accidents due to mechanical lose of metallic bridges, cars, aircrafts etc.
- ✓ Causes pollution due to escaping products from corrosion

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ELECTROCHEMISTRY AND CORROSION

CLASSIFICATION OR THEORIES OF CORROSION

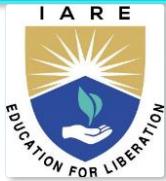
Based on the environment, corrosion is classified into

- (i) Dry or Chemical Corrosion
- (ii) Wet or Electrochemical Corrosion

S.No	Dry Corrosion	Wet Corrosion
1	It occurs in dry condition	It occurs in wet condition
2	If the corrosion takes place due to direct chemical attack (in the absence of moisture), corrosion is known as dry corrosion.	If the corrosion takes place due to electrochemical attack in presence of moisture or a conducting medium, corrosion is known as wet corrosion.
3	Explained by absorption mechanism	Explained by electrochemical mechanism
4	It occurs on both heterogeneous and homogeneous surfaces	It occurs only on heterogeneous metal surfaces
5	Corrosion is uniform	Corrosion is not uniform
6	It is a slow process	It is a fast process
7	Corrosion products accumulate at the place where corrosion occurs	Corrosion takes place at anode but products accumulate near the cathode

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ELECTROCHEMISTRY AND CORROSION



DRY or CHEMICAL CORROSION:

This type of corrosion is due to the direct chemical attack of metal surfaces by the atmospheric gases such as O₂, halogens, H₂S, SO₂, N₂ or anhydrous inorganic liquid, etc.

Silver materials undergo chemical corrosion by atmospheric H₂S gas



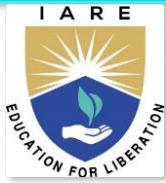
Polished Silver

Tarnished Silver



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ELECTROCHEMISTRY AND CORROSION



DIFFERENT TYPES OF DRY CORROSION (CHEMICAL CORROSION)

- 1.Corrosion by oxygen or oxidation corrosion
- 2.Corrosion by other gases
- 3.Liquid metal corrosion

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ELECTROCHEMISTRY AND CORROSION

1. CORROSION BY OXYGEN or OXIDATION CORROSION

Alkali metals (Li, Na, K etc.,) and alkaline earth metals (Mg, Ca, Sn, etc.,) are rapidly oxidized at low temperature. At high temperature, almost all metals (except Ag, Au and Pt) are oxidized

Mechanism:

1. Oxidation takes place at the surface of the metal forming metal ion



2. Oxygen is converted to oxide ion(O^{2-})due to the transfer of electrons from metal.



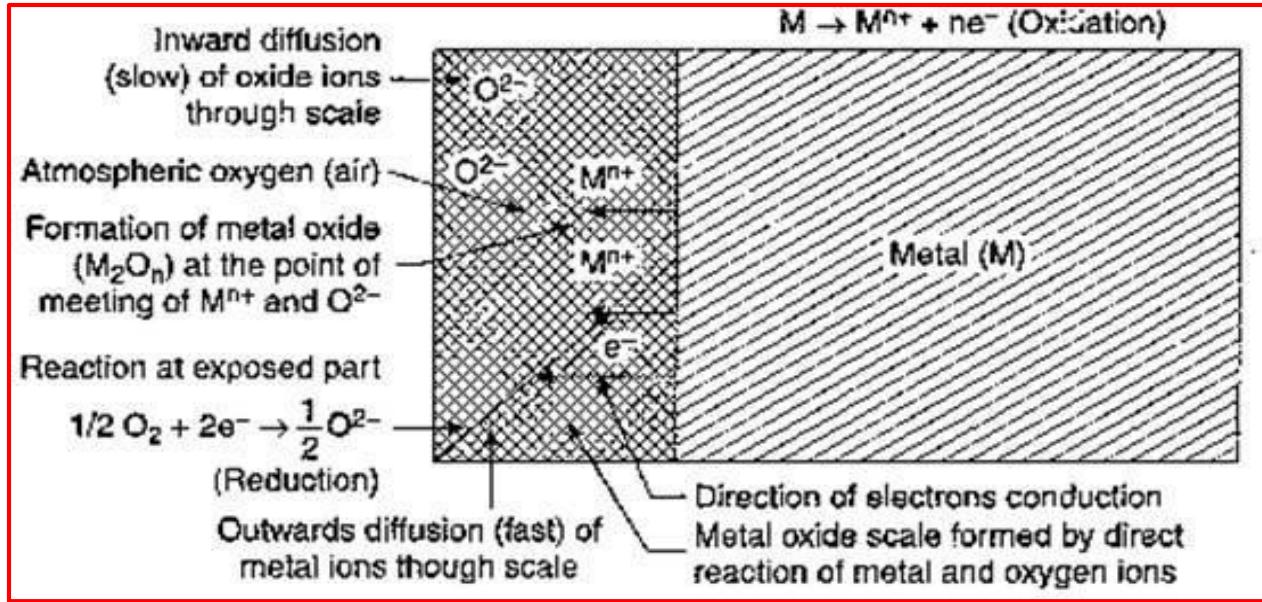
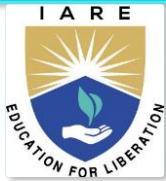
3. The overall reaction is oxide ion reacts with the metal ions to form metal oxide film.



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Metal + Oxygen \rightarrow Metal oxide (corrosion product)

ELECTROCHEMISTRY AND CORROSION



Oxidation corrosion

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ELECTROCHEMISTRY AND CORROSION



Mechanism: Initially the surface of metal undergoes oxidation and the resulting metal oxide scale forms a barrier which restricts further oxidation. The extent of corrosion depends upon the nature of metal oxide

a) If the metal oxide is stable, it behaves has a protective layer which prevents further Corrosion

E.g., the oxide films of Al, Sn, Pb, Cu, Cr, W etc. are stable and therefore further corrosion is prohibited

b) If the metal oxide unstable, the oxide layer formed decomposes back into metal and oxygen. Oxidation corrosion is not possible.



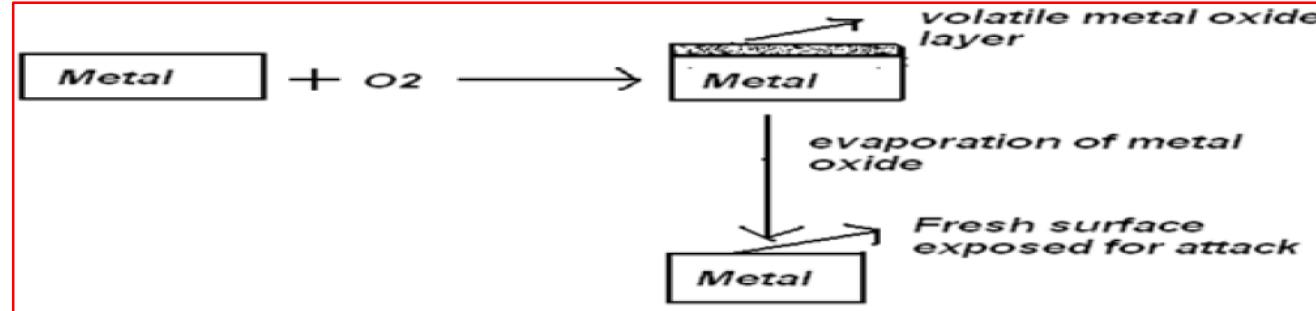
E.g., Ag, Au and Pt do not undergo oxidation corrosion.

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ELECTROCHEMISTRY AND CORROSION

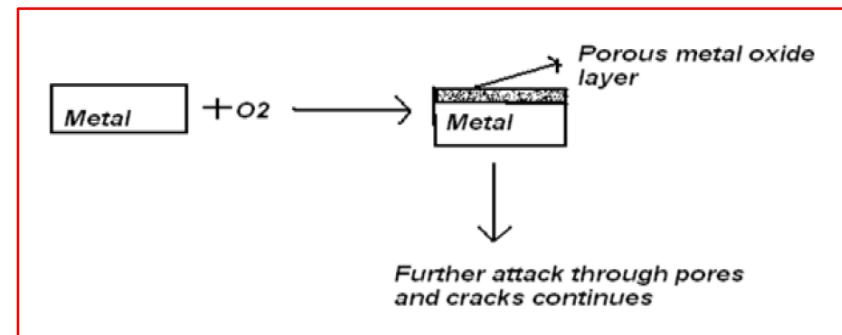


c) If the metal oxide layer is volatile, then the oxide layer volatilizes after formation and leaves the underlying metal surface exposed for further attack. This causes continuous corrosion which is excessive in molybdenum oxide (MoO_3).



d) If the metal oxide layer is porous, the oxide layer formed has pores or cracks. In this case the atmospheric oxygen penetrates through the pores or cracks and corrode the underlying metal surface. This cause continuous corrosion till conversion of metal into its oxide is completed.

E.g., Alkali and alkaline earth metals (Li, Na, K, Mg etc.)



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ELECTROCHEMISTRY AND CORROSION



2. CORROSION BY OTHER GASES

- Corrosion by other gases like SO_2 , CO_2 , H_2S etc. The degree of attack depends on the formation of protecting or non-protective films on the metal surface

a) If the film formation is protective or non-porous:

The intensity of corrosion decreases because of the film formed will protect the metal from the further corrosion

(E.g.: *AgCl film resulting from the attack of Cl_2 on Ag*).

b) If the film formation is non-protective or porous:

the surface of the whole is gradually destroyed

E.g.: Dry Cl_2 gas attacks on tin (Sn) forming volatile SnCl_4 there by leaving fresh surface for further corrosion

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3) Liquid metal corrosion

This is due to chemical action of flowing liquid metal at high temperatures on solid metal or alloy. Such corrosion occur in devices used for nuclear power.

The corrosion reaction involves either:

- (i) Dissolution of a solid metal by a liquid metal or
- (ii) Internal penetration of the liquid metal into the solid metal.

Eg. Coolant (sodium metal) leads to corrosion of cadmium in nuclear reactors

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ELECTROCHEMISTRY AND CORROSION



Pilling-Bedworth rule:

- The extent degree of corrosion attack depends on the formation of protective or non protective films on the metal surface which is explained on the basis of Pilling Bedworth rule.
- It is expressed in terms of specific volume ratio.

$$\text{Specific Volume ratio} = \frac{\text{Volume of metal oxide layer}}{\text{Volume of parent metal}}$$

- Smaller the specific volume ratio, greater is the rate of corrosion
- Eg. The specific volume ratio of W, Cr, and Ni are 3.6, 2.0 and 1.6 respectively. Consequently the rate of corrosion is least in Tungsten(W)
- If volume of metal oxide formed on the surface of a metal is more than or equal to the volume of metal from which it is formed, the oxide layer will be protective or non porous.
- If volume of metal oxide formed on the surface of a metal is less than the volume of metal from which it is formed, the oxide layer will be non-protective or porous.

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ELECTROCHEMISTRY AND CORROSION



Topics:

- wet or electrochemical corrosion definition
- Hydrogen evolution electrochemical corrosion
- Oxygen absorption electrochemical corrosion
- Differential aeration corrosion (oxygen corrosion cell)
- Factors effecting on rate of corrosion

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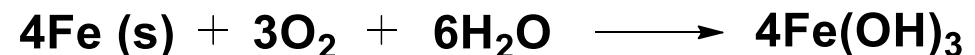
ELECTROCHEMISTRY AND CORROSION

When corrosion occurs under wet or moist conditions it is known as **electrochemical or wet corrosion**

It occurs when

- i) A metal is in contact with a conducting liquid
- ii) When metals of different reactivity's are in contact with solutions

Example: Rusting of iron



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ELECTROCHEMISTRY AND CORROSION



The Wet or electrochemical corrosion involves:

In presence of conducting medium metal undergoes following changes

1. Formation of anodic and cathodic areas
2. Corrosion of anodic parts only
3. Formation of corrosion product closer to the cathodic area.

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ELECTROCHEMISTRY AND CORROSION



- According to electrochemical theory, when a metal comes in contact with a conducting liquid a galvanic cell is formed within the metal. Some parts of the metal act as anode and rest act as cathode.
- Atmospheric gases and humidity present in the corrosive environment act as an electrolyte.
- Corrosion of anodic parts takes place due to oxidation at anode.
- Example for electrochemical corrosion is rusting of iron

a) Anodic Reaction:



These metal ions dissolves in solutions

b) Cathodic reaction

The occurs in two ways

- (i) Hydrogen evolution (in acidic environment)
- (ii) Oxygen absorption (in neutral or alkaline environment)

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ELECTROCHEMISTRY AND CORROSION

(i) Hydrogen evolution

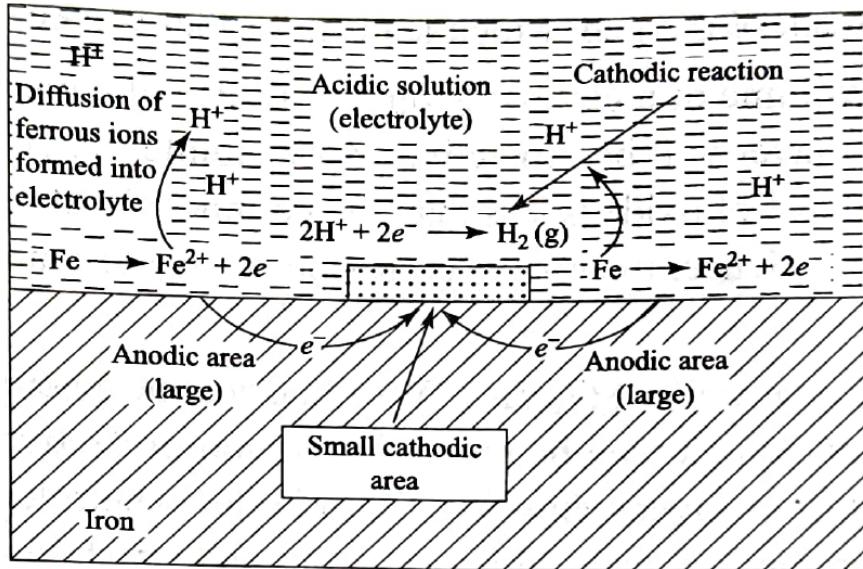
This type of corrosion occurs when

- i) Anodic areas are larger than cathodic areas
- ii) Oxygen is absent
- iii) Acidic environment required

Example rusting of Iron



These electrons flow through the metal, from anode to cathode, where H^+ ions of acidic solution are eliminated as hydrogen gas.



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ELECTROCHEMISTRY AND CORROSION



Oxygen Absorption Type

This type of corrosion occurs when

- i) Anodic areas are smaller than cathodic areas
- ii) Oxygen is present
- iii) Neutral or basic environment required

At Anode: Metal dissolves as ferrous ions with liberation of electrons.



At Cathode: The liberated electrons are intercepted by the dissolved oxygen.



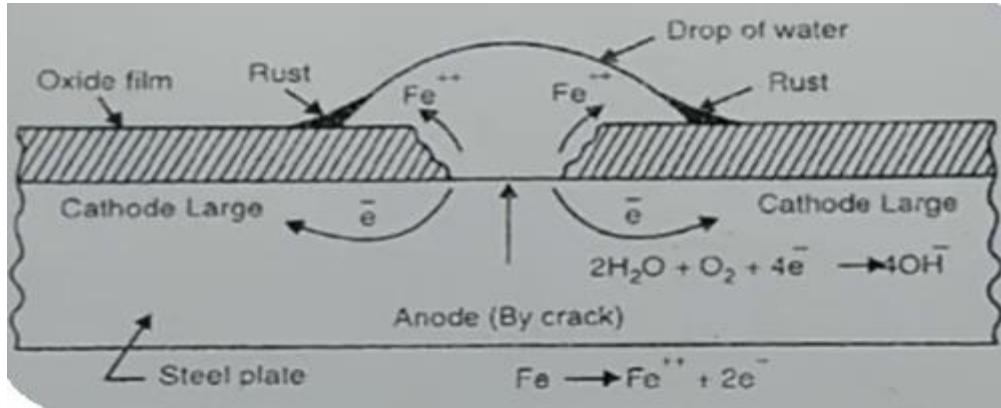
The Fe^{2+} ions and OH^- ions diffuse and when they meet, ferrous hydroxide is precipitated.



(i) If enough oxygen is present, ferrous hydroxide is easily oxidized to ferric hydroxide.



(ii) If the supply of oxygen is limited, the corrosion product may be even black anhydrous magnetite, Fe_3O_4 .



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ELECTROCHEMISTRY AND CORROSION



Types of wet/electrochemical corrosion

1. **Galvanic Corrosion (Differential Metal Corrosion)**
2. **Differential Aeration Corrosion**

- Waterline Corrosion
- Pitting Corrosion

Galvanic Corrosion (Differential Metal Corrosion)

- It is also called as *bi-metallic corrosion*.
- Galvanic corrosion occurs when two dissimilar metals (having different potentials) are electrically connected and jointly exposed to aqueous corrosive environment.
- The metal with the lower potential acts as anode and undergoes corrosion. The metal with higher potential acts as cathode and is protected.

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ELECTROCHEMISTRY AND CORROSION



Example: Iron pipes coupled with copper couplings

In the above example, iron (-0.44V) acts as anode and undergoes corrosion because its potential is less than that of copper (0.34V).

If anodic region is small it leads to severe corrosion.

Example: Pb-Sb soldering used on copper wire

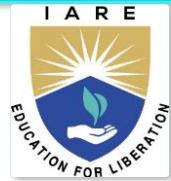
Pb is placed higher in the electrochemical series, acts as anode undergoes corrosion



Iron pipe connected to coupling.

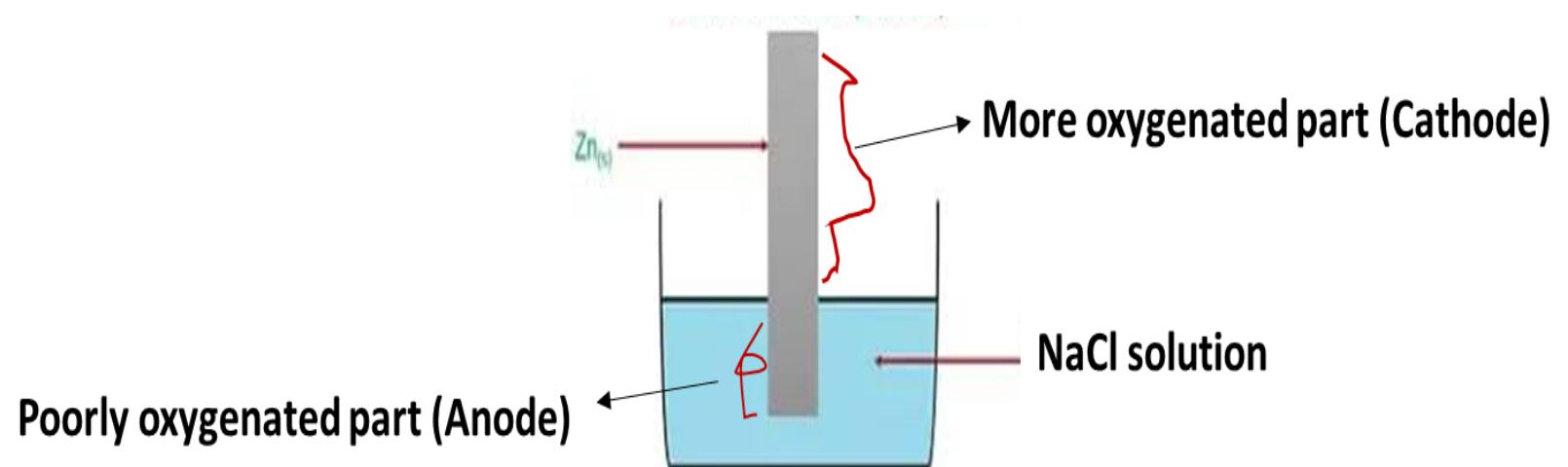
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ELECTROCHEMISTRY AND CORROSION



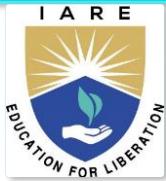
Differential aeration corrosion (oxygen corrosion cell) :

- It is a type of electrochemical corrosion that occurs when a metal in contact with conducting medium (corrosive medium) is exposed to different concentrations of oxygen
- The more oxygenated part of the metal becomes cathode and protected from corrosion
- Poorly oxygenated part of the metal becomes anode and undergoes corrosion



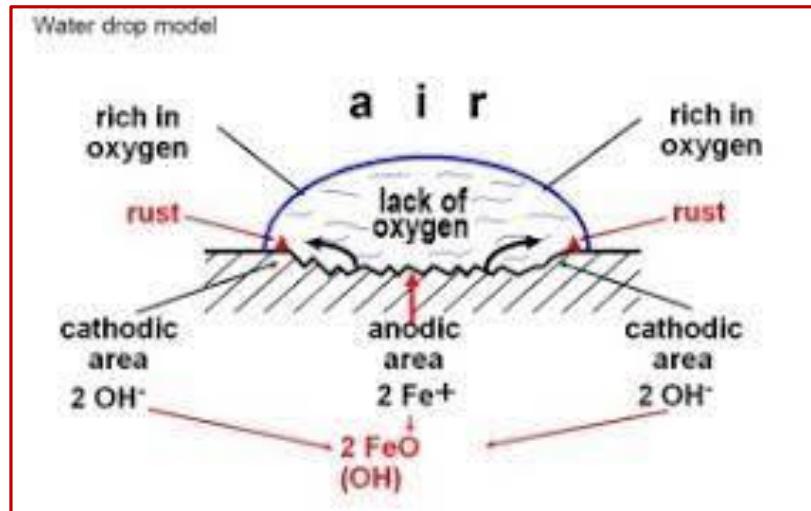
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ELECTROCHEMISTRY AND CORROSION



- Examples of this type of corrosion include drop corrosion, waterline corrosion, pitting corrosion.
- ✓ Also the areas below nuts, bolts, joints, areas covered by dust particles and welded areas are suffered from this type of corrosion.

Drop Corrosion

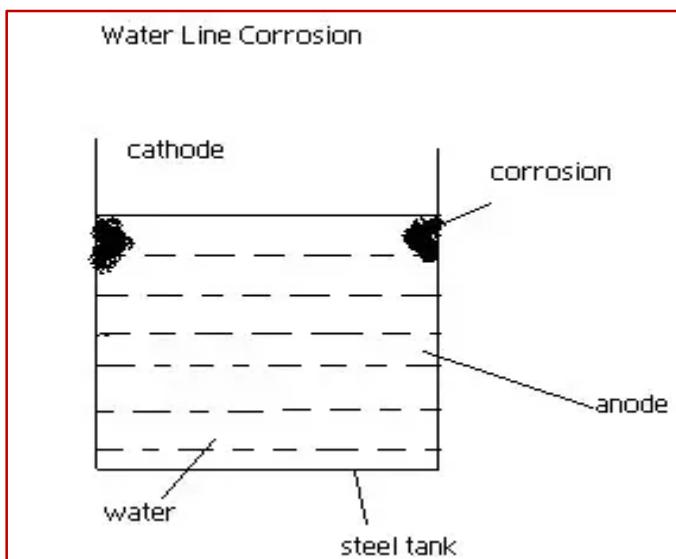


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ELECTROCHEMISTRY AND CORROSION

WATERLINE CORROSION

- Waterline corrosion a type of differential aeration corrosion.
- It occurs when a metal is partly submerged in water or a metallic tank is partially filled with water.
- *The part of metal below waterline is poorly oxygenated and acts as anodic area; while the part of the metal above the waterline is more oxygenated and acts cathodic area.*

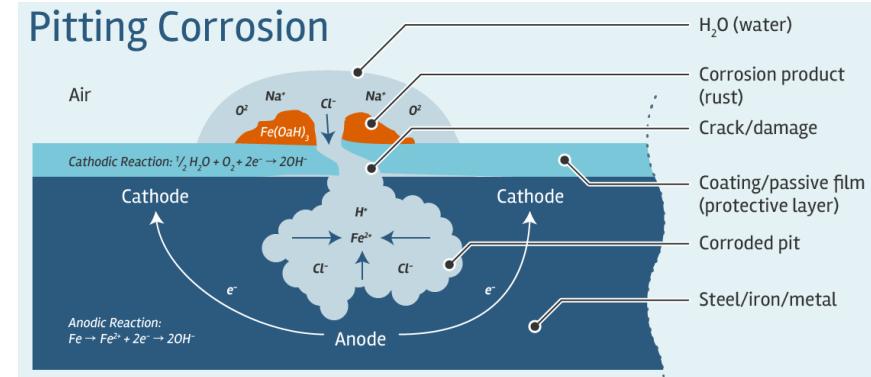


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ELECTROCHEMISTRY AND CORROSION

PITTING CORROSION

- Pitting corrosion is a localized form of corrosion resulting in the formation of pin holes or pits.
- When a small cracking, breaking of protective film on the metal surface occurs, small anodic areas and large cathodic areas are formed.
- The inner area of it is less aerated and the outer surface of the metal is well aerated.
- Therefore, the inner area of the pit acts as anode and under corrosion, while outer surface acts cathode and protected.



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ELECTROCHEMISTRY AND CORROSION

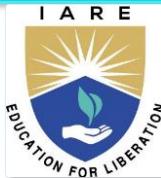


Topics:

- Metallic coatings
- Anodic metallic coatings
- Cathodic metallic coating
- Methods of application of metallic coatings

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ELECTROCHEMISTRY AND CORROSION



Metallic coatings

- The surface of the base metal coated with another metal (coating metal) is called metallic coatings
- Metallic coatings are broadly classified into two types
 - i) Anodic metallic coating
 - ii) Cathodic metallic coating

1. Anodic metallic coating:

- The metal used for the surface coating is more anodic than the base metal which is to be protected
- For example, coating of Al, Cd and Zn on steel surface are anodic because their electrode potentials are lower than that of the base metal iron
- Therefore, anodic coatings protect the underlying base metal sacrificially.

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ELECTROCHEMISTRY AND CORROSION



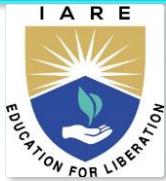
- The coating metal dissolves anodically and the base metal is protected
- If formation of pores and cracks over the metallic coating exposes the base metal and a galvanic cell is formed between the base metal and coating metal

2. Cathodic coating:

- Cathodic coatings are obtained by coating a more noble metal (i.e. metals having higher electrode potential like Sn, Au, Ag, Pt etc.) than the base metal
- They protect the base metal as they have higher corrosion resistance than the base metal
- Cathodic coating protects the base metal only when the coating is uniform and free from pores
- The formation of pores over the cathodic coating exposes the base metal (anode) to environment and a galvanic cell is set up. This causes more damage to the base metal.

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ELECTROCHEMISTRY AND CORROSION



Methods of application of metallic coatings

1. Hot dipping:

- Hot dipping process is applicable to the metals having higher melting point than the coating metal.
- It is carried out by immersing a well cleaned base metal in a bath containing molten coating metal
- Eg: Coating of Zn, Pb, Al on iron and steel surfaces
- The most widely used hot dipping processes are
 - (a) Galvanizing
 - (b) Tinning

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ELECTROCHEMISTRY AND CORROSION



Galvanizing:

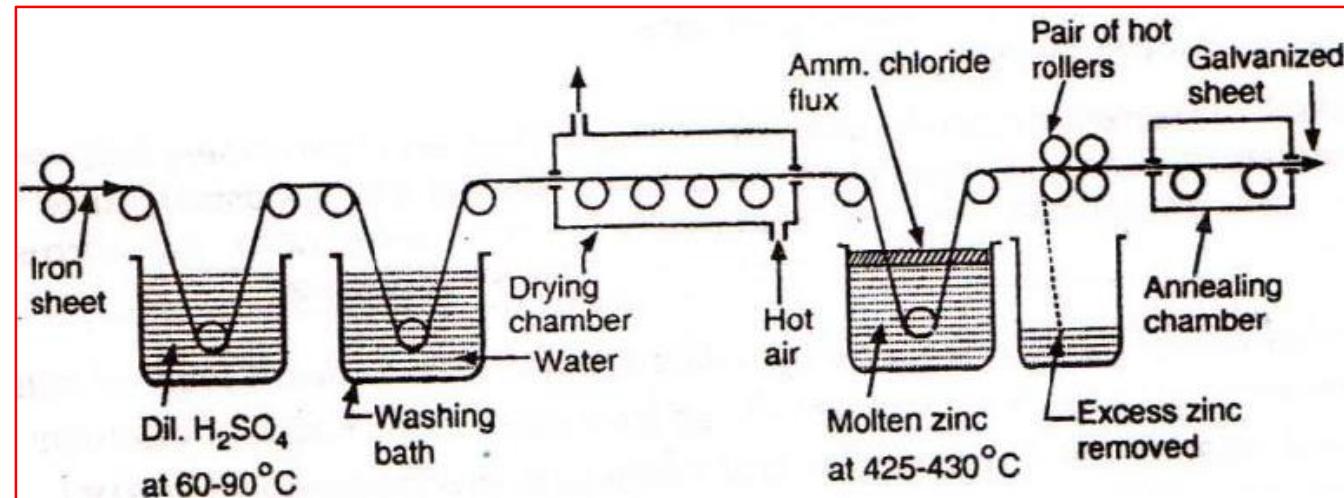
- Galvanizing is a process in which the iron base metal is protected from corrosion by coating it with a thin layer of zinc
- It is the anodic protection offered by the zinc
- In this process, at first iron or steel is cleaned by pickling with dil. H_2SO_4 solution for 15-20 minutes at 60-90 °C
- Dirt, oil, grease or rust and any other impurities are removed from the metal surface by pickling process
- The iron base metal is washed well and then dried.
- It is then dipped in bath of molten zinc maintained at 425-430 °C
- The surface of bath(molten zinc) is kept covered with ammonium chloride flux to prevent oxide formation

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ELECTROCHEMISTRY AND CORROSION



- The base metal is covered with a thin layer of zinc when it is taken out of bath.
- It is then passed through a pair of hot rollers, which removes any excess of zinc and produces a thin film of uniform thickness
- Then it is annealed and finally cooled slowly



- Galvanizing is widely used for protecting iron exposed to the atmosphere (roofs, wire fences, pipes etc.)
- Galvanized metallic sheets are not used for keeping eatables because of the solubility of zinc.

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ELECTROCHEMISTRY AND CORROSION

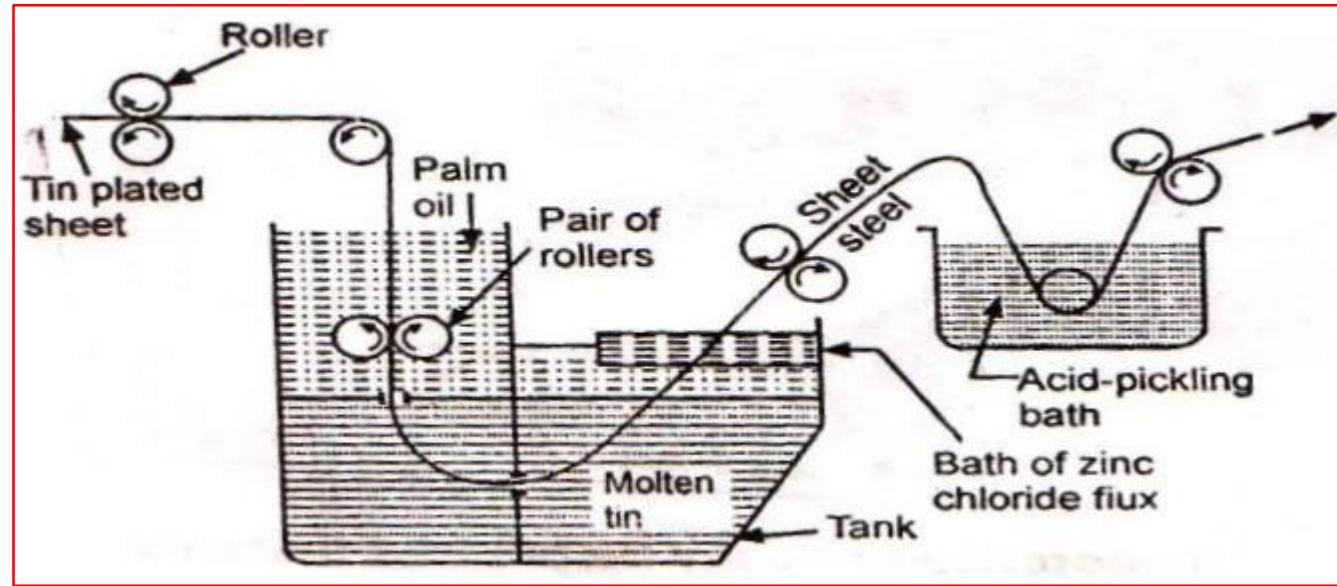
Tinning

- The process of coating tin over the iron or steel base metal to protect from corrosion is known as tinning
- Tin is a noble metal and therefore it possess more resistance to chemical attack
- It is the cathodic protection offered by the tin
- In this process, iron sheet is treated in dilute sulphuric acid (pickling) to remove any oxide film, if present.
- cleaned iron sheet is passed through a bath of $ZnCl_2$ molten flux followed by molten tin and finally through a suitable vegetable oil
- Palm oil protects the tin coated surface against oxidation
- Finally the sheet is passed through rollers to remove excess of tin and produce thin coat of tin of uniform thickness



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ELECTROCHEMISTRY AND CORROSION



Applications of Tinning:

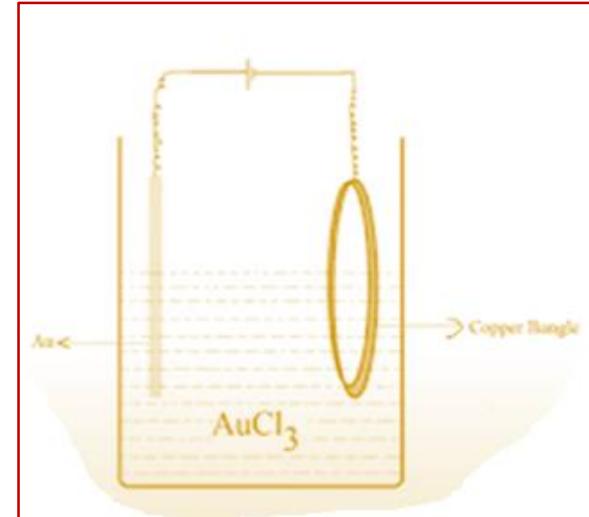
- Tin metal possess good resistance against atmospheric corrosion. Tin is non-toxic and widely used for coating steel, copper and brass sheets
- The containers coated with tin are used for storing food stuffs, ghee, oil etc and packing food materials
- Tinned copper sheets are used for making cooking and refrigeration equipment.

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ELECTROCHEMISTRY AND CORROSION

Electroplating

- The process of depositing the coating metal on the surface of base metal by electrolysis is called electroplating
- The base metal ornament (ex. Copper bangle) is connected to negative terminal of battery. It acts as cathode
- A pure metal (Au) which gives protective coating is connected to positive terminal of battery. It acts as anode
- The anodic metal salt solution i.e gold (III) chloride (AuCl_3) solution is taken as electrolyte
- Upon passing direct current from battery, electrolysis occur
- During the electrolysis process, anodic metal dissolves in electrolyte and deposits on the surface of base metal as coating
- Since the coated metal has noble character, it does not undergo corrosion



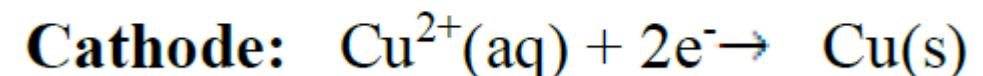
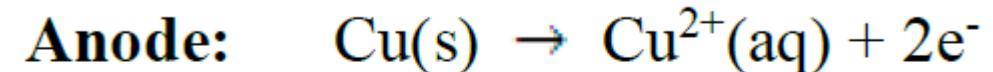
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ELECTROCHEMISTRY AND CORROSION



Electroplating- Copper plating

- For electroplating of copper on iron base metal the following are maintained
- Anode: Pure copper
- Cathode: Base metal article
- Electrolytic solution: CuSO₄
- When direct current is passed, the Cu²⁺ ions migrate to the cathode and deposit on the base metal article



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BATTERIES CHEMISTRY AND CORROSION



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MODULE II

WATER AND ITS TREATMENT

Dr. T. Dhananjay Rao
Assistant Professor
Department of Chemistry



Topic: Types of Hardness, units of Hardness

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MODULE II

WATER AND ITS TREATMENT



TOPICS

- **What is water?**
- **Introduction**
- **Sources of water**
- **Contamination of water**
- **Effect of water on rocks and minerals**
- **Classification of impurities**
- **Effect of impurities on natural water**
- **Soft water**
- **Hard water**
- **Disadvantages of hardwater**

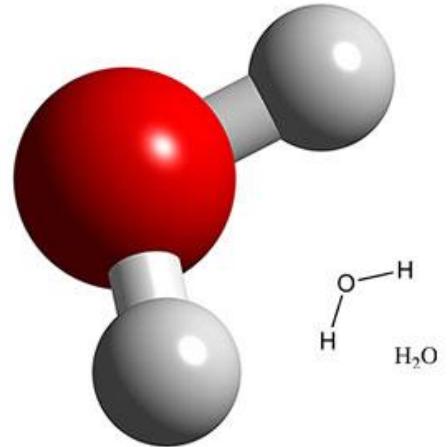
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MODULE II

WATER AND ITS TREATMENT

What is water?

- Water is made of tiny molecules of hydrogen and oxygen
- Pure water has no color, no taste and does not smell of anything
- Water exists in three forms on the earth
- Solid (ice, hail, snow or frost)
- Liquid (in lakes, oceans, rain, dew, fog or mist)
- Gas (steam or water vapour—invisible water in the air)



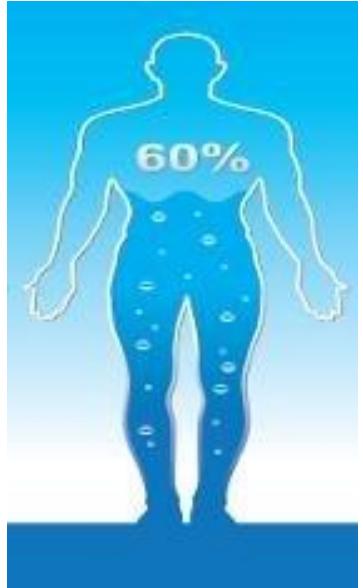
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MODULE II

WATER AND ITS TREATMENT



- ✓ Water is of major **importance** to all **living things**
- ✓ Up to **60 %** of the human body is water
- ✓ Therefore the **quality of water** we drink is very important
- ✓ The drinking water should be totally **clean, pure** and free of any disease causing microbes, and therefore be **properly treated** and **disinfected** before using it for drinking purposes.
- ✓ As an **engineering material** water is used for producing **steam**, in boilers to generate **hydro-electric power**, furnishing **steam** for engines, for construction of **concrete structures** & as a solvent in **chemical process**



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MODULE II

WATER AND ITS TREATMENT



Sources of Water

- ✓ There are **3 natural sources** of water
- ✓ Surface water (oceans, sea water, lakes, ponds)
- ✓ Above surface water (rain)
- ✓ Ground water (Springs or wells)
- ✓ **Surface water** collects on the ground or in a stream, river, lake, reservoir, or ocean.
- ✓ **Ground water** is located below the surface of the earth in spaces between rock and soil.
- ✓ It is stored in and moves slowly through geologic formations of soil, sand and rocks called aquifers.



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MODULE II

WATER AND ITS TREATMENT



Contamination of Water

❖ Surface waters

- ✓ Rain water – pure but **contaminated with gases**
- ✓ River water – **high dissolved salts** moderate organics
- ✓ Lake water – **constant composition** but high organics
- ✓ Sea water – **High salinity, pathogens, organics**

✓ Underground waters

- ✓ Spring/well water – **crystal clear but high dissolved salts**
and high impurity from organics



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MODULE II
WATER AND ITS TREATMENT



Effect of water on rocks and minerals

- ✓ **Dissolution:** Mineral constituents of rocks such as NaCl and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ readily dissolve in water
- ✓ **Hydration:** Minerals are easily hydrated causing disintegration of rocks
- ✓ **Effect of dissolved oxygen:** Oxidation and hydration of rocks
- ✓ **Effect of dissolved CO_2 :** Water containing CO_2 convert the insoluble carbonates of Ca, Mg and Fe to soluble bicarbonates



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MODULE II

WATER AND ITS TREATMENT

Classification of impurities

- ✓ **Dissolved Impurities:** Dissolved impurities may be organic or inorganic

- i. **Inorganic salts:**

Cations: Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Fe^{2+} , Al^{2+} and traces of Zn^{2+} and Cu^{2+}

Anions: Cl^- , SO_4^{2-} , NO_3^- , HCO_3^- , F^- , and NO_2^-

- ii. **Gases:** CO_2 , O_2 , N_2 , oxides of N_2 , NH_3 , H_2S

- iii. **Organic salts:** Organic water products, amino acids, proteins, etc.

Impurities
Present in Water

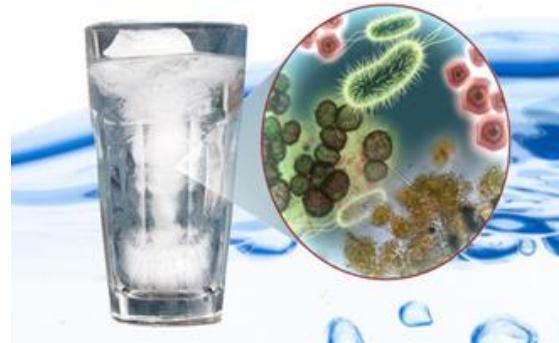


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MODULE II

WATER AND ITS TREATMENT

- ✓ **Suspended Impurities:**
- ✓ The impurities are **dispersion of solid particles** that are large enough to be removed by filtration on surface and heavier one settles down.
- ✓ It is of 2 types
 - i. **Inorganic** : sand & clay
 - ii. **Organic** : oil globules, vegetable and animal matter
- ✓ **Biological Impurities:** Micro-organisms like **pathogenic bacteria, fungi, algae etc.**



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MODULE II
WATER AND ITS TREATMENT



Effects of impurities in Natural Waters

- Various impurities **impart some properties** on the waters
- From the point of **industrial use**, the characteristics and effects of the impurities are as follows

1. Color
2. Tastes and odors
3. Turbidity and sediment
4. Micro-organisms
5. Dissolved mineral matter
6. Dissolved gases
7. Silica content and
8. Oxidability

- Hardness
- Alkalinity
- Total solids and
- corrosion



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MODULE II

WATER AND ITS TREATMENT

Effects of impurities in Natural Waters

1. Color

- ✓ Colors of natural waters range from pale yellow through yellowish-brown to dark brown
- ✓ Color in water is due to metallic salts of Fe, Mn and due to organic substances like humus, peat, algae, weed
- ✓ Colored water is objectionable in the industrial activities such as textile, paper & pulp, dyeing, tanneries
- ✓ Color intensities of water sample can be measured using tintometer using platinum cobalt standard color complex and expressed in "Hazen units"
- ✓ Removal or reduction of color is done by coagulation, settling, adsorption, and filtration



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MODULE II

WATER AND ITS TREATMENT

Tastes and odors

- ✓ **Taste:** Presence of dissolved salts and gases impart bitter, soapy, brackish and palatable taste which normally co-related with odor
- ✓ Bitter (Fe, Al, Mn, SO₄, Ca(OH)₂)
- ✓ Soapy (NaHCO₃)
- ✓ Brackish (High salt content NaCl)
- ✓ **Odour:** Domestic and industries activities cause undesirable odor to water
- ✓ Industrial effluent of organic, sewage discharge, presence of N, S and P contains compounds, metal ion pollution like Fe
- ✓ Substances like algae, peat, bacteria
- ✓ Grassy odor, peaty odor, offensive odor, tarry and faint odor



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MODULE II

WATER AND ITS TREATMENT



Turbidity and sediments

- ✓ It is due to **colloidal, extremely fine suspension** such as clay, slit, finely divided matters, sometimes microorganisms
- ✓ It reflects the **optical properties of water** in terms of light scattering ability instead of transmitting in straight lines



- ✓ Material which is so **coarse** that it rapidly tends to drop **out of suspension** is called “**sediment**”
- ✓ Turbidity is often measured by nephelometer or turbidimeter and expressed in “**formazin turbidity units**” or “**nephelometric turbidity units**”



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MODULE II
WATER AND ITS TREATMENT

Dissolved mineral matter

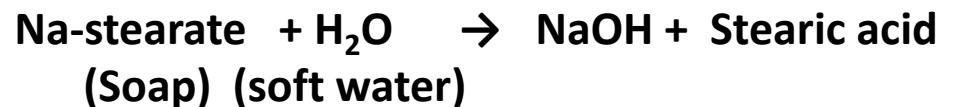
- **Hardness**
- **Alkalinity**
- **Total solids and**
- **Corrosion**
- **Mineral matter that effects the industrial applications of water are the hardness and alkalinity**
 - **Hardness:** it is the **soap consuming capacity** of a water sample
 - **There are 2 types of hardness:** temporary and permanent
 - **Alkalinity** of water is the total substances that increase the OH^- ions concentrations

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- The pure water is composed of two parts of hydrogen and one part of oxygen by volume and dissolves many substances.
- Water is a very good solvent.
- It is called as universal solvent.

Soft water

- ✓ The water which does not contain dissolved salts of Ca^{+2} and Mg^{+2}
- ✓ The water which can give lather with soap easily is called as softwater.



Stearic acid + Na-stearate \rightarrow formation of lather

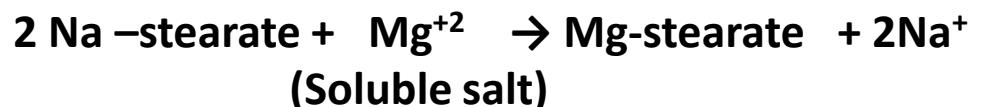
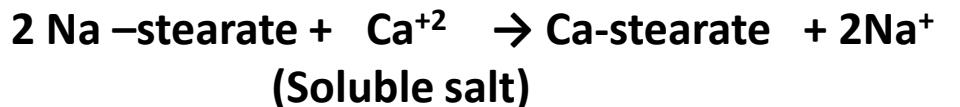


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Hard water

The water contains dissolved salts of Ca^{+2} and Mg^{+2}

The water which cannot give lather with soap easily is called as hard water.



- Minerals in hard water reacts with soap and form scum
- Interferes with soap's ability to lather
- So more soap is needed to form lather. Hence they are not suitable for washing.



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- **Washing and Bathing** : Hard water, does not produce lather freely with soap. Thus, the **cleaning quality of soap** is depressed and a lot of it is wasted.
- **Cooking**: The boiling point of water is increased because of presence of salts. Hence **more fuel and time** are required for cooking.
- **Drinking**: Hard water causes bad effects on our digestive system. Moreover, the possibility of forming **calcium oxalate crystals** in urinary tracks is increased.



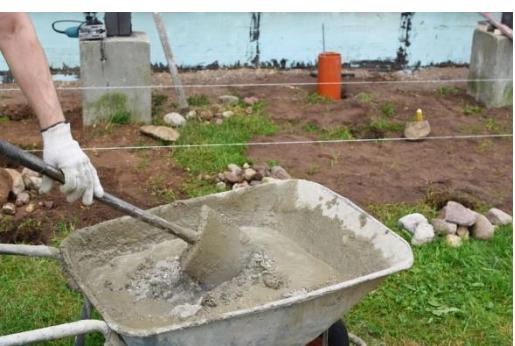
Industrial use

- ✓ **Textile industry:** Hard water causes wastage of soap. Precipitates of calcium and magnesium soaps adhere to the fabrics and cause problem.
- ✓ **Sugar Industry:** Water containing sulphates, nitrates, alkali carbonates etc. if used in sugar refining, causes difficulties in the crystallization of sugar. Moreover, the sugar so produced may be de-liquiscent.
- ✓ **Dyeing industry:** The dissolved salts in hard water may react with costly dyes forming precipitates.



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- ✓ **Paper Industry:** Calcium, magnesium, iron salts in water may affect the quality of paper.
- ✓ **Pharmaceutical Industry:** Hard water may cause some undesirable products while preparation of pharmaceutical products.
- ✓ **Concrete making:** Water containing chlorides and sulphates, if used for concrete making, affects the hydration of cement and the final strength of the hardened concrete.
- ✓ **Laundry:** Hard water, if used in laundry, causes much of the soap used in washing to go as waste iron salts may even causes coloration of the cloths.



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Disadvantages of Hard water

If hard water is used in boilers, it may lead to

- ✓ Boiler corrosion
- ✓ Scale and sludge formation
- ✓ Priming and foaming
- ✓ Caustic embrittlement pharmaceutical industry

BOILER CORROSION



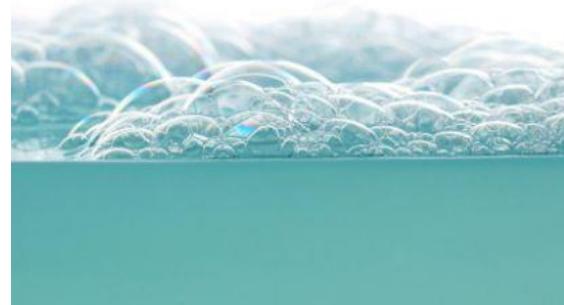
SLUDGE AND SCALE FORMATION



CAUSTIC EMBRITTLEMENT



PRIMING AND FOAMING



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MODULE II
WATER TECHNOLOGY

Dissolved solids

Total solid content comprises of **total dissolved solids** and **suspended solids**

Corrosion

- The corrosiveness of a raw water is determined by the **nature of impurities present in it**
- Under boiler conditions, **concentrated alkalis can attack steel**
- **Loss of mechanical strength**
- **Pitting and perforation of metal**
- **Contamination of water**
- **Interference with heat transfer**



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MODULE II
WATER TECHNOLOGY

Dissolved gases

- ✓ Carbon dioxide: amount of CO₂ picked up by rain water is very small. However lakes and rivers contain high CO₂ due to decay of organic matter
- ✓ Oxygen: dissolved O₂ is corrosive to iron, steel and brass
- ✓ Nitrogen: it is inert and has no corrosive effect on metals
- ✓ Hydrogen sulfide: sulfur waters are corrosive with offensive odor
- ✓ Methane: well waters contain methane. It is advisable to aerate water prior to its use so as to avoid fire



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Silica content

- ✓ It is the concentration of silicic acid present in the water
- ✓ The presence of SiO_2 in boiler feed water forms silicate scales and deposits in blades and nozzles of turbines



Oxidability

- ✓ Contamination of water by organic substances
- ✓ It is expressed as mg of oxygen required for oxidizing 1kg of organic substances
- ✓ Also expressed as amount of KMnO_4 spent to oxidize the organic substances



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Topics

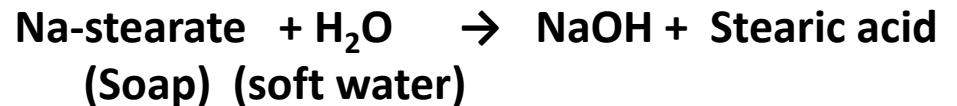
- **Soft water**
- **Hard water**
- **Types of hardness of water**
- **Units of hardness of water**

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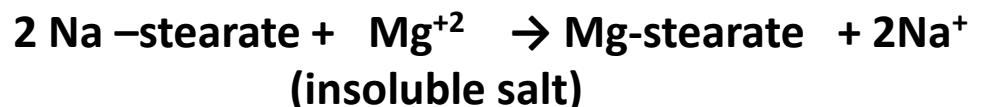
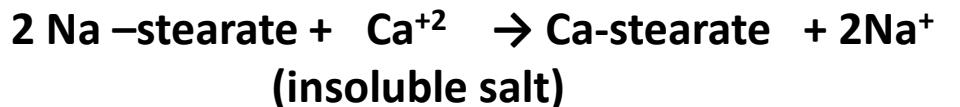


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Hard water

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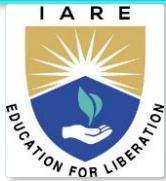


- Minerals in hard water reacts with soap and form scum
- Interferes with soap's ability to lather
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WATER TECHNOLOGY



Difference between hard and soft water:

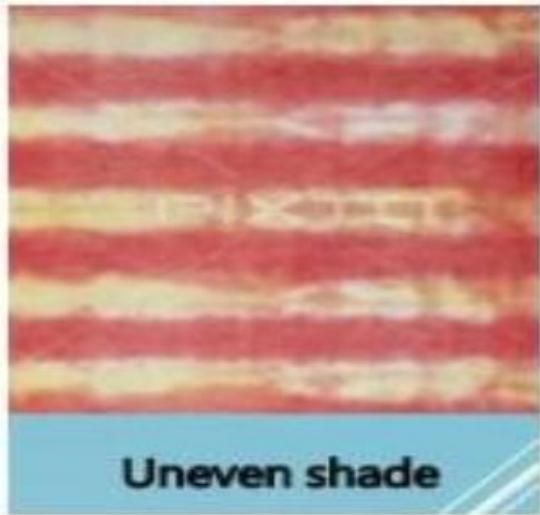
HARD WATER	SOFT WATER
Soap is not so effective	Soap is easily effective
No foam and lather from soaps	foam and lather from soaps
Leaves spots on the washed dishes after they are dried	Does not leave any spots on dishes after they are dried
Contains minerals like magnesium and calcium	Contains sodium ion
Example: Groundwater like deep wells	Example: Rainwater

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MODULE II
WATER TECHNOLOGY

Disadvantages of hard water

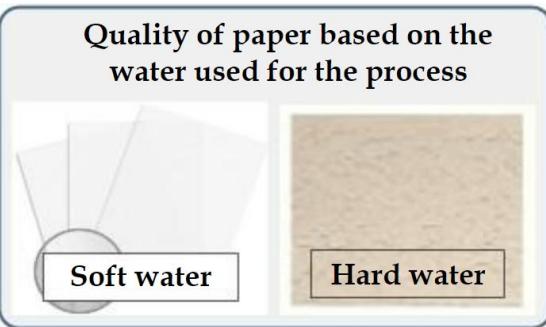
- ✓ **Textile industry:** Ca^{2+} and Mg^{2+} ions of hard water react with dye molecules and precipitate the dye. Precipitates of calcium and magnesium soaps adhere to the fabrics and cause problem.
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MODULE II
WATER TECHNOLOGY

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Causes of hardness:

The natural water is usually contaminated by different types of impurities

1. Physical impurities
2. Chemical impurities
3. Biological impurities

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Physical impurities

Physical impurities causes following impurities

- 1) Turbidity
- 2) Color
- 3) Taste
- 4) Odor
- 5) Temperature
- 6) Radioactive substances

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Turbidity

- Presence of suspended or colloidal insoluble particles present in the water is called turbidity
- Example: mud, sand, sediment, clay etc. they settle rapidly on standing
- The turbidity of feed water should not exceed 5 ppm.
- These materials can be removed by settling, filtration and coagulation methods

Color

- The water gets color from discharges industries like chemical, textile, paper etc.
- Yellowish color indicates the presence of chromium and organic matter
- Yellowish red color indicates the presence of iron

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Taste

- Taste for water obtained due to the presence of dissolved minerals
- Bitter taste can be due to the presence of iron, aluminum, manganese, sulphate or excess of lime
- Soapy tasty can be due to the presence of large amount of sodium bicarbonate
- Slightly salty due to the presence of dissolved gases and minerals like chlorides, nitrates in water

Odor

- Waste products discharge from industries gives odor to water
- Strong smelling compounds like chlorine, hydrogen, sulphide

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Temperature

- Temperature is an important factor for assessing water quality
- Temperature alters the various physical and chemical properties of the water
- Water is more denser at 4 °C , and less denser at either high or low temperature

Radioactive substances

- The discharges from nuclear power plant or research center discharge radioactive substance.
- These can seriously effect human health and life

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Chemical impurities

i) Acids

- The waste products of some industries such as battery factories, explosive factories contain acids.
- If these waste products are directly discharged into river then it will be harmful to life and will destroy the self purification property of water

ii) Inorganic compounds

- The waste products of industries like fertilizer industries contain certain inorganic compounds
- These compounds mainly consists of sulphides, ammonia etc.

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iii) Organic compounds

- Organic compounds may exist in the water due to presence of fats, protein, and carbohydrates
- The suspended organic compounds may develop due to decayed fruits and dead animals

ii) Inorganic compounds

- The waste products of industries like fertilizer industries contain certain inorganic compounds
- These compounds mainly consists of sulphides, ammonia etc.

iii) Biological impurities of water

- Biological contamination of water is caused by living organisms like algae, bacteria, protozoa, pathogens etc.

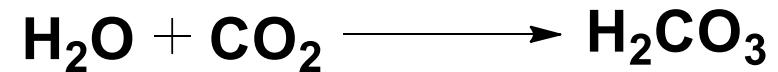
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WATER TECHNOLOGY

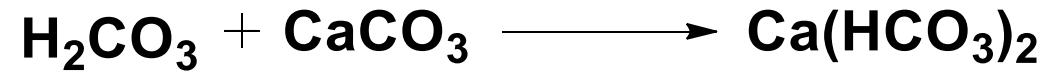


Causes of hardness of water

- Rain water absorbs carbon dioxide from air and also from decaying plants on soil form carbonic acid



- Such water containing carbonic acid, when flows over the rocks containing calcium and magnesium carbonates forms calcium and magnesium bicarbonates

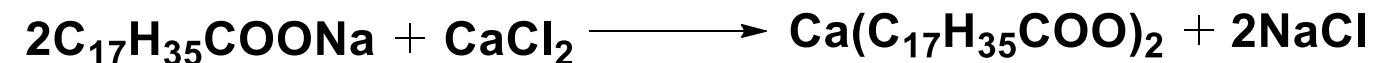


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WATER TECHNOLOGY



- On the surface layer, along with calcium, magnesium carbonates corresponding chlorides and sulphates also present
- The water containing carbonic acids reacts with calcium, magnesium chlorides and sulphates forms water soluble products
- Water containing these dissolved products is called hard water, it does not produce good lather with soap solution
- Soap is a mixture of sodium salts of fatty acids like steric acids, oleic acid, palmitic acid
- When soap is added to hard water containing calcium and magnesium salts (i.e Ca^{+2} and Mg^{+2}), insoluble calcium and magnesium salts are obtained by double decomposition

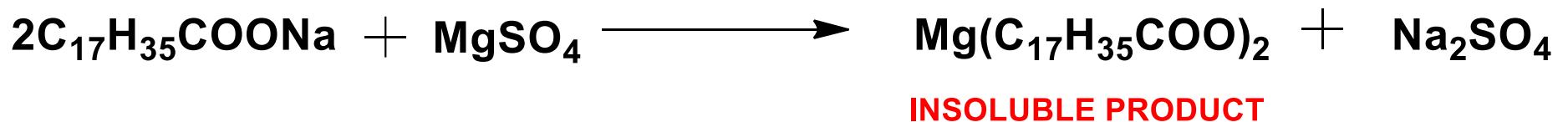
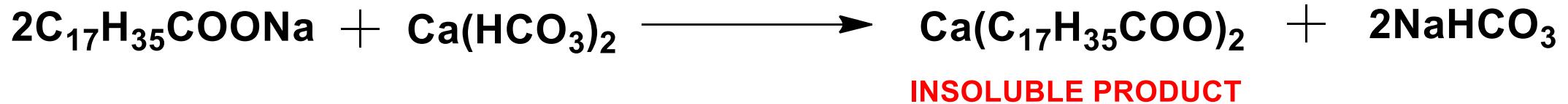
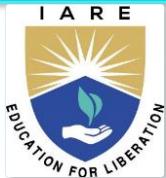


Soluble sodium sterate salt(soap)

INSOLUBLE PRODUCT

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WATER TECHNOLOGY



- This insoluble calcium or magnesium salts are formed when soap reacts with hard water

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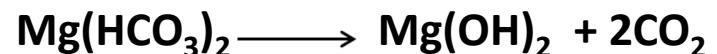
TYPES OF HARDNESS

Hardness in water is of two types.

- i. Temporary hardness and
- ii. Permanent hardness

Temporary hardness:-

- The hardness that can be removed simply by boiling is called the temporary hardness.
- It is due to the presence of magnesium and calcium hydrogen carbonates.
- On boiling $\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$ are precipitated as insoluble salts, which can be removed through filtration.



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Permanent Hardness:

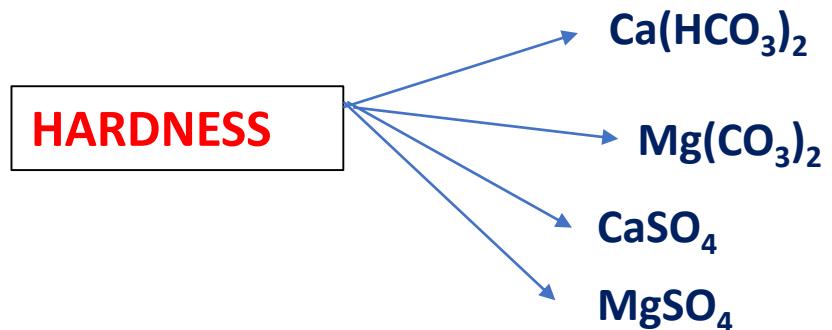
- Permanent hardness cannot be removed by boiling.
- It is due to CaCl_2 , CaSO_4 , MgCl_2 , MgSO_4 and nitrates in H_2O . These salts cannot be removed.
- Fe^{3+} , Al^{3+} & Mn^{2+} also cause hardness in water.



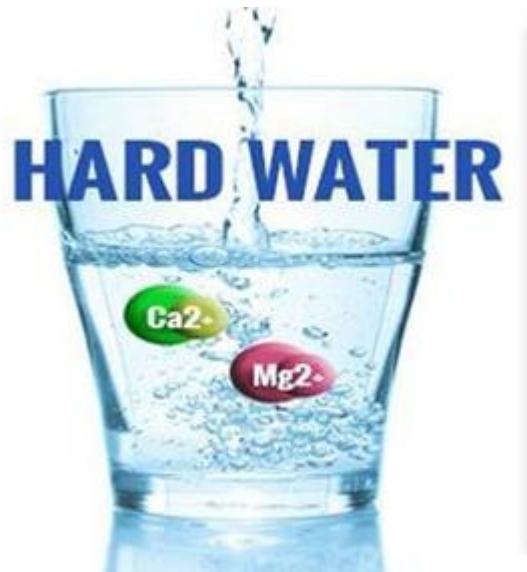
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Equivalents of CaCO_3 / Degree of Hardness

- To express concentrations of hardness impurities as well as some non-hardness impurities.



- Even if we take same amount (weight) of above salts will not give equal hardness
- To compare the hardness of above salts we have to convert those salts into CaCO_3 equivalents.



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Why CaCO_3 ?

1. The molecular weight of CaCO_3 is 100 and its equivalent weight becomes 50

So the equivalent CaCO_3 calculations are very easy compare with other salts

2. CaCO_3 is very insoluble precipitate in water.

- when certain methods are carried out to make hard water soft then dissolved salts of water i.e calcium hydrogen carbonate, calcium chloride and calcium sulphate are converted to insoluble calcium carbonate.
- so quantity of calcium carbonate obtained gives the information regarding concentration of dissolved salts in water.

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Conversion to CaCO_3 equivalents

CaCO_3 equivalent = mass of hardness producing substance x multiplication factor ($\frac{100}{\text{M.w of salt}}$)

- NaCl , KCl , Fe_2O_3 , SiO_2 All these salts do not impart any kind of hardness to water hence we should not consider for calculations

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UNITS OF HARDNESS



- i. **Parts per million (ppm):-** It is the number of parts of equivalents of CaCO_3 hardness causing salt present in one million parts (10^6) of water.

$1\text{ppm} = 1 \text{ part of } \text{CaCO}_3 \text{ equivalent present in } 10^6 \text{ parts of water}$

- i. **Miligram per litre (mg/L):-** number of milligrams of CaCO_3 equivalent hardness causing salt present in one liter of hard water.

E.g.: - 1mg/L means $1 \text{ mg of equivalent } \text{CaCO}_3$ present in one litre of hard water

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UNITS OF HARDNESS

iii. **Degree Clarke ($^{\circ}\text{Cl}$)**:- it is the number of parts of CaCO_3 equivalents of hardness causing salt in 70,000 parts of water.

$1 \ ^{\circ}\text{Cl} = 1 \text{ part of } \text{CaCO}_3 \text{ eq hardness per 70,000 parts of water}$

iv. **Degree French ($^{\circ}\text{Fr}$)**:- It is a French unit. The number of parts of CaCO_3 equivalents of hardness causing substance in 10^5 parts of water.

Inter conversion: - $1\text{ppm} = 1\text{mg/l} = 0.07 \ ^{\circ}\text{Cl} = 0.1 \ ^{\circ}\text{Fr}$

$$1 \ ^{\circ}\text{Cl} = 1.43 \ ^{\circ}\text{Fr} = 14.3 \text{ ppm} = 14.3 \text{ mg/l}$$

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A Water sample contains 204 mg of CaSO_4 , per litre, calculate hardness (in ppm, degree Clark and degree French) in terms of CaCO_3 equivalents

CaCO_3 equivalents = mass of hardness producing salt \times multiplication factor

$$= 204 \text{ mg/L} \times \frac{100}{136}$$

$$= 150 \text{ mg/L or } 150 \text{ ppm hardness}$$

Inter conversion: - 1ppm = 1mg/l = 0.07 ° Cl = 0.1 ° Fr

$$1\text{ppm} = 1\text{mg/l} = 0.07 \text{ }^{\circ}\text{Cl}$$

$$= 150 \text{ ppm} = 150 \times 0.07 \text{ }^{\circ}\text{Cl}$$

$$= 10.5 \text{ }^{\circ}\text{Cl hardness}$$

$$1\text{ppm} = 0.1 \text{ }^{\circ}\text{Fr}$$

$$150 \text{ ppm} = 150 \times 0.1 \text{ }^{\circ}\text{Fr} = 15 \text{ }^{\circ}\text{Fr}$$

Solved Problem

1. A sample of hard water contains the following dissolved salts per liter. $Mg(HCO_3)_2=14.6\text{mgs}$; $Ca(HCO_3)_2=16.2\text{mgs}$; $CaCl_2=11.1\text{mgs}$; $CaSO_4=1.36\text{mgs}$; Silica=40mgs; Turbidity=10mgs. determine the temporary, permanent and total hardness of water in ppm, degree Clark and degree French

Compound	Wt of compound (mg/L)	Type of hardness	$CaCO_3$ equivalents (mg/L)
$Mg(HCO_3)$	14.6	Temporary	$(14.6 \times 100)/146 = 10$
$Ca(HCO_3)_2$	16.2	Temporary	$(16.2 \times 100)/162 = 10$
$CaCl_2$	11.1	permanent	$(111 \times 100)/111 = 100$
$CaSO_4$	1.36	permanent	$(1.36 \times 100)/136 = 1$

Temporary hardness = hardness due to $Mg(HCO_3)_2$ + hardness due to $Ca(HCO_3)_2$ =

$$10 + 10 = 20 \text{ mg/L} = 20 \text{ ppm} = 1.4 \text{ }^{\circ}\text{Cl} = 2 \text{ }^{\circ}\text{Fr}$$

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Permanent hardness = hardness due to CaSO_4 + hardness due to CaCl_2
= $100 + 1 = 101 \text{ mg/L} = 101 \text{ ppm} = 7.07 \text{ }^{\circ}\text{Cl} = 10.1 \text{ }^{\circ}\text{Fr}$

Total Hardness of water = Temporary hardness + Permanent hardness
= $20 + 101 = 121 \text{ mg/L} = 121 \text{ ppm} = 8.47 \text{ }^{\circ}\text{Cl} = 12.7 \text{ }^{\circ}\text{Fr}$

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Calculate the temporary and permanent hardness (in degree clerk) of water sample having the following constituents per litre:

$\text{Ca}(\text{HCO}_3)_2 = 162\text{mg}$ $\text{Mg}(\text{HCO}_3)_2 = 73\text{mg}$ $\text{MgCl}_2 = 95\text{mg}$ $\text{NaCl} = 585\text{mg}$ $\text{CaSO}_4 = 136\text{mg}$

SALT	Mass of the sample	TYPE OF HARDNESS	CaCO_3 equivalent
$\text{Ca}(\text{HCO}_3)_2$	162mg	temporary	$162 \times \frac{100}{162} = 100 \text{ ppm}$
$\text{Mg}(\text{HCO}_3)_2$	73mg	temporary	$73 \times \frac{100}{146} = 50 \text{ ppm}$
MgCl_2	95mg	permanent	$95 \times \frac{100}{95} = 100 \text{ ppm}$
CaSO_4	136mg	permanent	$136 \times \frac{100}{136} = 100 \text{ ppm}$
NaCl	585mg	Not effect	--

Temporary hardness = $100 + 50 = 150 \text{ ppm}$; we know $1\text{ppm} = 0.07^\circ \text{Cl}$ then $150 \text{ ppm} = 10.5^\circ \text{Cl}$

Permanent hardness = $100 + 100 = 200 \text{ ppm}$; we know $1\text{ppm} = 0.07^\circ \text{Cl}$ then $200 \text{ ppm} = 14^\circ \text{Cl}$

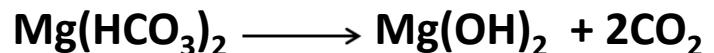
Question bank questions

1. One liter of water sample collected from a water source in telangana has shown the Following analysis. $Mg(HCO_3)_2 = 14.6$ mg, $MgSO_4 = 12$ mg, $Ca(HCO_3)_2 = 16.2$ mg, $CaCl_2 = 22.2$ mg, $MgCl_2 = 9.5$ mg and organic impurities 100 mg. determine temporary and permanent hardness in Degree French and degree Clark.
2. One liter of water from an underground reservoir in thirupathi town in andhrapradesh showed the Following analysis for its contents $Mg(HCO_3)_2 = 42$ mg, $MgSO_4 = 48$ mg, $Ca(HCO_3)_2 = 146$ mg, $CaCl_2 = 71$ mg, determine temporary and permanent hardness of the sample of 10000 liters of water
3. A water sample contains the following. $Mg(HCO_3)_2 = 73$ mg/l; $MgCl_2 = 95$ mg/l; $NaCl = 410$ mg/l. Calculate temporary, permanent and total hardness of the sample water in ppm, degree Clark and degree French.
4. Determine temporary and permanent hardness of a water sample in ppm which contains 6.8mg of $CaSO_4$, 33mg of $CaCl_2$, 40mg of $MgCl_2$, 24mg of $MgSO_4$ per liter of the water sample.(Given Molar mass of Ca=40g, Mg=24g, S=32g, O=16g, Cl=35g).

TYPES OF HARDNESS

Temporary hardness:-

- It is due to the presence of magnesium and calcium hydrogen carbonates.
- The hardness that can be removed simply by boiling is called the temporary hardness.
- On boiling $\text{Ca}(\text{HCO}_3)_2$, $\text{Mg}(\text{HCO}_3)_2$ are precipitated as insoluble salts, which can be removed through filtration.



Permanent Hardness:

- Permanent hardness cannot be removed by boiling.
- It is due to CaCl_2 , CaSO_4 , MgCl_2 , MgSO_4 and nitrates in H_2O .

These salts cannot be removed.

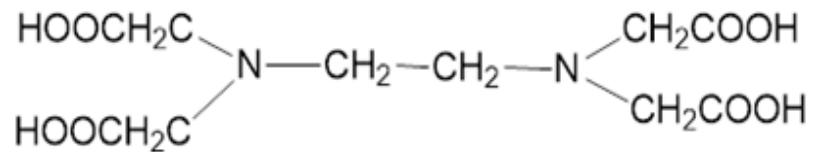
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ESTIMATION OF HARDNESS OF WATER

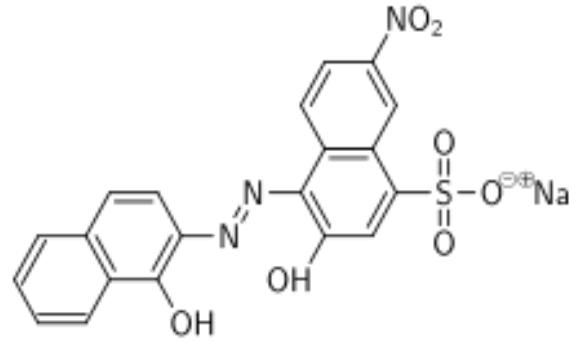
EDTA Complexometric titration

- Ethylenediaminetetraacetic acid (EDTA) is used to determine the hardness of water with the help of complexometric titration.

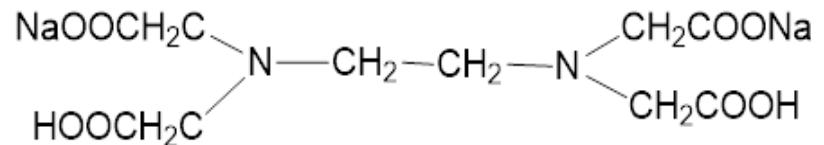
Chemicals Required



Ethylenediamine tetraacetic acid



Eriochrome Black-T



Disodium ethylenediamine tetraaceticacid

Ammonical Buffer

$(\text{NH}_4\text{OH} + \text{NH}_4\text{Cl})$

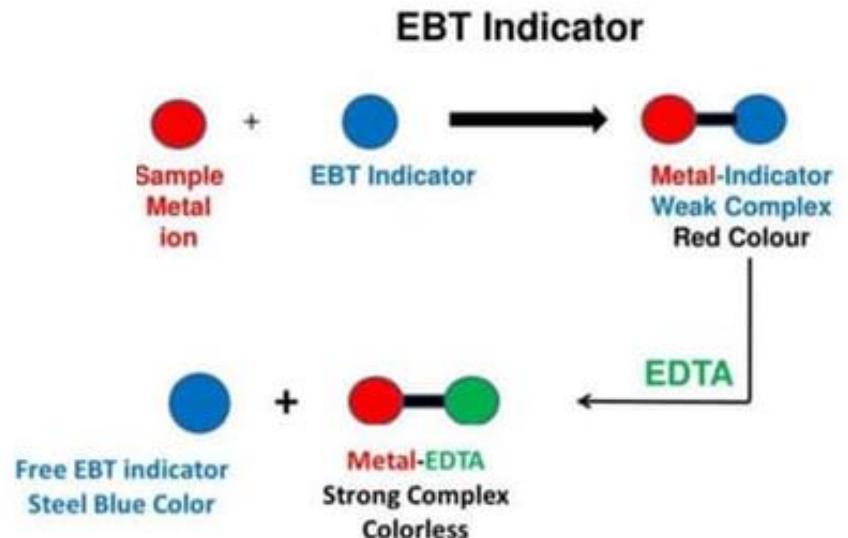
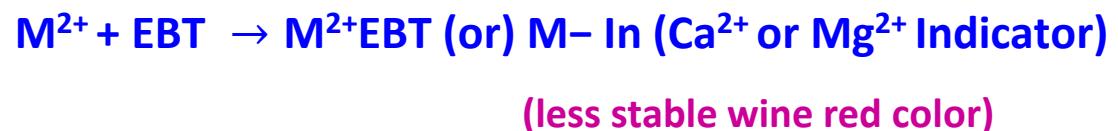
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ESTIMATION OF HARDNESS OF WATER

Principle:-

- The Ca^{2+} & Mg^{2+} ions present in water are responsible for hardness.
- These ions form selectable complexes with the indicator (EBT) and these metal ions forms stable complexes with EDTA.
- This fact is used to estimate the hardness of water sample.
- The metal ions Ca^{2+} & Mg^{2+} , EBT indicator and forms a less stable complex at $\text{pH}-10$.

pH 9-10:

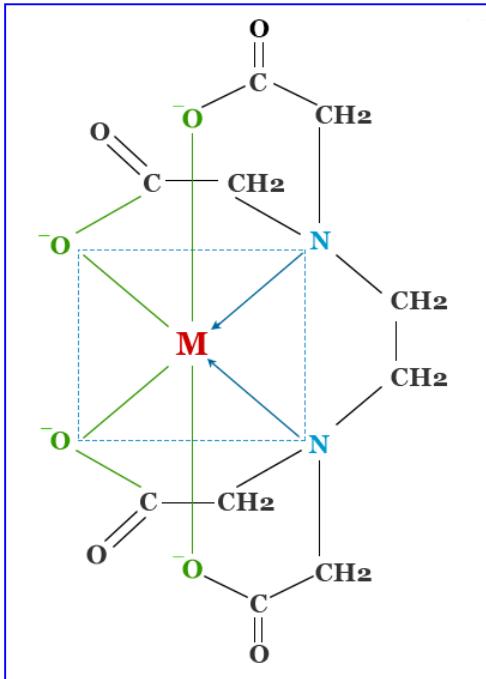


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ESTIMATION OF HARDNESS OF WATER



- whenever we are adding EDTA solution to the **wine-red color (M-In) solution**, the metal ions form more stable complex with EDTA.
- When all the metal ions in the sample complexed with EDTA, further addition of EDTA liberates the free indicator solution at pH-10 which in **blue color** indicates the end point of the titration.



M= bivalent metal



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ESTIMATION OF HARDNESS OF WATER

Step I PREPARATION OF STANDARD SOLUTION OF $\text{MgSO}_4/\text{CaCO}_3$

Weigh the approx 0.25gm of MgSO_4 and transfer into 100ml standard flask through the funnel and dissolve in minimum quantity of distilled water.

Make up the solution up to the mark with distilled water and shake the flask well for uniform concentration then calculate the Molarity of MgSO_4

Molecular Weight of $\text{MgSO}_4 = 246.48\text{gm}$

Molarity of $\text{MgSO}_4 = 0.01\text{M}$

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ESTIMATION OF HARDNESS OF WATER

Step II Find out the concentration of EDTA Solution

- Pipette out 20ml of MgSO_4 solution into a clean conical flask.
- Add 2ml of buffer solution and add 2 to 3 drops of EBT indicator and it gets wine red color solution.
- Take EDTA solution in a burette after titrate with EDTA solution till wine red color changes to blue color
- Note the burette reading and repeat the titration to get concurrent values.

M_1 = MgSO_4 molarity

V_1 = volume of MgSO_4

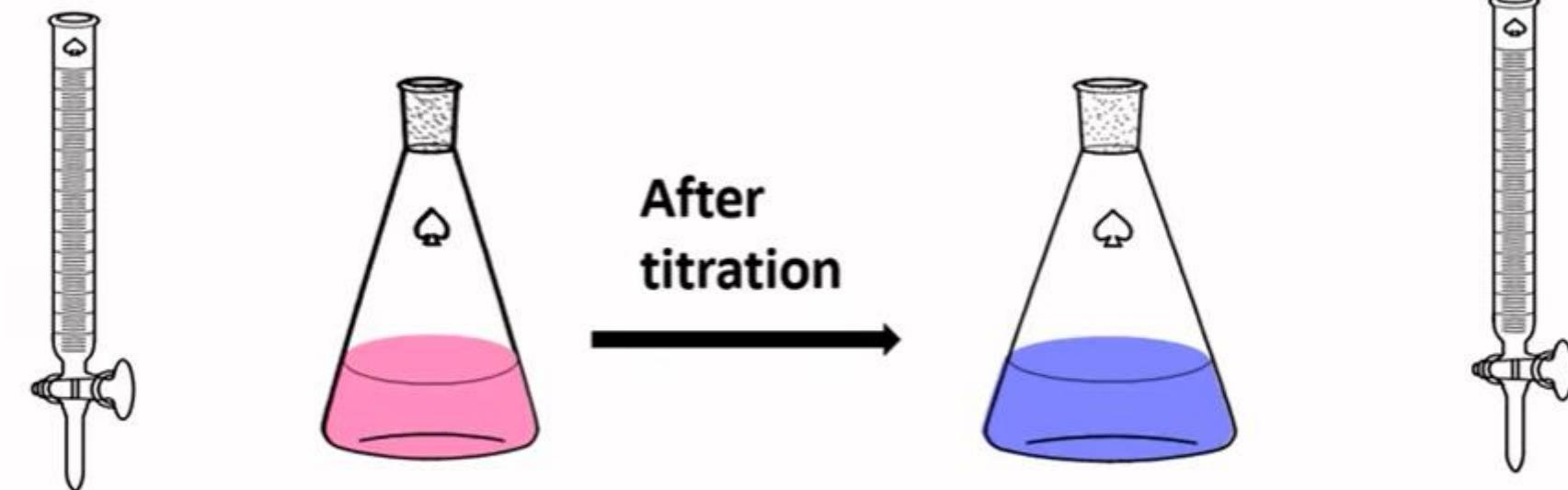
M_2 = EDTA molarity

V_2 = volume of EDTA consumed

$$M_1V_1 = M_2V_2$$

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Standardization of EDTA solution



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ESTIMATION OF HARDNESS OF WATER

Step III Estimation of Hard water

- A known volume (V_1) of hard water sample is titrated with about 3 ml of buffer solution and 4- 5 drops of EBT indicator.
- Pipette out 20ml of tap water into a 250ml conical flask add 2 ml of buffer solution and add 2-3drops of EBT indicator.
- Titrate the wine red color solution with EDTA taken in burette, till a blue color end point is obtained.
- Repeat the titration to get concurrent values.

M_3 = molarity of hard water M_2 = EDTA molarity

V_3 = volume of Hard water V_2^1 = volume of EDTA consumed

$$M_3 V_3 = M_2 V_2^1$$

$$M_3 = M_2 V_2^1 / V_3$$

Total hardness= $M_3 \times 100 \times 1000$ = -----PPM

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Step IV: CALCULATION OF PERMANENT HARDNESS OF WATER

- Pipette out 100ml of hard water sample into a beaker containing 250 ml and boil the water till volume reduces to 50ml (all the bicarbonates of Ca^{2+} , Mg^{2+} decomposes to CaCO_3 and Mg(OH)_2 respectively).
- Cool the solution and filter the water into beaker then pipette out 20ml of this cool water sample in to 250ml conical flask add 2ml of buffer solution and 2-3 drops of EBT indicator
- Titrate the wine red color solution with EDTA taken in the burette, till a blue colored solution end point is obtained. Repeat the titration to get concurrent values.

M_4 = molarity of hard water M_2 = EDTA molarity

V_4 = volume of hard water V_2^{II} = volume of EDTA consumed

$$M_4 V_4 = M_2 V_2^{\text{II}}$$

$$M_4 = M_2 V_2^{\text{II}} / V_4$$

Permanent hardness = $M_4 \times 100 \times 1000 = \dots \text{PPM}$

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ESTIMATION OF HARDNESS OF WATER



RESULT:

Total hardness in _____ PPM

2) Permanent hardness in _____ PPM

3) Temporary hardness in _____ PPM (Total hardness – Permanent hardness)

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Topics covered

- **Potable water**
- **Specifications**
- **Water treatment steps**
- **Disinfection methods**

- Potable water** is water that has been treated and tested as safe for human consumption, also known as drinking water.
- This includes tap water, bottled water, filtered water, and any other water considered safe for drinking and food preparation.

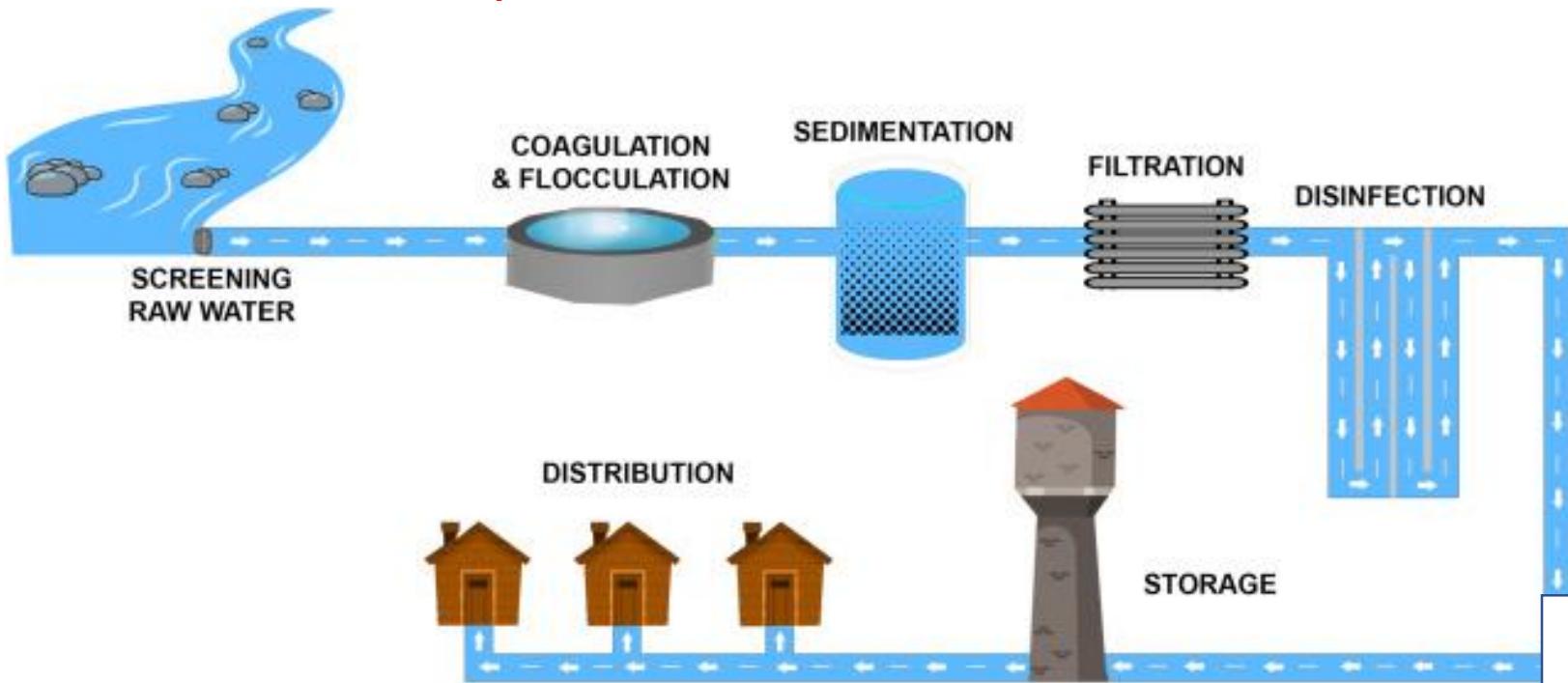


Specifications

- The water should be clear, colorless and odorless.
- The turbidity should not exceed 10 ppm.
- Total dissolved salts (TDS) should not exceed 500 ppm.
- The hardness of water must be less than 125 ppm and P^H must be 7.0 to 8.5.
- The water should be free from heavy metals like Pb, As, Cr, Mn and dissolved gases such as H₂S and SO₂.
- The water should be free from pathogenic micro organisms.

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Steps involved in treatment of potable water



- a. Screening
- b. Sedimentation
- c. Coagulation
- d. Filtration
- e. Disinfection

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- The type of treatment is given to water largely depends upon the quality of raw water and also upon specified standards
- Steps involved in treatment of potable water

(i) Removal of suspended impurities

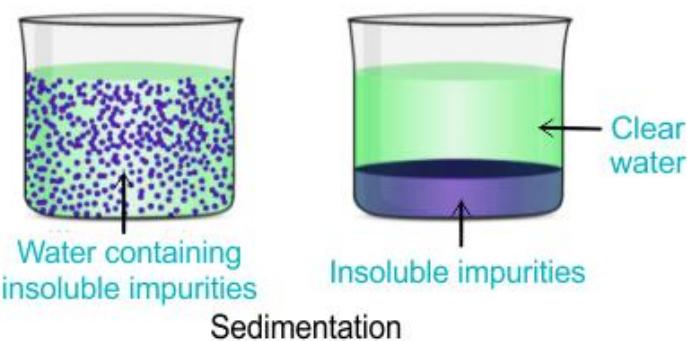
- a) **Screening:** the raw water is passed through screens having large no. of holes where floating materials are retained.
- b) **Sedimentation:** It is a process of allowing water to stand undisturbed in big tanks about 5m deep when most of the suspended particles settle down at the bottom due to force of gravity



Screening



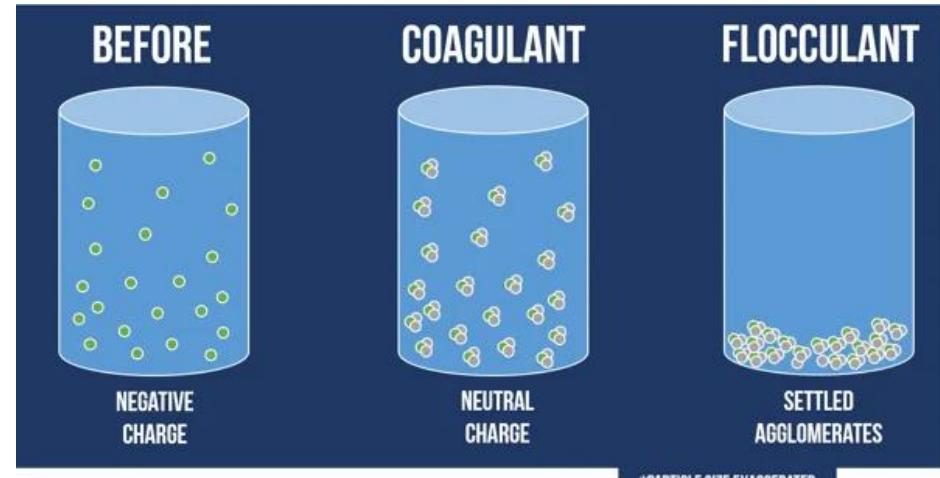
Sedimentation



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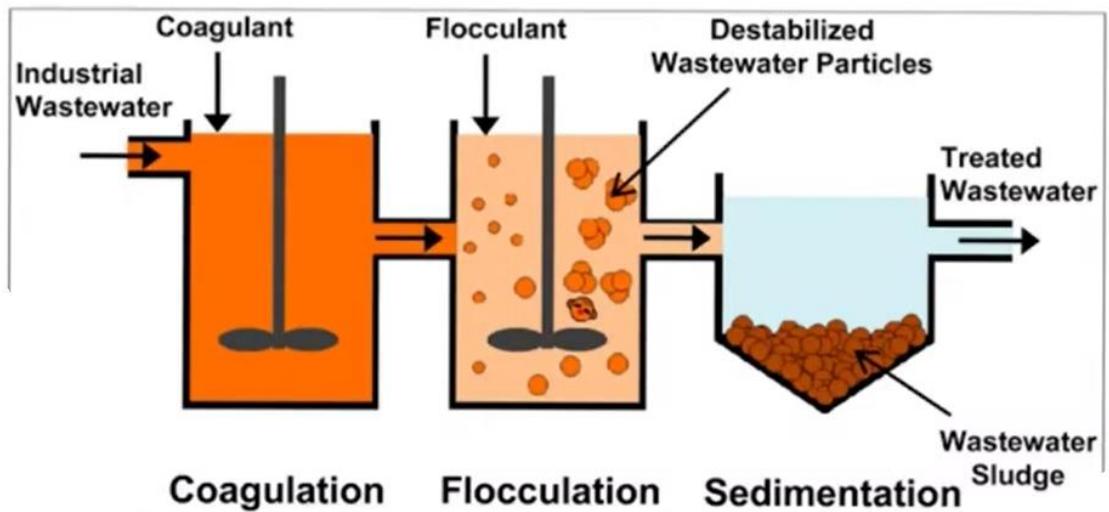
C. Coagulation and flocculation

- ❑ Sedimentation with coagulation is the process of removing fine suspended and colloidal impurities by addition of coagulants (chemicals) to water before sedimentation.
- ❑ The difference between the two is coagulation is the coming together, or clumping of particles, and flocculation is the settling of coagulated particles
- ❑ Coagulant when added to water form insoluble gelatinous, flocculant precipitate which descent through the water, adsorbs and entangles very fine suspended impurities forming bigger flocs, which settle down easily.



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Eg. Alum $[K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O]$, $NaAlO_2$, $FeSO_4 \cdot 7H_2O$.



d) **Filtration:** the process of removing colloidal matter and most of the bacteria, microorganism by passing water through a bed of fine sand and other proper sized granular materials.

A sand filter consists of a thick top layer of fine sand placed over coarse sand layer and gravels.

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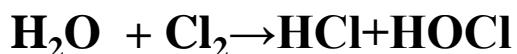
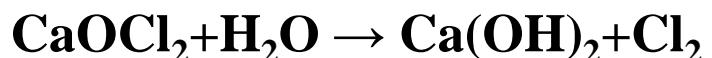
ii) Removal of Microorganisms

Disinfection: the process of destroying/killing the disease producing bacteria, microorganisms etc from the water and making it safe is called disinfection

(a) Boiling: Boil water for 10-15 min, all the disease producing bacteria are killed and water become safe for use

Bleaching powder: The purification is achieved by dissolving 1 kg of bleaching powder in 1000 kilo litres of water

✓ This dissolved water produces a powerful germicide hypochlorous acid.

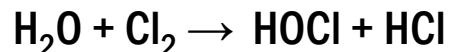


germs → germs are killed → water purified

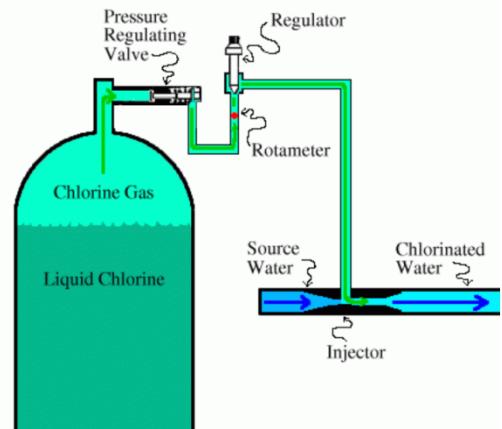
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Chlorination:

Chlorination is the process of purifying the drinking water by producing a powerful Germicide like hypochlorous acid. When this chlorine is mixed with water it produces Hypochlorous acid which kills the Germs present in water.



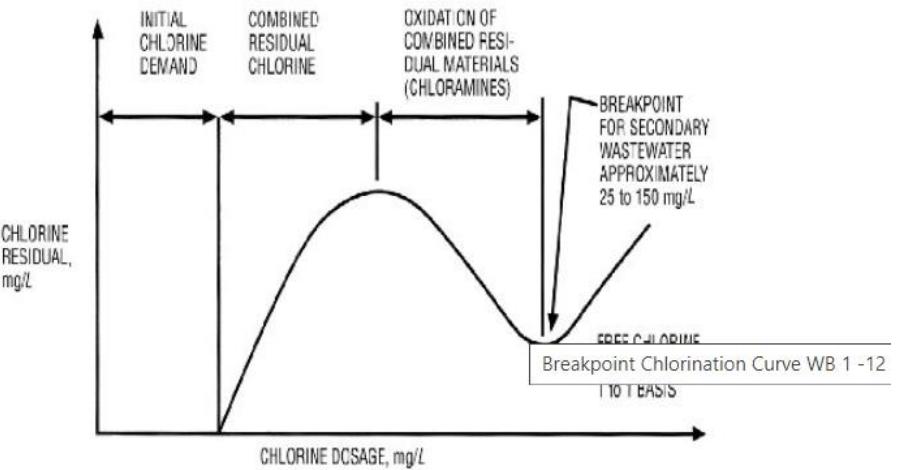
Chlorine is basic (means P^{H} value is more than 7) disinfectant and is much effective over the germs. Hence chlorine is widely used all over the world as a powerful disinfectant. Chlorinator is an apparatus, which is used to purity the water by chlorination process.



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Break- Point Chlorination:

- ✓ When chlorine is added to water it is used for different reactions like
- ✓ Oxidation of reducing substances
- ✓ Chlorination of ammonia
- ✓ Chlorination of organic substances
- ✓ Disinfection of pathogens



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Break- Point Chlorination:

✓ It is defined as it is the point where the demand of chlorine has been fully satisfied in terms of chlorine addition to water, Breakpoint chlorination is an experimental technique used to estimate the amount of chlorine required for complete destruction (Oxidation) of organic, Ammonia, inorganic impurities.

✓ When chlorine added to water



When chlorine is added to a sample of water and its amount is estimated experimentally after a few minutes addition, it is found that the available chlorine is not equal to the amount of chlorine added.

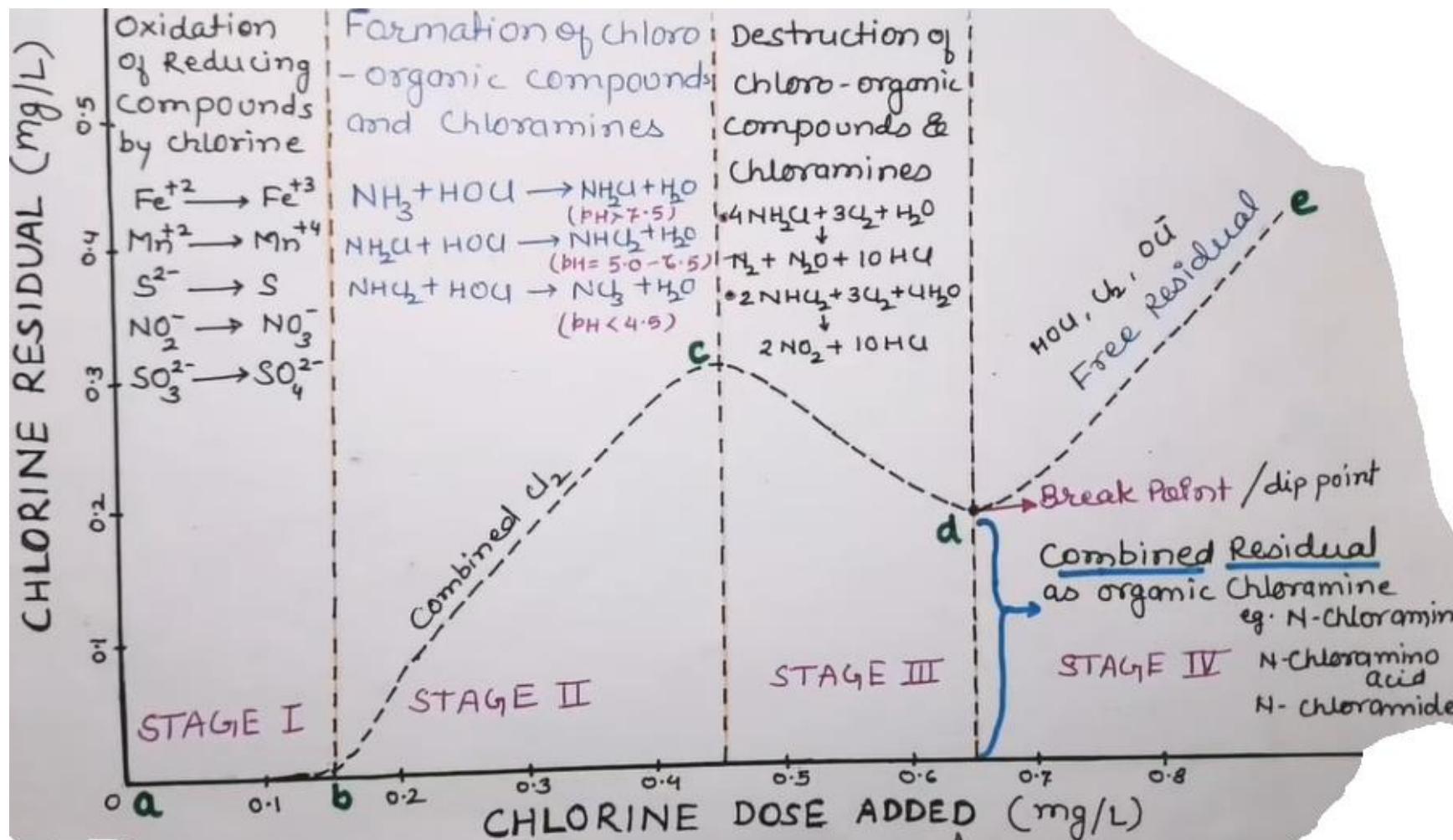
✓ A relationship between amount of chlorine added to water and residual chlorine is shown by Breakpoint chlorination curve.

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Residual chlorine = Free available chlorine + combined chlorine

Free available Cl_2 = $\text{Cl}_2 + \text{HOCl} + \text{OCl}^-$

Combined Chlorine = $\text{NH}_2\text{Cl} + \text{NHCl}_2 + \text{NCl}_3$ (Organic chloramines)



Ozonisation:

- Ozone gas is faintly blue gas of pungent odour and is excellent disinfectant.
- It can be produced by passing high tension electric current through the stream of air in closed chamber.



- Ozone being unstable decomposes by giving nascent oxygen which is capable of destroying the Bacteria.



- This nascent oxygen acts as powerful oxidising agent.
- This nascent oxygen removes the colour and taste of water and oxidizes the organic matter present in water.



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SOFTENING OF WATER

- The process of removing or reducing the hardness of water irrespective of whether it is temporary or permanent is called softening of water
- Removing of hardness means removing of hardness causing salts or ions (Ca^{+2} , Mg^{+2})
- These salts are completely soluble in water, we cannot remove by simple filtration



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SOFTENING OF WATER

➤ It is very essential process since hard water is unsuitable for domestic as well as industrial use. one of the most important applications of water is in steam production for the generation of electricity. For this water need to be fed to boilers.

Treatment of Boiler Feed Water :

- The Hard water using in boilers creates large number of problems like corrosion, scale and sludge formation,
- The treatment of water includes the removal of hardness causing salts either by precipitation or by complex formation.
- There are two types of treatments.
 - (a) External treatment
 - (b) Internal treatment

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Treatment of Boiler Feed Water :

External treatment:

- The treatment given to water for the removal of hardness causing salts before it is taken in to the boiler is called external treatment of water.
- This treatment prevents boiler problems.
- It can be done by lime-soda, zeolite and ion-exchange process.

Internal treatment:

- Internal treatment of boiler feed water refers to the conditioning of water in the boiler itself by the addition of chemicals.
- This is essentially corrective method to remove those salts which are not completely removed by external treatment of water softening.
- The conditioning methods used in internal treatment are colloidal, phosphate, calgon and carbonate conditioning.

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Ion exchange process/De-Mineralization/De-Ionization process

- In this method ion exchange resins are used as softening materials
- In this process cations and cations (Ca^{+2} and Mg^{+2}) and anions (Cl^- , SO_4^{-2}) are removed respectively by cation exchange resins and anion exchange resins
- At the end of the process outcome water does not posses any type of ions means deionized water

Ion exchange resins

- Ion exchange resins are insoluble, cross linked, long chain organic polymers with a microporous structure
- The functional groups attached to the chains are responsible for the ion- exchanging properties

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Ion-Exchange resins classified as:

Cation exchange resin (R^-H^+)

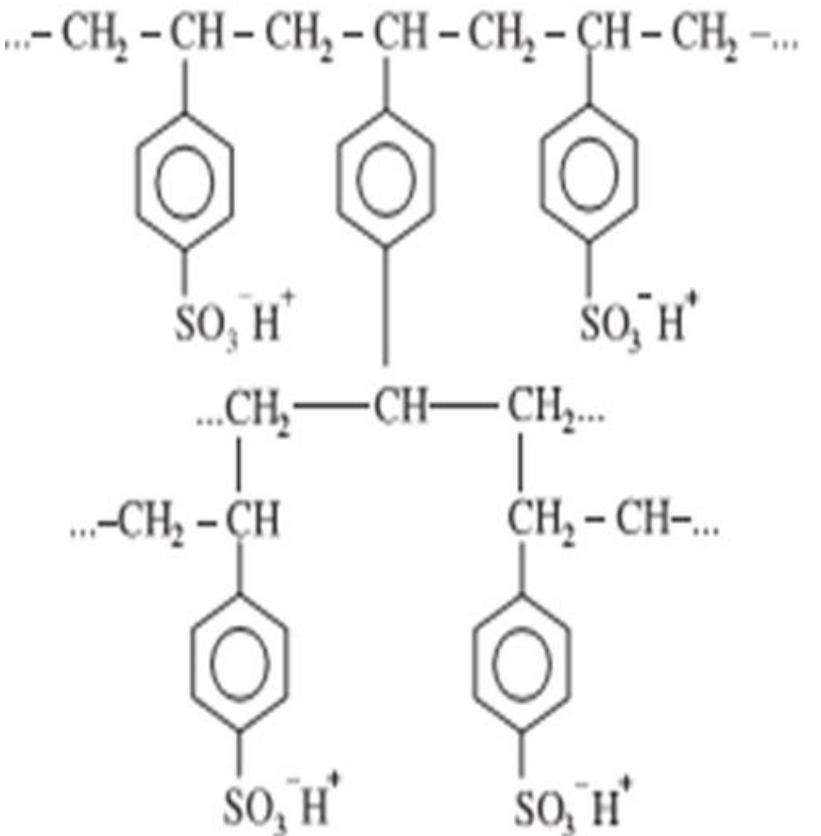
Anion exchange resin (R^+OH^-)

➤ **Cation exchange resin (R^-H^+):** Cation exchangers are capable of exchanging their H^+ ions with cations of the dissolved salts, which comes in their contact. The cation exchangers are represented by general formula RH, are mainly styrene-divinyl benzene copolymers containing the functional groups $-COOH$, or $-SO_3H$.

➤ **R** is the general structure of resin and **H** is exchangeable with cation.

- Examples i) sulphonated coals
➤ ii) sulphonated polystyrene

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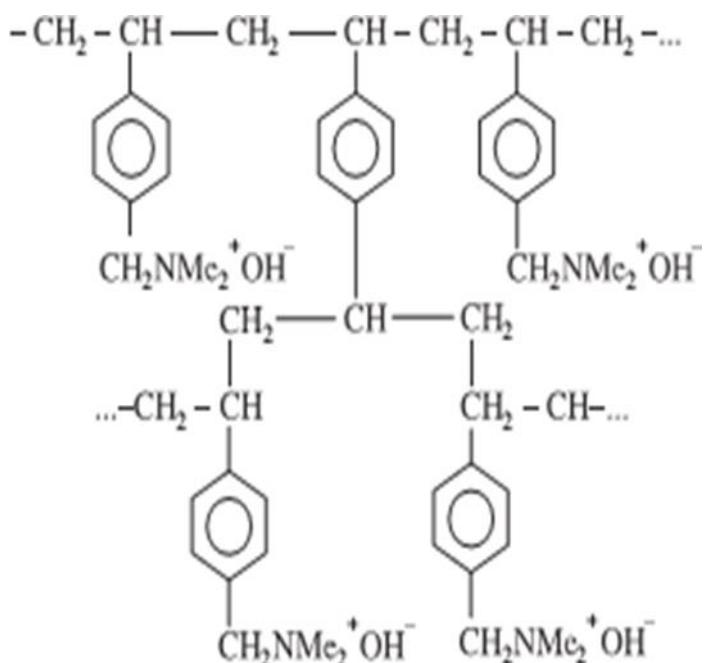
Cation exchange resin

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Anion exchange resin (ROH^-)

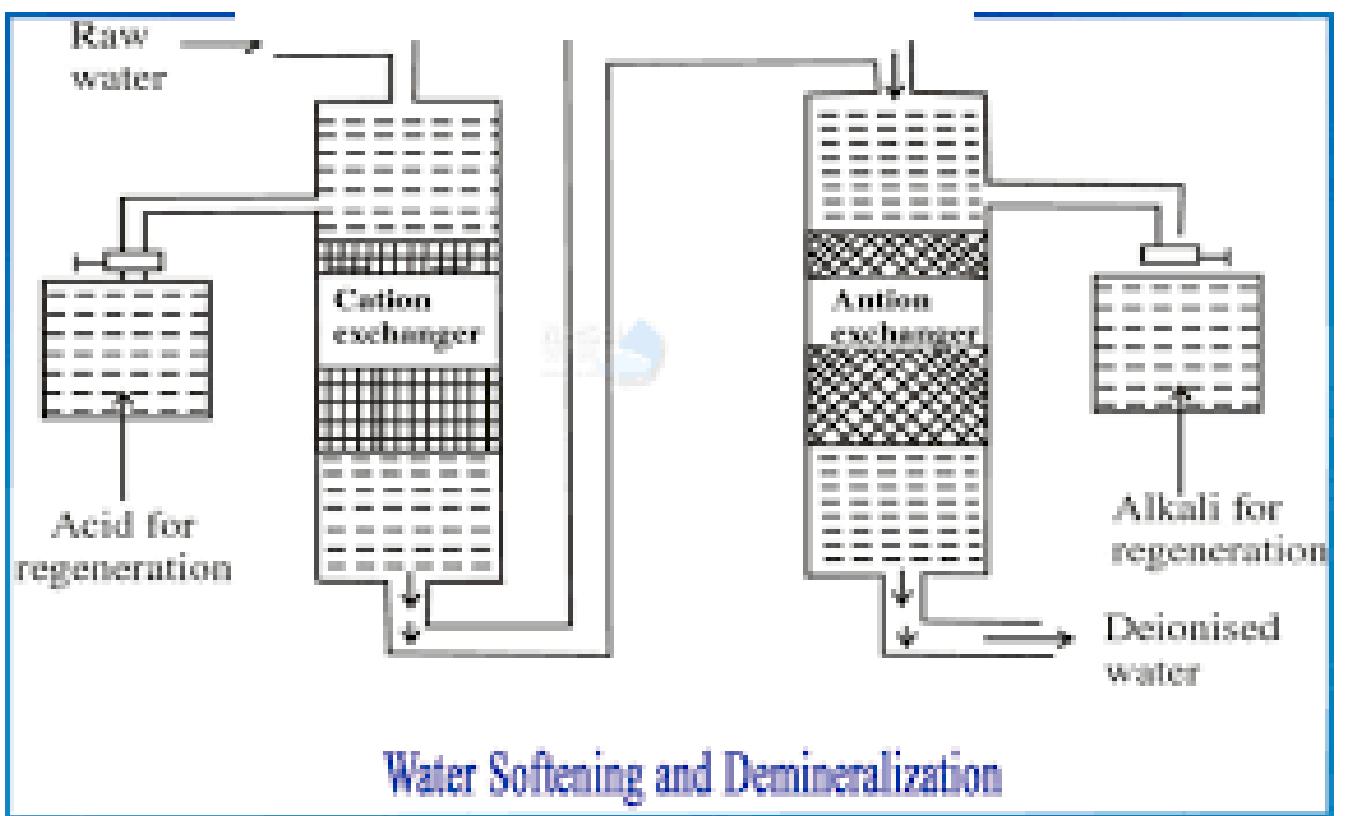
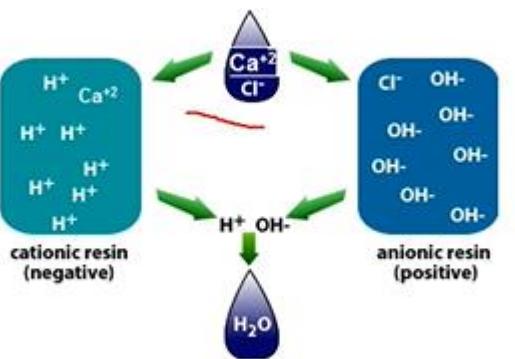
➤ Cation exchangers are capable of exchanging their OH^- ions with cations of the dissolved salts, which comes in their contact. The cation exchangers are represented by general formula R^+OH^- , are mainly styrene-divinyl benzene copolymers containing the functional groups $-\text{R-OH}$, or R-SNH_2 .

- i) Cross linked quaternary ammonium salts
- ii) Urea-formaldehyde resin ($\text{R-NR}_3\text{OH}$)



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WATER TECHNOLOGY



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In cationic Exchange Resin



In Anionic Exchange Resin



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Regeneration of exhausted resins

- The saturated cation exchanger is gotten back by passing dilute HCl solution



$CaCl_2$ and $MgCl_2$ are removed by washing

- The saturated anionic exchanger is gotten back by passing dilute NaOH solution



$NaCl$ and Na_2SO_4 are removed by washing, The regenerated ion exchanger can be used again

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- Thus the water coming out from the anion and cation exchangers is free from both cations and anions
- This water is known as ion free water or deionized or demineralize water

Advantages

- It produces water hardness is very low (2 ppm)
- This process can remove both anions and cations
- It can be also used to soften the high acid or basic hard water

Disadvantages

- Equipment chemical resins are more expensive

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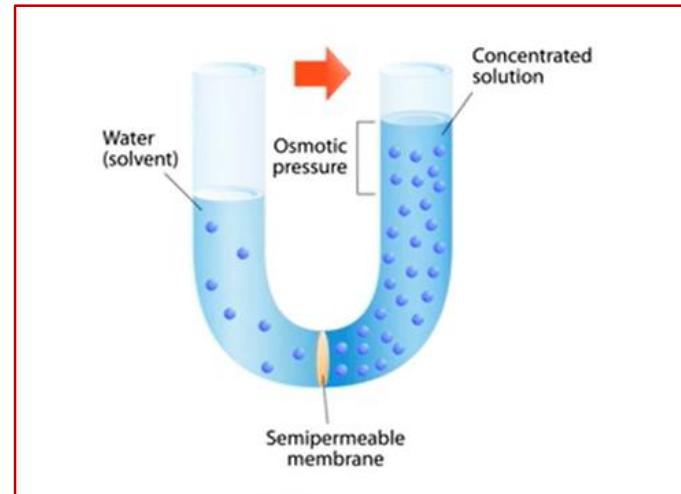
BRACKISH WATER AND DESALINATION

- The water containing dissolved salts with peculiar salty taste is called Brackish water or saline water
- The process of removing common salt (NaCl) from the sea water is known as desalination
- The common methods used for desalination are
 - i) electrodialysis
 - ii) Reverse osmosis

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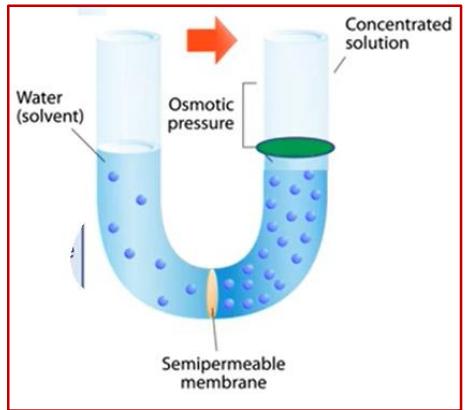
Reverse osmosis/ Desalination

- **Osmosis:** The spontaneous flow of water from low concentrated (dilute) to more concentrated side through semipermeable membrane.
- Semi permeable membrane is one which permits only water (solvent) molecules to pass through it
- Cellulose acetate, polyamide, egg membrane, goats bladder can acts as semipermeable membrane

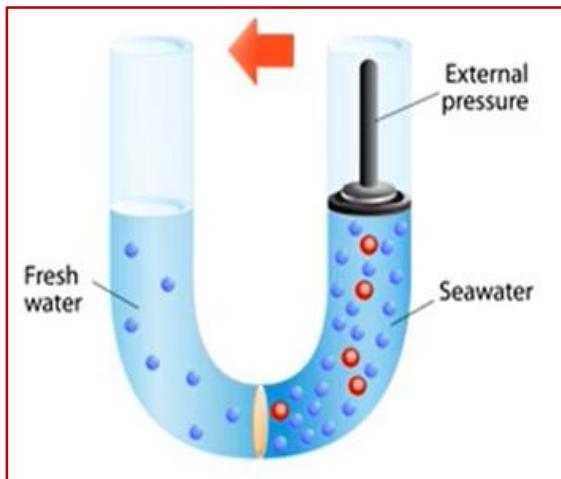


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The pressure required to stop the spontaneous osmosis process is called osmotic pressure



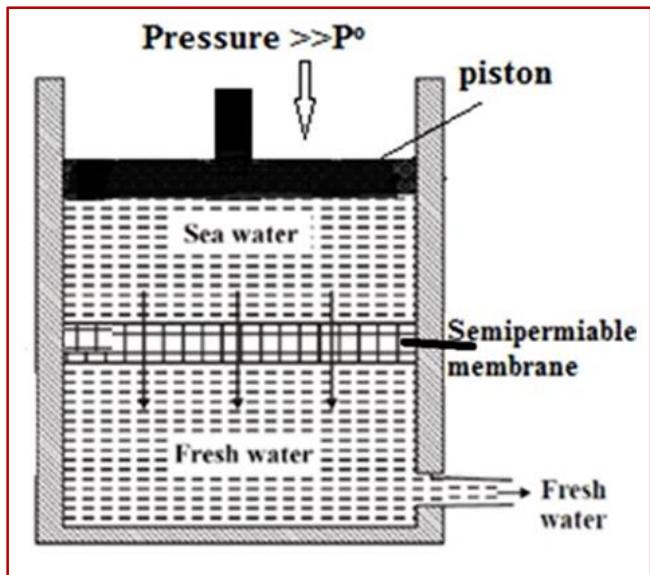
If pressure is applied (**more than osmotic pressure**) on concentration side the osmosis will be reversed



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Reverse osmosis

- In the reverse osmosis, the pure water is separated from the contaminated salt water



- This type of membrane filtration is called **super filtration** or **hyper filtration**

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Advantages of RO process

- This method has greater advantages of removing ionic, non-ionic, colloidal and high molecular weight organic matter
- The life time of membrane is quite high (2 years)
- The membrane can be replaced within few minutes. It provides nearly uninterrupted water supply
- Due to low capital cost, low operating cost and high reliability, this method is superior than other methods.

Applications

- RO plays a major role in providing potable water defined by the WHO criterion of <500 ppm of dissolved solids (TDS).
- Extremely high quality water required for nuclear power plants can be made from sea water by reverse osmosis

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Water Technology

1. A sample water of 100 ml required 12.6 ml of 0.02M EDTA solution with EBT as indicator and 8.4 ml of 0.02 M EDTA for the same volume of water after removing the carbonate hardness. Calculate the total, permanent hardness in terms of calcium carbonate equivalents.

- 100 ml required 12.6 ml of 0.02M EDTA solution
- 8.4 ml of 0.02 M EDTA for the same volume of water after removing the carbonate hardness
- M_3 = molarity of hard water M_2 = EDTA molarity
- V_3 = volume of Hard water V_2^l = volume of EDTA consumed
- $$M_3 V_3 = M_2 V_2^l$$
- $$M_3 = M_2 V_2^l / V_3$$
- $$M_3 = 0.02 \times 12.6 / 100 = 0.00252M$$
- Total hardness = $M_3 \times 100 \times 1000 = 0.0025 \times 100 \times 1000 = 252 \text{ PPM}$

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Water Technology

8.4 ml of 0.02 M EDTA for the same volume of water after removing the carbonate hardness

- M_4 = molarity of hard water M_2 = EDTA molarity
- V_4 = volume of hard water V_2'' = volume of EDTA consumed
- $M_4 V_4 = M_2 V_2''$
- $M_4 = M_2 V_2'' / V_4$
- $M_4 = 0.02 \times 8.4 / 100 = 0.00168 \text{ M}$
- Permanent hardness = $0.00168 \times 100 \times 1000 = 168 \text{ PPM}$
- Temporary hardness of the water sample = (Total hardness – Permanent hardness)
= $(M_3 \times 100 \times 1000 - M_4 \times 100 \times 1000) \text{ ppm.}$
- $= (0.0025 \times 100 \times 1000 - 0.00168 \times 100 \times 1000)$
- $= (250 - 168) = 84 \text{ ppm}$

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Water Technology

2. A sample water of 20 ml required 18.2 ml of 0.01M EDTA solution with EBT as indicator and 4.6 ml of 0.01 M EDTA for the same volume of water after removing the carbonate hardness. Calculate the total, permanent hardness in terms of calcium carbonate equivalents.

- 20 ml required 18.2 ml of 0.01M EDTA solution with EBT as indicator and
- 4.6 ml of 0.01 M EDTA for the same volume of water after removing the carbonate hardness.
- M_3 = molarity of hard water M_2 = EDTA molarity
- V_3 = volume of Hard water V_2^l = volume of EDTA consumed
- $$M_3 V_3 = M_2 V_2^l$$
- $$M_3 = M_2 V_2^l / V_3$$
- $$M_3 = 0.01 \times 18.2 / 20 = 0.0091M$$
- Total hardness = $M_3 \times 100 \times 1000 = 0.0091 \times 100 \times 1000 = 910 \text{ PPM}$

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Water Technology

4.6 ml of 0.01 M EDTA for the same volume of water after removing the carbonate hardness.

- M_4 = molarity of hard water M_2 = EDTA molarity
- V_4 = volume of hard water V_2'' = volume of EDTA consumed
- $M_4 V_4 = M_2 V_2''$
- $M_4 = M_2 V_2'' / V_4$
- $M_4 = 0.01 \times 4.6 / 20 = 0.0023 \text{ M}$
- Permanent hardness = $0.0023 \times 100 \times 1000 = 230 \text{ PPM}$
- Temporary hardness of the water sample = (Total hardness – Permanent hardness)
- = $(M_3 \times 100 \times 1000 - M_4 \times 100 \times 1000) \text{ ppm.}$
- = $(0.0091 \times 100 \times 1000 - 0.0023 \times 100 \times 1000)$
- = $(910 - 230) = 680 \text{ ppm}$

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MODULE-II

1. One gram of CaCO_3 was dissolved in dil. HCl and the solution was diluted to one litre. 100 ml of this solution required 90 ml of EDTA solution, while 100 mL of sample water required 40 ml of EDTA solution. On the other hand, 100 ml of boiled water sample, when titrated against EDTA, consumed 20ml of the solution. Calculate total , permanent and temporary hardness of water sample in ppm.

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Water and Its Treatment



2. one gram of CaCO_3 was dissolved in dil. HCl and the solution was diluted to one litre. 100 mL of this solution required 20 mL of EDTA solution, while 100mL of sample water required 10 mL of EDTA solution. On the other hand, 100 ML of boiled water sample, when titrated against EDTA, consumed 5 mL of the solution. Calculate total , permanent and temporary hardness of water sample in ppm.

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Water and Its Treatment



3. 0.5 gm of CaCO₃ was dissolved in dil.HCl and the solution was diluted to 1000mL. 50 mL of this solution required 48 mL of EDTA solution, while 50 mL of sample water required 15mL of EDTA solution. On the other hand, 50 ML of boiled water sample, when titrated against EDTA, consumed 10 mL of the solution. Calculate each type of hardness in ppm.

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water softening by external treatment methods:

Ion-Exchange process:

- **Ion-exchange:** ion exchange is a process by which ions held on a porous, especially insoluble solid are exchanged for ions in solution that is brought in contact with it.
- **Ion-exchange resins:** ion-exchange resins are insoluble, cross-linked, high molecular weight, organic polymers with a porous structure and the functional groups attached to the chains are responsible for the ion-exchange properties.

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Water and Its Treatment

Ion-Exchange resins classified as:

Cation exchange resin (RH^+)

Anion exchange resin (ROH^-)

- **Cation exchange resin (RH^+):** Cation exchangers are capable of exchanging their H^+ ions with cations of the dissolved salts, which comes in their contact. The cation exchangers are represented by general formula **RH**, are mainly styrene-divinyl benzene copolymers containing the functional groups **-COOH**, or **-SO₃H**.
- **R** is the general structure of resin and **H** is exchangeable with cation.

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Water and Its Treatment

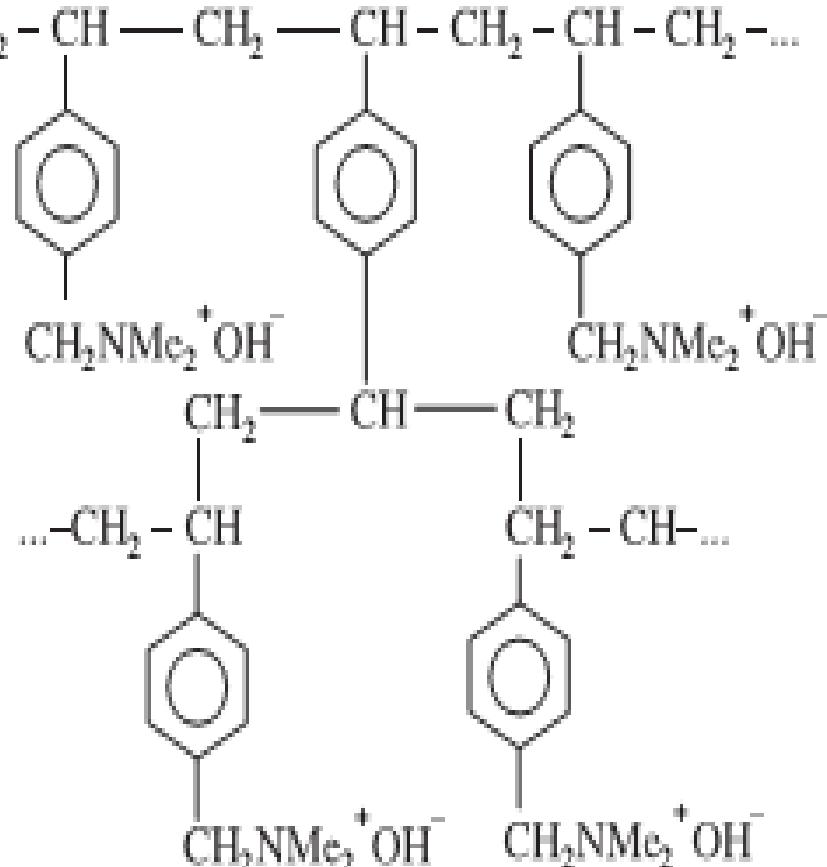
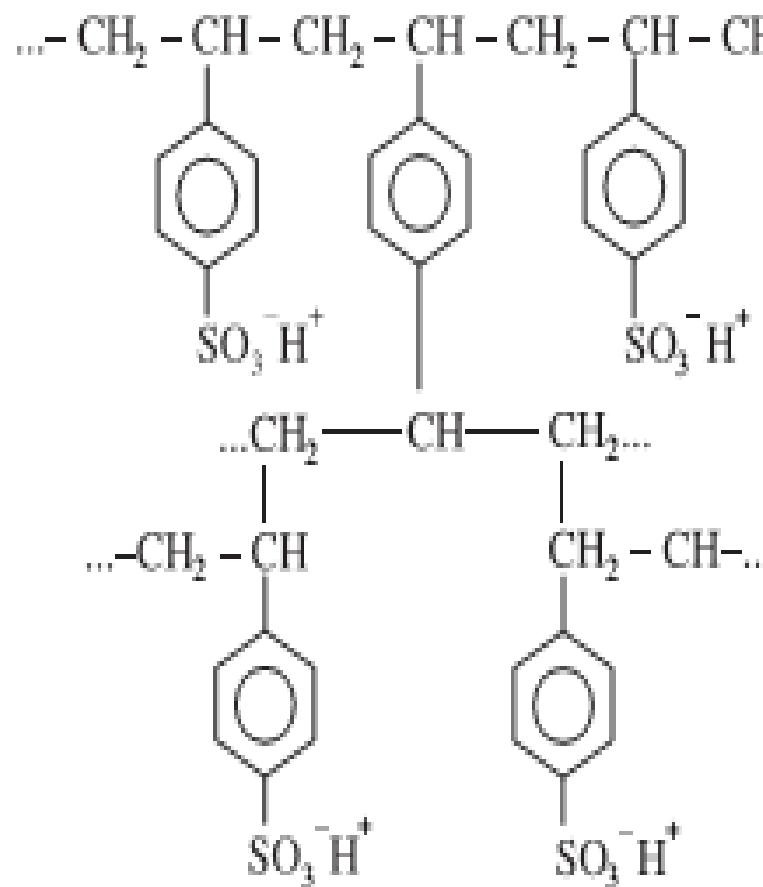
Anion exchange resin (ROH-)

- Anion exchangers are styrene-divinyl benzene copolymers containing the functional groups phenol-formaldehyde or amine formaldehyde which exchange their OH- ion with any anion present in the dissolved salt.
- The anion exchangers are represented by general formula ROH-.
- R is representation of the general structure of resin and OH is exchangeable with anion.
- Thus all the cations and anions present in the dissolved salts are exchanged with cation exchanger resin and anion exchanger resin.

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Water and Its Treatment

Cation and Anion Exchangers:



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Water and Its Treatment

Ion-exchange process:

- Ion-exchange process includes the exchange of the cations and anions of the dissolved salts with H⁺ and OH⁻ ions respectively.

Process:

Cation exchange process:

The hard water is first passed through cation exchange column where all the cations like Ca²⁺, Mg²⁺ are removed from it and equivalent amount of H⁺ ions are released from this column to water.



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Water and Its Treatment

Cation-exchange process:



The Ca^{2+} and Mg^{2+} are retained by the cation exchanges as CaR and MgR releasing H^+ into water. Thus the water coming out of the resin is highly acidic because the H^+ released by the cation exchange combine with anion of the dissolved salt to produce the acids.

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MODULE II
WATER TECHNOLOGY



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POLYMER TECHNOLOGY

Dr. T. Dhananjay Rao
Assistant Professor
Department of Chemistry

Topic: Classifications of polymers



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POLYMER TECHNOLOGY

Definition of polymer: Polymers can be defined as the large molecules (macro molecular) formed by the linkage of small molecules called monomers

(In Greek language poly means **many** & Mer means **units**)

E.g.: - poly ethylene



- Thus, the repeated unit of **monomer** is called polymer
- The number of repeating units in a polymer chain is called **degree of polymerization**.

For e.g.: - if 100 molecules of ethylene polymerize to give the polymer chain, the degree of polymerization is 100.

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POLYMER TECHNOLOGY



- Polymers form very important components in our daily life.
- The polymers are highly useful in domestic industrial & medical fields.

The following are the reasons for the extensive use of polymers

- Most of the polymers are non-toxic & safe to use
- They have low densities (light in weight) so transportation polymers will be easy.
- They possess good mechanical strength.
- These are resistant to corrosion and will not absorb moisture when exposed to the atmosphere
- These can function as good thermal & electrical insulators.
- These can be molded and fabricate easily
- many of the carbohydrates, Proteins & enzymes, DNA & RNA are natural polymers.

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POLYMER TECHNOLOGY

Classification of polymers based on origin

Natural polymers:

- ❖ Those Polymers which occurs in nature are called natural polymers.
- ❖ e.g.: - starch, cellulose, proteins, natural rubber.

Synthetic polymers: The polymers which are prepared in the laboratory are known as synthetic polymers.

- ❖ Ex: -PVC, polyethylene, synthetic rubber, nylon-6,6

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POLYMER TECHNOLOGY

Polymerization:

- It is a fundamental process. The low m.wt of compound converted into high m.wt compound through linkages that process is called **polymerization**.

Types of Polymerizations:

There are three types of polymerizations. They are

1) Addition Polymerization

- i) Homo-polymerization
- ii) Copolymerization

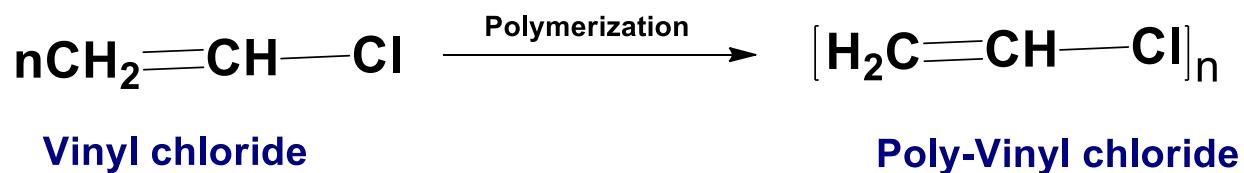
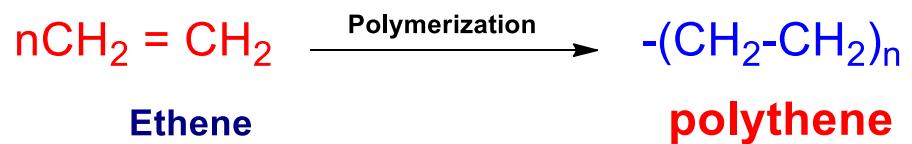
2) Condensation Polymerization

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POLYMER TECHNOLOGY

1. Addition Polymerization:(Chain Polymerization)

- Addition polymers are formed by adding monomer units without any loss of atoms or groups
- These polymers formed by the polymerization of monomers containing double or triple bonds (Unsaturated compounds).



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POLYMER TECHNOLOGY

Types of Addition polymerization

Homo polymer: Polymer made up of only one type of monomer

e.g.: - polyethylene, PVC



Copolymer: Polymer formed by the reaction between different monomers

eg: buna-s rubber

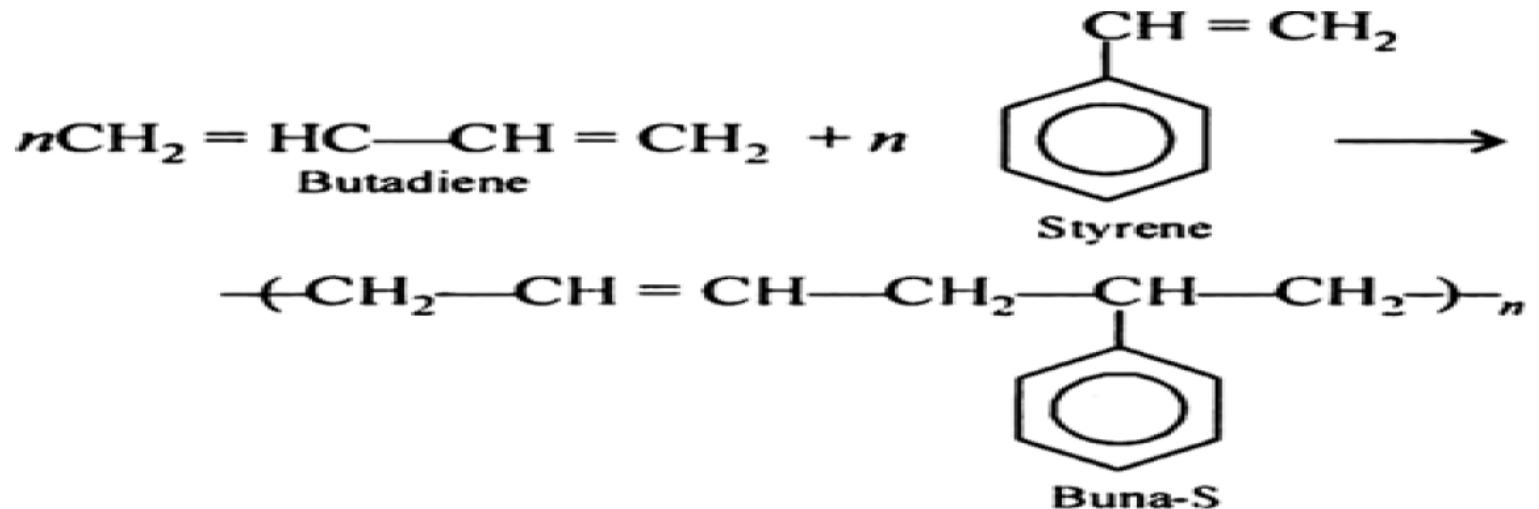


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POLYMER TECHNOLOGY

Co-polymerization:

- The polymers which are obtained by the polymerization of two or more monomers are called copolymers.
- This process is called co-polymerization.



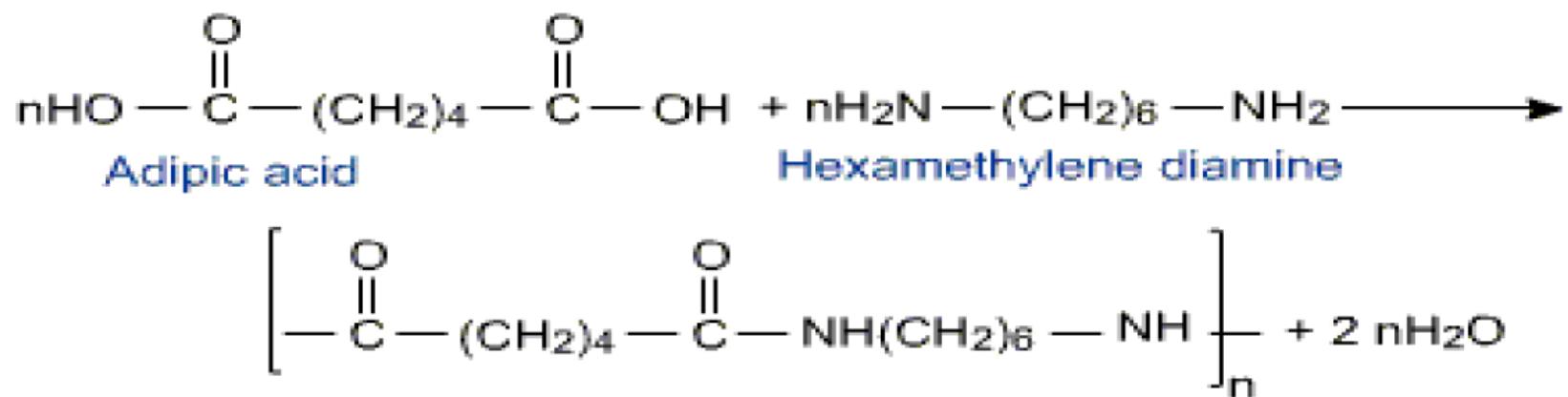
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POLYMER TECHNOLOGY

Condensation polymerization:

- polymers formed from the functional group of monomers with the elimination of a bi product and with the formation of a new functional groups are known as condensation polymers.

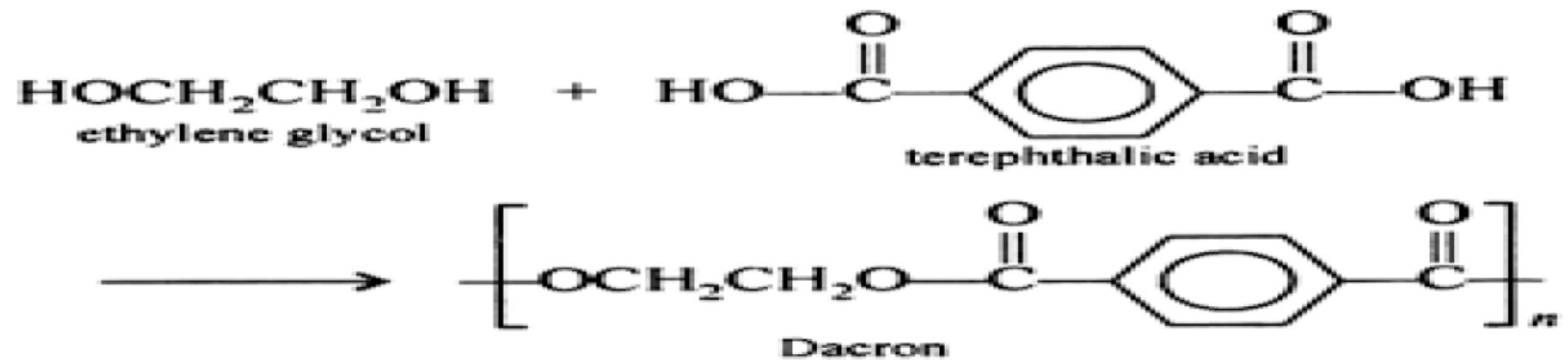
Ex: -1) Nylon-6,6



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POLYMER TECHNOLOGY

Ex: - 2) Terylene



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3) Differences between Addition and condensation polymers:

Addition or chain polymerization	Condensation/step polymerization
1. The monomer must have at least one multiple bond eg $\text{CH}_2=\text{CH}_2$	1. The monomer must have at least two identical or different functional groups. Eg. Glycol, nylon 6,6
2. Monomer add on to give a polymer and no other byproduct is formed	2. Monomers condense to give a polymer and by products such as H_2O , CH_3OH etc.
3. The addition of monomers results in the formation of the polymer.	3. The condensation reaction between monomers results in the formation of the polymer.
4. The molecular weight of the resultant polymers is a multiple of the monomer's molecular weight	4. The molecular weight of the resultant polymer is not a multiple of the monomer's molecular weight.
5. Lewis acids or bases, radical initiators are catalysts, in addition polymerization	5. Different molecules are used as catalysts in the process of condensation polymerization
6. Common examples of addition polymerization are PVC, polyethene, Teflon etc.	6. Common examples of condensation polymerization are nylon, Bakelite, silicon, etc.

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POLYMER TECHNOLOGY

Introduction to plastics:

- The word **plastics** derived from Greek in which **plastics** means **mouldable**. these are **high molecular weight organic materials**.
- **Plastics are made by polymers and additives.**
- **Polymers which can be moulded into hard, tough and utility articles by the application of heat and pressure are called plastics.**
- **Polymers may be natural or synthetic but plastics are synthetic only**

All plastics are polymers but all polymers are not plastics

- **Poly Ethelene, Poly Styrene, nylon, Poly esters etc.**

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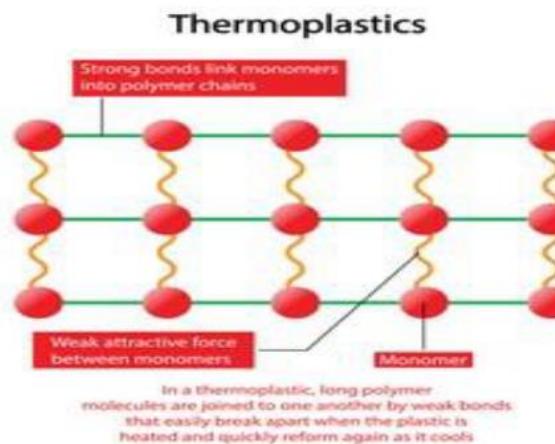
Plastics as engineering materials

Advantages of plastics in engineering materials.

- (1) Low fabrication cost, low thermal & electrical conductivities, high resistance to corrosion & solvents.**
 - (2) The stress – strain relationship of plastics is similar to that of the metals.**
 - (3) Plastics reduce noise & vibration in machines**
 - (4) Plastics are bad conductors of heat are useful for making handles used for hot objects, most plastics are inflammable.**
 - (5) Plastics are electrical insulators & find large scale use in the electrical industry.**
 - (6) Plastics are resistance to chemicals.**
 - (7) Plastics are clear & transparent so they can be given beautiful colors.**
- **Plastics are classified into two main types**
 - i. Thermo plastic
 - ii. Thermosetting plastic

POLYMER TECHNOLOGY

- Thermoplastics can be softened on heating & hardened on cooling. They are generally soluble in organic solvents. Once cooled, they show no changes in chemical properties, meaning they can be re-melted and re-used several times
- Ex: poly ethylene, poly vinyl chloride.
- Thermoplastics are prepared by addition polymerization.
- They are straight chain or slightly branched polymers and various chains are held together by weak Van der Waals forces of attraction.



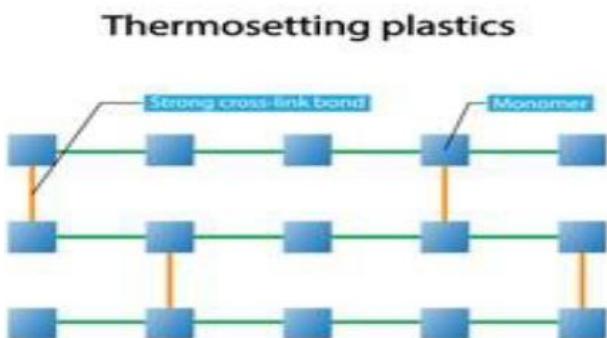
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POLYMER TECHNOLOGY

Thermosetting plastics or thermosets

- Thermosetting plastics get harden on heating and once harden they cannot be softened again
- Thermosetting plastics are prepared by condensation polymerization
- Various polymer chains are held together by strong covalent bond (called crosslinks)
- They are almost insoluble in organic solvents.

Examples: Bakelite, polyester.



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POLYMER TECHNOLOGY

Difference Between Thermoplastic and Thermosetting Plastic	
Thermoplastic	Thermosetting Plastic
Thermoplastics are usually formed by the addition of polymerization.	Thermosetting plastics are often formed by the condensation polymerization.
It contains long-chain linear polymers and held together by weak Van der Waal forces.	It contains a 3D network structure constructed with strong covalent bonds.
Usually becomes soft on heating and stiffen on cooling.	It does not become soft on heating.
They are expensive.	They are cheap.
Thermoplastic is soluble in organic solvents.	Thermosetting plastics are insoluble in organic solvents.
They are usually soft, weak and less brittle in nature.	They are usually hard, strong and more brittle in nature.
Can be remolded.	They can't be remolded.
An example of thermoplastic is polythene.	An example of Thermosetting plastic is Bakelite.

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POLYMER TECHNOLOGY

Contents:

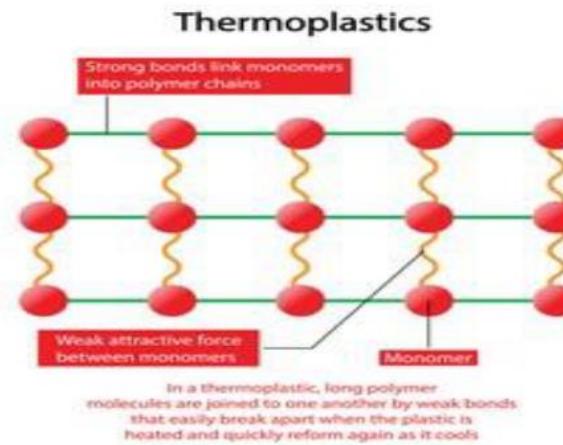
- Thermoplastics
- Preparation of PVC
- Properties and uses of PVC
- Preparation of Nylon 6,6
- Properties and uses of Nylon 6,6

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POLYMER TECHNOLOGY

Thermoplastics:

- Thermoplastics can be softened on heating & hardened on cooling. They are generally soluble in organic solvents. Once cooled, they show no changes in chemical properties, meaning they can be re-melted and re-used several times
- Ex: poly ethylene, poly vinyl chloride.
- Thermoplastics are prepared by addition polymerization.
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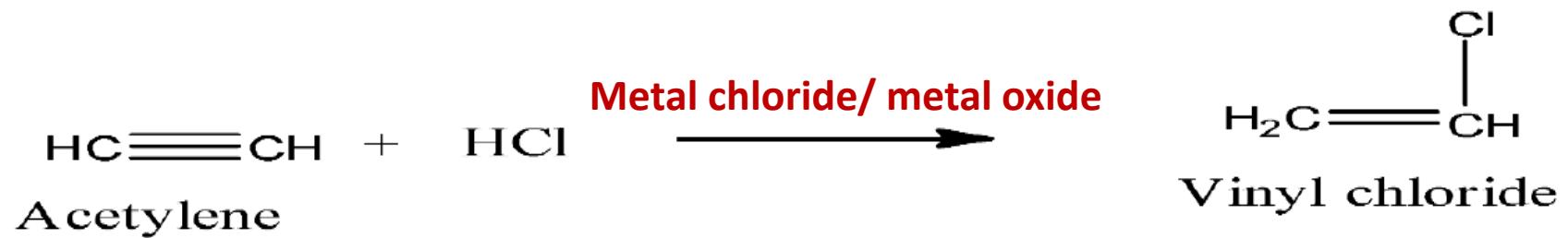
POLYMER TECHNOLOGY

Chemistry of some important thermoplastic

i. Preparation, properties and uses of PVC:

Preparation:

step I: vinyl chloride is prepared by treating acetylene with hydrogen chloride at 60-80 ° C in the presence of metal chloride as catalyst.

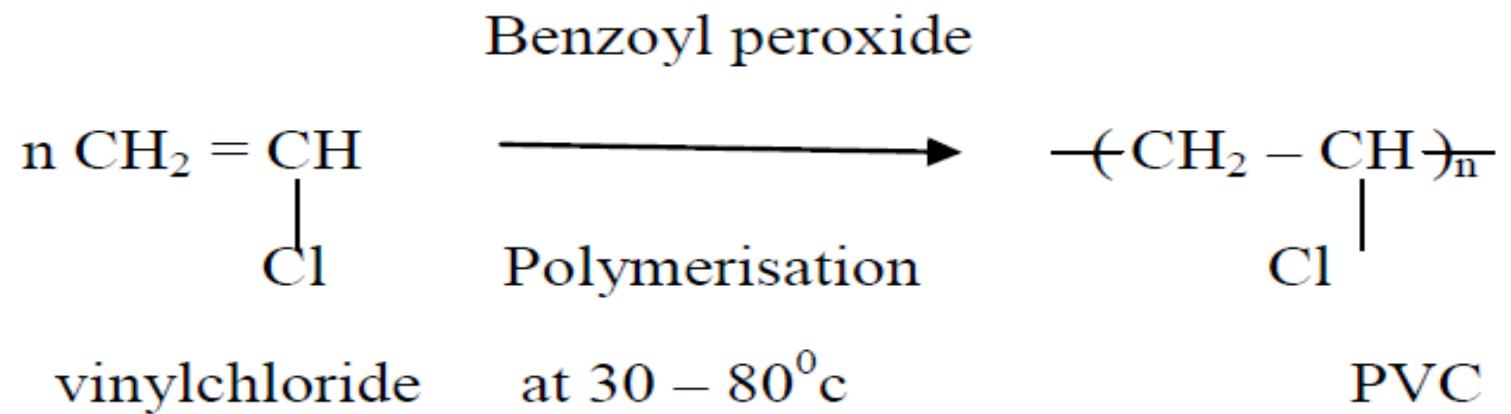


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POLYMER TECHNOLOGY

Step 2: Poly vinyl chloride is produced by heating vinyl chloride in presence of **benzyl peroxide or H₂O₂** under pressure.

- It follows addition mechanism



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POLYMER TECHNOLOGY

Properties:

- PVC is very light weight polymer
- PVC is colorless, odor less and chemically inert powder.
- it is insoluble in inorganic acids and alkalis, but soluble in hot chlorinated hydro carbons such as ethyl chloride.
- it undergoes degradation in presence of heat or light.
- PVC can be made more flexible and softer by adding plasticizers such as phthalate and can be bent as per requirement
- PVC products are self-extinguishing due to high chlorine content
- It can withstand extreme climatic conditions, shock and is free from corrosion
Hence, it is the preferred method for several outdoor applications.

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POLYMER TECHNOLOGY

Uses:

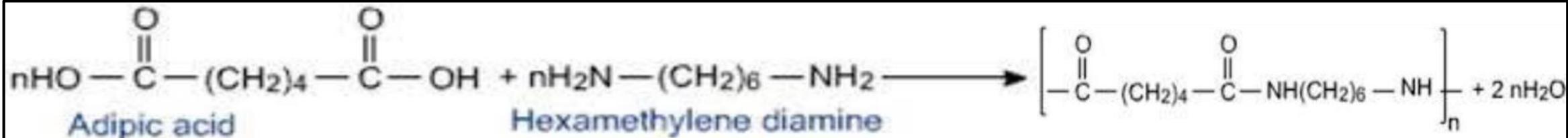
- it is used in the production of pipes, cables insulations, table covers and rain – coats etc.
- It is also used for making sheets, which are employed for tank – linings, light fittings, refrigerator components etc.
- It is used in making sewage pipes and other pipe applications
- Used in construction fields for insulation on electrical wires or in flooring for hospitals, schools, homes, and other areas where a sterile environment is a priority.
- It is used in various industries like building, electronics, electrical, automotive, medical and packaging.
- PVC fabric is used in the manufacture of aprons shower curtains, raincoats, jackets and sports bags.

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POLYMER TECHNOLOGY

Nylon -6,6:

- It is obtained by the polymerisation of adipic acid with hexamethylene diamine at high temperature and pressure(Condensation polymerization).



Properties

- nylons are translucent, whitish, high melting polymers
- High mechanical strength
- They possess high temperature stability and good abrasion resistance (Rubbing or Friction)
- They are insoluble in common organic solvents and soluble in phenols and formic acid
- Good electrical insulating properties
- No resistance to UV rays
- Lightweight; sometimes used in applications in place of metals
- Does not absorb water
- Dries quickly

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POLYMER TECHNOLOGY

Uses of nylon 6, 6 :

- nylons are used for making filaments for ropes, bristles for tooth – brushes and films etc.
- Nylon – 6,6 is used for which is used in making socks, dresses, carpets etc
- It is used for making sheets
- It also can be used for surgical items
- To prepare textile fabrics

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POLYMER TECHNOLOGY

Dr. T. Dhananjay Rao
Assistant Professor
Department of Chemistry

Topic: Bakelite synthesis and properties



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POLYMER TECHNOLOGY

Contents:

- Thermosetting resins
- Bakelite synthesis
- Properties of Bakelite
- Applications of Bakelite

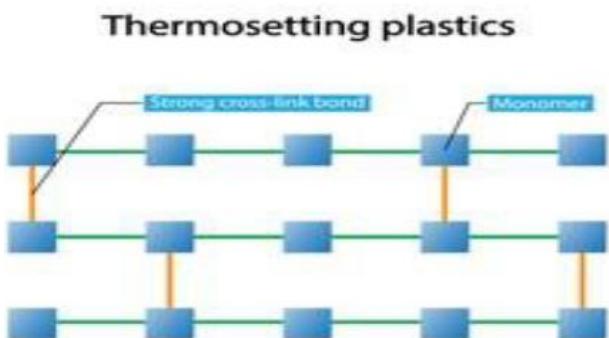
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POLYMER TECHNOLOGY

Thermosetting plastics or thermosets

- Thermosetting plastics get harden on heating and once harden they cannot be softened again
- Thermosetting plastics are prepared by condensation polymerization
- Various polymer chains are held together by strong covalent bond (called crosslinks)
- They are almost insoluble in organic solvents.

Examples: Bakelite, polyester.



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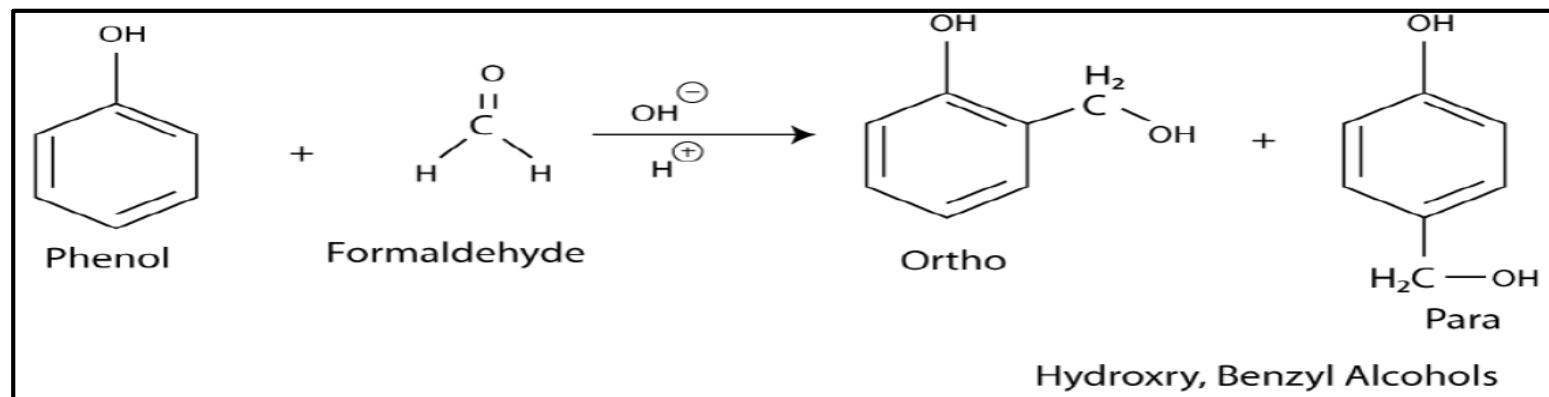
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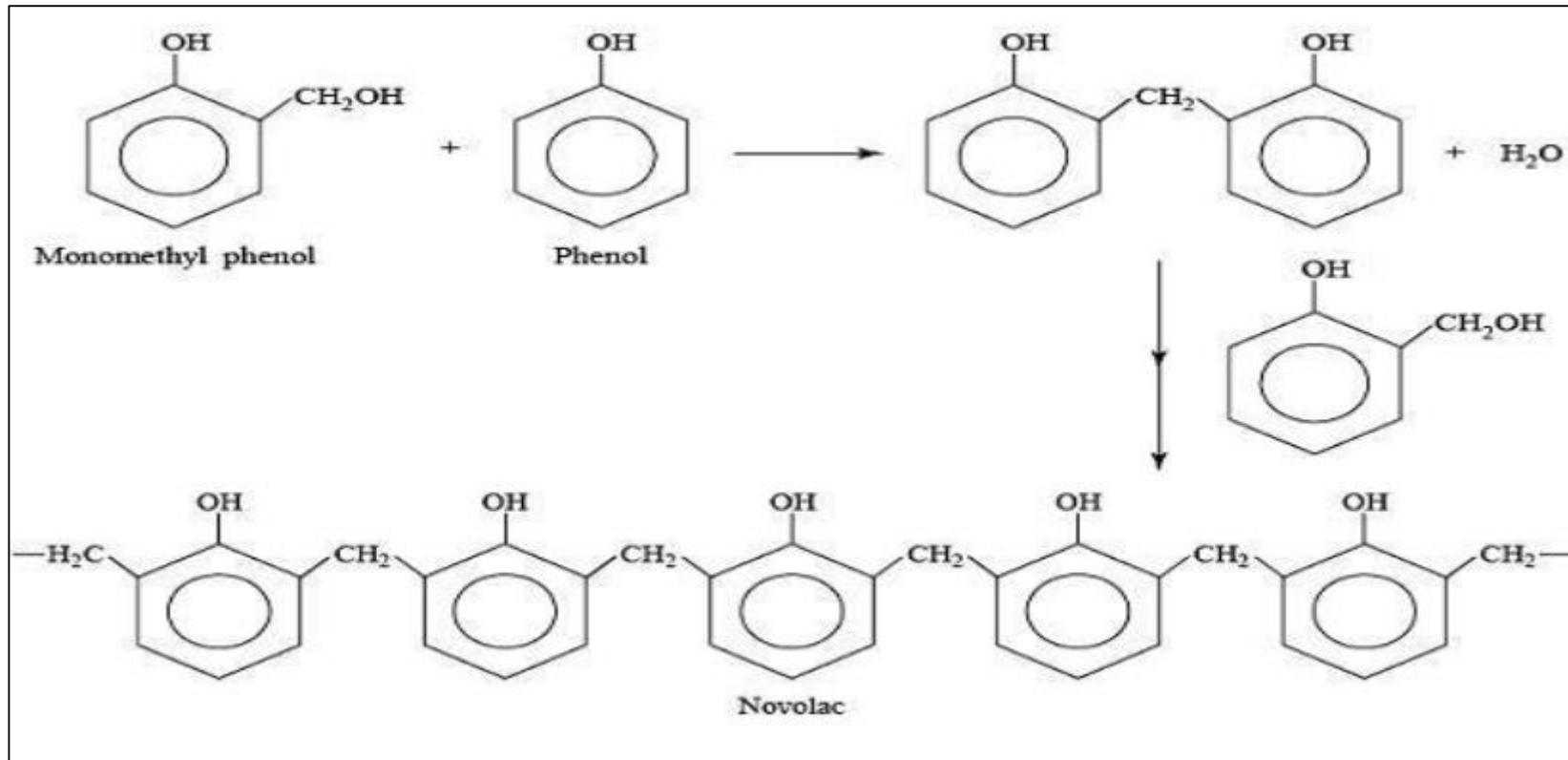
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POLYMER TECHNOLOGY

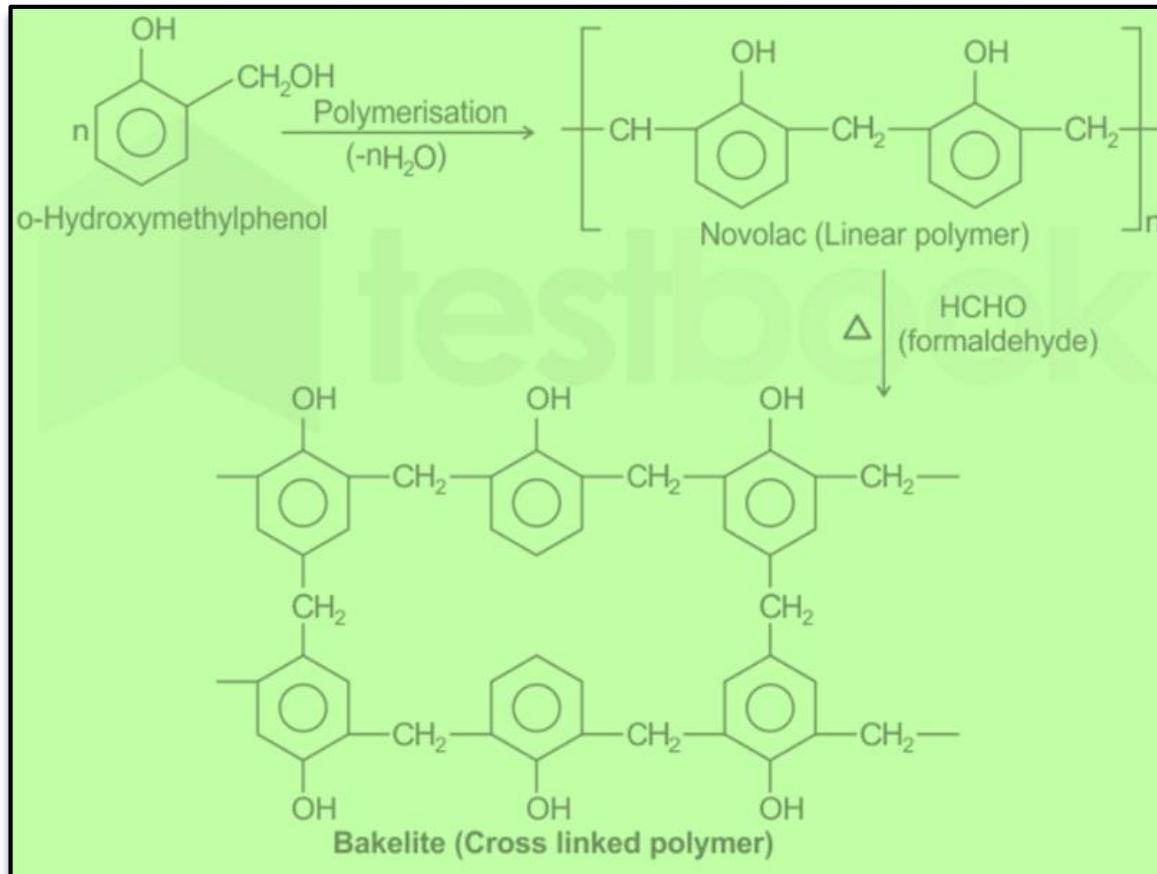
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POLYMER TECHNOLOGY

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POLYMER TECHNOLOGY

Properties:

- It is a thermosetting polymer that cannot be reused or remolded
- Bakelite is a resistant to acids, salts, and most organic solvents
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- It possesses excellent electrical insulating property

Uses:

- Bakelite is used as a plywood laminations & grinding wheel etc.
- It is also widely used in paints, varnishes.
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- It is used for making combs, phonograph records, handles of various utensils.

POLYMER TECHNOLOGY

Dr. T. Dhananjay Rao
Assistant Professor
Department of Chemistry

Topic: Bio-degradable polymers



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POLYMER TECHNOLOGY

Biodegradable polymers:

- Generally, polymers do not undergo bio degradation, even after a long time.
- It is very difficult to manage the polymer waste in the environment
- To avoid this, bio degradable polymers usage
- They degrade quickly & do not cause such environmental problems

Definition:

- biodegradable polymers are polymers which undergo degradation by the naturally occurring micro-organisms like algae, fungi and bacteria.

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Biodegradable polymers are classified in to two types:

- i) **Natural biodegradable polymers:** These polymers undergo biodegradation by enzyme – catalysed reaction in aqueous media
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Advantages of bio degradable polymers

- It is cheaper than normal polymers
- The emission of CO₂ is reduced
- It takes less time to break down
- These polymers are renewable.
- It is good to the environment.

These are nontoxic, easy to recycle and requires less energy to produce.

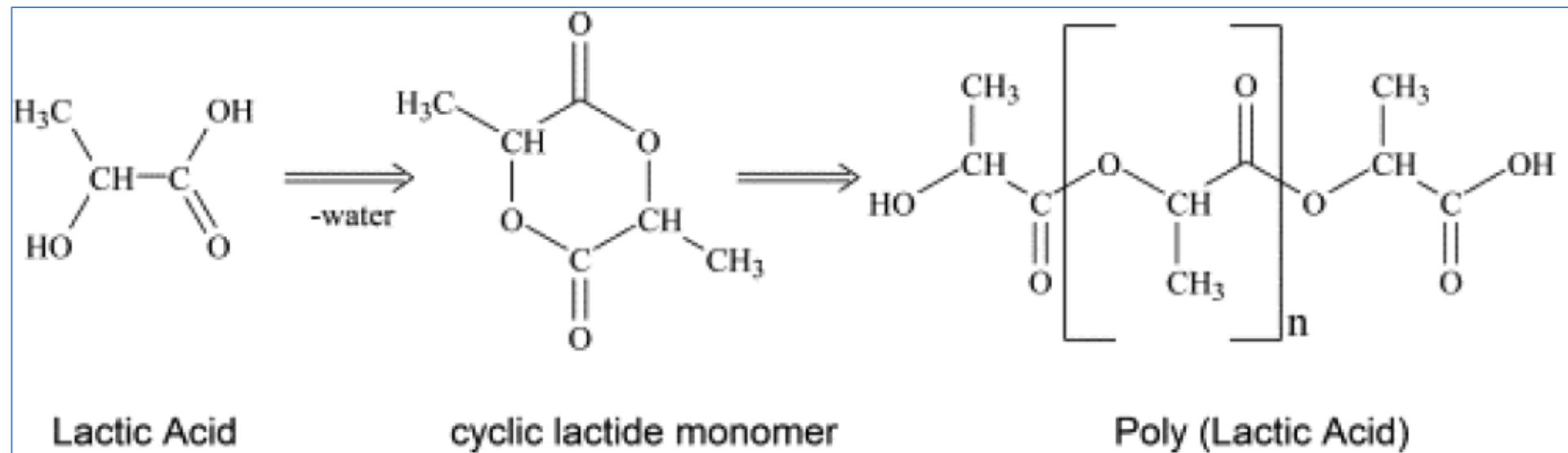
POLYMER TECHNOLOGY

Polylactic acid:

- It is derived from renewable sources such as starch, sugarcane etc

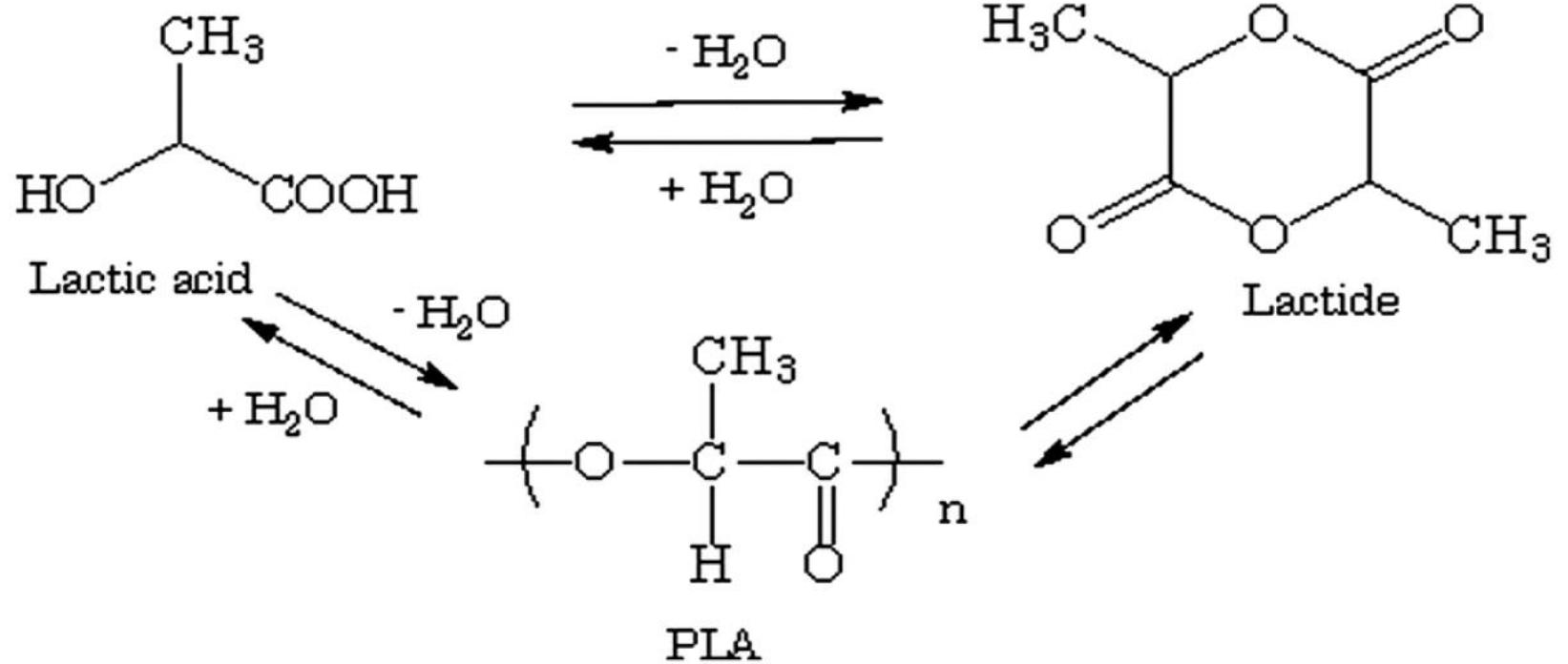
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POLYMER TECHNOLOGY

OR



POLYMER TECHNOLOGY

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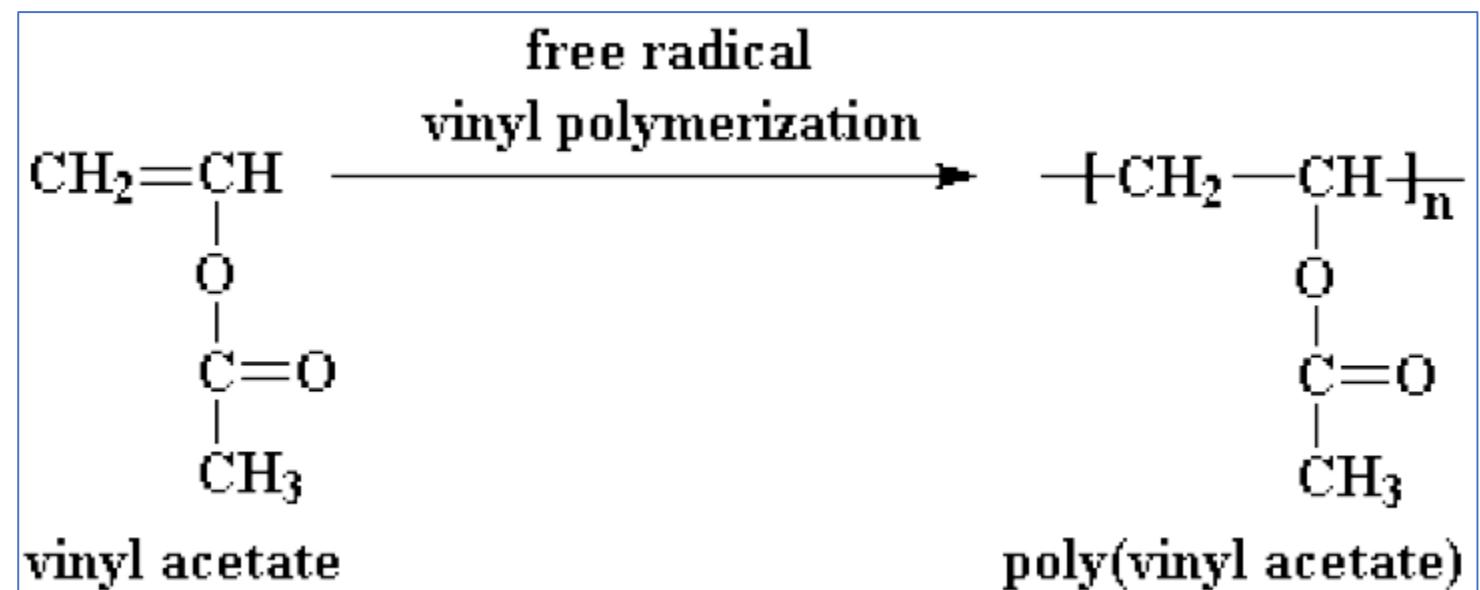
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POLYMER TECHNOLOGY



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- It undergoes pyrolysis at higher temperature.
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POLYMER TECHNOLOGY

Topics going to be covered

- Rubbers
- Natural Rubber
- Vulcanization
- Elastomers/synthetic rubber
- Buna-S Rubber
- Thiokol Rubber

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POLYMER TECHNOLOGY

Rubbers

- Rubber is a common name. Elastomer is a technical name. polymers which will have rubber like elasticity are called elastomer.
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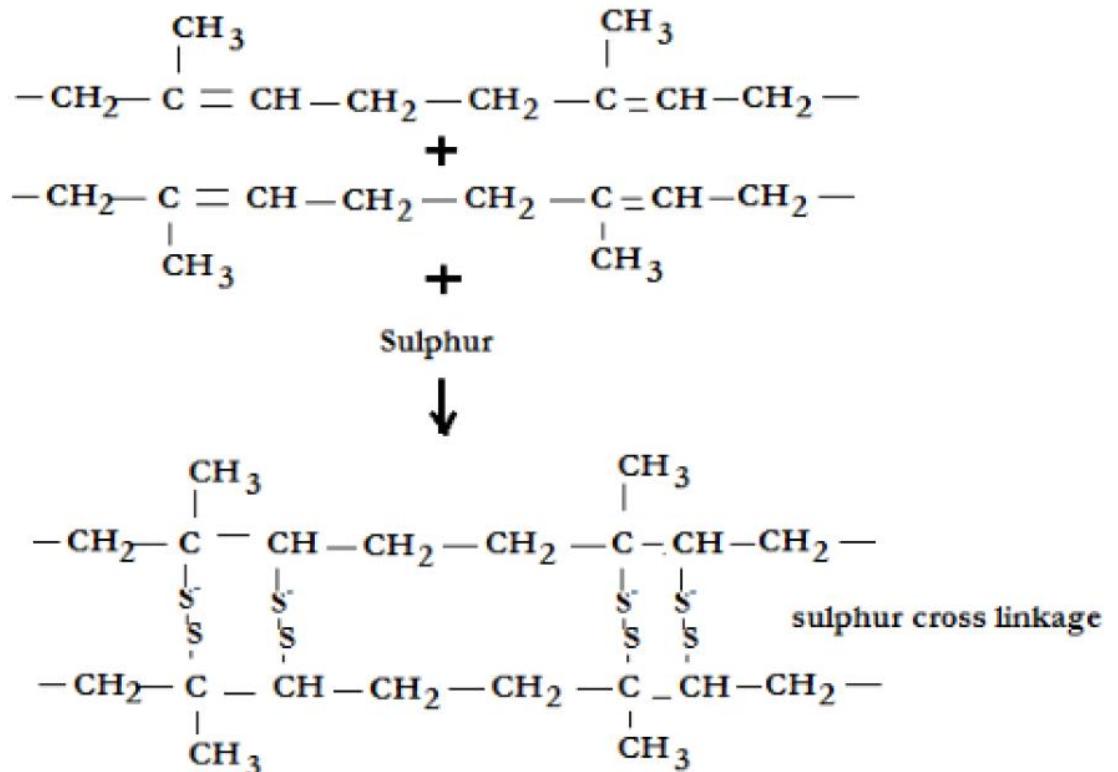
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- He observed that when rubber is heated with sulphur at $100-140^{\circ}\text{C}$ its tensile strength elasticity and resistance to swelling are increased tremendously.

POLYMER TECHNOLOGY

- The Sulphur combines chemically at the double bonds in the rubber molecule bringing about excellent changes in its properties eg resistance to changes in temperature, increased elasticity & tensile strength, durability & chemical resistance.



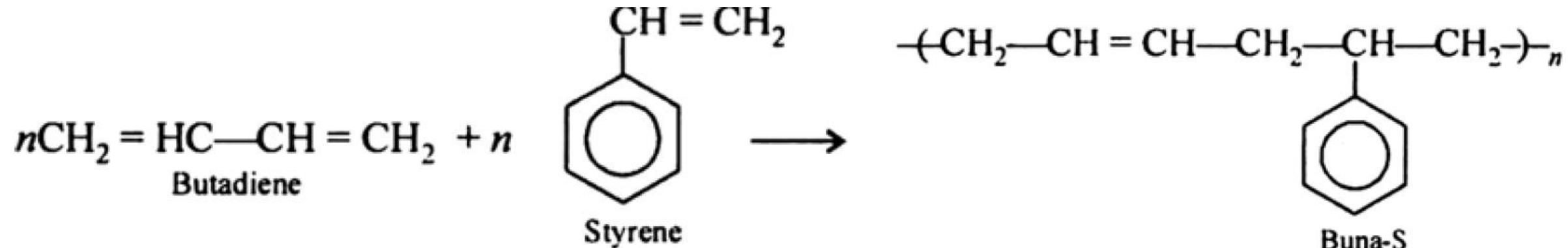
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POLYMER TECHNOLOGY

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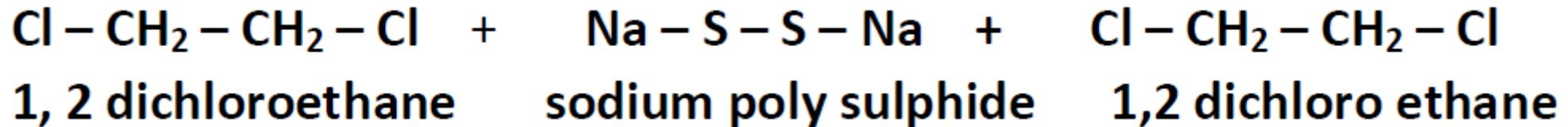
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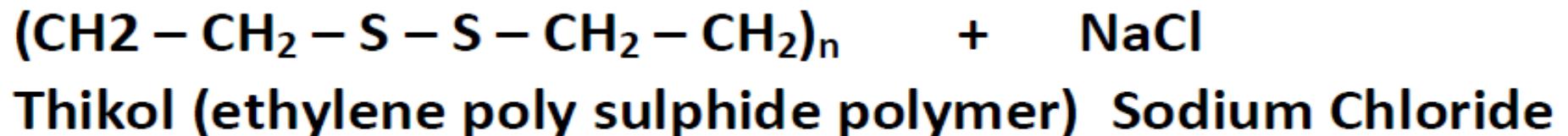
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POLYMER TECHNOLOGY

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POLYMER TECHNOLOGY

Chemistry of some important thermoplastic & thermoset Resins:- :

i. Preparation, properties and uses of PVC:

Preparation:

Step I: vinyl chloride is prepared by treating acetylene with hydrogen chloride at 60-80 ° C in the presence of metal chloride as catalyst.



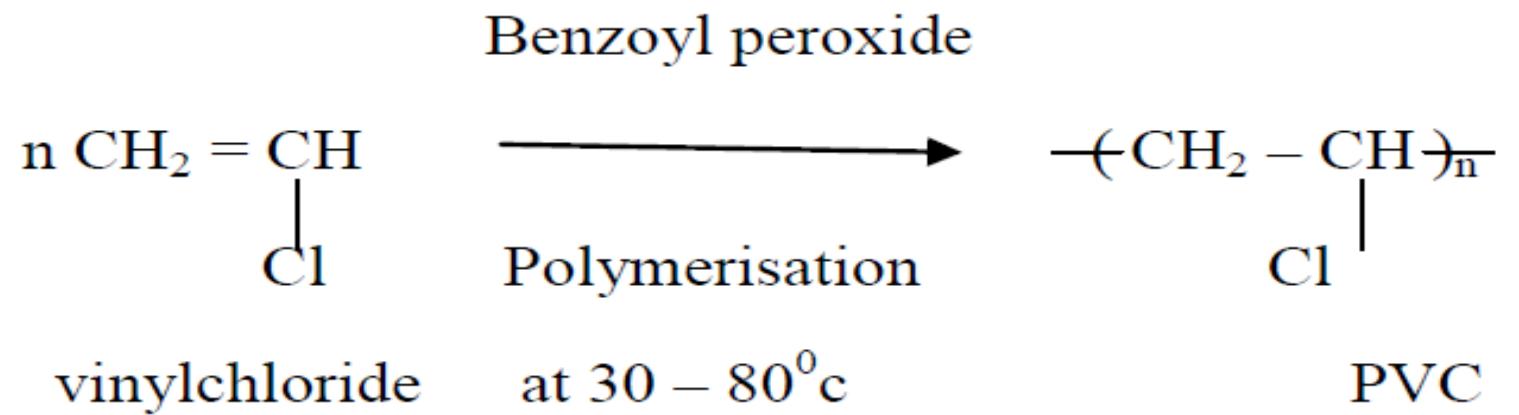
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POLYMER TECHNOLOGY



Step 2: Poly vinyl chloride is produced by heating vinyl chloride in presence of **benzyl peroxide** or **H₂O₂** under pressure.

- It follows addition mechanism



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POLYMER TECHNOLOGY

Properties:

- PVC is very light weight polymer
- PVC is colorless, odor less and chemically inert powder.
- it is insoluble in inorganic acids and alkalis, but soluble in hot chlorinated hydro carbons such as ethyl chloride.
- it undergoes degradation in presence of heat or light.
- PVC can be made more flexible and softer by adding plasticizers such as phthalate and can be bent as per requirement
- PVC products are self-extinguishing due to high chlorine content
- It can withstand extreme climatic conditions, shock and is free from corrosion
Hence, it is the preferred method for several outdoor applications.

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POLYMER TECHNOLOGY

Uses:

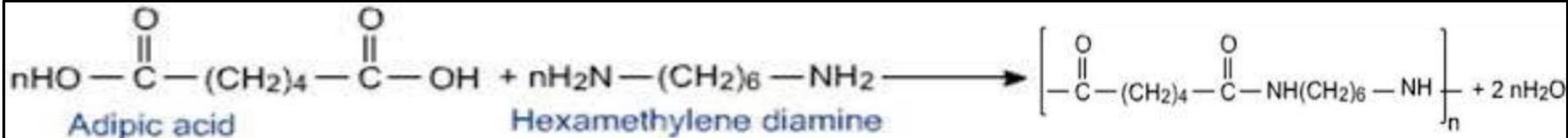
- it is used in the production of pipes, cables insulations, table covers and rain – coats etc.
- It is also used for making sheets, which are employed for tank – linings, light fittings, refrigerator components etc.
- It is used in making sewage pipes and other pipe applications
- Used in construction fields for insulation on electrical wires or in flooring for hospitals, schools, homes, and other areas where a sterile environment is a priority.
- It is used in various industries like building, electronics, electrical, automotive, medical and packaging.
- PVC fabric is used in the manufacture of aprons shower curtains, raincoats, jackets and sports bags.

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POLYMER TECHNOLOGY

Nylon -6,6:

- It is obtained by the polymerisation of adipic acid with hexamethylene diamine at high temperature and pressure(Condensation polymerization).



Properties

- nylons are translucent, whitish, high melting polymers
- High mechanical strength
- They possess high temperature stability and good abrasion resistance (Rubbing or Friction)
- They are insoluble in common organic solvents and soluble in phenols and formic acid
- Good electrical insulating properties
- No resistance to UV rays
- Lightweight; sometimes used in applications in place of metals
- Does not absorb water
- Dries quickly

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POLYMER TECHNOLOGY

Uses of nylon 6, 6 :

- nylons are used for making filaments for ropes, bristles for tooth – brushes and films etc.
- Nylon – 6,6 is used for which is used in making socks, dresses, carpets etc
- It is used for making sheets
- It also can be used for surgical items
- To prepare textile fabrics

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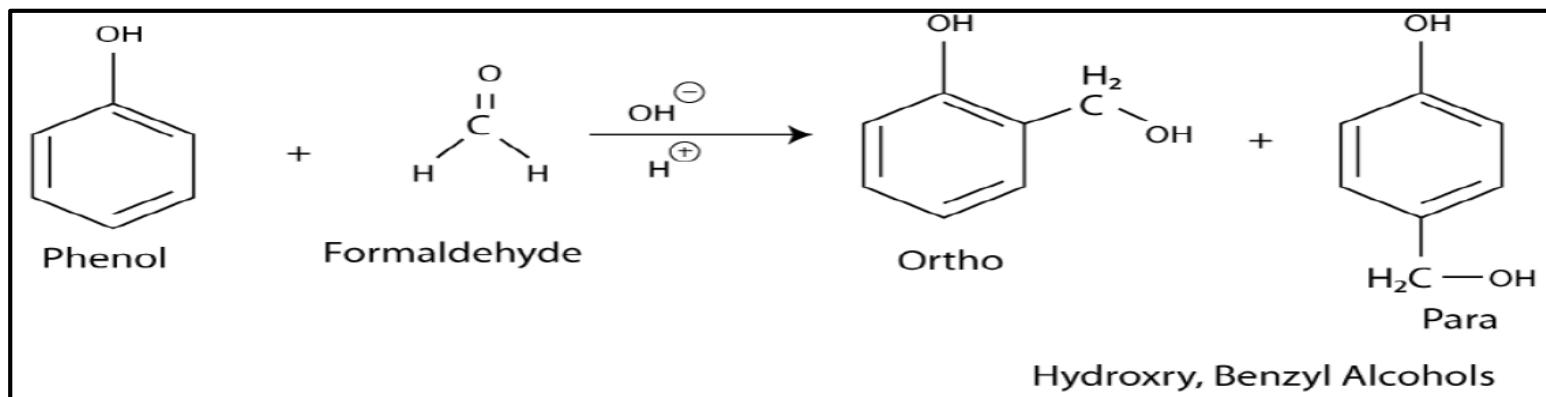
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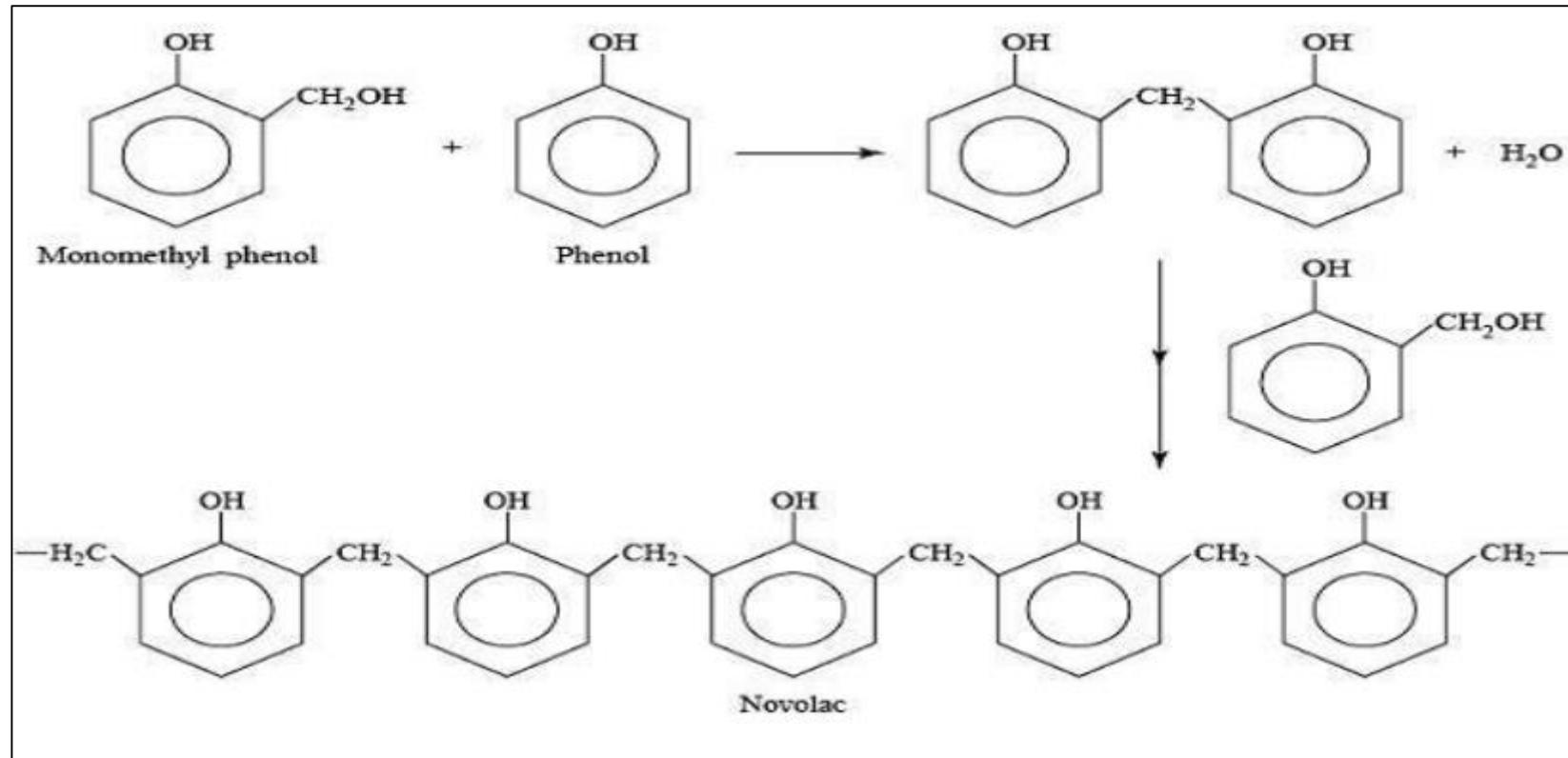
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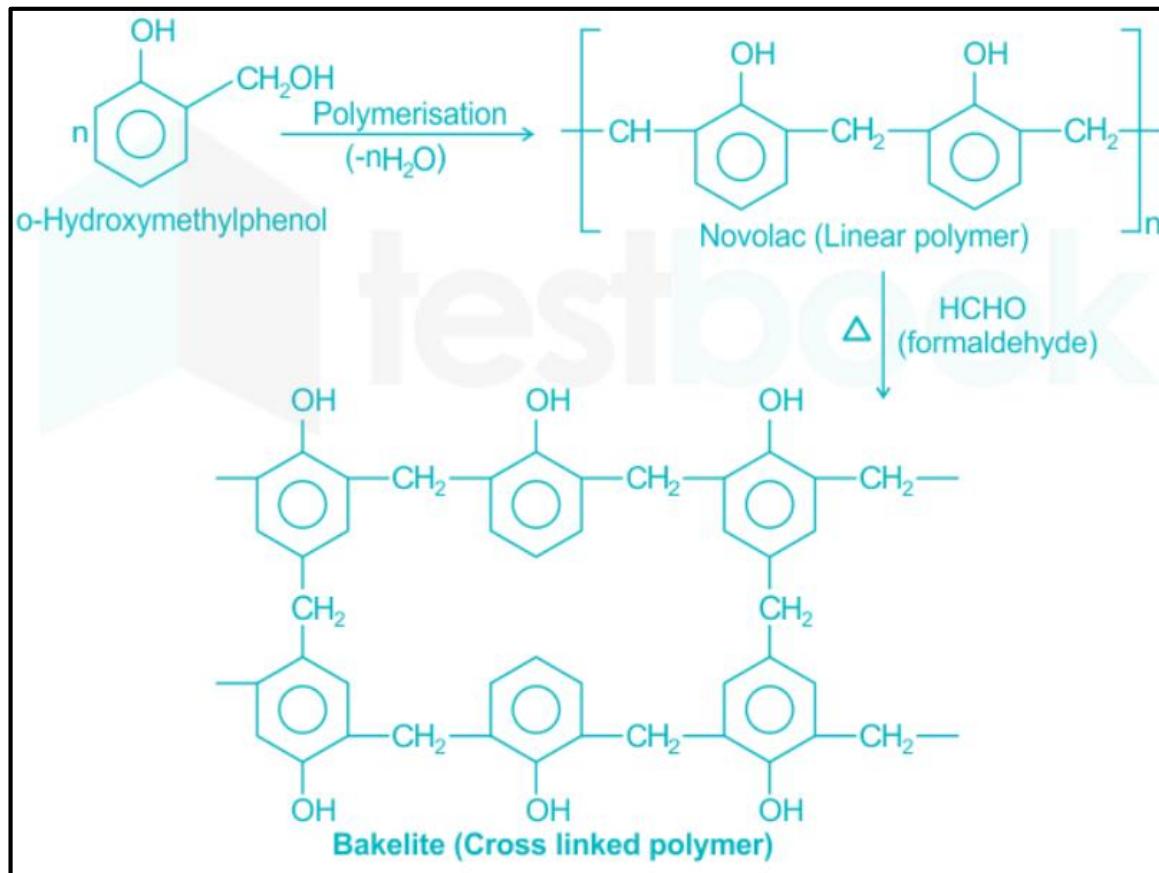
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POLYMER TECHNOLOGY

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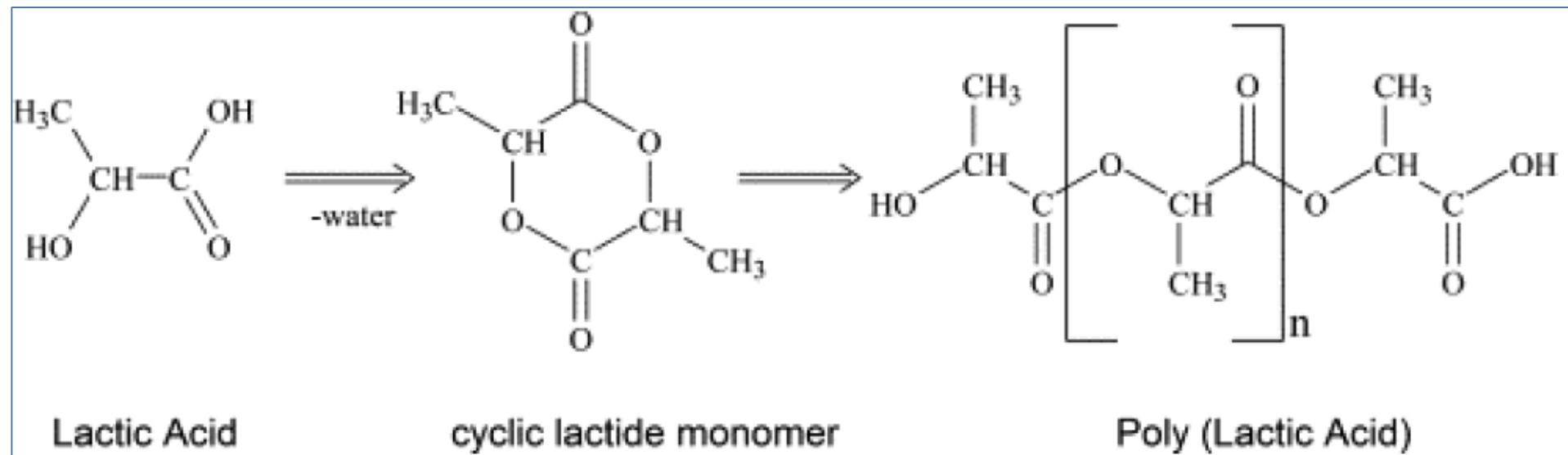
POLYMER TECHNOLOGY

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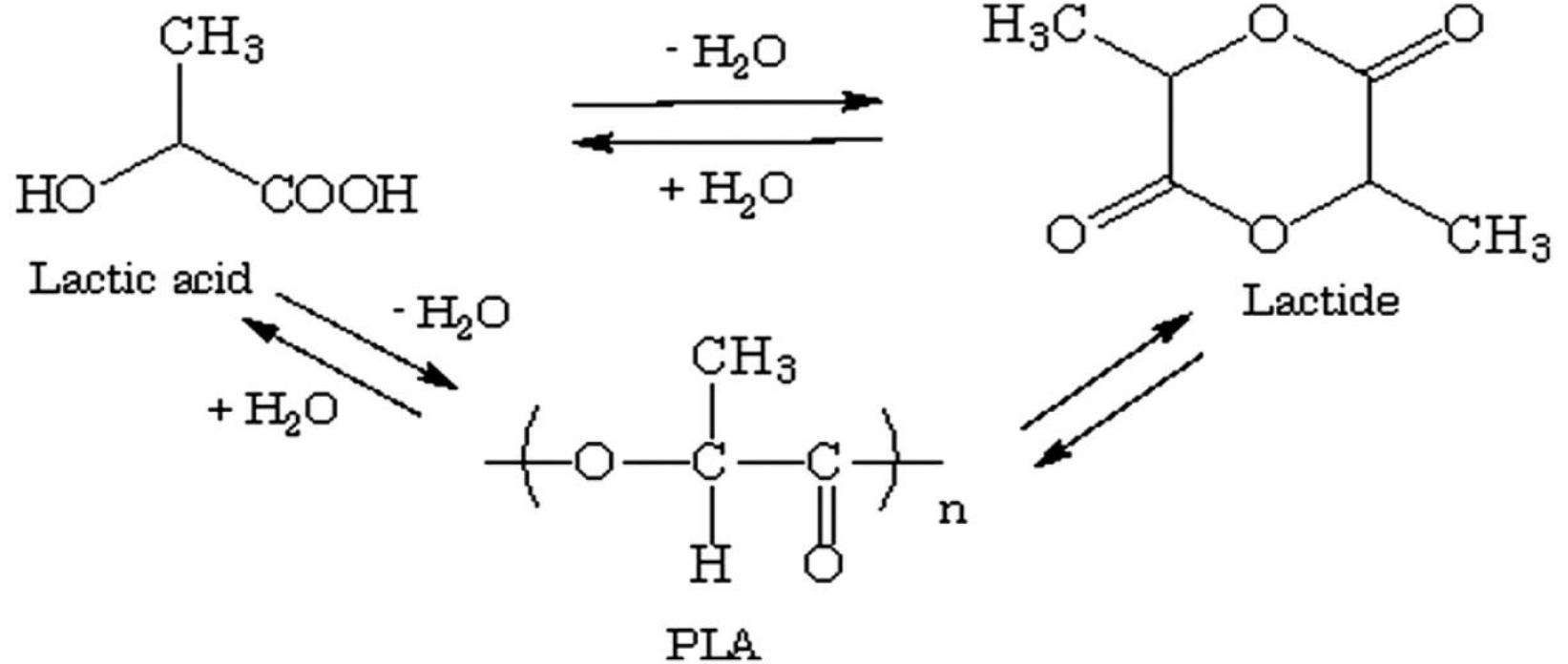
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POLYMER TECHNOLOGY

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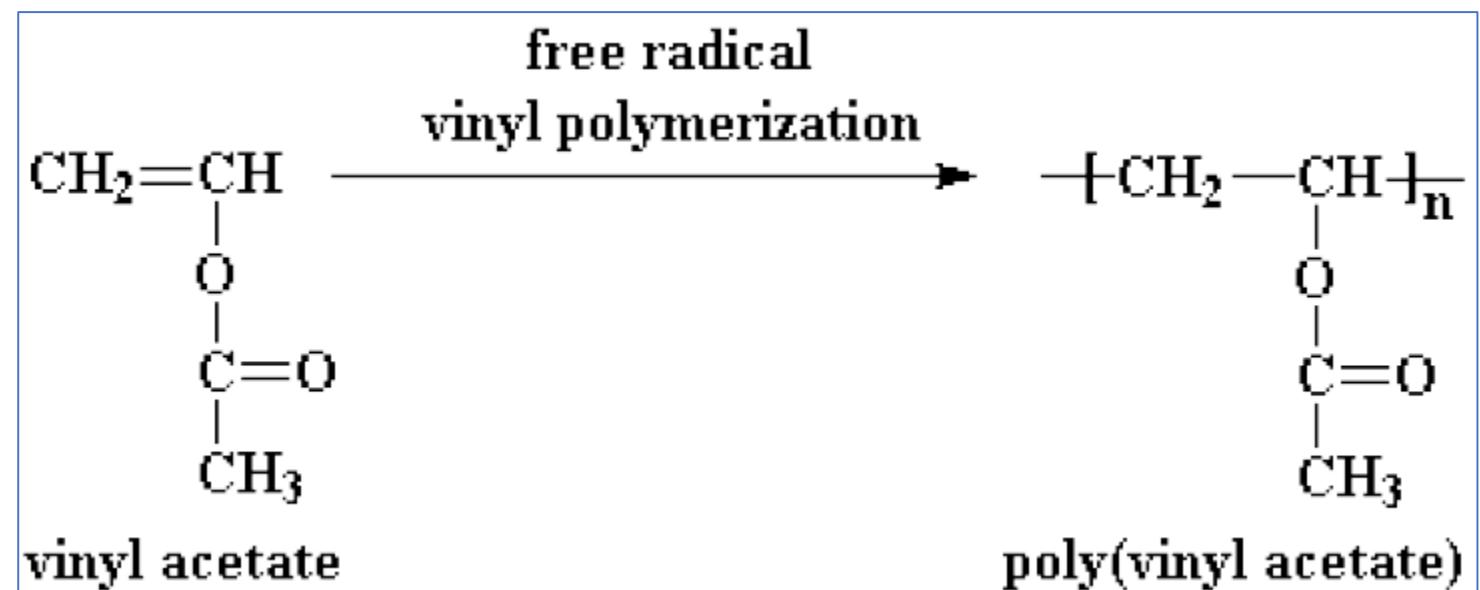
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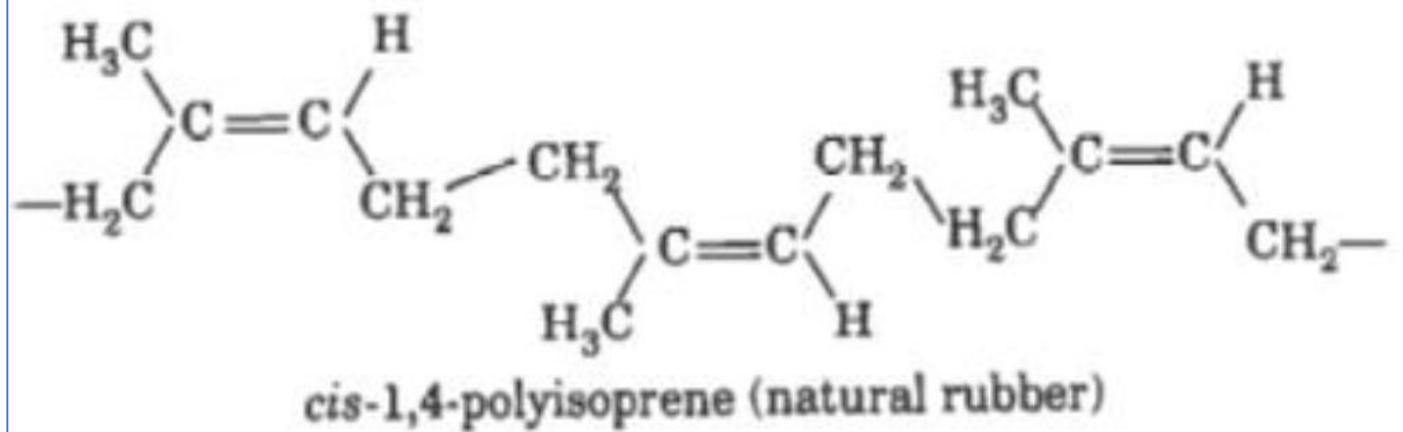
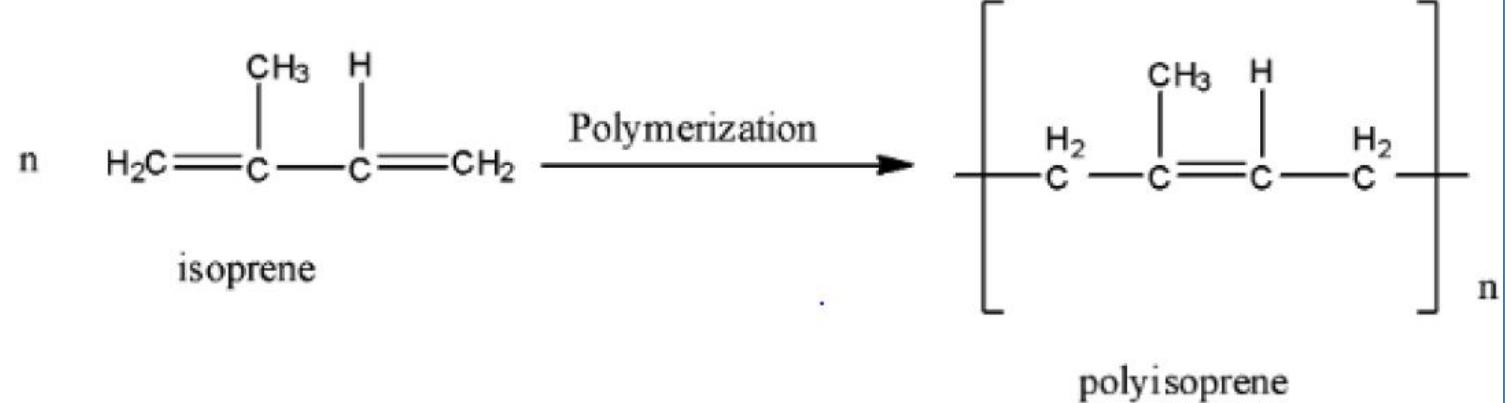
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POLYMER TECHNOLOGY



POLYMER TECHNOLOGY

Natural Rubber:

Processing of Natural Rubber:

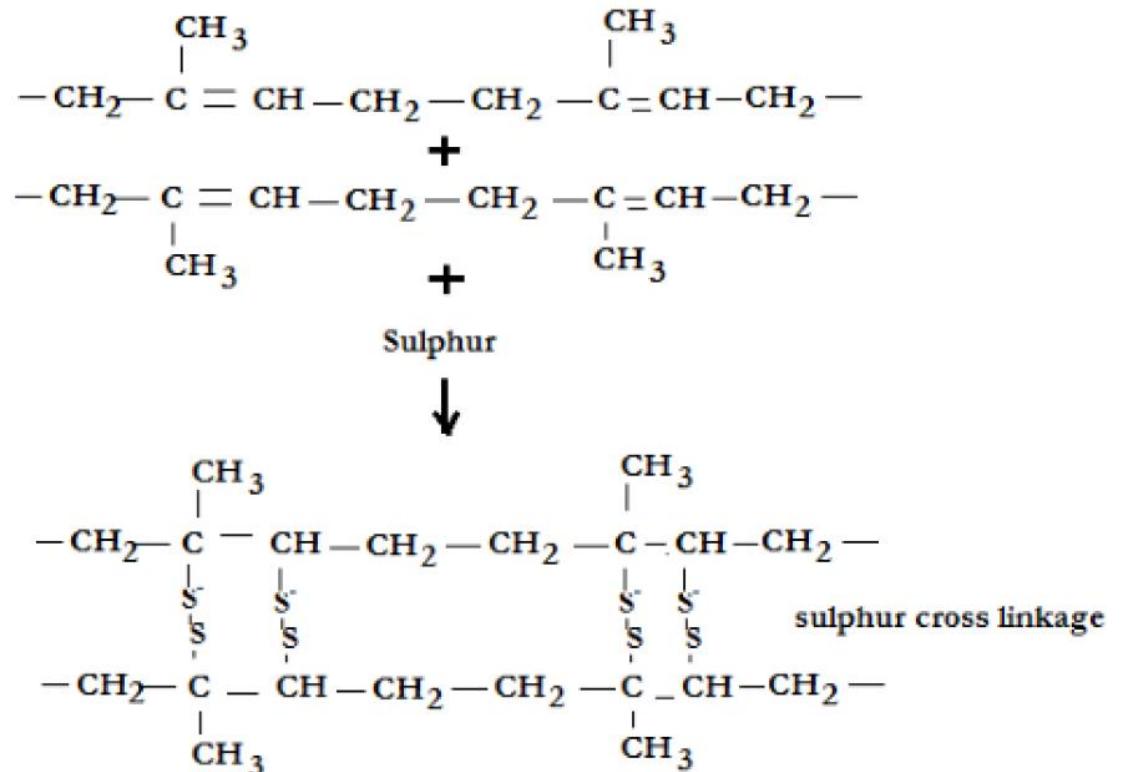
- By cutting the bark of rubber tree the milky colloidal rubber milk is obtained. The main constituent of rubber latex is 25-45% of rubber and the remaining are water, protein & resinous materials.
- The rubber latex is coagulated by using 5% acetic acid and made in to sheets.
- The rubber sheets are cured under mild heat and then subjected to further processing.

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- It is the process of improving the properties of rubber, compound with same chemicals like sulphur hydrogen sulphide, benzoyl chloride etc. most important is addition of sulphur.
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POLYMER TECHNOLOGY

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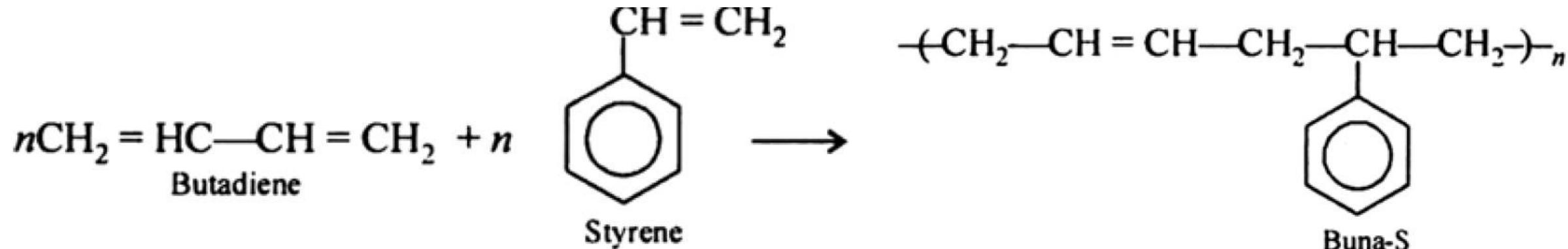


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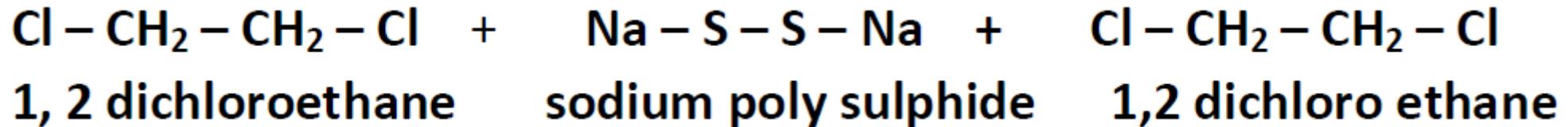
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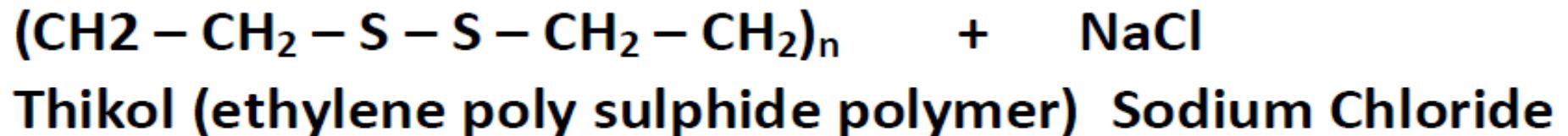
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Energy sources

Dr. T. Dhananjay Rao
Assistant Professor
Department of Chemistry

Topic: Introduction to Fuels



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Energy sources

FUEL

- Fuel is a chemical substance, which on **combustion** produces a large amount of heat.
- The produced heat is used for domestic and industrial purpose
- Fuels contain carbon, hydrogen and oxygen as main constituents
- A fuel may also contain sulphur, nitrogen as contaminants

COMBUSTION

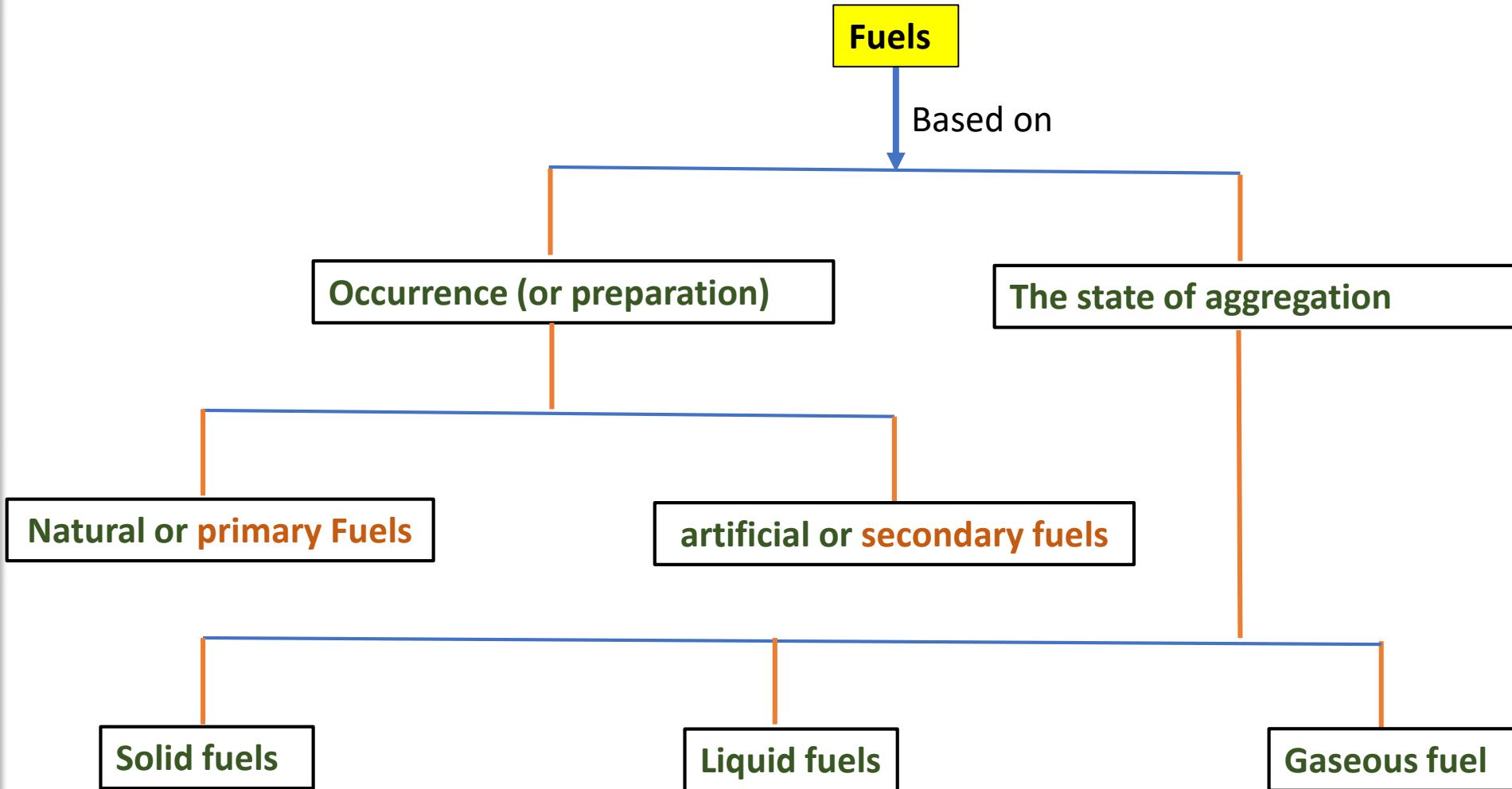
- Any substance burns completely in presence of oxygen is called combustion



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Energy sources

- Classification of Fuels:



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Energy sources

Natural or primary fuels: These are found in nature such as Wood, peat, coal, Petroleum, natural gas etc.

artificial or secondary fuels: These are prepared artificially from the primary fuels.

Ex: - charcoal, coke, kerosene, diesel, petrol, coal gas, oil gas, producer gas, blast Furnace gas etc.

Type of fuel	Natural or primary fuel	Artificial or secondary fuel
Solid	Wood, peat, lignite, dung, bituminous coal and anthracite coal	Charcoal, coke etc
Liquid	Crude oil	Petrol, diesel and various other fractions of petroleum
Gaseous	Natural gas	Coal gas, oil gas, bio gas, water gas etc.

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Energy sources

Characteristics of good fuels:

- Higher calorific value
- Moderate ignition temperature
- Low moisture content
- Low non-combustible matter
- Moderate velocity of combustion
- Less toxic combustible gases
- A good fuel should be readily available in bulk at low cost
- Handling and transport of fuel should be easy

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Energy sources

Characteristic properties of solid, liquid and gaseous fuels

Characteristic property of a fuel	Solid fuels	Liquid fuels	Gaseous fuels
example	Coal	Crude oil	Coal gas
Cost	Cheap	Costlier than solid fuels	Costly
Storage	Easy to store	Closed containers should be used for storing	Storage space required is huge and should be leak proof.
Risk towards fire hazards	Less	More	Very high, since these fuels are highly inflammable
Combustion rate	It is a slow process	Fast process	Very rapid and efficient
Combustion control	Cannot be controlled	Cannot be controlled or stopped when necessary	Controlled by Regulating the supply of air

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Characteristic properties of solid, liquid and gaseous fuels

Characteristic property of a fuel	Solid fuels	Liquid fuels	Gaseous fuels
Handling cost	High since labors required in their storage & transport.	Low, since the fuel can be transported through pipes	Low, similar to liquid fuels, these can be transported through pipes
Ash	Ash is produced and its disposal also possess problems	No problem of ash	No problem of ash
Smoke	Produce smoke invariably	Clean, but liquids associated with high carbon and aromatic fuels produce smoke	Smoke is not produced
Calorific value	Least	High	Highest
Combustion rate	It is a slow process	Fast process	Very rapid and efficient
Heat efficiency	Least	High	Highest efficiency

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Energy sources

Solid Fuels:

- The main solid fuels are wood, peat, lignite, coal and charcoal

Coal:

- Coal is a fossil fuel which occurs in layers in the earth's crust
- It is formed by the partial decay of plant materials accumulated millions of years ago and further altered by action of heat and pressure

The process of conversion of wood into coal can be represented as

Wood → Peat → Lignite → Bituminous Coal → Anthracite

Peat:- Peat is brown-fibrous jelly like mass.

Lignite:- these are soft, brown colored, lowest rank coals

Bituminous coals:- These are pitch black to dark grey coal

Anthracite:- It is a class of highest rank coal

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Energy sources

Fuel	Percentage of carbon	Calorific value (k.cal/kg)	Applications
Wood	50	4000-4500	Domestic fuel
Peat	50-60	4125-5400	Used if deficiency of high rank coal is prevailing
Lignite	60-70	6500-7100	For steam generation in thermal power plants
Bituminous	80-90	8000-8500	In making coal gas and Metallurgical coke
Anthracite	90-98	8650-8700	In households and for steam raising

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Energy sources

Analysis of Coal:

- The analysis of coal is helpful in its ranking
- Classification and quality of coal
- Elemental analysis
- Industrial applications
- The assessment of the quality of coal is carried out by these two types of analyses.
 - A) Proximate analysis
 - B) Ultimate analysis

Proximate analysis:

- In this analysis, the percentage of carbon is indirectly determined
- It is a quantitative analysis of the following parameters.
 1. Moisture content
 2. Volatile matter
 3. Ash
 4. Fixed carbon

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Energy sources



Moisture Content:

- About 1 gram of finely powdered air-dried coal sample is weighed in a crucible.
- The crucible is placed inside an electric hot air-oven, maintained at 105 to 110 °C for one hour.
- The crucible is allowed to remain in oven for 1 hour and then taken out, cooled in desiccators and weighed.
- Loss in weight is reported as moisture

$$\text{Percentage of moisture} = \frac{\text{Loss in weight}}{\text{weight of coal taken}} \times 100$$

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Volatile Matter:

- The dried sample taken in a crucible in and then covered with lid and placed in an electric furnace or muffle furnace, maintained at 925 ± 20 °C.
- The crucible is taken out of the oven after 7 minutes of heating
- The crucible is cooled first in air, then inside desiccators and weighed again.
- Loss in weight is reported as volatile matter on percentage-basis.

$$\text{Percentage of volatile matter} = \frac{\text{Loss in weight}}{\text{weight of coal taken}} \times 100$$

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Ash:

- The residual coal sample taken in a crucible and then heated without lid in a muffle furnace at 700 ± 50 °C for $\frac{1}{2}$ hour.
- The crucible is then taken out, cooled first in air, then in desiccators and weighed.
- Heating, cooling and weighing are repeated, till a constant weight is obtained
- The residue is reported as ash on percentage-basis.

$$\text{Percentage of ash} = \frac{\text{Weight of ash left}}{\text{Weight of coal taken}} \times 100$$

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Fixed Carbon:

- Percentage of fixed carbon = $100 - \% \text{ of } (\text{Moisture} + \text{Volatile matter} + \text{ash})$

Significance of proximate analysis

- Proximate analysis provides following valuable information's in assessing the quality of coal.

Moisture:

- Moisture is coal evaporates during the burning of coal and it takes some of the liberated heat in the form of latent heat of evaporation.
- Therefore, moisture lowers the effective calorific value of coal. Moreover over, it quenches the fire in the furnace, hence, lesser, the moisture content, better the quality of coal as a fuel.
- However, presence of moisture, up to 10%, produces a more uniform fuel-bed and less of "fly-ash".

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Volatile matter:

- **a high volatile matter content means that a high proportion of fuel will distil over as gas or vapor, a large proportion of which escapes un-burnt**
- **So, higher volatile content in coal is undesirable.**
- **A high volatile matter containing coal burns with a long flame, high smoke and has low calorific value.**
- **Hence, lesser the volatile matter, better the rank of the coal**

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Ash:

- Ash is a useless, non-combustible matter, which reduces the calorific value of coal.
- Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature.
- This in-turn causes obstruction to air supply; thereby the burning of coal becomes irregular.
- Hence, lower the ash content, better the quality of coal.
- The presence of ash also increases transporting, handling and storage costs.
- It also involves additional cost in ash disposal.
- The presence of ash also causes early wear of furnace walls, burning of apparatus

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Fixed Carbon:

- Higher the percentage of fixed carbon, greater is its calorific and betters the quality coal.
- Greater the percentage of fixed carbon, smaller is the percentage of volatile matter
- The percentage of fixed carbon helps in designing the furnace and the shape of the fire-box, because it is the fixed carbon that burns in the solid state.

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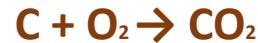
Energy sources

Ultimate analysis:

- This is the elemental analysis and often called as qualitative analysis of coal.
- analysis involves the determination of carbon and hydrogen, nitrogen, sulphur and oxygen.

1. Carbon and Hydrogen:

- About 1 to 2 gram of accurately weighed coal sample is burnt in a current of oxygen in a combustion apparatus.
- C and H of the coal are converted into CO_2 and H_2O respectively.
- The gaseous products of combustion are absorbed respectively in KOH and CaCl_2 tubes of known weights
- The increase in weights of these are then determined



12 44



2 18



Energy sources

$$\text{Percentage of C} = \frac{\text{Increase in weight of KOH tube}}{\text{Weight of Coal sample taken}} \times \frac{12}{44} \times 100$$

$$\text{Percentage of H} = \frac{\text{Increase in weight of CaCl}_2\text{ tube}}{\text{Weight of Coal sample taken}} \times \frac{2}{18} \times 100$$

2. Nitrogen :

- About 1 gram of accurately weighed powdered coal is heated with concentrated H_2SO_4 along with K_2SO_4 (catalyst) in a long-necked Kjeldahl's flask
- Sample + H_2SO_4 $\xrightarrow{\text{K}_2\text{SO}_4}$ Clear solution + KOH $\xrightarrow{\text{Heat}}$ $\text{NH}_3 + \text{Acid}$ \longrightarrow Non-consumed acid + base

Consumed acid can be measured

Back Titration

Energy sources

- After the solution becomes clear, it is treated with excess of KOH and the liberated ammonia is distilled over and absorbed in a known volume of standard acid solution.
- The unused acid is then determined by back titration with standard NaOH solution.
- By the above process, we can measure the how much volume of acid consumed neutralize the base NaOH
- From the volume of acid used by ammonia liberated, the percentage of N in coal is calculated as follows:

$$\text{Percentage of N} = \frac{\text{Volume acid} \times \text{Normality of acid} \times 1.4}{\text{Weight of Coal sample taken}}$$

Energy sources

3. Sulphur

- Known weight of coal combusted in Bomb calorimeter presence of BaCl₂
- If any Sulphur present in sample it converted into solid BaSO₄
- BaSO₄ is separated as solid and measured its weight
- S + O₂ → SO₄⁻² → BaCl₂ → BaSO₄

$$\text{Percentage of S} = \frac{\text{Weight of BaSO}_4 \text{ obtained}}{\text{Weight of Coal sample taken in bomb}} \times \frac{32}{233} \times 100$$

Energy sources

By ultimate analysis of coal percentage of Carbon, Hydrogen, Nitrogen, Sulphur, Ash, Oxygen in the coal can be calculated

% Ash:

Ash determination is carried out in proximate analysis

$$\text{The Percentage of Ash} = \frac{\text{Weight of ash left} \times 100}{\text{Weight of Coal taken}}$$

% Oxygen:

$$\% \text{ Oxygen} = 100 - \% \text{ of } (C + H + S + N + \text{Ash})$$

$$\text{Percentage of C} = \frac{\text{Increase in weight of KOH tube}}{\text{Weight of Coal sample taken}} \times \frac{12}{44} \times 100$$

$$\text{Percentage of H} = \frac{\text{Increase in weight of CaCl}_2\text{ tube}}{\text{Weight of Coal sample taken}} \times \frac{2}{18} \times 100$$

$$\text{Percentage of N} = \frac{\text{Volume acid} \times \text{Normality of acid} \times 1.4}{\text{Weight of Coal sample taken}}$$

$$\text{Percentage of S} = \frac{\text{Weight of BaSO}_4\text{ obtained}}{\text{Weight of Coal sample taken in bomb}} \times \frac{32}{233} \times 100$$

Energy sources

Significance of ultimate analysis:

Carbon and Hydrogen: Greater the percentage of carbon and hydrogen better is the coal in quality and calorific value.

Nitrogen : Nitrogen has no calorific value and hence, its presence in coal is undesirable

Thus, a good quality coal should have very little Nitrogen content.

Energy sources

Sulphur :

- Sulphur, although contributes to the heating value of coal, yet on combustion produces acids like SO_2 , SO_3 , which have harmful effects of corroding the equipment's and also cause atmospheric pollution.
- Sulphur is, usually, present to the extent of 0.5 to 0.3% and derived from ores like iron, pyrites, gypsum, etc., mines along with the coal.
- Presence of sulphur is highly undesirable in coal to be used for making coke for iron industry
- Since it is transferred to the iron metal and badly affects the quality and properties of steel.
- Moreover, oxides of sulphur pollute the atmosphere and leads to corrosion

Ash :

- Ash is a useless, non-combustible matter, which reduces the calorific value of coal
- Moreover, ash causes the hindrance to the flow of air and heat, thereby lowering the temperature.
- Hence, lower the ash content, better the quality of coal.
- The presence of ash also increases transporting, handling and storage costs.
- The presence of ash also causes early wear of furnace walls, burning of apparatus

Oxygen:

- Oxygen content decreases the calorific value of coal.
- oxygen is a combined form with hydrogen in coal and thus, hydrogen available for combustion is lesser than actual one.
- An increase in 1% oxygen content decreases the calorific value by about 1.7% and hence, oxygen is undesirable.

A sample of coal weighing 1.98 gm, on heating for 1 hour at 110 °C for one hour, left a residue weighed 1.78gms. The residue was heated in a suitable crucible with a lid at a at 950 ° C for exactly 7 min The residue weighed 1.59 gms. The residue was heated in presence of air till a constant weight was obtained. This residue weighed 0.231 gms. Calculate the proximate analysis of coal.

Weight of coal taken = 1.98 gm

Mass of moisture in coal = 1.98 – 1.78 gm = 0.2

$$\text{Percentage of moisture} = \frac{\text{Loss in weight}}{\text{weight of coal taken}} \times 100 = \frac{0.2}{1.98} \times 100 = 10.1 \%$$

Mass of volatile matter = 1.78 – 1.59 = 0.19gm

$$\text{Percentage of volatile matter} = \frac{\text{Loss in weight}}{\text{weight of coal taken}} \times 100 = \frac{0.19}{1.98} \times 100 = 9.59 \%$$

Mass of residue after ignition = 0.231 gm

$$\text{Percentage of ash} = \frac{\text{Weight of ash left}}{\text{Weight of coal taken}} \times 100 = \frac{0.231}{1.98} \times 100 = 11.66 \%$$

- Percentage of fixed carbon = 100 - % of (Moisture + Volatile matter + ash)
- % of fixed carbon = 100 – (10.1 + 9.59 + 11.66) = 68.65

Energy sources

Liquid Fuels

- Liquid fuels are the important commercial and domestic fuels used these days.
- Most of these fuels are obtained from the naturally occurring petroleum or crude oil.

Primary Petroleum:

- Petroleum or crude oil is a dark greenish brown, viscous oil found deep in the earth crust.
- Crude oil is a source of many liquid fuels that are in current use

The composition of crude petroleum approximately is

C = 80-85%, H= 10-14%

S= 0.1-3.5% and N=0.1-0.5%.

Energy sources

Refining: The process of purification and separation of various fractions present in petroleum/crude oil by fraction distillation is called refining of petroleum

Refining of petroleum is done in different stages:

a. Removal of solid impurities:

- The crude oil is a mixture of solid, liquid and gaseous substances
- This is allowed to stand undisturbed for some time, when the heavy solid particles settle down and gases evaporate.
- The supernatant liquid is then centrifuged where in the solids get removed.

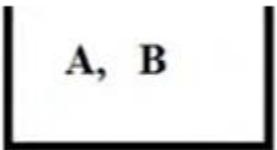
b. Removal of water (Cottrell's process):

- The crude oil obtained from the earth's crust is in the form of stable emulsion of oil and brine.
- This mixture when passed between two highly charged electrodes will destroy the emulsion films and the colloidal water droplets coalesce into bigger drops and get separated out from the oil.

Energy sources

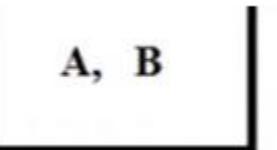
Removal of harmful impurities:

- In order to remove Sulphur compounds in the crude oil. It is treated with copper oxide.
- The sulphur compounds get converted to insoluble copper sulphide, which can be removed by filtration.
- Substances like NaCl and MgCl₂ it present will corrode the refining equipment and result in scale formation.
- These can be removed by techniques like electrical desalting and dehydration.



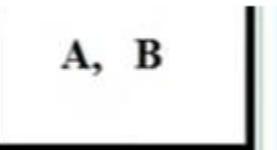
Case-1

Heating at : 40°C



Case-2

70°C



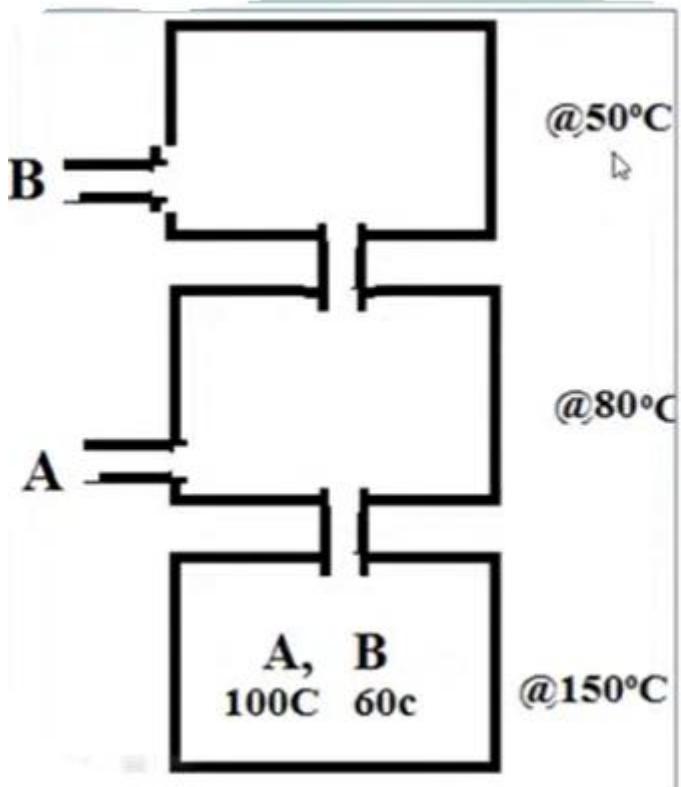
Case-3

120°C

Case-1: -----

Case-2: -----

Case-3: -----

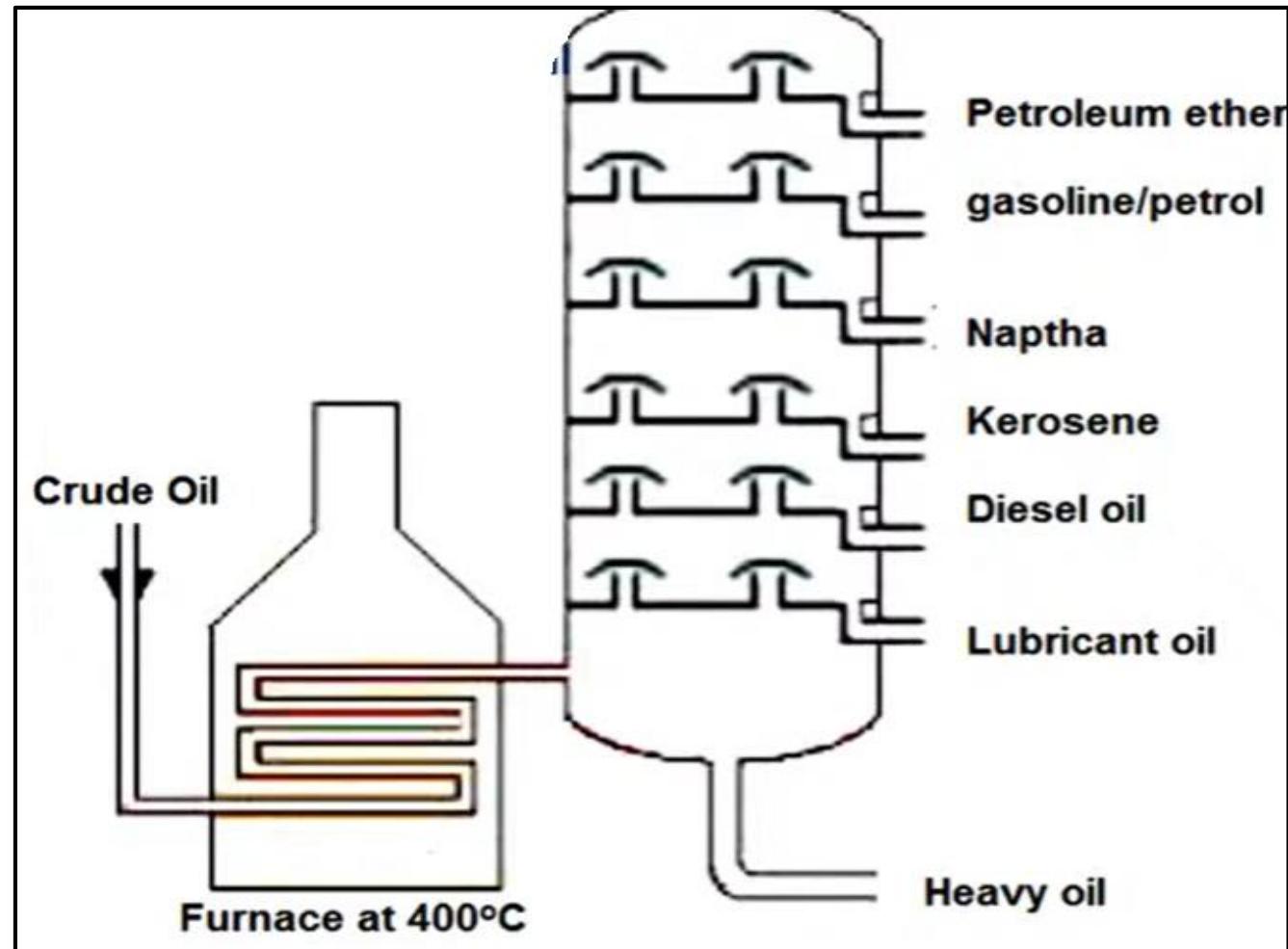


Fractional distillation

Energy sources

Fractional Distillation:

- Heating of crude oil around 400°C in an iron retort, produces hot vapor which is allowed to pass through fractionating column.
- It is a tall cylindrical tower containing a number of horizontal stainless trays at short distances and is provided with small chimney covered with loose cap.
- As the vapors go up they get cooled gradually and fractional condensation takes place.
- Higher boiling fraction condenses first later the lower boiling fractions.



Refining petroleum

Properties and uses of fractions of petroleum:

Fraction	Boiling point range ($^{\circ}\text{C}$)	Composition	Uses
Petroleum gas	< 30	$\text{C}_1\text{-C}_4$	Petroleum gas is change into liquid under pressure and used as a household fuel (LPG)
Petroleum ether	30-70	$\text{C}_5\text{-C}_7$	As a solvent
Gasoline / petrol	40-120	$\text{C}_5\text{-C}_9$	As a solvent and in dry cleaning
Naphtha	120-180	$\text{C}_9\text{-C}_{10}$	As solvent for paints, varnishes and in dry cleaning
Kerosene	180-250	$\text{C}_{10}\text{-C}_{16}$	As household fuel in pressure stoves, lanterns, petromax lamps etc.
Diesel oil	250-320	$\text{C}_{10}\text{-C}_{19}$	As Diesel engine fuel
Heavy oil	320-400	$\text{C}_{17}\text{-C}_{30}$	Used for getting high quality petrol by Cracking

Energy sources

Gaseous Fuels:

- The gaseous fuels are most preferred because of their ease of storage, transport, handling and ignition.
- These are classified into two types.

i) Primary fuels :

Ex:- Natural gas

ii) Secondary fuels :

Ex: - Coal gas, producer gas, water gas

Energy sources

Natural gaseous:

1. Natural gas is primary gaseous fuel. It is a fossil fuel
2. It is obtained from oil wells dug in the earth crust during mining of petroleum
3. It is mainly composed of methane and small quantities of ethane along with other Hydrocarbons
4. It is also known as *methane gas or marsh gas* as it majorly contains methane

5. Composition of Natural gas:

CH_4 - 88.5% C_2H_6 - 5.5% Propane - 3.7%

Butane - 1.8% H_2 , CO , CO_2 - 0.5%

6. Calorific value varies from 12000-14000 Kg/m³

7. It is used as a very good domestic fuel

Energy sources

- It is used in the preparation of ammonia
- It is used to prepare carbon black for rubber industry
- It is used to prepare some synthetic proteins which are used as animal feed

Energy sources

LPG (Liquefied Petroleum Gas)

- The gas is obtained from natural gas or as a byproduct in refineries during cracking of heavy petroleum products.
- Nowadays LPG has been a common fuel for domestic work and also in most of the industries.
- The main components of LPG are n-butane, isobutane, butylenes and propane (traces of propene and ethane).
- The hydrocarbons are in gaseous state at room temperature and 1 atmospheric pressure but can be liquefied under higher pressure.
- LPG is kept in metallic cylinder attached with burner through pipe.
- It has two stoppers, one at the cylinder and other at burner
- LPG has special odour due to the presence of organic sulphides which are added specially for safety measure

Characteristics of LPG:

1. It has high calorific value ($27,800\text{kcal/m}^3$)
2. It gives less CO and least unburnt hydrocarbons. So it causes least pollution.
3. It gives moderate heat which is very good for cooking
4. Its storage is simple. It is colorless
5. It has tendency to mix with air easily
6. Its burning gives no toxic gases though it is highly toxic
7. It neither gives smoke nor ash content
8. It is cheaper than gasoline and used as fuel in auto vehicles also
9. It is dangerous when leakage is there

Applications of LPG:

In Food industry :

- LPG is widely used in the food industry like hotels, restaurants, bakeries, Canteens etc.
- Low sulphur content and controllable temperature makes LPG the most preferred fuel in the food industry.

In Glass & Ceramic:

The use of a clean fuel like LPG enhances the product quality thereby reducing technical problems related to the manufacturing activity of glass and ceramic products.

In Building industry:

LPG being a premium gaseous fuel makes it ideal for usage in the Cement manufacturing process.

In Automotive Industry:

The main advantage of using automotive LPG is, it is free of lead, Very low in sulphur, other metals, aromatics and other contaminants

In Forming Industry :

LPG in the farming industry can be used for the following:

- Drying of crops
 - Cereal drying
 - Curing of tobacco and rubber
 - Soil conditioning Horticulture etc
- LPG is used in metal industry, aerosol industry, textile industry and it can also be used in Steam rising.

CNG (Compressed Natural Gas):

- Natural gas contains mainly CH_4
- When natural gas is compressed at high pressure (1000atm) or cooled to -160°C , it is converted to CNG.
- It is stored in cylinder made of steel.
- It is now replacing gasoline as it releases less pollutant during its combustion.
- In some of the metro cities, CNG vehicles are used to reduce pollution.

Characteristics of CNG:

- CNG being lead/sulphur free, its use substantially reduces harmful engine emissions
- CNG being lighter than air, will rise above ground level and disperse in the atmosphere, in the case of a leakage.
- CNG in the gaseous state, and is colorless
- Predominantly Methane is available in the lean gas, hence CNG contains mostly methane

Applications of CNG gas

- It was used to generate electricity, heat buildings, fuel vehicles, power industrial furnaces and Air conditioners.
- Natural gas is also consumed in homes for space heating and for water heating
- It is used in stoves, ovens, clothes dryers and other appliances.
- In some of the metro cities, CNG vehicles are used to reduce pollution.

Energy sources

- Energy resources may be defined as “any property which can be converted into work” .
- Energy is defined as the capacity to do work

Energy sources need

- Energy essential for human societies.
- Energy required for domestic as well as industrial process like mining transport, lighting, and heating.
- Energy consumption of India is increasing rapidly because of growing population and rapid urbanization of country
- The lifestyles of are changing from a simple way to a luxurious lifestyle, which further increases dependency on energy. India is world's 6th largest consumer. (Industry, transportation, residential sector)
- Presently, 95% of energy is available only from the fossil fuels such as coal, oil and natural gas.

Classification of Energy sources

- Based on continual utility, energy sources can be classified into 2 types

Renewable energy resources:

- These resources can be generated continuously and are inexhaustible
- Ex: wood, solar energy, wind energy, hydro power, tidal energy, geothermal energy etc.

Non-renewable energy resources:

- These resources are natural, that cannot be regenerated once they are exhausted
- They cannot be used again

Ex: Coal, petroleum, natural gas, nuclear fuels

Non Conventional Energy sources

- These are renewable
- These are continuously available
- No need to conserve
- Pollution free
- Eg. Solar energy, wind energy

Conventional Energy sources

- These are non-renewable
- These will be exhausted one day
- Necessary to conserve
- Cause more pollution
- Eg. Coal, LPG

Renewable energy resources:

1. Solar energy:

- Sun is the ultimate source of energy.
- Energy is derived from the sun's radiation is called solar energy.
- Traditionally solar energy is used for drying clothes & food grains
- preservation of eatables
- obtaining salt from sea water.

Advantages of solar energy:

- Solar energy is freely available
- It does not produce ash, fumes and noise pollution hence it is clean, noise less and environment friendly
- It saves money in long run.
- It is renewable from of energy.

Disadvantages of solar energy:

- Initial cost is very large.
- Energy should be stored in batteries.
- Large space is needed for installation
- Energy generated is depend on solar intensity

Now we have several techniques for harnessing solar energy.

- Photo voltaic cell is a device which converts solar radiation into electrical energy by using the semiconductor device

Solar cells:

- Solar cell is a device that converts photons from the sun (solar light) into electricity.
- They are also known as photo voltaic cells solar cells are made up of semiconductor materials like silicon & gallium.
- When solar radiations fall on them a potential difference is produced which causes flow of electrons and produces electricity.
- By using gallium arsenide, cadmium sulphide or boron, efficiency of the PV cells can be improved.

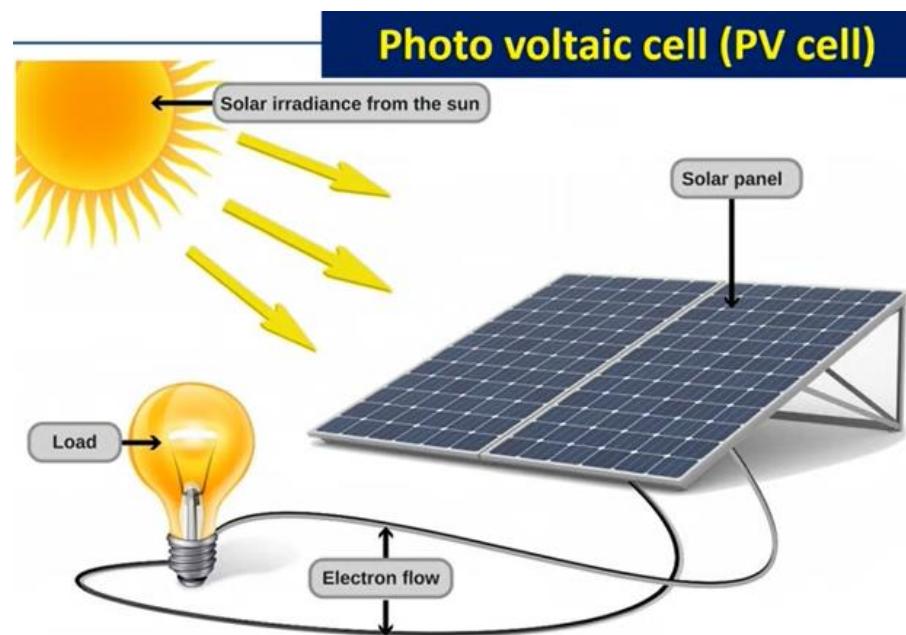


Photo voltaic cells are made up of semiconductors, such as doped silicon materials.

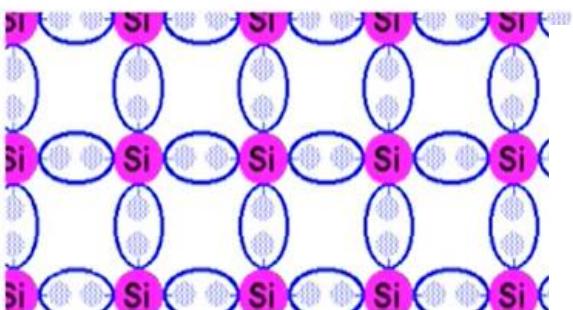
Electronic Configuration of:

B (Z=5): $1S^2 2S^2 2P^1$

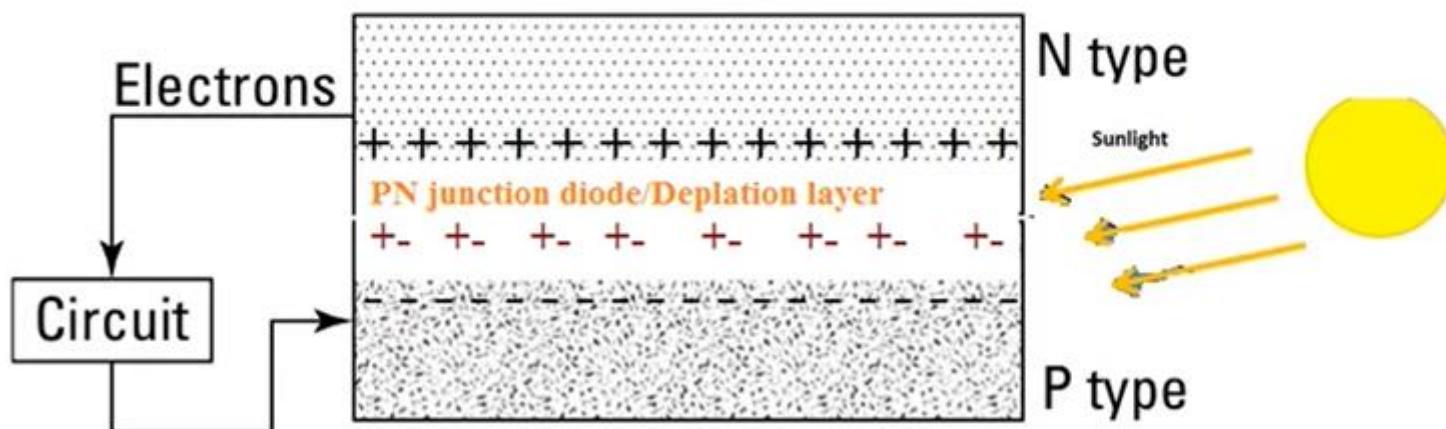
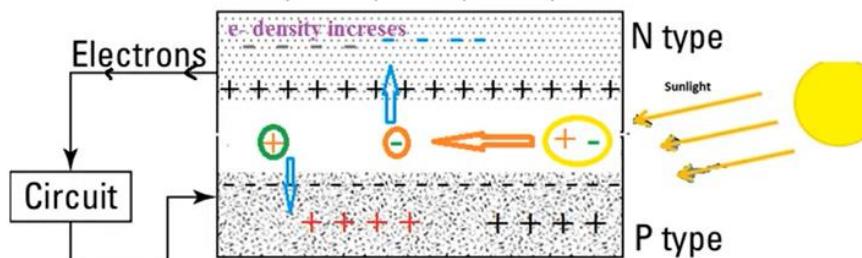
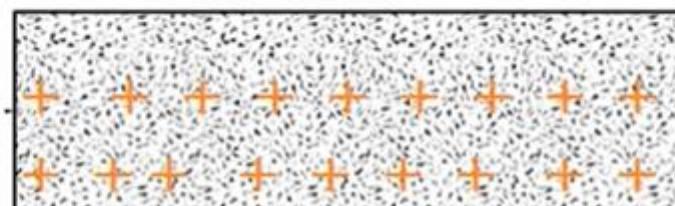
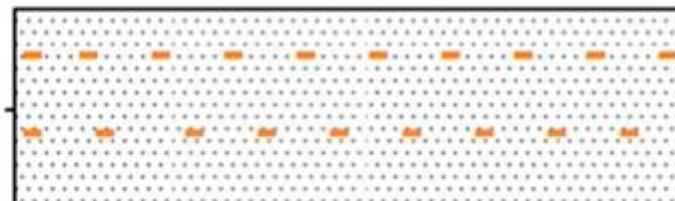
Si (Z=14): $1S^2 2S^2 2P^6 3S^2 3P^2$

P (Z=15): $1S^2 2S^2 2P^6 3S^2 3P^3$

There are two types of semiconductor material, called positive type (P-type) and negative (N-type) semi conductors.



PN junction diode

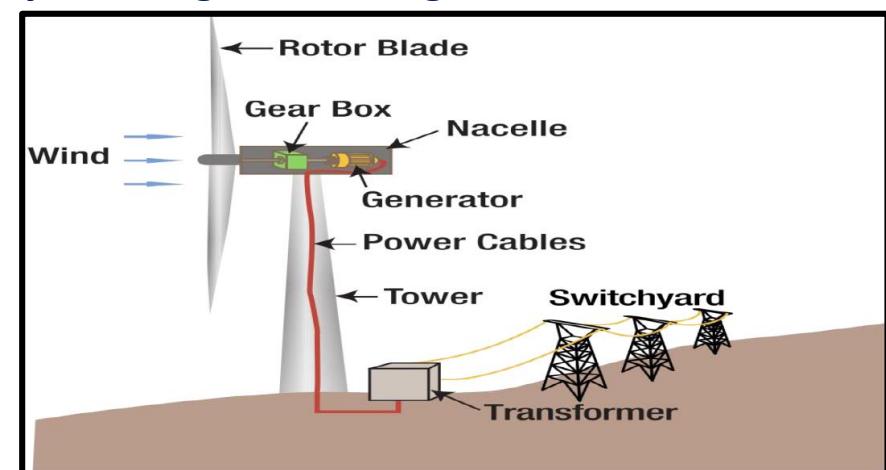


Wind energy:

- The high-speed winds have lot of energy in them as kinetic energy, due to their motion.

Wind mill:

- The wind energy is harnessed by making use of wind mills.
- The blades of the wind mill keep on rotating continuously due to the force of striking wind.
- The blades are linked to gear box and AC generator, which can drive number of machines like water pump heater, flour mills, electric generator etc.
- A large number of wind mills are installed in clusters called wind farms.
- The minimum wind speed required for satisfactory working of a wind generator is 15 km/ hr.



Advantages of wind energy:

- The electricity produced from wind power is said to be eco-friendly because its generation produces no pollution or greenhouse gases.
- It is good for health and environmentally safe
- Available for free of cost.
- Wind is a renewable energy resource, it is inexhaustible
- From wind energy one can locally produce electricity

Disadvantages of wind energy:

- Generates noise pollution
- The amount of electricity generated depends on the strength of the wind - if there is no wind, there is no electricity
- Wind energy is that winds can never be predicted
- Wind mill kills birds
- Tornadoes, hurricanes and cyclones cause heavy damage
- Skilled manpower is required for installation

Hydropower energy



- The flowing in a river is collected by constructing a big dam where the water is stored and allowed to fall from a height.
- The blades of the turbine located at the bottom of the dam move with fast moving water which in turn rotate the generation and producers produces electricity.
- The minimum height of the water falls should be 10 meters
- The hydropower potential of India is estimated to be about 4×10^{11} KW – hours.
- Hydropower does not cause pollution it is renewable.

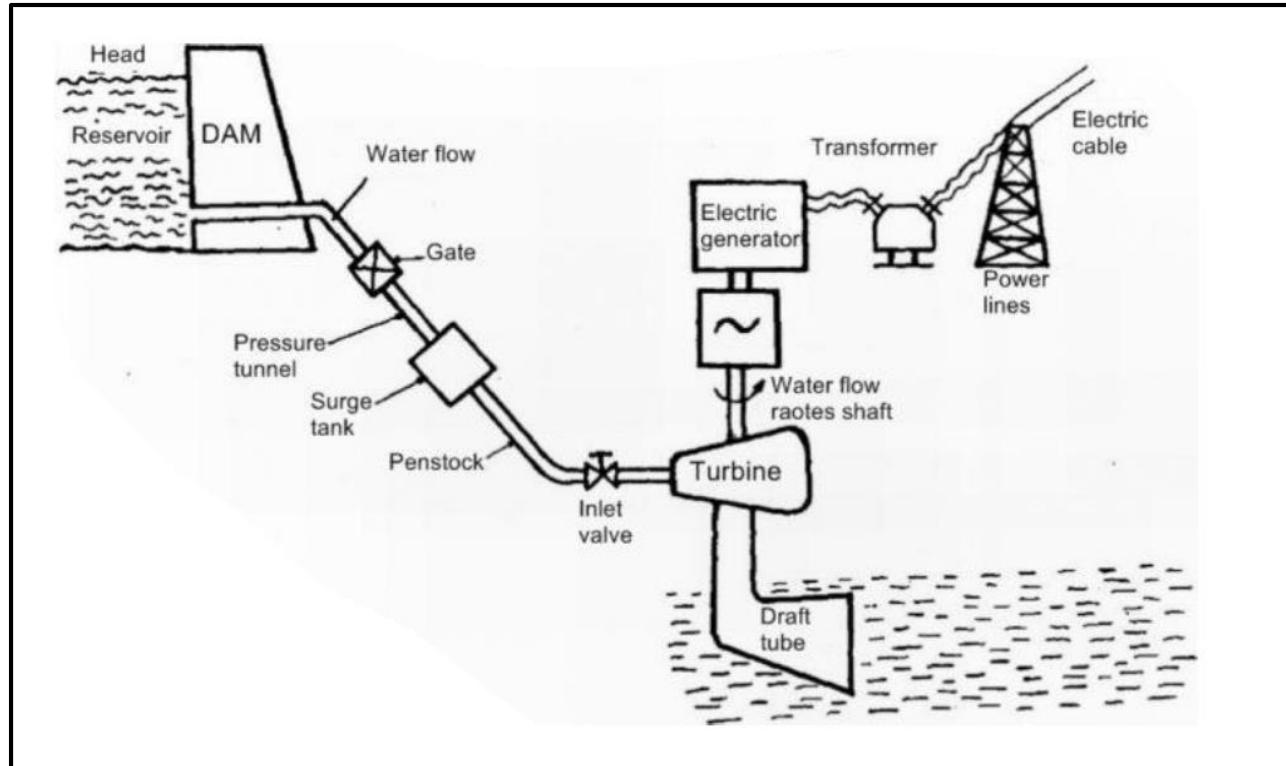
Advantages:

- Hydropower is fueled by water, so it's a clean fuel source
- Hydropower doesn't pollute the air like power plants that burn a fossil fuel, such as coal or natural gas
- Hydropower is a domestic source of energy

Hydropower is generally available as needed; engineers can control the flow of water through the turbines to produce electricity on demand.

Advantages:

- Hydropower plants provide benefits in addition to clean electricity.
- Other benefits may include water supply and flood control





Disadvantages:

- Fish populations can be impacted if fish cannot migrate one place to another place
- Hydropower can impact water quality and flow
- Hydropower plants can cause low dissolved oxygen levels in the water
- When water is not available, the hydropower plants can't produce electricity.
- New hydropower facilities impact the local environment and may compete with other use for the land.
- Humans, flora, and fauna may lose their natural habitat.

Calorific value:

- The primary property of a fuel is its capacity to supply heat
- Fuels essentially consist of carbon, hydrogen, oxygen and some hydrocarbons and the heat that a particular fuel can give is due to the oxidation of carbon and hydrogen
- Further the heat produced is different for different fuels and is termed as its calorific value.

Calorific value of fuel may be defined as “the total quantity of heat liberated, when a unit mass (or volume) of a fuel is burnt completely”.

“Calorific value is the amount of heat liberated by the complete combustion of a unit weight of the fuel and is usually expressed as cal gm⁻¹ or kcal gm⁻¹ or B.Th.U.

The calorific value of a fuel can be defined as “the total quantity of heat liberated when a unit mass of the fuel is completely burnt in air or oxygen”.

There are different units for measuring the quantity of heat. They are

1. Calorie
2. Kilocalorie
3. British thermal unit(B.Th.U)
4. Centigrade heat unit(C.H.U)

Units of calorific value:

For solid or liquid fuels: cal/g or k.cal/kg,

For gaseous fuels: k.cal/cubic meter or k.cal/m³

British Thermal unit (B.T.U) and Centigrade Heat unit (C.H.U)

$$1 \text{ k.cal} = 1000 \text{ cal}$$

$$1 \text{ k.cal} = 3.968 \text{ B.Th.U}$$

$$1 \text{ k.cal} = 3.968 \text{ B.Th.U} = 2.2 \text{ C.H.U}$$

$$1 \text{ B.Th.U} = 252 \text{ cal} = 0.252 \text{ k.cal}$$



- Fuels contains Carbon, Hydrogen, oxygen as main constituents

Latent Heat of vaporization: It is defined as heat required to vaporize one mole of liquid under standard atmospheric pressure

Latent Heat of Condensation: it is energy released when water vapor condenses to form liquid droplets

- Evaporation requires energy
- condensation releases energy



Types of Calorific value:

Which salary is high Gross salary or net salary?

- When Calorific value measured in openly the produced vapor escape into atmosphere and loose some heat energy (**LCV**)
- When Calorific value measured in closed vessel the produced vapor condensed and released vapor energy (**HCV**)
 - **HCV = GCV**
 - **LCV = NCV**

Calorific value: The total quantity of heat liberated, when unit mass of the fuel is completely burnt (Combustion)

Higher or Gross calorific value (HCV/GCV) : The total quantity of heat liberated when a unit mass of the fuel is completely burnt and the combustion products are condensed at room temperature

Less or Net calorific value (LCV/NCV) : The total quantity of heat liberated when a unit mass of the fuel is completely burnt and the combustion products are allowed to escape into environment

Problems on HCV and LCV

Dulong's Formula :

- In this formula the calorific value (HCV) of a fuel is the total calorific value of each of the components.

$$\text{GCV or HCV} = \frac{1}{100} [8080 C + 34500 (H - \frac{O}{8}) + 2240 S] \text{ cal/gm}$$

$$\text{NCV or LCV} = \text{HCV} - [9 \times \frac{H}{100}] \times 587 \text{ cal/gm}$$

- Where C, H, O, S are the percentages of carbon, hydrogen, oxygen and sulphur respectively as determined by the ultimate analysis of coal.

Fuels and Combustion

1. A sample of coal contains Carbon=60%, Hydrogen=6%, Oxygen=33%, Sulphur=0.5%, Nitrogen=0.2% and Ash=0.3%. Calculate the HCV and LCV calorific values of the fuel.

$$\begin{aligned} \text{HCV} &= 1/100[8080 \text{ C} + 34500 (\text{H} - \text{O}/8) + 2240 \text{ S}] \text{ cal/gm} \\ &= 1/100[8080 \times 60 + 34500 (6 - 33/8) + 2240 \times 0.5] \text{ cal/gm} \\ &= 1/100[4,84,800 + 64,687.5 + 1,120] \text{ cal/gm} \\ &= 1/100[5,50,607.5] \text{ cal/gm} \end{aligned}$$

$$\text{HCV} = 5,506.07 \text{ cal/gm}$$

$$\begin{aligned} \text{LCV} &= \text{HCV} - 9 \times \text{H}/100 \times 587 \\ &= 5.506.07 - 9 \times 6 / 100 \times 587 \\ &= 5.506.07 - 316.98 = 5198.095 \text{ cal/gm} \end{aligned}$$

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Fuels and Combustion

2. Calculate the gross and net calorific values of a coal sample having the following composition
**Carbon=80%, Hydrogen=7%, Oxygen=3%,
Sulphur=3.5%, Nitrogen=2% and Ash=5%.**

$$\begin{aligned} \text{GCV} &= 1/100[8080 \text{ C} + 34500 (\text{H} - \text{O}/8) + 2240 \text{ S}] \text{ cal/gm} \\ &= 1/100[8080 \times 80 + 34500 (7 - 3/8) + 2240 \times 3.5] \text{ cal/gm} \\ &= 1/100[646400 + 228562.5 + 7840] \text{ cal/gm} \\ &= 1/100[882802.5] \text{ cal/gm} \end{aligned}$$

$$\text{GCV} = 8,828.025 \text{ cal/gm}$$

$$\begin{aligned} \text{NCV} &= \text{GCV} - 9 \times \text{H}/100 \times 587 \\ &= 8,828.025 - 9 \times 7 /100 \times 587 \\ &= 8,828.025 - 369.81 = 8458.21 \text{ cal/gm} \end{aligned}$$

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Fuels and Combustion

3. A sample of coal contains the following composition Carbon=84%, Hydrogen=12%, Oxygen=2%, Sulphur =1% and the remainder being ash. Calculate the gross and net calorific values of the fuel.

$$\begin{aligned} \text{GCV} &= 1/100[8080 \text{ C} + 34500 (\text{H} - \text{O}/8) + 2240 \text{ S}] \text{ cal/gm} \\ &= 1/100[8080 \times 84 + 34500 (12 - 2/8) + 2240 \times 1] \text{ cal/gm} \\ &= 1/100[678720 + 413999.7 + 2240] \text{ cal/gm} \\ &= 1/100[1094959.7] \text{ cal/gm} \end{aligned}$$

$$\text{GCV} = 10949.59 \text{ cal/gm}$$

$$\begin{aligned} \text{NCV} &= \text{GCV} - 9 \times \text{H}/100 \times 587 \\ &= 10949.59 - 9 \times 2 /100 \times 587 \\ &= 10949.59 - 105.66 = 10843.93 \text{ cal/gm} \end{aligned}$$

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Fuels and Combustion

1. A sample of coal weighing 1.98 gm, on heating for 1 hour at 110°C for one hour, left a residue weighed 1.78gms. The residue was heated in a suitable crucible with a lid at a at 950°C for exactly 7 min. The residue weighed 1.59 gms. The residue was heated in presence of air till a constant weight was obtained. This residue weighed 0.231 gms. Calculate the proximate analysis of coal.
2. A sample of coal was analysed as follows: 0.9824 g of an air dried coal sample was weighed in a silica crucible. After heating for 1 hour at $105 - 110^{\circ}\text{C}$, the dry coal residue weighed 0.9668g. The residue was covered with a vented lid and then heated strongly for exactly 7 min. at 950°C . The residue weighed 0.7900g. The crucible was then heated strongly in air until a constant weight was obtained. The last residue was found to weigh 0.1200g. Calculate the proximate analysis of the coal sample

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Fuels and Combustion

- 1. Calculate the gross and net calorific values of a coal sample containing 84% of carbon, 1.5 % of Sulphur, 6% of nitrogen, 5.5% of hydrogen and 8.4% of oxygen. The calorific value of carbon, hydrogen and Sulphur are 8080 kcal/kg, 34500 kcal/kg and 2240 kcal/kg, respectively, and latent heat of steam is 587 cal/g.**

- 2. Determine the gross and net calorific values of a coal sample having the following composition Carbon=87%, Hydrogen=5%, Oxygen=3%, Sulphur=0.5%, Nitrogen=0.5% and Ash=4%. and the latent heat of steam is 587 cal/gm.**

- 3. Determine the gross and net calorific values of a coal sample having the following composition Carbon=80%,**
 - Hydrogen=7%,**
 - Oxygen=3%,**
 - Sulphur=3.5%,**
 - Nitrogen=2% and**
 - Ash=5%..**

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Fuels and Combustion



4. Determine the gross and net calorific values of a coal sample having the following composition Carbon=80%, Hydrogen=7%, Oxygen=3%, Sulphur=3.5%, Nitrogen=2% and Ash=5%.

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Theoretical calculation of calorific value:

The calorific value of a fuel can approximately be calculated by noting the amount the components constituting the fuel. In such cases we can into consideration the heat of the reaction which is defined as the amount of heat produced when one gram molecule of the reactants is burnt in the presence of oxygen.

C, H, O, S are % in each fuel

100 Kg fuel contain C Kg carbon

1Kg fuel contains $\frac{C}{100}$ kg of carbon



 12 gm 32 gm 44 gm

12 Kg of carbon liberates 96960 calories of heat

1 Kg of carbon liberates = ? = $96960 / 12 = 8080 \text{ calories}$

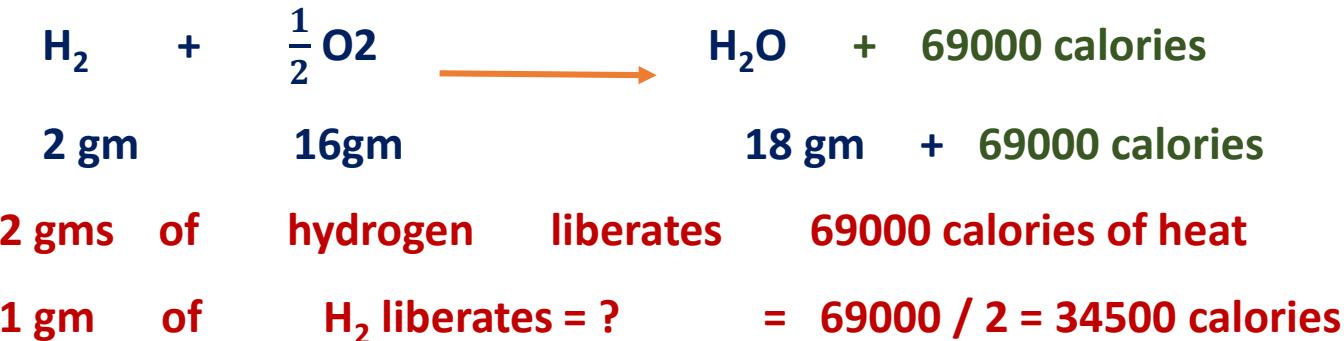
The HCV of the carbon is 8080 cal

1Kg carbon has HCV = 8080 cal

$\frac{C}{100}$ kg carbon has HCV = $8080 \times \frac{C}{100}$

For Hydrogen and oxygen

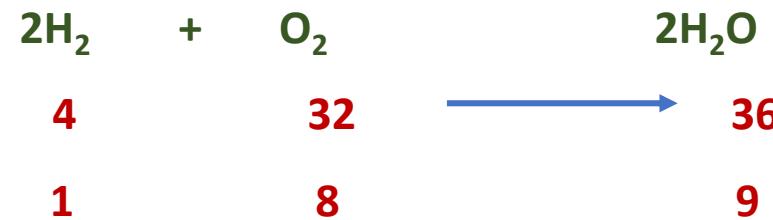
➤ H₂ burns in the presence of O₂ resulting in the formation of water



HCV of hydrogen is 34500 Kcal/Kg

- But if oxygen present in fuel then it is assumed that it must be combined with hydrogen and form water
- The amount of hydrogen which gets combined with oxygen do not take part in combustion and known as Fixed Hydrogen
- So the amount of Hydrogen available for combustion is some what lower than the total hydrogen present in fuel
- Amount of Hydrogen available for combustion = Total hydrogen in fuel – fixed hydrogen
- Total Hydrogen in fuel = H
- Total oxygen in fuel = O

➤For fixed Hydrogen.



8 part oxygen combine with 1 part H

O part oxygen combine with $\frac{1}{8} \times O$ part H = $\frac{o}{8}$ = fixed hydrogen

Therefore fixed hydrogen = $\frac{\text{mass of oxygen in the fuel}}{8}$

Amount of hydrogen available for combustion = Total hydrogen - Fixed hydrogen = $[\text{H} - \frac{o}{8}]$

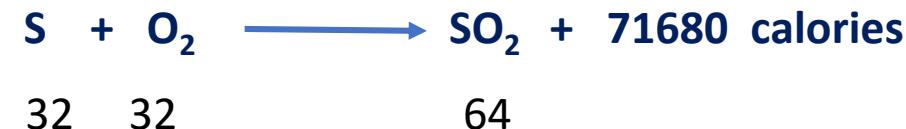
100 Kg fuel contains combustible Hydrogen = $[\text{H} - \frac{o}{8}]$

1 Kg fuel contains combustible Hydrogen = $[\text{H} - \frac{o}{8}] \times \frac{1}{100}$

We know that HCV of Hydrogen fuel is 34500 Kcal/kg

1kg hydrogen has calorific value 34500 Kcal/kg

= $[\text{H} - \frac{o}{8}] \times \frac{1}{100}$ kg hydrogen has cv = $34500 \times [\text{H} - \frac{o}{8}] \times \frac{1}{100}$



32 gms of S produces 71680 calories

1 gm of S produces = $71680 / 32 = 2240$ calories.

We know that HCV of S = 2240 Kcal/kg

1 kg S has CV = 2240

$$\frac{S}{100} \text{ kg S has } CV = 2240 \times \frac{S}{100} = \frac{1}{100}[2240S]$$

The calorific value of the components of the fuels

constituent	calorific value (cal/gm)
Carbon	8080
Hydrogen	34500
Sulphur	2240

Total HCV of fuel = CV of [C + H + S] present in fuel

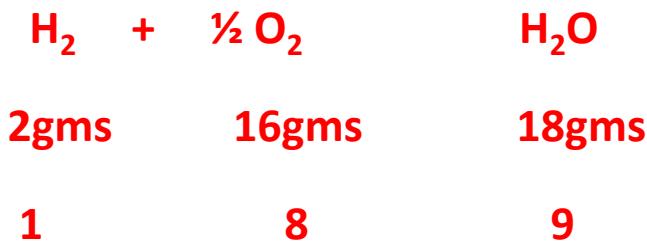
$$= [8080x \frac{C}{100} + 34500 (H - \frac{O}{8})x \frac{1}{100} + 2240x \frac{S}{100}]$$

$$= \text{HCV} = \frac{1}{100} [8080C + 34500 (H - \frac{O}{8})x \frac{1}{100} + 2240xS] \text{ Kcal/Kg}$$

Net calorific value is the excluding the latent heat of condensation of water from gross calorific value (the weight of water formed is nine times the weight of hydrogen in the fuel).

Therefore,

- LCV or NCV = HCV – Latent heat of water vapor formed
- Since 1 part by mass of hydrogen produces 9 parts by mass of water as given by the equation



Hence LCV = HCV – (Mass of hydrogen x 9 x latent heat of steam).

- Latent heat of steam is 587 kcal/kg of water vapor formed at room temperature (Latent heat of vaporization is the amount of heat required to convert 1 Kg of liquid to vapor or steam)

➤ Net calorific value is the gross calorific value excluding the latent heat of steam and percentage of hydrogen.

$$NCV = GCV - \frac{9 \times H}{100} \times 587$$

$$= GCV - (0.09 \times H \times 587)$$

Where H= % of hydrogen in the fuel

Fuels

Example 4

A fuel contains C = 75%; H = 4%; O = 5%; S = 7%; remaining ash. Calculate the minimum quantity of air required for complete combustion of 1 kg of the fuel.

Solution

1. 1 kg of the fuel contains

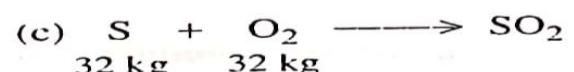
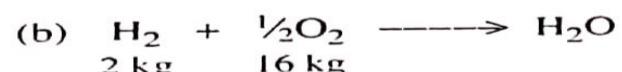
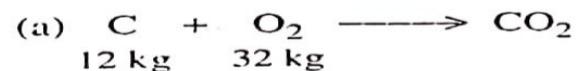
$$\frac{75}{100} = 0.75 \text{ kg of carbon}$$

$$\frac{4}{100} = 0.04 \text{ kg of hydrogen}$$

$$\frac{5}{100} = 0.05 \text{ kg of oxygen}$$

$$\frac{7}{100} = 0.07 \text{ kg of sulphur}$$

2. The combustion equations of the various elements present in the fuel are as follows



(a) 12 kgs of carbon requires 32 kgs of oxygen

Fuels



$$\therefore 0.75 \text{ kg of carbon requires} = \frac{32 \times 0.75}{12}$$

$$= 2 \text{ kg of oxygen}$$

(b) 2 kgs of hydrogen requires 16 kgs of oxygen

$$\therefore 0.04 \text{ kg of hydrogen requires} = \frac{16 \times 0.04}{2}$$

$$= 0.32 \text{ kg of oxygen}$$

(c) 32 kgs of sulphur requires 32 kgs of oxygen

$$\therefore 0.07 \text{ kg of sulphur requires} = \frac{32 \times 0.07}{32}$$

$$= 0.07 \text{ kg of oxygen}$$

$$\text{Total amount of O}_2 \text{ required} = 2 + 0.32 + 0.07 = 2.39 \text{ kgs}$$

But, the amount of O₂ already present in the fuel = 0.05 kg

∴ Net amount of O₂ required = Total amount of O₂ - O₂ already present in the fuel.

$$= 2.39 - 0.05 = 2.34 \text{ kgs}$$

We know that

23 kgs of O₂ is supplied by 100 kgs of air

$$2.34 \text{ kgs of O}_2 \text{ is supplied by} = \frac{100 \times 2.34}{23}$$

$$= 10.174 \text{ kgs of air}$$

∴ The minimum amount
of air required for complete
combustion of 1 kg of a fuel } = 10.174 kgs

1. Calculate the minimum amount of air required for complete combustion of 1kg of coal sample having the following compositions: C=80%, S=2%, H=5%, N=1% and ash=4%. Oxygen in air is 23% by weight.
2. The percentage composition of a sample of bituminous coal was found to be as under: C = 75.4%; H = 5.3%; O = 12.6%; N = 3.2%; S = 1.3% and Ash = rest. Calculate the minimum weight of air necessary for complete combustion of 1 Kg of coal. Oxygen in air is 23% by weight.
3. A sample of coal was found to have the following percentage composition: C=75%, S=1.2%, H=5.2%, N=3.7%, O=12.8% and ash=2.1%. Oxygen in air is 23% by weight. Calculate the minimum amount of air required for complete combustion of 1kg of coal sample.





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ENGINEERING CHEMISTRY

TOPIC: Properties of lubricants

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TOPICS:

- Lubricants
- Properties of lubricants: viscosity, flash and fire point, cloud and pour point.

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Lubricant: Lubricant is a substance used in between two moving surfaces to reduce the friction.

Lubrication: Lubrication is a process of reducing friction and wear between two moving surfaces by adding lubricant in between them.

Functions of a lubricant:

- ✓ It prevents the direct contact between the moving surfaces & reduces wear and tear & surface deformation of the concerned parts.
- ✓ It reduces wastage of energy so that efficiency of the machine enhanced.
- ✓ It reduces the frictional heat & prevents the expansion of metals.
- ✓ It acts as a coolant by removing the frictional heat generated due to rubbing of surfaces.
- ✓ It minimizes corrosion.



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Properties of lubricants:

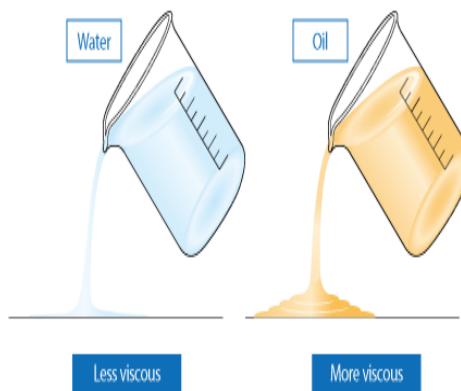
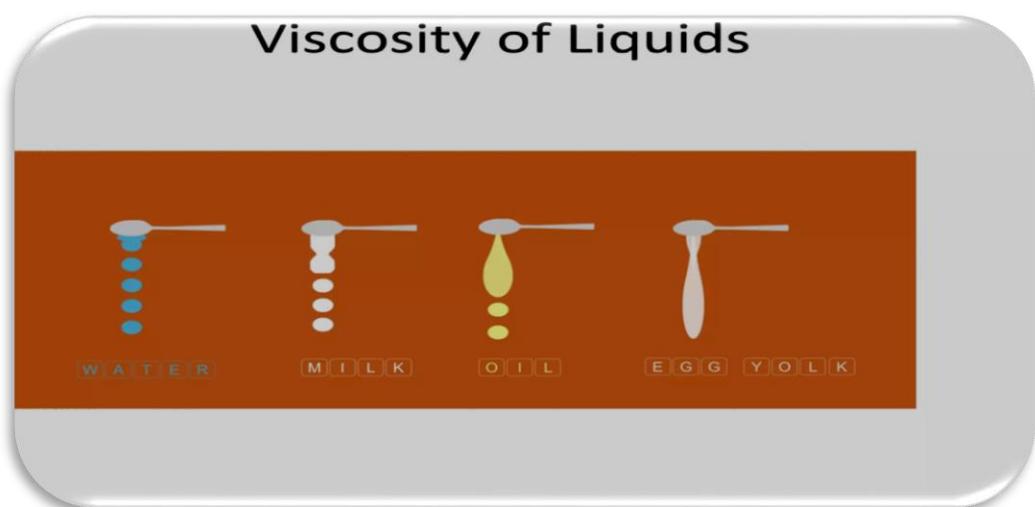
1) Viscosity: viscosity is a measure of the internal resistance of a liquid during its flow. It is expressed in centipoise.

The viscosity of an oil is the time in seconds for a given quantity of oil to pass through a standard orifice under the specified conditions.

Significance: If the viscosity of the lubricating oil is too high the movement of the machine is restricted due to excessive friction.

If the viscosity of the lubricating oil is too low, the liquid oil film can not be maintained and excessive wear will take place.

A good lubricant should have moderate viscosity



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2. Viscosity index: The viscosity of oil decreases with increase in temperature.

- If the viscosity of oil decreases rapidly with the increase in temperature it has **low viscosity index**.
- If the viscosity of an oil is slightly affected with the increase in temperature, it has **higher viscosity index**.
- For every 1°C rise in temperature the viscosity index decreases by 2%.

A good lubricant should have a high viscosity index.

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2) Flash point: It is the lowest temperature at which the oil gives off enough vapour that ignites for a moment, when a small flame is brought near it.

Fire point: It is the lowest temperature at which the vapour of the oil burns continuously for at least 5 seconds, when a small flame is brought near it. Generally, the fire point is 5- 40° C higher than flash point.

Significance: A knowledge of flash and fire point is useful in providing protection against fire hazard during transport and storage.

Lubricating oils of paraffinic base possess higher flash points than those of naphthenic base. Hence the determination of flash & fire points is helpful in identifying the type of lubricating oil.

A good lubricating oil should have flash & fire points higher than the operating temperature of the machine.



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Determination of Flash and Fire points:

Description:

1. The apparatus consists of a brass cup
2. This cup should be dried and no moisture should be allowed to remain inside it. The level up to which oil is to be filled in the cup is marked at about 1 cm below the top of the cup.
3. The lid of the cup is provided with four openings of standard sizes which are meant for special type of stirrer, a standard thermometer, an inlet for air and the fourth for introducing a flame.
4. At the top of the cup, a shutter is provided. By moving the shutter, openings for the test flame and air are opened and the flame exposure device dips into the opening over the surface of the oil.
5. The whole assembly is kept on an electrical heater which can be heated in a controlled manner.

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LUBRICANTS

Determination of Flash and Fire points:

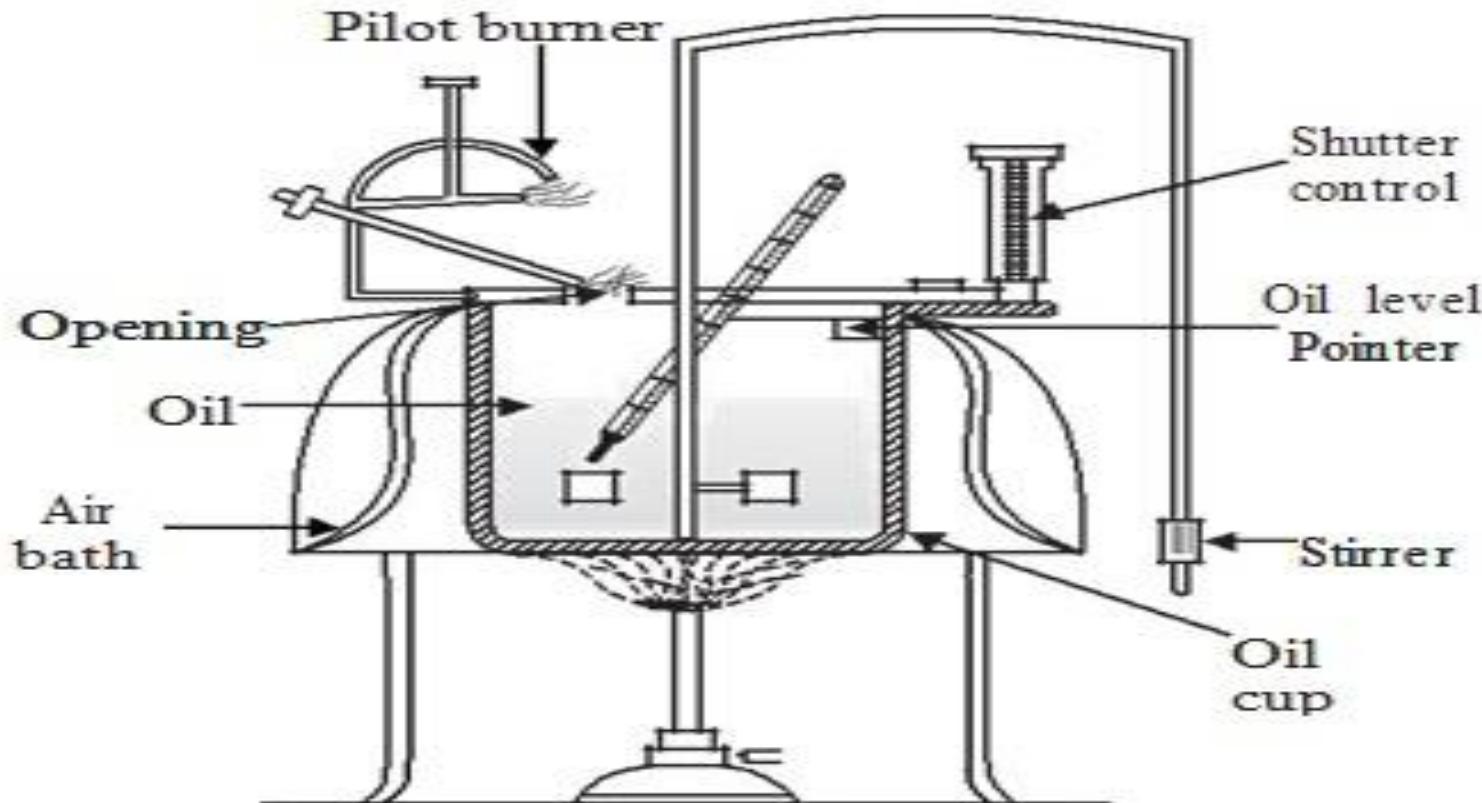


Fig. Pensky Marten's flash point apparatus

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Determination of Flash and Fire points:



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Procedure:

- Clean the oil cup thoroughly and fill the oil cup with the sample oil to be tested up to the mark.
- Insert the thermometer into the oil cup through a provision, which measures the rise of oil temperature.
- Using the Energy regulator, control the power supply given to the heater and rate of heating.
- The oil is heated slowly when temperature of oil rises, it is checked for the flash point for every one degree centigrade rise in temperature.

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LUBRICANTS

Procedure:

- After determining the flash point, the heating shall be further continued.
- The temperature at which time of flame application which causes burning for a period at least 5 seconds shall be recorded as the fire point.
- Repeat the experiment 2 or 3 times with fresh sample of the same oil.
Take the average value of flash and fire points.

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LUBRICANTS

Determination of Flash and Fire points:

(a)



(b)



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3) CLOUD & POUR POINT:

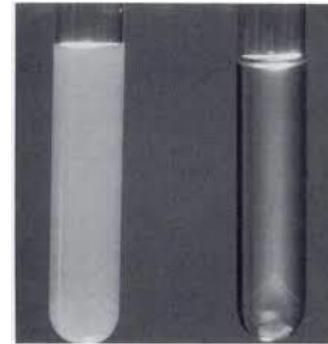
cloud point: When an oil is cooled slowly the temperature at which the oil becomes cloudy in appearance is called its cloud point.

or The temperature at which the impurities begin to separate from the solution and lubricating oil becomes cloudy or hazy in appearance is called cloud point.

Pour point: The temperature at which the oil ceases to flow or pour is called its pour point.

Significance: Most of the petroleum based lubricating oils contain dissolved paraffin wax & asphaltic impurities. When the oil is cooled these impurities undergo solidification which cause jamming of the machine so the cloud & pour points indicate the suitability of the lubricants in cold condition.

A good lubricant must have low cloud & pour points.



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Cloud and Pour Points:

- In order to understand the suitability of lubricants in cold conditions, we make use of cloud point and pour points.
- Usually lubricating oils derived from petroleum contains dissolved paraffin wax and other asphaltic impurities.
- These impurities tend to separate out of the oil at lower temperatures.
- Further solidification of lubricant normally causes jamming of the machine.

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Cloud and Pour Points:

- The cloud-point is the temperature at which crystallization of solids in the form of a cloud or haze first becomes noticeable, when the oil is cooled in a standard apparatus at a standard rate.
- The pour point is the temperature at which the oil just ceases to flow when cooled at a standard rate in a standard apparatus.

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Cloud and Pour Points :

- The pour point has a greater significance for lubricating oils.
- It determines the suitability of a lubricant or a hydraulic oil for low temperature installations.
- Important examples are refrigerator plants and air-craft engines, which may be required to start and operate at sub-zero temperature.

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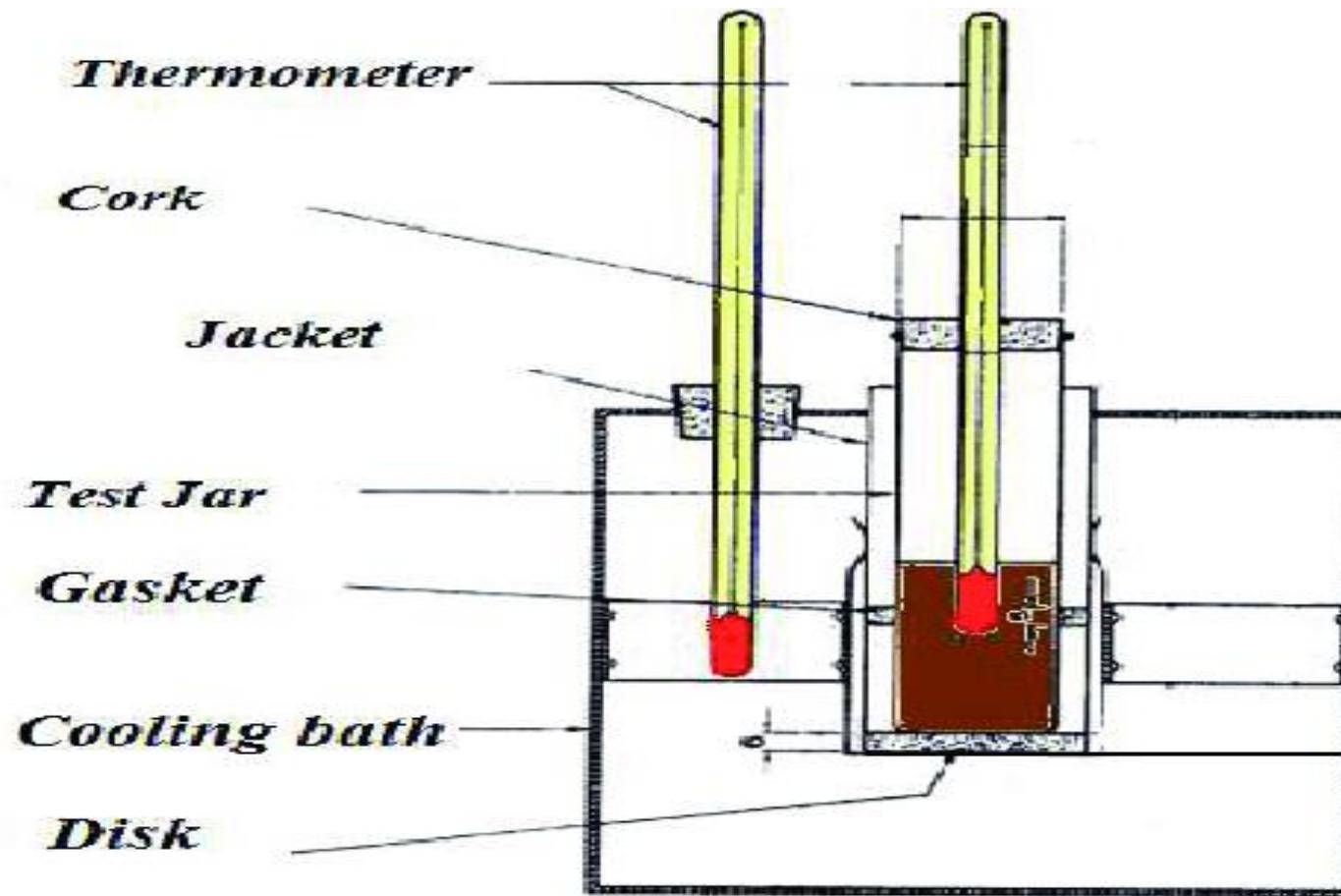
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Cloud and Pour Point:

- The apparatus used for conducting both these tests.
- 1. The apparatus consists of a flat bottomed tube enclosed in an air jacket.
- 2. This tube is placed in a glass jar having suitable freezing mixture and a thermometer.
- 3. Different freezing mixtures are tried depending on the type of lubricating oil.
- 4. Mixture of ice and salt, ice and water, ice and CaCl_2 , solid CO_2 and acetone are commonly used.

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LUBRICANTS



Cloud and Pour Points

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Cloud and Pour Points:

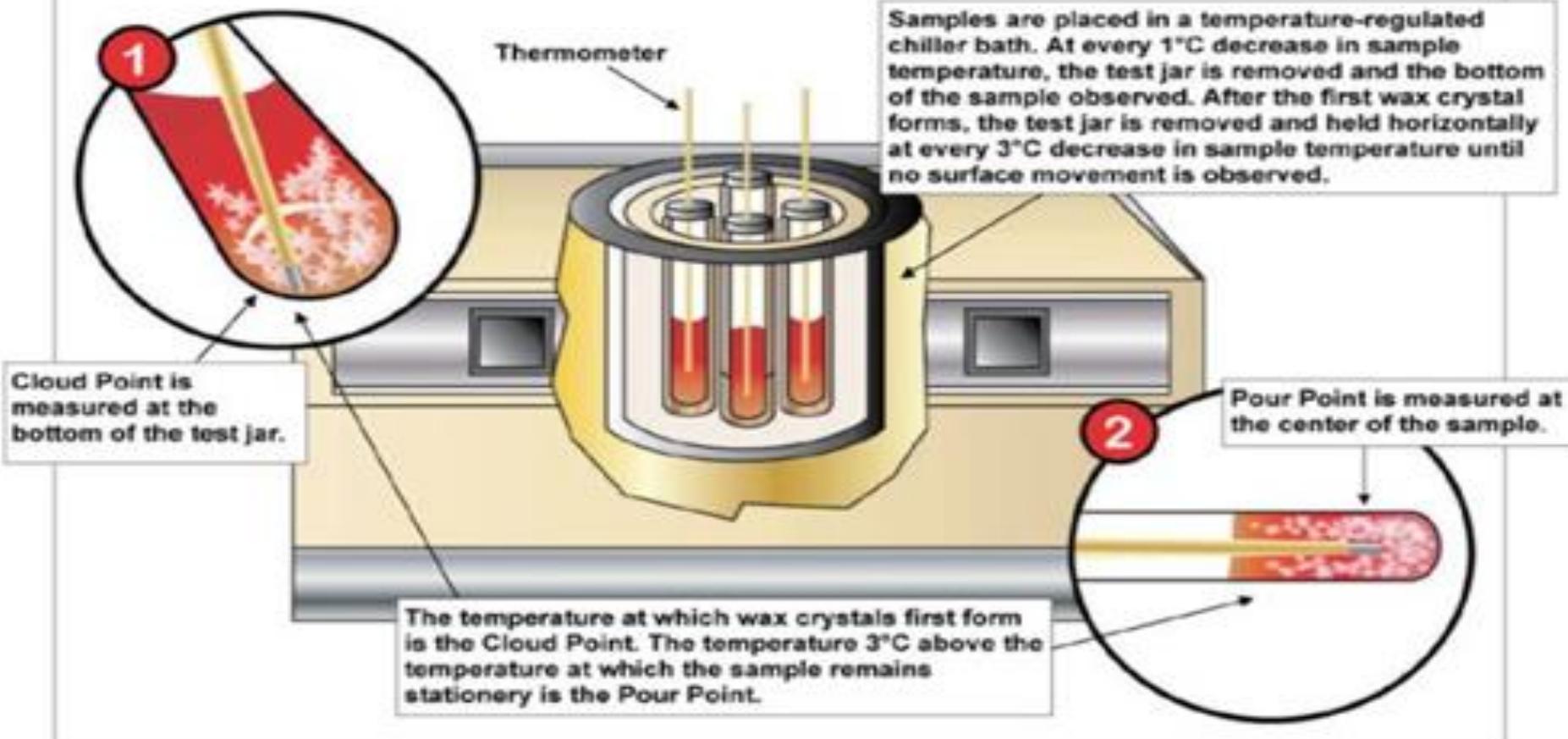
Procedure:

- The oil is first dried by shaking it with small amount of anhydrous sodium sulphate and it is filtered through filter papers.
- The oil is filled up to the mark inside the flat bottomed glass tube and the cork is fitted with a thermometer dipping inside the oil.
- The tube is then kept freezing mixture. The temperature of the oil falls on cooling. The tube is taken out of the freezing mixture, for every 1 °C fall of temperature of the oil and then inspected for a moment.

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LUBRICANTS

CLOUD & POUR POINT



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Cloud and Pour Points:

- The temperature at which cloudiness or haziness is first noticed represents the cloud-point.
- As the cooling is further continued ,at a particular temperature the oil just ceases to flow or pour as observed from tilting the test jar.
- This particular temperature at which the oil does not flow in the test jar for 5 seconds on tilting in horizontal position is reported a the pour point.

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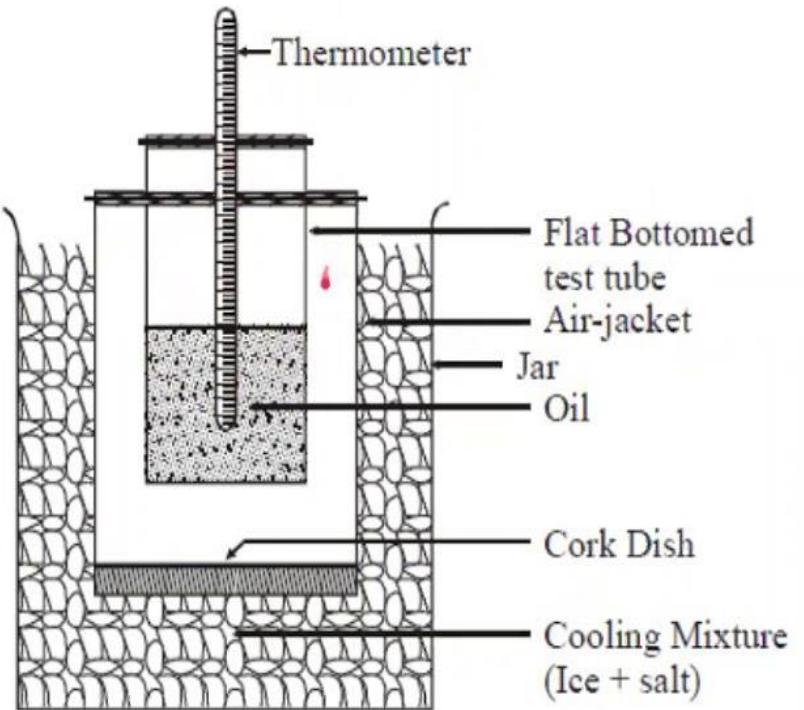
Cloud and Pour Points:

- Cloud point is useful for estimating the temperature at which filter screens in the fuel intake system of diesel engines might become clogged because of separation of wax.
- Pour point values of petroleum and non-petroleum lubricants are necessary when functioning under sub-freezing conditions.
- A good lubricating oil should possess low cloud and pour points.

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Cloud and Pour Point Apparatus



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4) Oiliness :

It is one of the most important property of lubricants which posses by oils. It is a property by virtue of which an oil remains adhered to the lubricating surface.



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Oiliness of lubricants:

- It is the property of the lubricant to stick on to the surface under the conditions of high speed and heavy load.
- oiliness is directly related to specific gravity of oil.
- Lower the specific gravity(density) higher is oiliness.
- The oils are generally either saturated and unsaturated fatty acids.
- The vegetable/animal oils are with high oilness compared to mineral oils.
- Oilness is an oil enhancement property provided through the use of chemical additives known as antiwear agents. These are generally used in extreme pressure lubrication.

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Understanding these properties and selecting lubricants based on the specific requirements of an application is crucial for ensuring optimal performance and longlife of machinery.



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TOPICS:

- Lubricants
- characteristics of lubricants
- Mechanism of lubrication – thick film, thin film, extreme pressure lubrication

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Lubricants:

- ✓ In all type of machines, the moving surfaces rub against each other. Due to this rubbing, a resistance is offered to their movement.
- ✓ This resistance is known as friction. This friction will cause a lot of wear & tear of surfaces of moving parts.
- ✓ Due to the friction large amount of energy is dissipated in the form of the friction, large amount of energy is dissipated in the form of heat, thereby the efficiency of machine gets reduced.



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Lubricant: Lubricant is a substance used in between two moving surfaces to reduce the friction.

Lubrication: Lubrication is a process of reducing friction and wear between two moving surfaces by adding lubricant in between them.

Functions of a lubricant:

- It prevents the direct contact between the moving surfaces & reduces wear, tear & surface deformation of the concerned parts.
- It reduces wastage of energy so that efficiency of the machine enhanced.
- It reduces the frictional heat & prevents the expansion of metals.
- It acts as a coolant by removing the frictional heat generated due to rubbing of surfaces.
- It minimizes corrosion.



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Characteristics of a good lubricant:

- ❖ A good lubricant should not undergo any decomposition, oxidation, reduction at high temperature.
- ❖ A good lubricant should have higher flash and fire points than the operating temperature.
- ❖ A good lubricant should not corrode the machine parts.
- ❖ A good lubricant should have high oiliness, viscosity index, aniline point.



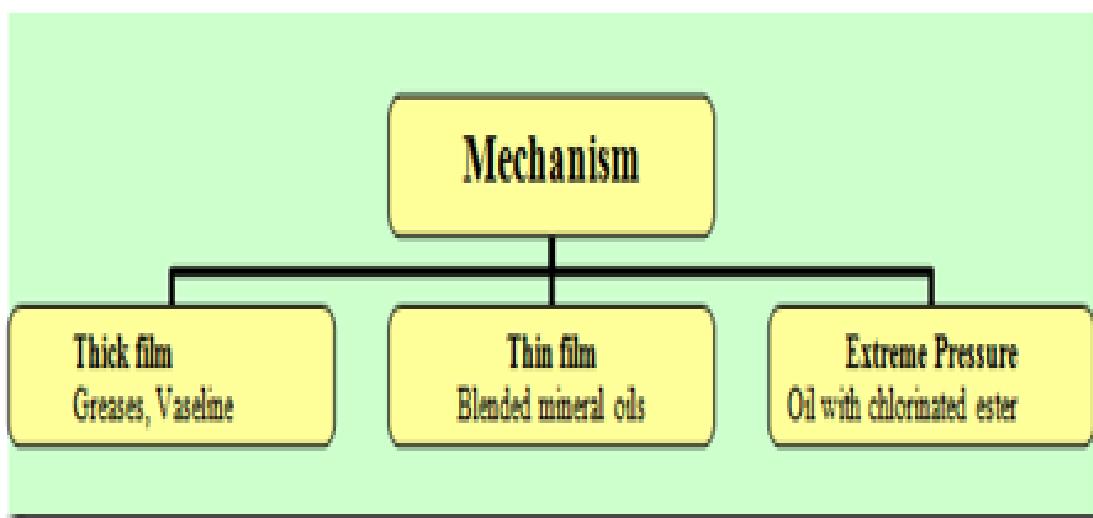
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Mechanism of lubrication (Types of lubrication):

Lubrication film between the two contact surfaces is thick enough and two contact surfaces are separated completely by viscous oil film. At this time, frictional force of two contact surfaces are determined by viscous resistance of lubricant and it can be take a very small value (coefficients of friction can be 0.0001).

- 1) Thick film or fluid film or hydrodynamic lubrication
- 2) Thin – film or boundary lubrication
- 3) Extreme pressure lubrication



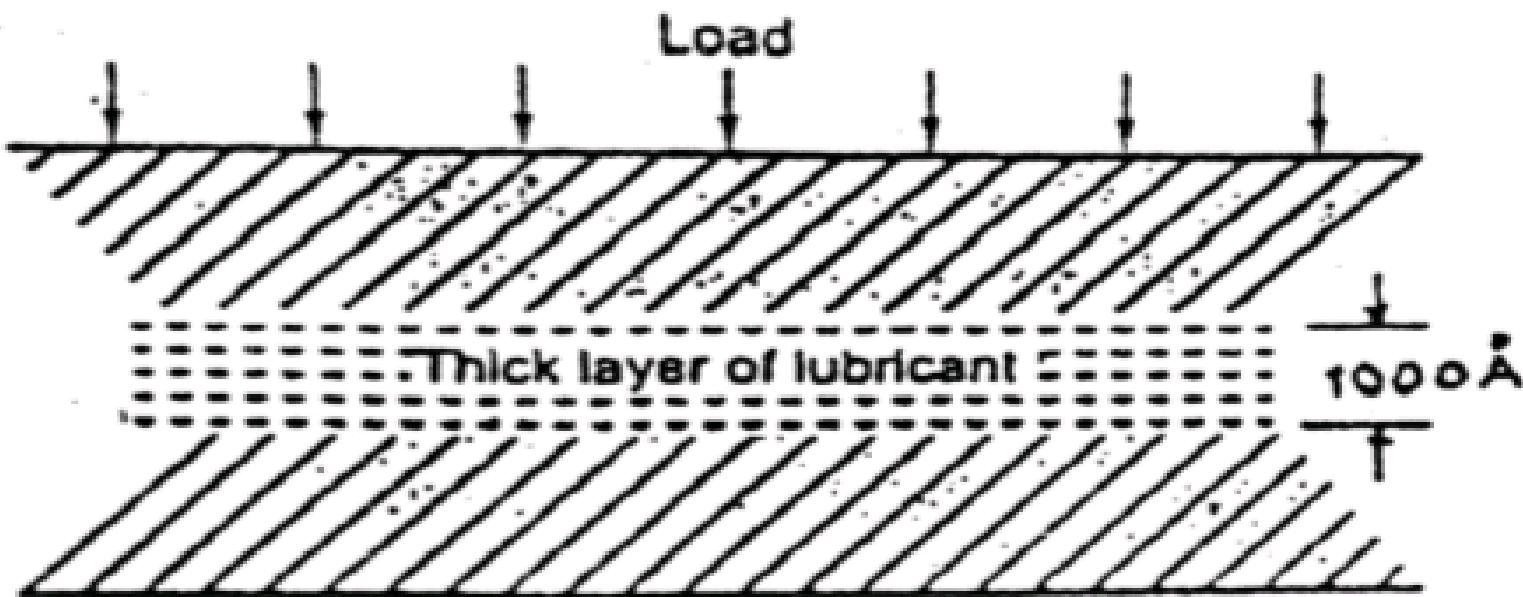
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Thick film or fluid film or hydrodynamic lubrication:-

Condition: Under low load & high speed

- Under low load & high speed, a thick fluid film of lubricant is maintained between the two solid surfaces. The thickness of fluid film is at least 1000 \AA .
- Since the thick fluid film separates the two solid surfaces there is no direct contact between the solid surfaces.
- This reduces wear & tear is no direct contact between the solid surfaces. This reduces wear & tear. The coefficient of friction in such cases is as low as 0.001 to 0.03.



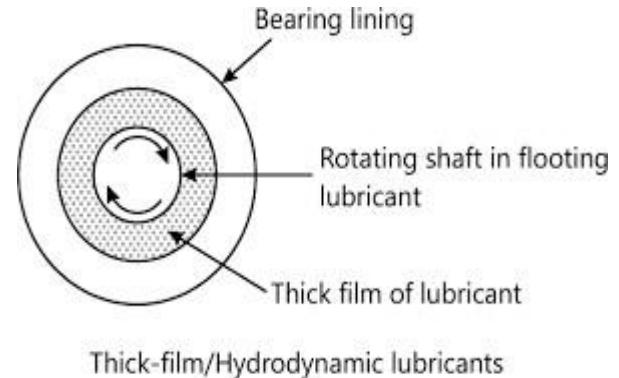
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Thick film or fluid film or hydrodynamic lubrication:-

Ex: consider the rotation of a shaft with respect to a stationary bearing.

- When a lubricant is added to the system, it occupies the annular surface between the shaft and the bearing and forms a hydrodynamic remain & prevents contact between the two solid surfaces.
- When the load becomes very high, the lubricant will be squeezed out of the wedge and friction will occur.



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Thick film or fluid film or hydrodynamic lubrication:-

Condition: Under low load & high speed

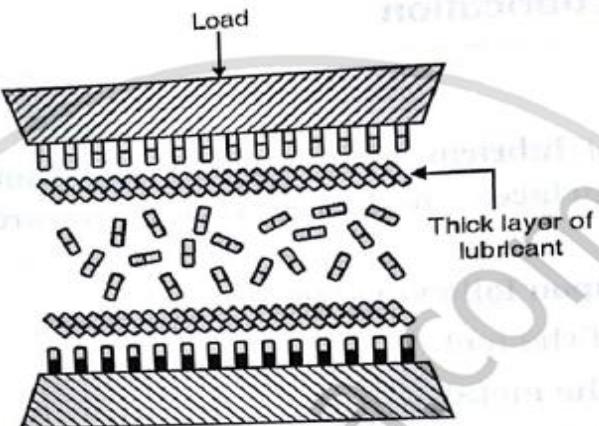
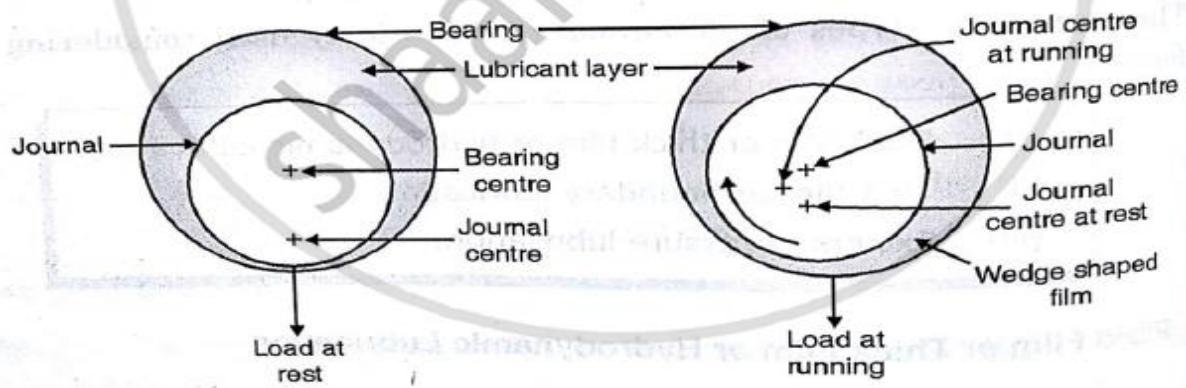


Fig. 3.3.1(a) : Hydrodynamic lubrication or fluid film lubrication



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The hydrocarbon lubricating oils contain small quantities of unsaturated hydrocarbons, which gets oxidized under working conditions and form gummy products. To prevent this antioxidants like aminophenols are added to lubricating oils.

Delicate instruments, light machines, watches, clocks, guns, sewing machines, scientific instruments etc. are provided with this type of lubrication.

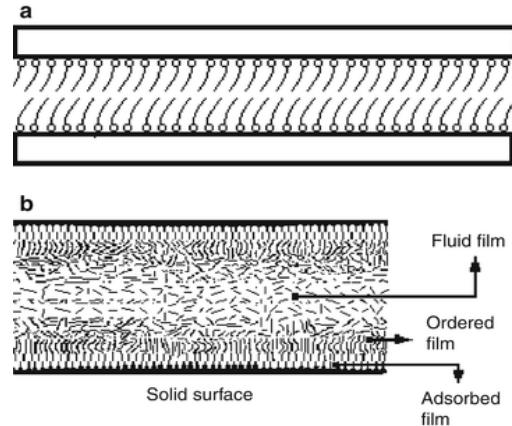
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Thin – film or boundary lubrication:-

Condition: under high load & slow speed.

- Under the conditions of high load and slow speed, a continuous fluid film cannot be maintained between the moving surfaces.
- Under such conditions, the thickness of the fluid film should be less than 1000 \AA^0 . such a thin film, consists of 2 or 3 molecules thick.
- To form a thin film the lubricant has to be adsorbed on the metal surfaces by physical or chemical forces.
- In some cases, the lubricant will react chemically with the metal surface forming a thin film of metal soap, which will act as a lubricant.
- This thin film is known as boundary film. The co – efficient of friction in such cases is around 0.05 to 0.15.



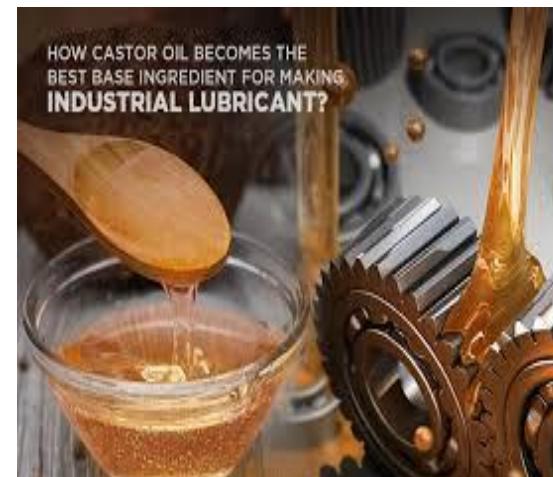
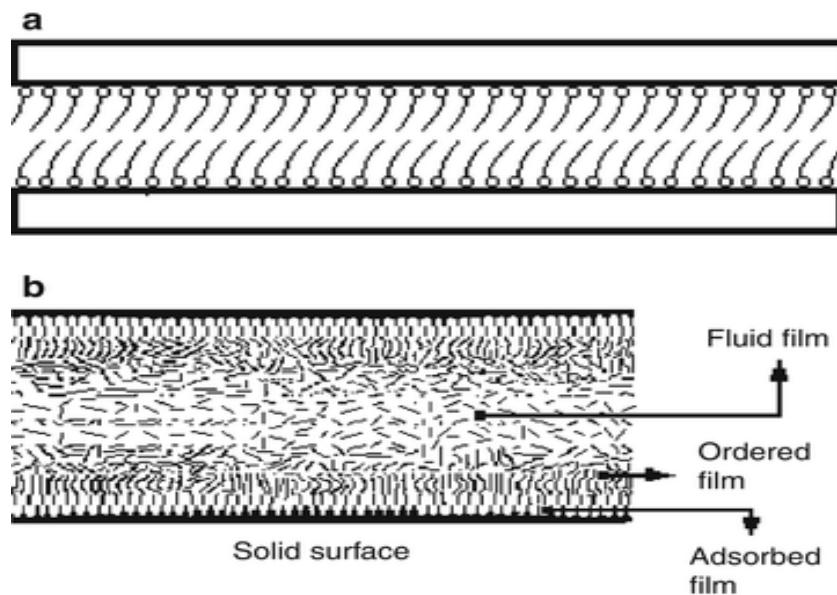
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Thin – film or boundary lubrication:-

The effectiveness of boundary lubrication depends on the oiliness of the lubricant. Oiliness is the ability of a lubricant to stick on to the surface. Vegetable oil and their fatty acids have more oiliness.

Ex: Oleic acid ($C_{17}H_{33}COOH$), stearic acid ($C_{17}H_{35}COOH$). The polar group carbonyl (- COOH) of these oils reacts with the metal surface to form a continuous thin film of lubricant. Hydro carbon chain of the fatty acid gets oriented out wards in a perpendicular direction.



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The conditions of the lubricant which ought to be satisfied for boundary lubrication are:

1. Long hydrocarbon chains
2. Polar groups to promote wetting or spreading over the surface.
3. High viscosity index.
4. Good oiliness.
5. Low pour point and oxidation.
6. Active functional groups which can form chemical bonds with the metals or other surfaces.
7. Resistant to heat.

Solid lubricants, greases and oils with proper additives, function as lubricants in this type of lubrication.

For example graphite, molybdenum disulphide(MoS₂),mineral oils with additives of fatty acids and vegetable and animals oils and their soaps.

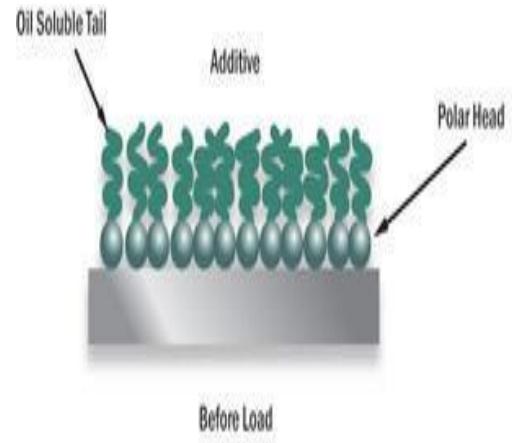
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Extreme pressure lubrication:-

Condition: under high load & high speed.

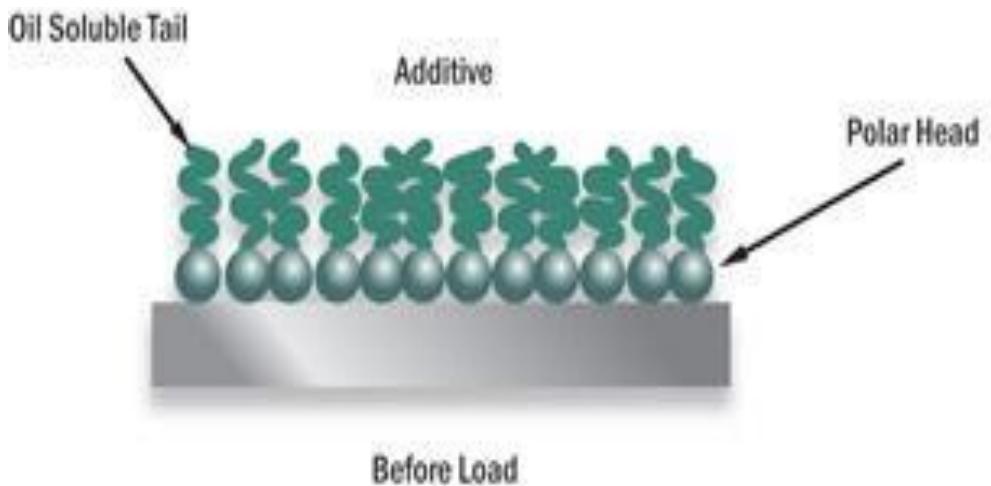
- Under the conditions of high load (high pressure) and high speed, more heat is generated between the moving surfaces.
- As a result of this, the liquid lubricant fails to stick and undergoes decomposition or evaporation. Under these conditions, for effective lubrication, special additives known as extreme pressure additives are used along with the lubricants.
- Important extreme pressure additives are organic compounds having active radicals or groups such as chlorine (ex: sulphurised oils) etc.
- These compounds react with metallic surfaces to form metallic chlorides, sulphides etc. These metallic compounds possess high melting points & serve as good lubricant under extreme pressure conditions.



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Extreme pressure lubrication:-

Condition: under high load & high speed.



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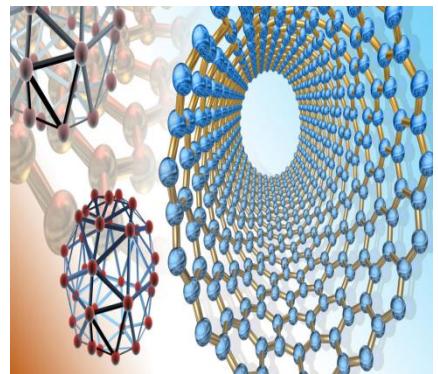
- Nano materials Introduction
- Preparation of nanoparticles by sol-gel method.

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What are nanomaterial's?

- Nano— Derived from a Greek word “Nanos” meaning Dwarf or small.
- The prefix "nano" means one-billionth, or 10^{-9} ; therefore one nanometer is one-billionth of a meter.
- Nanoparticles are particles between 1 and 100 nanometers in size (1-100nm).
- Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers.
- Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge.
- These emergent properties have the potential for great impacts in electronics, medicine, and other fields.



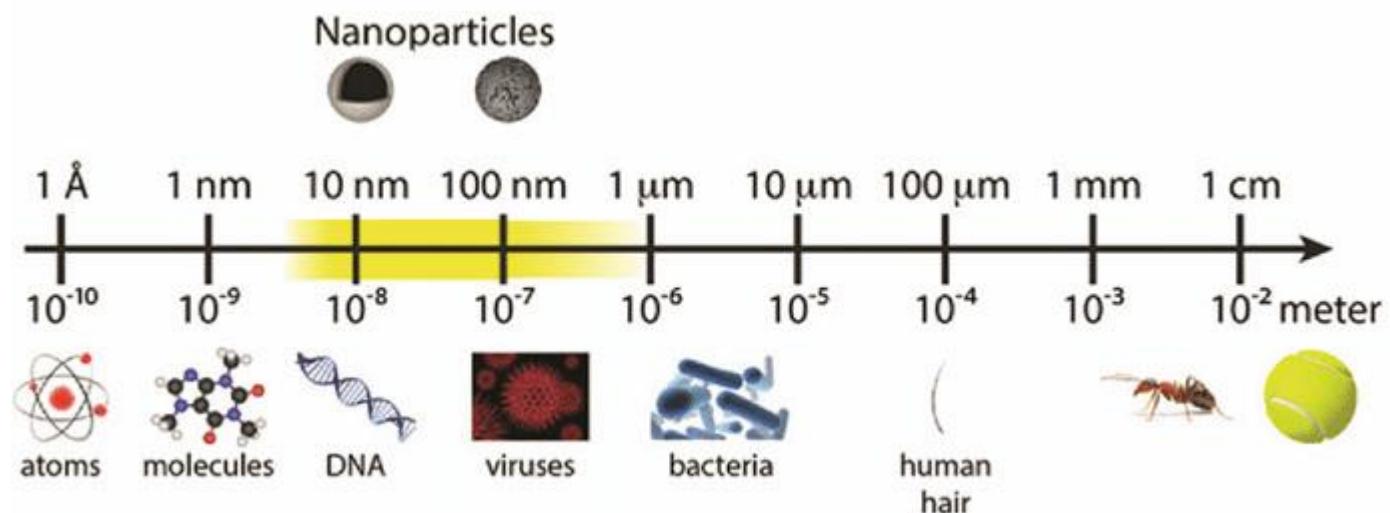
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Nanoscale:

The nanoscale is an incredibly small scale of measurement. It describes objects, processes, and phenomena that measure less than 100 nanometers in size. A nanometer is one-billionth of a meter, which means that the nanoscale is incredibly small.

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Nano materials:

The materials of at least one dimension between 1nm to 100nm are known as nanomaterials.

Nano science:

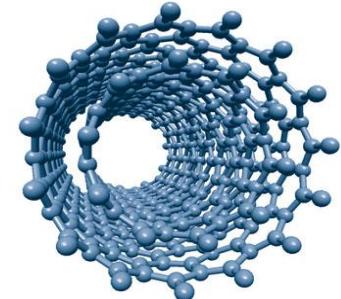
study of materials and their properties at the length scale of few nanometers is called nanoscience.

Nanotechnology:

The techniques involved in the preparation , characterization and use of the properties of nanomaterials in different applications are collectively called as nanotechnology.

or

It is design, characterization ,production and application of structures, devices and systems by controlling their shape and size at nanoscale.



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Synthesis of nanomaterials:

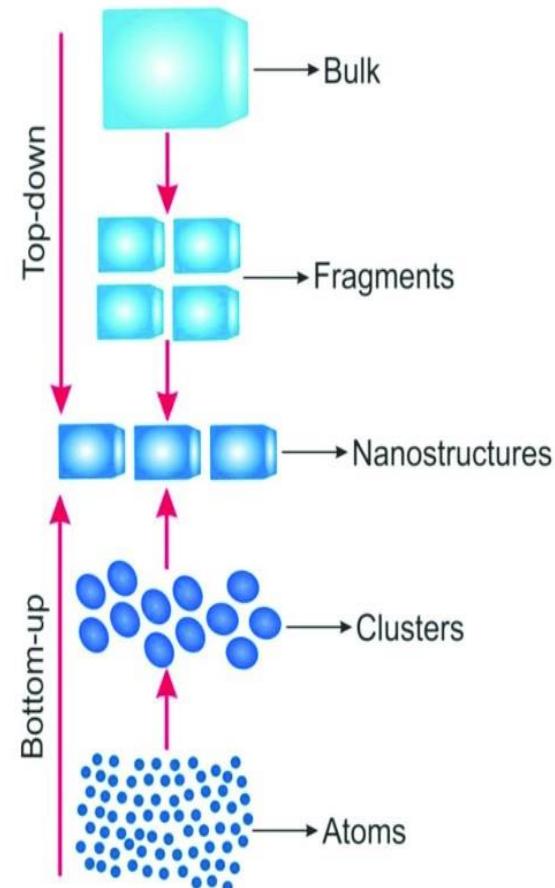
There are two methods of preparing nano materials. One is top-down approach & the other is bottom-up approach.

1. In top-down approach: The material is reduced from bulk size to nano scale.(macro to micro)

Examples for top-down approach are ball milling method & nano lithography.

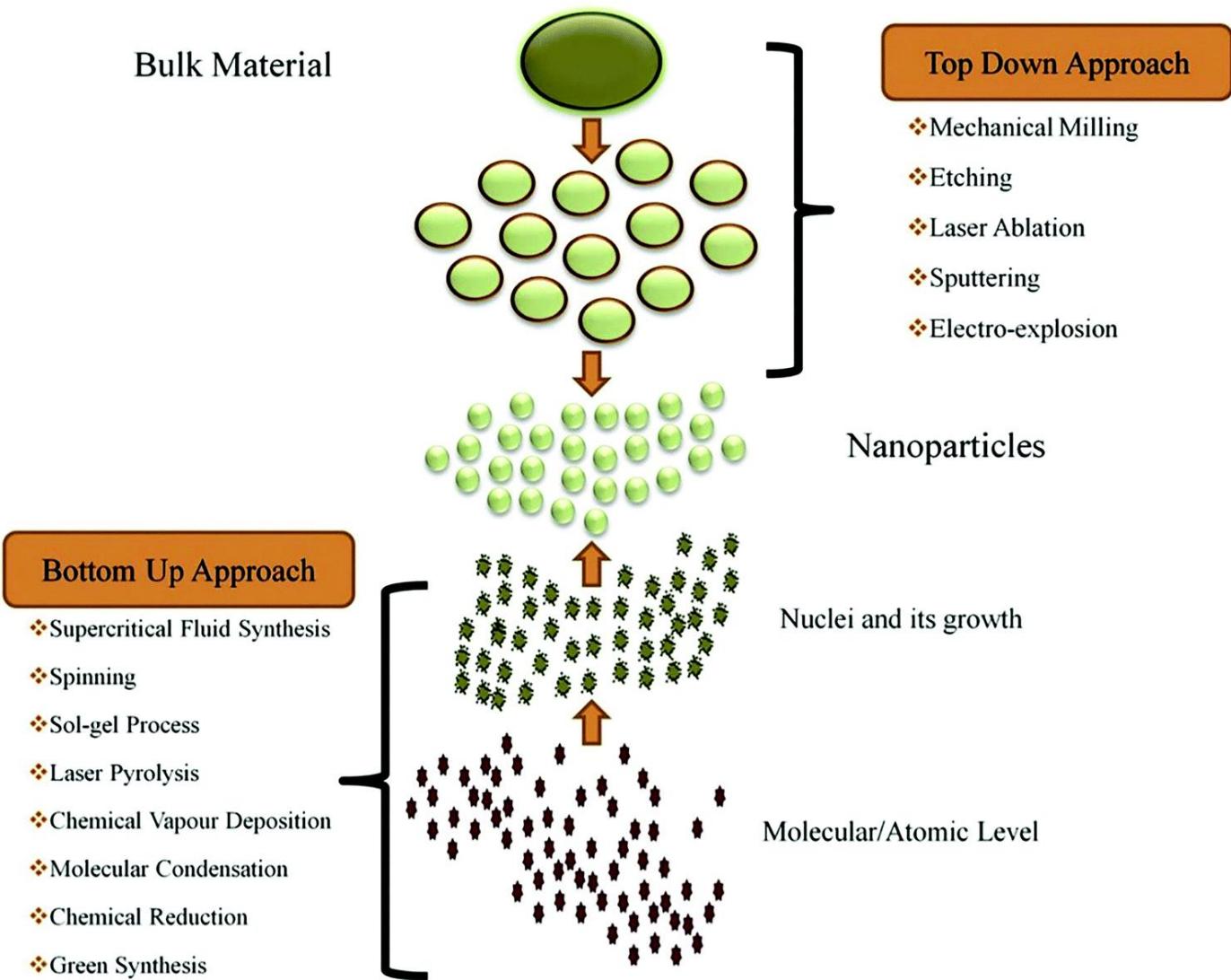
2. In bottom-up approach: Matter in atomic or molecular level gets assembled to form tiny clusters which grow to reach nano-size. (micro to macro)

Examples for bottom-up approach are chemical vapor deposition, physical vapor deposition & sol gel method.



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Nanomaterial synthesis by SOL – GEL PROCESS:

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

This method is mainly used for preparation of metal oxide nano materials.

Examples: Zinc oxide nanoparticles, TiO_2 nanoparticles can be synthesized by this method.

It is a good example for bottom up approach.

It is a wet chemical technique.



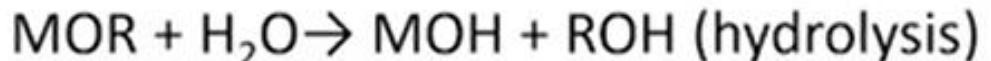
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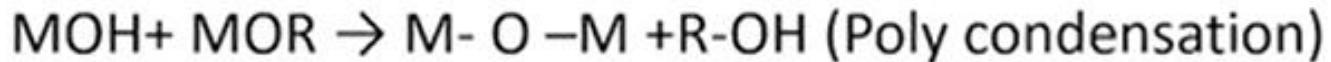
The following steps are involved in the synthesis of nanomaterial's by sol-gel process.

a) preparation of sol: In this method, metalalkoxide is used a precursor to synthesis nanoparticles of a metal oxide.

Metalalkoxide is dissolved in alcohol and then water is added under acidic, neutral or basic conditions. Addition of water leads to hydrolysis in which alkoxide ligand is replaced with a hydroxyl ligand.

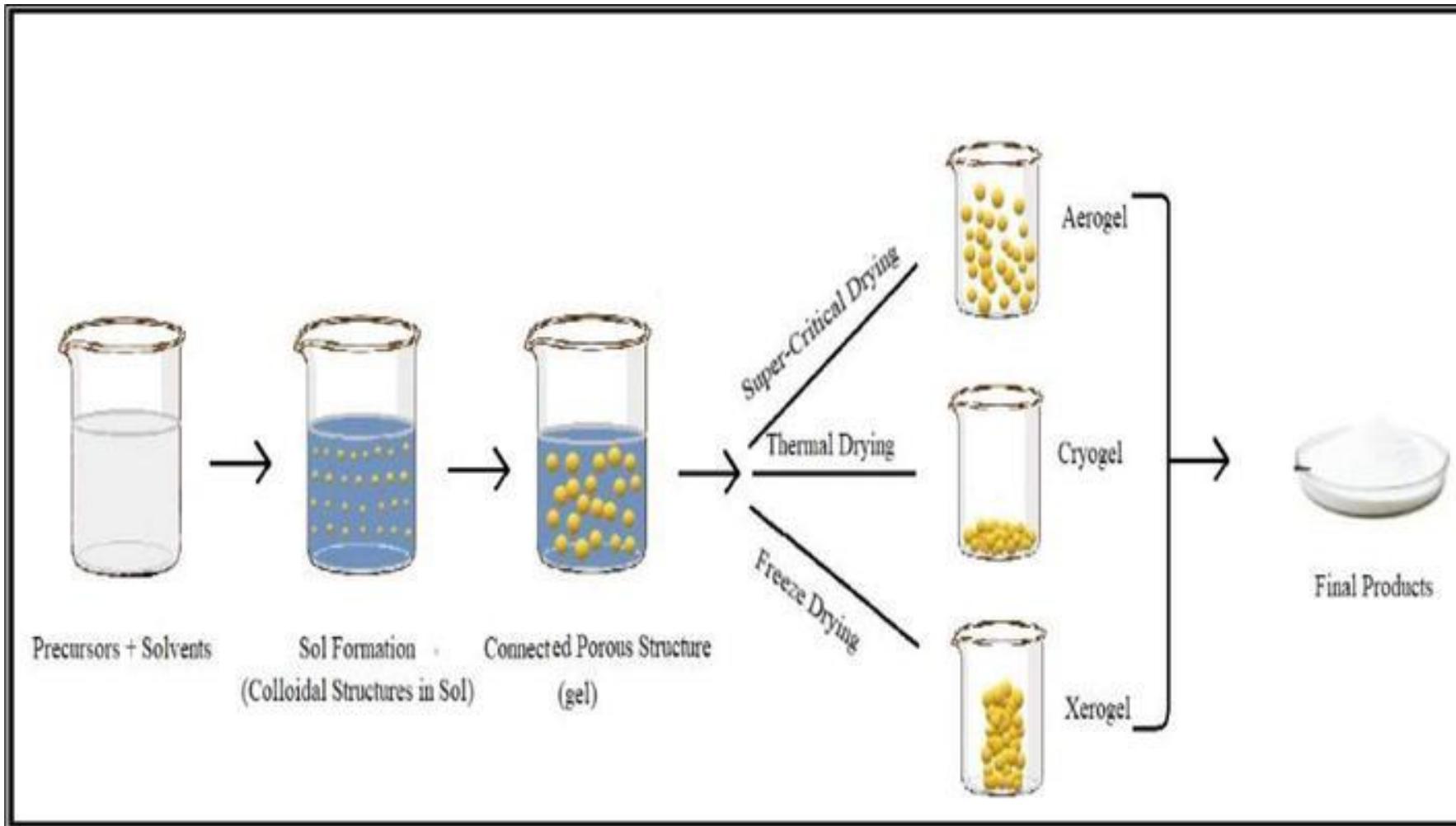


b) Conversion of sol to gel : The polycondensation reaction between MOH and MOR results in the formation of an oxide (M-O-M) or alcohol -(M-OH-M)bridged network(gel), that leads to increase in the viscosity of the solution.



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c) Aging of the gel: The reaction mixture is allowed to continue polycondensation reactions until the gel transforms into a solid mass(evaporation of solvent).

d) Removal of a solvent or Drying of gel: The water and other volatile liquids are removed from the gel network.

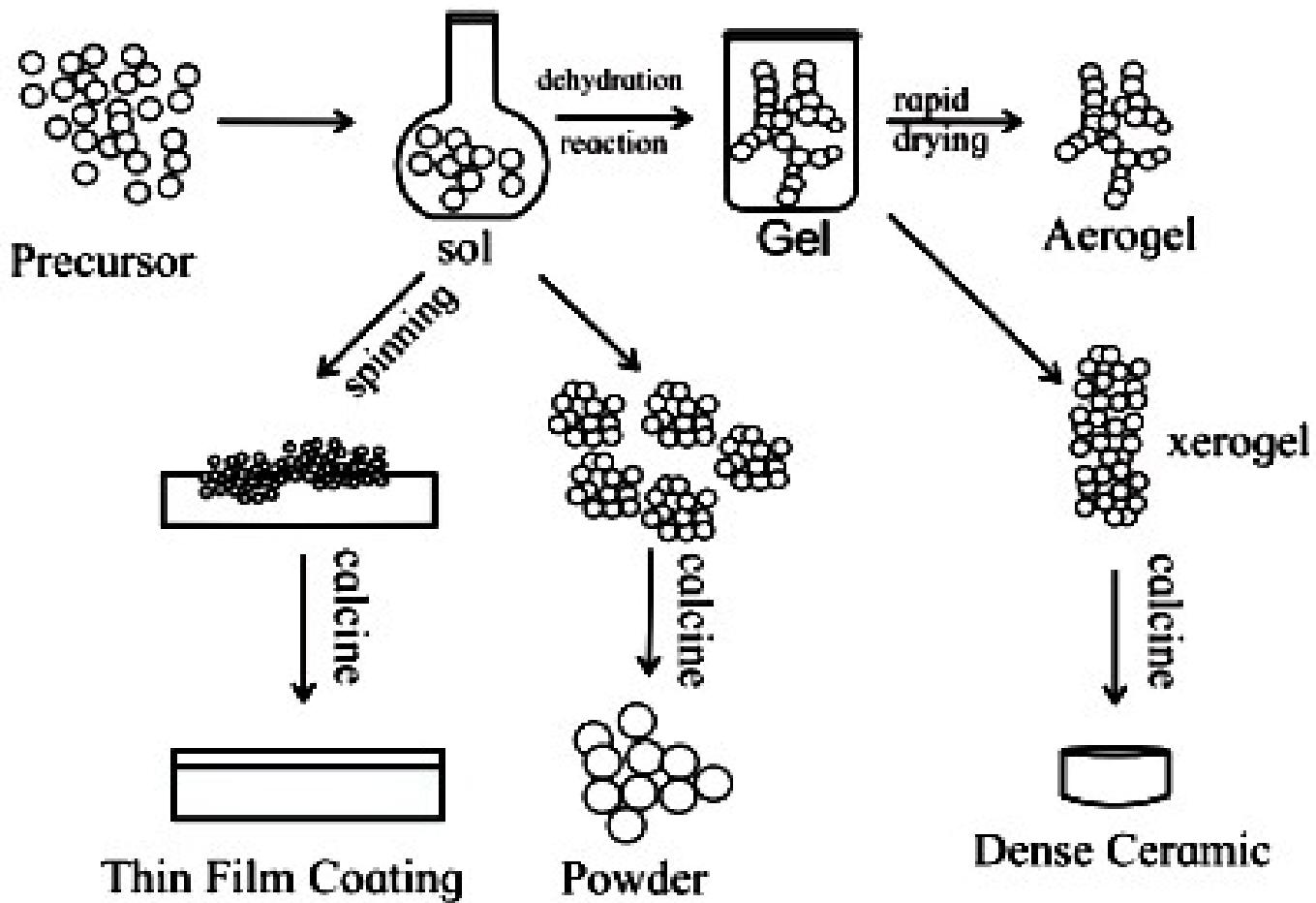
If isolated by thermal evaporation, the resulting product is termed a xerogel.

If the solvent is extracted under supercritical conditions, resulting product is termed an aerogel.

e) Heat treatment: The sample obtained is calcined at high temperature (800°C) to obtain nanoparticles. Nanoparticles formed by sol-gel process commonly have a size ranging from 1 to 100 nm.

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Advantages of the sol-gel process:

The main advantages of the sol-gel process are

- The high purity of the product,
- The narrow particle size distribution
- The achievement of uniform nanostructure at low temperatures.

Disadvantages of the sol-gel process:

The cost of the raw materials (the chemicals) may be high.

Applications of sol-gel method:

The materials obtained from the sol-gel method are used in various optical, electronic, energy, surface engineering, biosensors, and pharmaceutical and separation technologies (such as chromatography).

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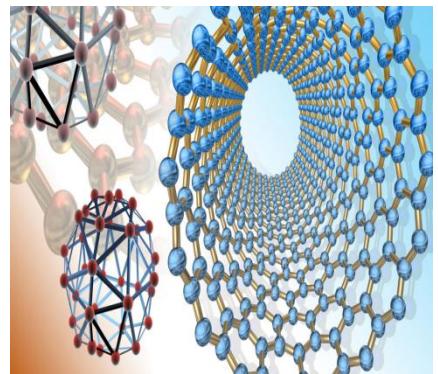
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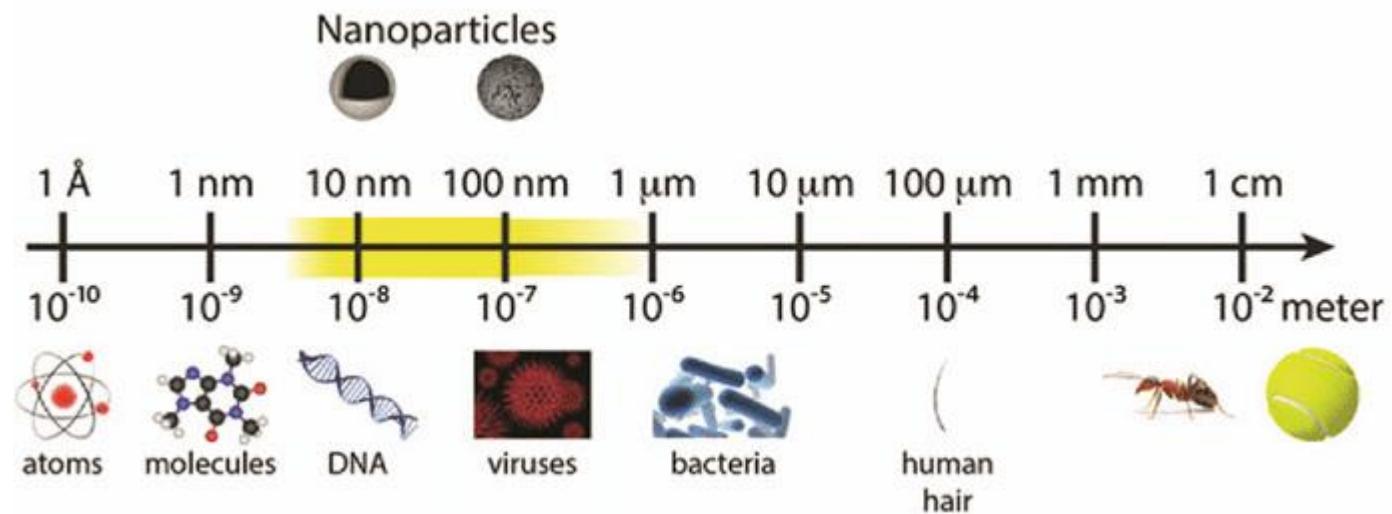
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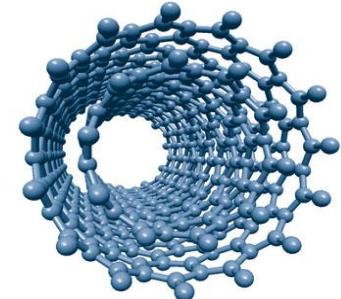
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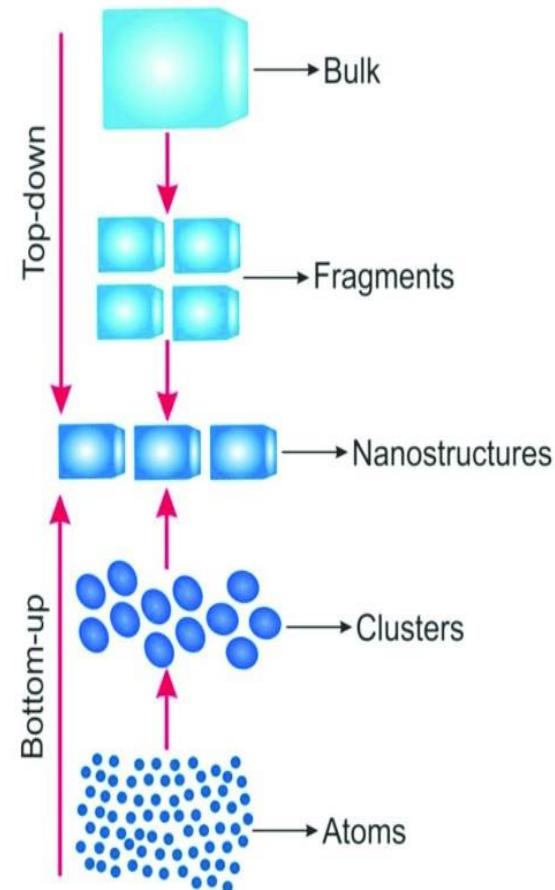
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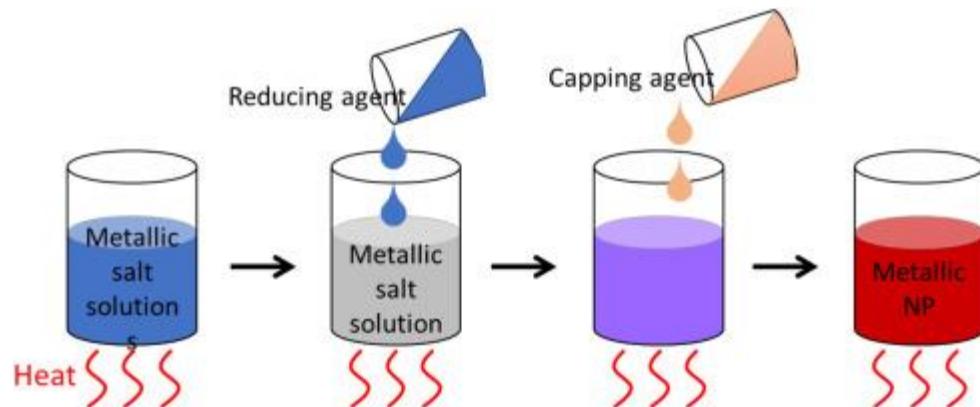
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Nanomaterial synthesis by chemical reduction method :

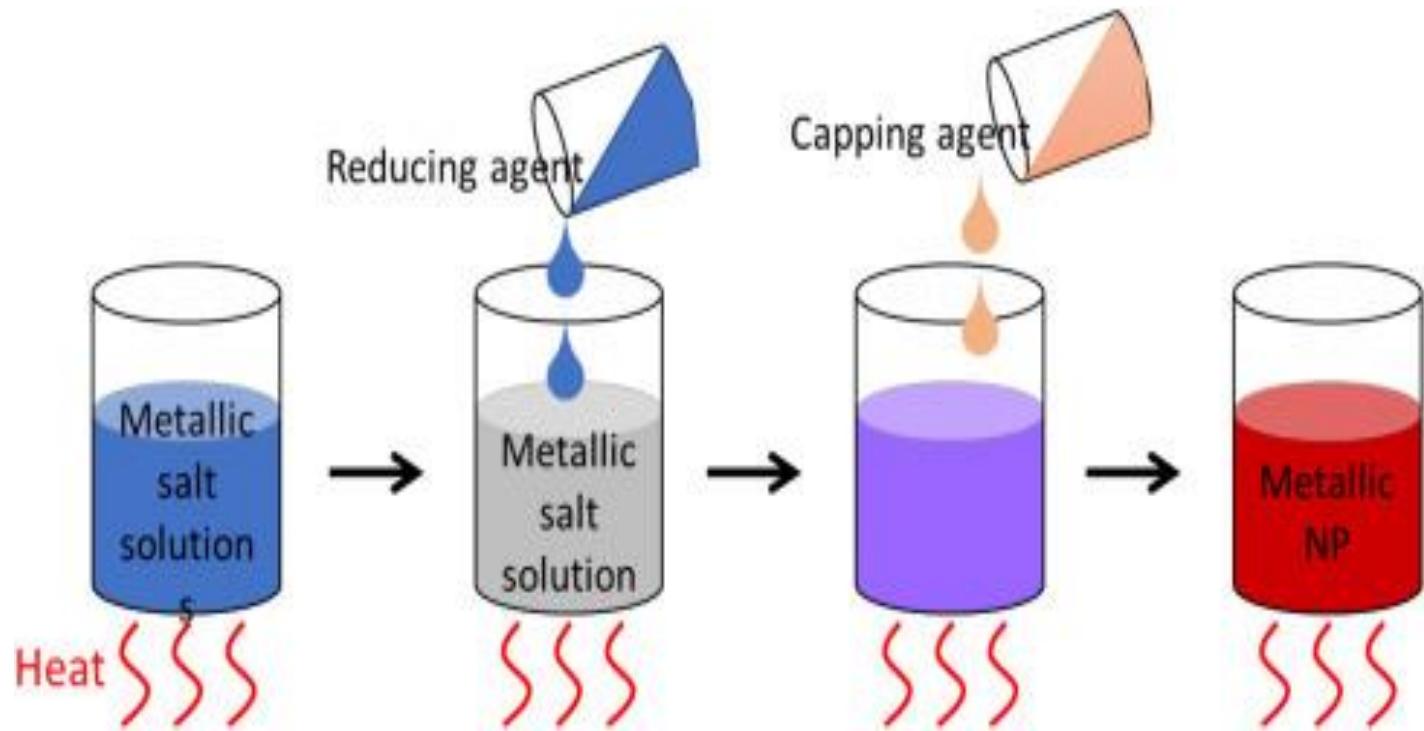
Nanoparticles of different metals can be synthesized by chemical reduction method.

- It is a bottom up approach.
- In this method metal precursor solution such as metal salt solution is treated with suitable reducing agent and appropriate stabilizing agents are added.
- After further treatment and drying, nanoparticles of metal are formed.
- For ex:- synthesis of silver nanoparticles by chemical reduction method



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Nanomaterial synthesis by chemical reduction method :



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synthesis of silver nanoparticles by chemical reduction method:

- Silver nitrate solution is taken as metal precursor and hydrazine hydrate as a reducing agent.
- Sodium dodecyl sulphate(SDS) and citrate of sodium are used as stabilizing agents. The reaction is carried out at room temp.
- The transparent colourless solution converted to the characteristic pale yellow and pale red color which indicates the formation of silver nanoparticles.
- The silver nanoparticles are purified by centrifugation. To remove excess silver ions, the silver colloids were washed at least 3 times with deionized water under nitrogen stream.
- Dried powder of nanosize silver can be obtained by freeze drying.
- The particle size of silver nanoparticle can be from 15 to 48nm.

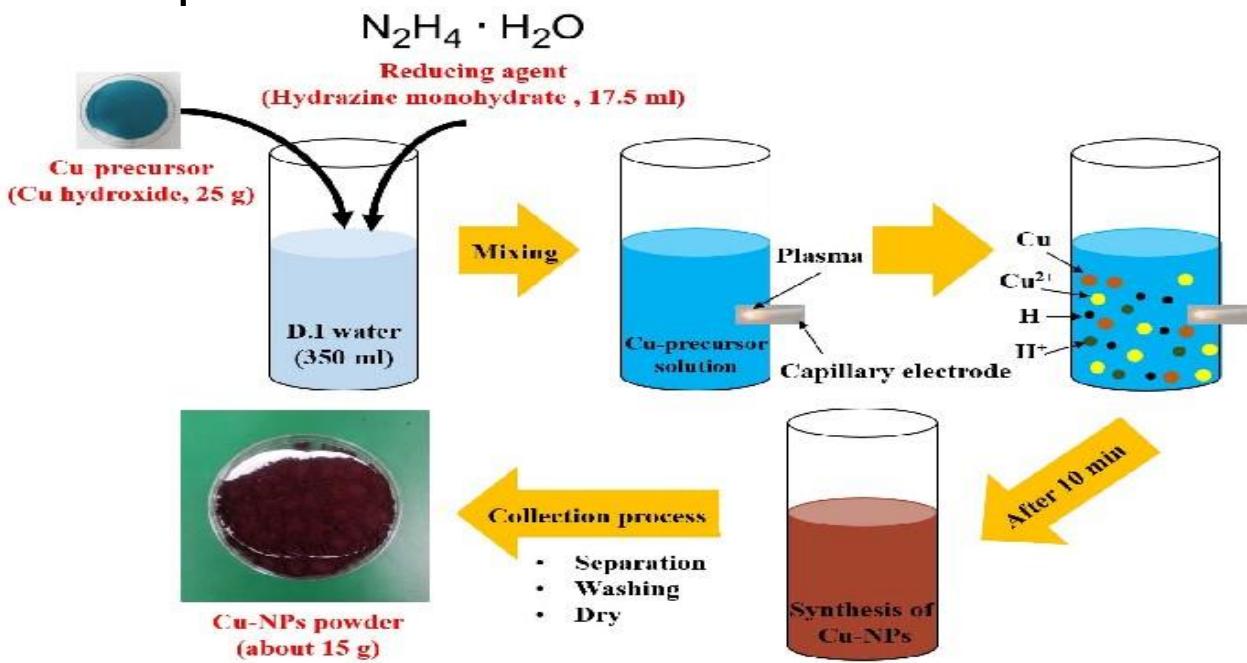


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synthesis of copper nanoparticles by chemical reduction method:

- copper nanoparticles also can be prepared by this chemical reduction method in which copper salt is reduced by reducing agents such as sodium borohydride or hydrazine, ascorbic acid are used as capping agents.
- Chemical reduction method also can be used for preparation of different metal nano particles.



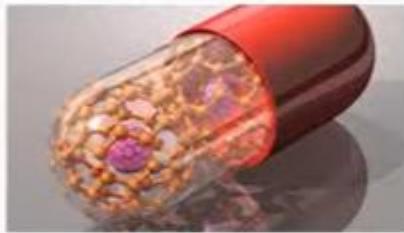
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Applications of NanoTechnology

1. In Medicines

- ✓ Targeted drug delivery
- ✓ Reduces side effect
- ✓ Early diagnosis of decease



2. In Electronics

- ✓ Reduced Power Consumption
- ✓ Less Size and weight of components
- ✓ Smaller and faster processors



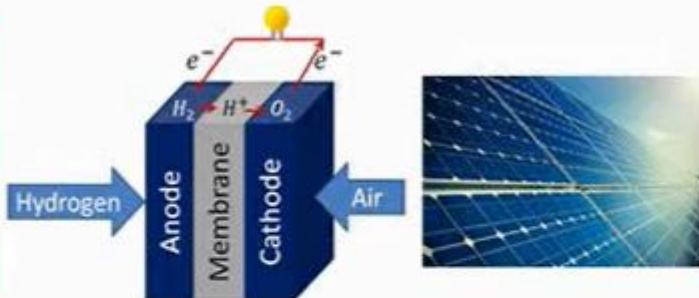
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Applications of NanoTechnology

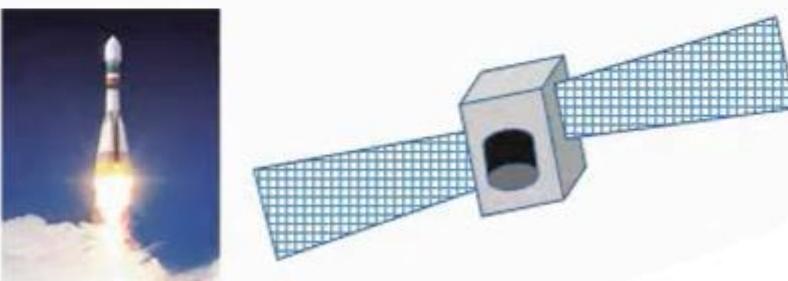
3. In Energy

- ✓ Reduce cost of catalysts in fuel cells
- ✓ Can increase efficiency of solar cells
- ✓ Increased energy density of batteries



4. In Space Technology

- ✓ Lightweight spacecraft
- ✓ Reduction in rocket fuel
- ✓ Larger material strength
- ✓ Low temperature coefficient of expansion



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Applications of NanoTechnology

5. In Automobiles

- ✓ High strength of metal
- ✓ Increased fuel efficiency
- ✓ Quality of paints



6. Environmental

- ✓ Sensors detecting pollution level
- ✓ Harmful emissions can be controlled



7. Textiles

- ✓ Water repellent clothes
- ✓ Wrinkle free clothes



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Applications of nanomaterials:

Nanomaterials, materials with structures or features on the nanoscale (typically between 1 and 100 nanometers), exhibit unique properties and behaviors compared to their bulk counterparts.

These distinctive characteristics make nanomaterials applicable in various fields.

Here are some notable applications of nanomaterials:

1. Medicine and Healthcare:

Drug Delivery Systems: Nanomaterials can be designed to carry and deliver drugs with precision, improving targeted therapy and minimizing side effects.

Diagnostic Imaging: Nanoparticles can enhance contrast in medical imaging techniques like MRI, CT scans, and ultrasound.

Biosensors: Nanomaterial-based biosensors enable highly sensitive and specific detection of biomolecules, helping in early disease diagnosis.



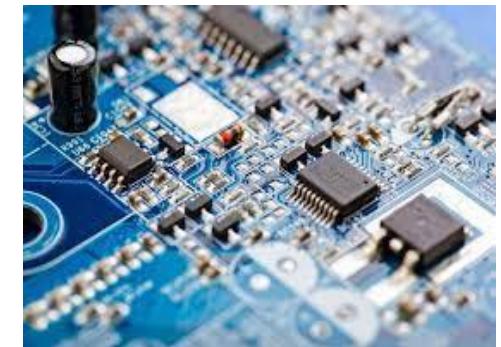
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2. Electronics:

1. Nanoelectronics: Nanomaterials contribute to the development of smaller, faster, and more efficient electronic devices.

2. Flexible Electronics: Nanomaterials enable the fabrication of flexible and transparent electronics, such as flexible displays and wearable devices.



3. Energy:

1. Solar Cells: Nanomaterials enhance the efficiency of solar cells by improving light absorption and charge transport.

2. Energy Storage: Nanomaterials are used in batteries and super capacitors to enhance energy storage capacity and charging/discharging rates.



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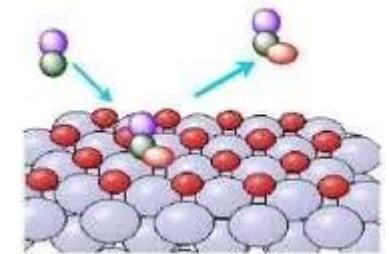
4.Catalysis:

Catalysts: Nanomaterials provide a high surface area, leading to improved catalytic activity in chemical reactions. This is crucial in industrial processes and environmental remediation.

5.Materials Science:

Strengthening Materials: Incorporating nanomaterials can enhance the mechanical and thermal properties of materials, leading to stronger and more durable products.

Self-Healing Materials: Nanomaterials are used to develop materials that can repair themselves when damaged.

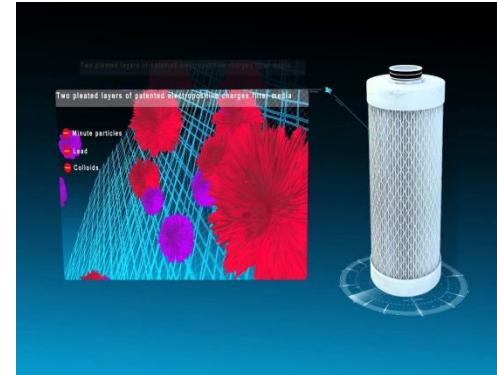


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6. Environmental Remediation:

Water Purification: Nanomaterials like nanoparticles and nano composites are used for efficient removal of pollutants and contaminants from water.



Air Filtration: Nanomaterials are employed in air filtration systems to capture and remove harmful particulate matter.

7. Textiles:

Smart Fabrics: Nanomaterials are integrated into textiles to impart properties like water resistance, UV protection, and antimicrobial activity.



Sensors in Clothing: Nanoscale sensors embedded in fabrics can monitor physiological parameters and provide health-related information.

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8. Food Industry:

Food Packaging: Nanomaterials are used in food packaging to enhance barrier properties, delay spoilage, and monitor food freshness.

Food Safety: Nano sensors can detect contaminants and pathogens in food, ensuring safety and quality.

9. Aerospace and Automotive:

Lightweight Materials: Nanomaterials contribute to the development of lightweight and strong materials, improving fuel efficiency in vehicles and aircraft.

Coatings: Nano coatings provide protection against corrosion, wear, and environmental degradation.



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10.Consumer Products:

Cosmetics: Nanomaterials are used in cosmetics for improved UV protection, enhanced drug delivery in skincare products, and better color dispersion.

Electronics: Nanomaterials contribute to the development of smaller and more efficient consumer electronics.

It's important to note that while nanomaterials offer numerous benefits, their potential environmental and health impacts are also subjects of ongoing research and consideration. Ethical and responsible use of nanomaterials is crucial for ensuring their safe and sustainable application across various industries.



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TOPICS:

- Cement: composition of Portland cement,
- setting and hardening of cement

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Cement:

- ❑ Concrete is most widely used non-metallic material in construction of buildings, dams, bridges, high ways etc.
- ❑ In concrete, cement is the essential bonding material which binds sand and rock when mixed with water.
- ❑ Cement is a grey-green or blue-grey heavy powder and finds its importance as a building material.
- ❑ It can be described as material possessing adhesive and cohesive properties and capable of bonding materials like stones, bricks, building blocks etc.
- ❑ Cement has the property of setting and hardening in the presence of water. So it is called as hydraulic cement.
- ❑ The essential constituents of cement used for constructional purposes are compounds of calcium (calcareous) and Al + Si (argillaceous).



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Composition of the cement

Component	Percentage range by mass
Lime (CaO)	60-69
Silica (SiO_2)	17-25
Alumina (Al_2O_3)	3-8
Iron oxide (Fe_2O_3)	2-4
Magnesium oxide (MgO)	1-5
Sulphur trioxide (SO_3)	1-3
Alkali oxides ($\text{Na}_2\text{O} + \text{K}_2\text{O}$)	0.3-1.5



Classification: -

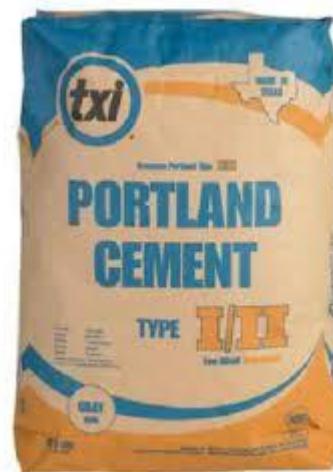
Cement is classified into four types, based on the chemical composition.

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

Of these, Portland cement is the most widely used cement.

Portland cement: It is most widely used non-metallic material of construction. It is a mixture of calcium silicates and calcium aluminates with small amount of gypsum.

The name Portland cement is used because this powder on mixing with water gives a hard, stone like mass which resembles Portland rock.



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Functions of the ingredients in cement:

- 1. Lime:-** lime is the principle constituent of cement. Excess of lime reduces the strength of cement, because it makes the cement to expand and disintegrate.(due to quick setting)
- 2. Silica:-** It imparts strength to cement.
- 3. Alumina:-** It is responsible for the setting action of cement. Excess of alumina makes the cement quick setting.
- 4. Iron Oxide:** It provides color strength and hardness to the cement.
- 5. Sulfur Trioxide:** Presence small amount of SO_3 imparts soundness to cement .
- 6. Gypsum:** It acts as a retarding agent for quick setting of cement.

Properties:- All Portland cements are hydraulic in nature

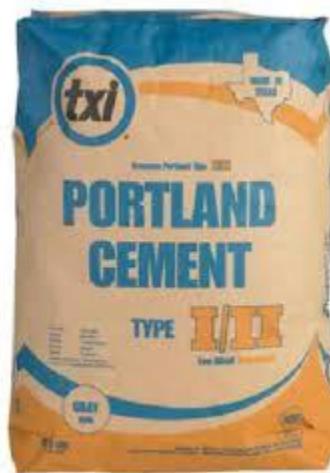
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Chemical composition of Portland cement:-

Portland cement is chemically defined as a finely ground mixture of silicates and aluminates of calcium of varying compositions. its approximate chemical composition is

S.NO	Name of the Bogue compondus	Formula	symbol	Percent
1	Di-calcium silicate	$2\text{CaO} \cdot \text{SiO}_2$	C_2S	25
2	Tri-calcium silicate	$3\text{CaO} \cdot \text{SiO}_2$	C_3S	45
3	Tri-calcium aluminate	$3\text{CaO} \cdot \text{Al}_2\text{O}_3$	C_3A	10
4	Tetra-calcium alumino ferrite	$4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$	C_4AF	9
5	Calcium Oxide	CaO	-	2
6	Magnesium Oxide	MgO	-	4
7	Calcium Sulphate	CaSO_4	-	5



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Setting and Hardening of cement:

- Cement when mixed with water forms a plastic mass called cement paste.
- During hydration reaction, gel and crystalline products are formed. The insoluble gels and crystals have the ability to surround inert materials like sand, bricks, crushed stones, etc.
- This process of solidification comprises of
 - (i) setting and then (ii) hardening
- **Setting:-** It is defined as stiffening of the original plastic mass, due to the formation of tobermonite gel .
- **Hardening:-** It is defined as the development of strength, due to formation of crystals.
- The setting and hardening of cement is due to the formation of inter locking crystals reinforced by rigid gels formed by the hydration and hydrolysis of the constitutional compounds.



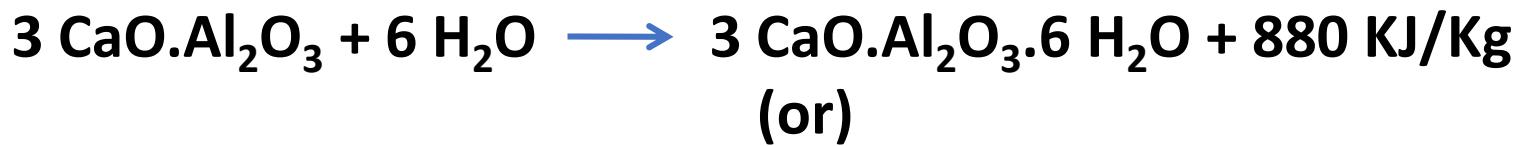
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In setting process C_3A , C_4AF , C_2S interact with water and forms gels

Reactions involved in setting and hardening of cement:-

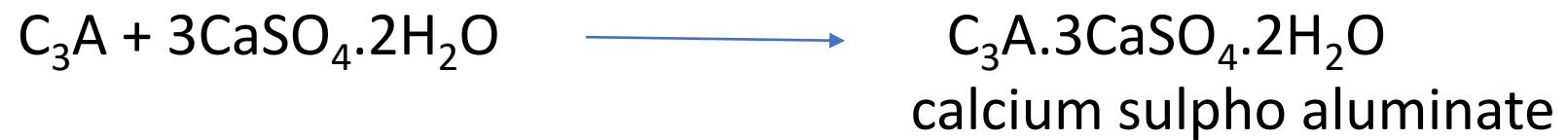
i) Day-1:- When the cement is mixed with water, at first hydration of tricalcium aluminate takes place rapidly (within 1 day) and the paste becomes quite rigid within a short time which is known as initial set or flash set.



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In order to retard the rapid hydration of C₃A (early initial setting), gypsum is added during grinding of cement clinkers. Gypsum reacts with C₃A to give insoluble calcium sulpho aluminate complex, which does not possess hydrating property and retards early setting of cement.

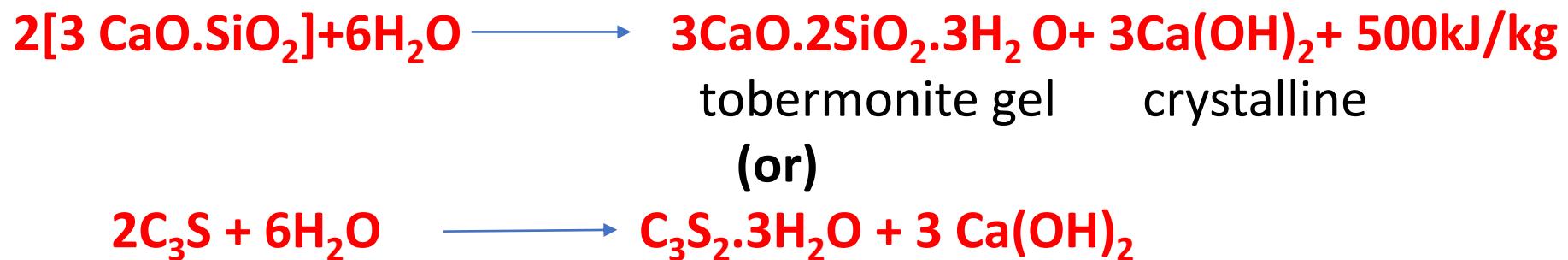


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ii) Day-2 to 7:

After the hydration of C_3A , C_3S begins to hydrate to give tobermonite gel and crystalline $Ca(OH)_2$. This is responsible for the development of initial strength of cement. The hydration of C_3S gets completed within 7 days. It does not contribute much to the strength of cement.

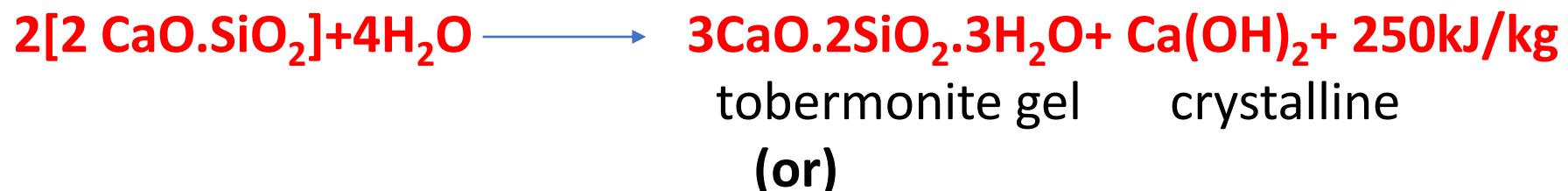


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iii) Day-7 to 28:

Dicalcium silicate(C_2S) reacts with water very slowly and gets completed in 7 to 28 days.

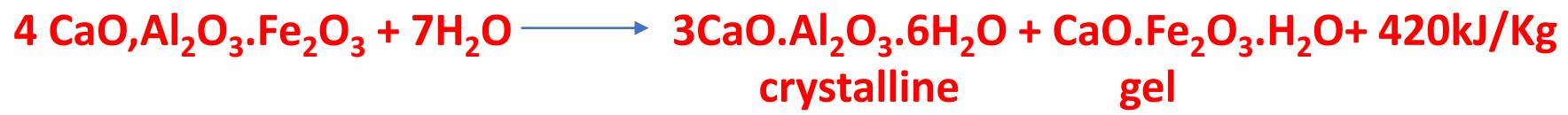


The increase in strength between 7 to 28 days is due to the formation of tobermonite gel and crystalline Ca(OH)_2 of both C_2S and C_3S .

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iv) Though the hydration of tetra calcium alumino ferrite(C_4AF) takes place initially, the hardening takes place finally through crystallization, along with C_2S .



(Or)



Thus the final setting and hardening of cement is due to the formation of tobermorite gel plus crystallization of $\text{Ca}(\text{OH})_2$ and hydrated tri calcium aluminate.

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Setting and Hardening of Cement

Setting of Cement	Hardening of Cement
Setting is the term used to describe the stiffening of the cement Paste	Hardening refers to the gain of strength of a set of cement paste
It refers to a change from a fluid to a rigid state	It refers to formation of solid mass possessing good compressive strength.
The setting of Cement Starts after 30 minutes from the instant when water is added to cement and compacted within 10 hours	The process of hardening of cement continues for a period more than 1 year.
To know the setting of cement, initial setting time test and final setting time test are conducted	To know the hardening of cement, compressive strength test is conducted.

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Conclusion:

Understanding the setting and hardening processes of cement is essential for achieving the desired performance and durability of concrete structures. Proper mix design, curing, and quality control during construction are crucial aspects of ensuring optimal cement setting and hardening.

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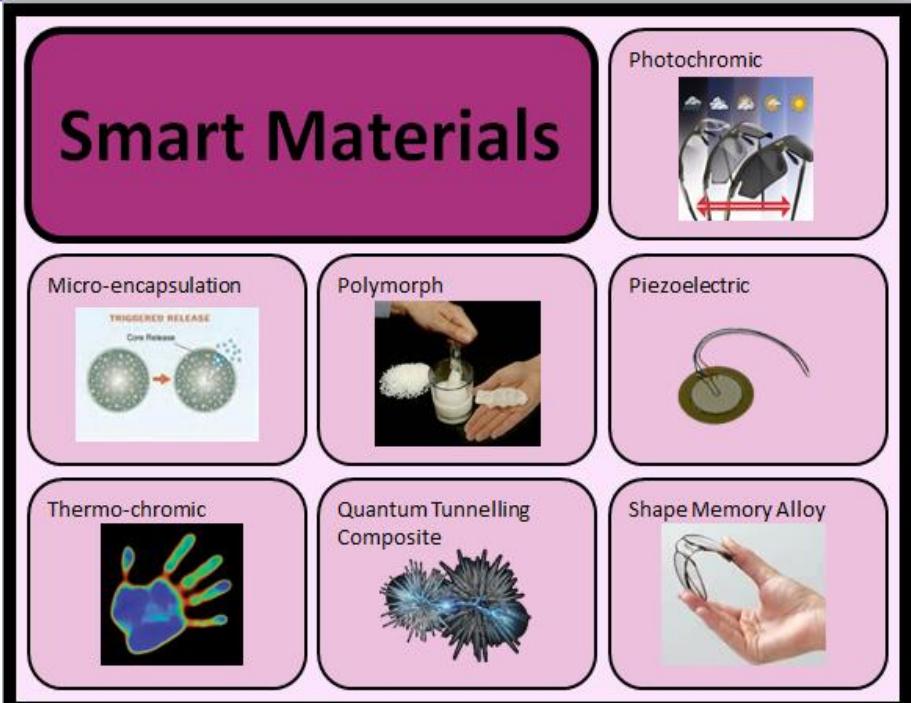
TOPICS

- Smart materials and their engineering applications
- Shape memory materials, Poly L-Lactic acid

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Smart materials

- Smart materials have properties that react to changes in their environment.
- Their properties can be changed by external conditions, such as temperature, light, pressure, electricity, voltage, pH, or chemical compounds.
- This change is reversible and can be repeated many times.
- These materials play a crucial role in various engineering applications and other fields.
- Smart materials, also called **intelligent or responsive materials** are designed materials that have one or more properties that can be significantly changed in a controlled fashion by external stimuli, such as stress, moisture, temperature, light.,etc.



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► Three basic components of a smart system are

◆ SENSOR

◆ PROCESSOR

◆ ACTUATOR

► Example: Smart concrete building

(suitable to earth quake areas)

Sensor : optical fibers(embedded in concrete)

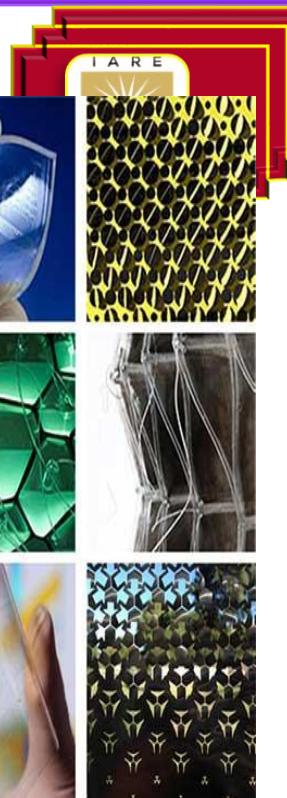
Processor: smart wires(automatic shrink/expand)

Actuator :chemically active smart materials

(fillers preventing crack propagation)

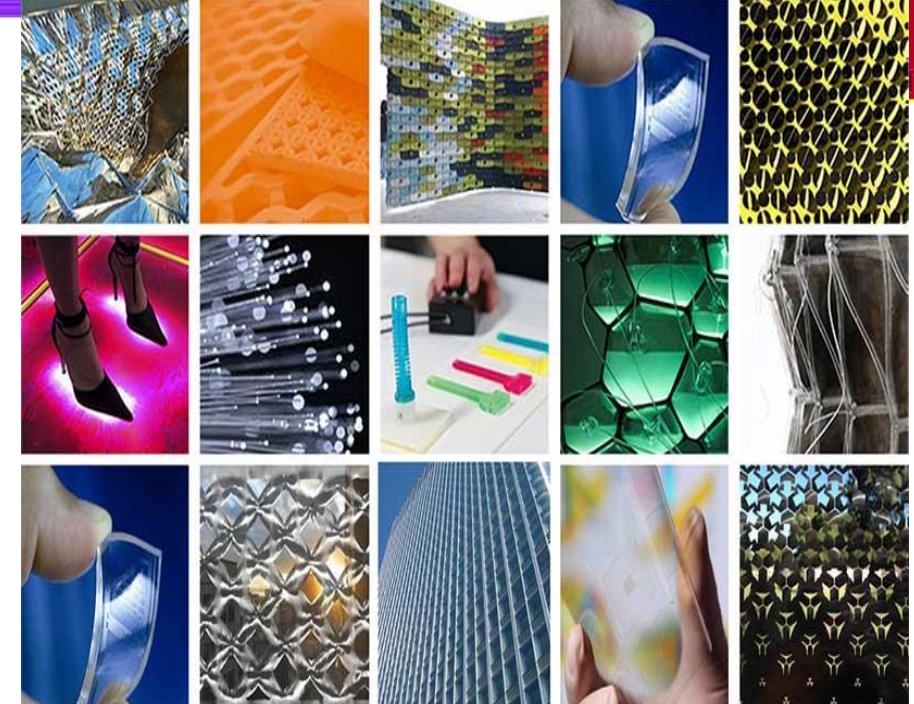
Smart materials can respond to a change & are

- able to receive information(sensing the problem)
- able to analyze & decide(processing the information)
- able to act on the decision(actuating the process)



Classification of smart materials:

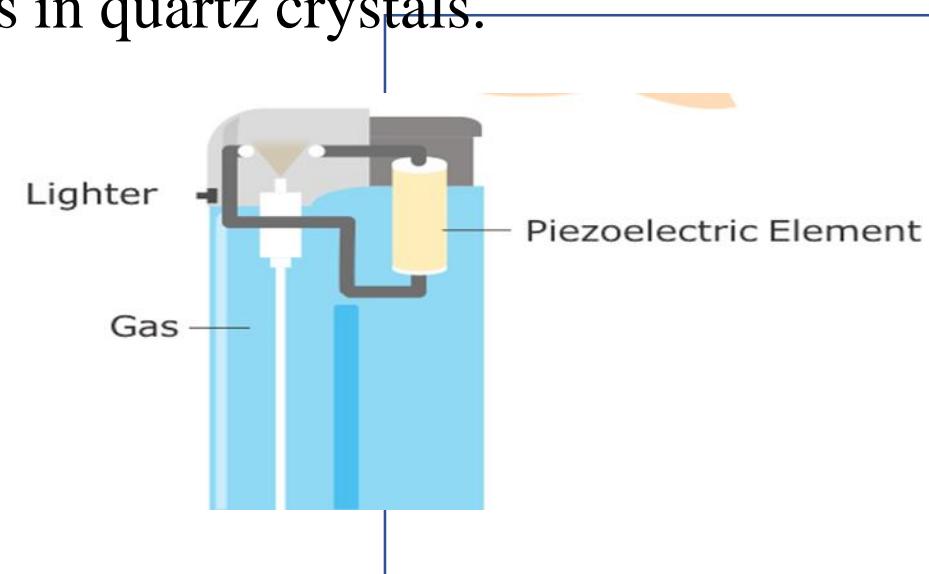
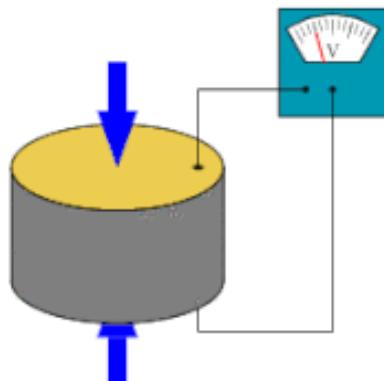
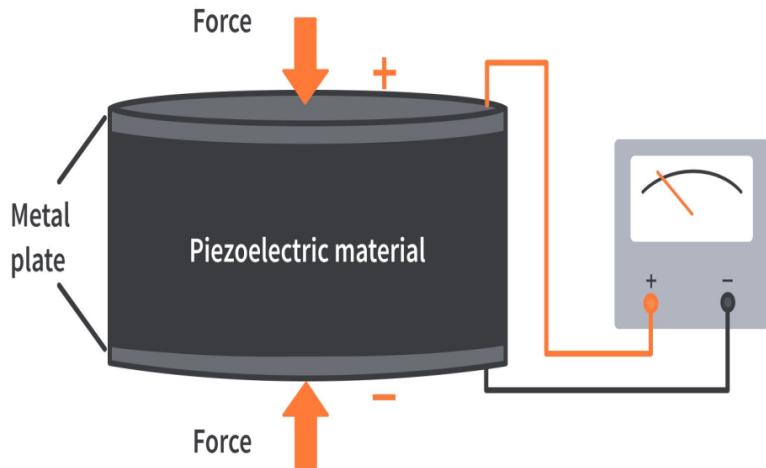
1. Piezoelectric Materials
2. Shape Memory Alloys (SMA)
3. Magnetostrictive Materials
4. Electrorheological(ER) and Magnetorheological (MR) Fluids
5. Smart Polymers
6. Thermochromic and Photo chromic Materials
7. Hydrogels



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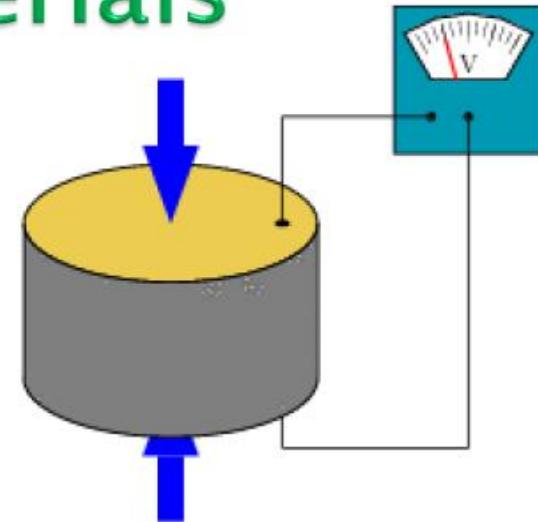
1. Piezoelectric Materials:

- Piezoelectric materials or piezoelectrics are the materials that can produce electric energy upon application of mechanical stress.
- A commonly known piezoelectric material is quartz.
- The mechanism involves development of electric charge due to movement of electron upon application of stress.
- Piezoelectricity was discovered in 1880 by Curie brothers in quartz crystals.



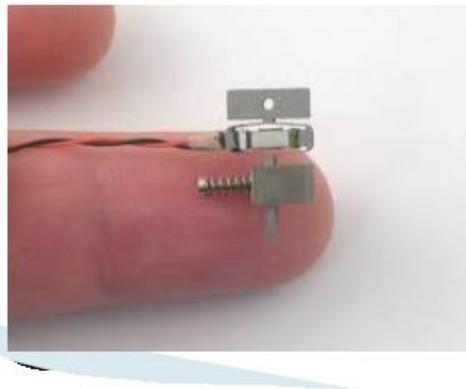
Piezoelectric Materials

- ▶ Materials that produce a voltage when stress is applied.(An applied mechanical stress will generate a voltage)
- ▶ Example:Quartz,BaTiO₃,GaPO₄
- ▶ The piezoelectric effect describes the relation between a mechanical stress and an electrical voltage in solids.
- ▶ In physics, the piezoelectric effect can be described as the link between electrostatics and mechanics.
- ▶ An LED is wired to a piezoelectric transducer. The LED briefly lights when the device is flicked & shows that electricity has been generated by stress and strain.



Applications of piezo electric effect

- ▶ In lighters or portable sparkers with a piezo fuze a sudden and strong pressure is used to produce a voltage. The spark then ignites the gas.
- ▶ A piezo motor is based on the change in mechanical shape of a piezoelectric material when an tension is applied. The material produces ultrasonic or acoustic vibrations and produces a linear or rotary motion.
- ▶ Piezo elements are used in music for acoustic instruments. They are inserted in stringed instruments such as guitar, violin or Mandoline. The dynamic deformation/vibration of the cords is converted into a small alternating voltage.



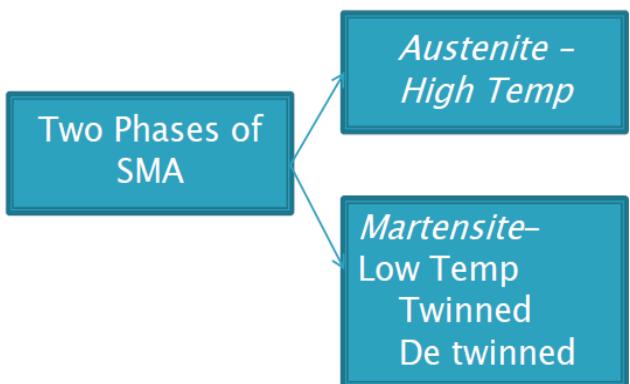


2. Shape Memory Alloys (SMA)

- A shape-memory alloy (SMA) is an alloy that can be deformed when cold but returns to its pre-deformed ("remembered") shape when heated.(depends on temperature)

Shape Memory Alloys

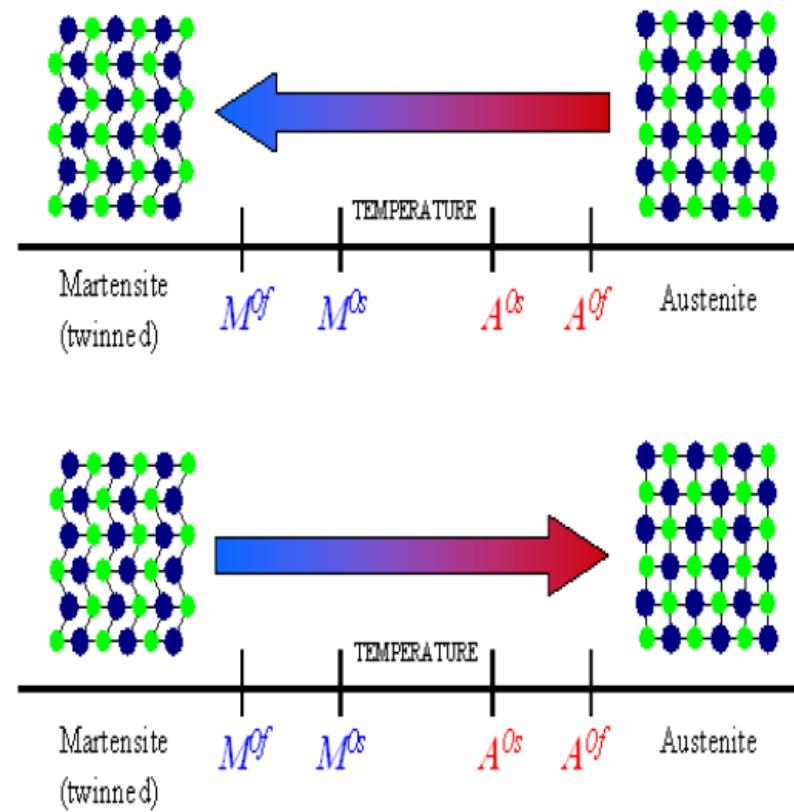
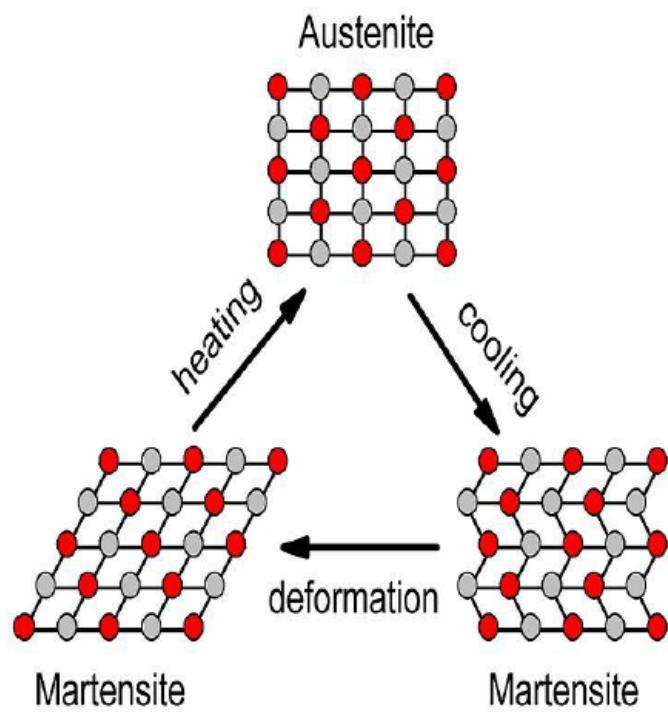
- Shape Memory Alloys (SMAs) are a unique class of metal alloys that can recover apparent permanent strains when they are heated above a certain temperature.



- A phase transformation which occurs between these two phases upon heating/cooling is the basis for the unique properties of the SMAs.

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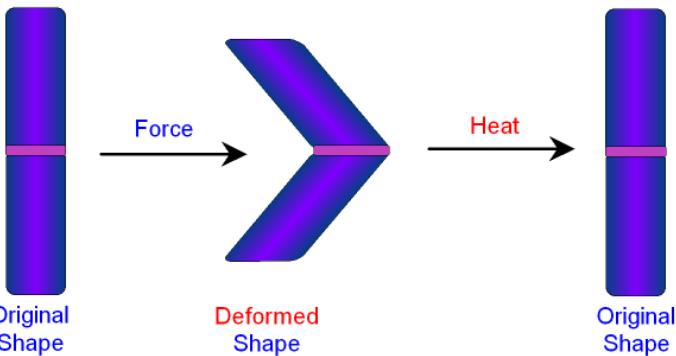
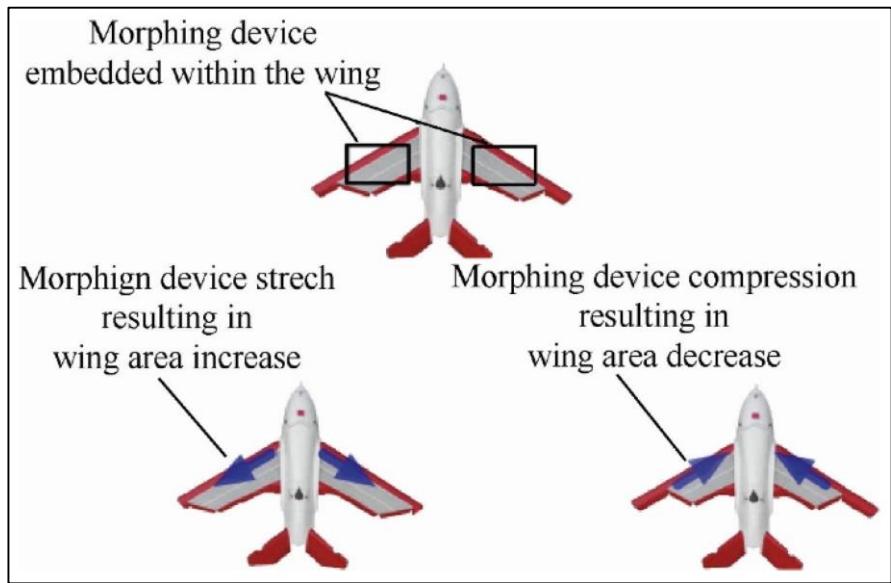
SHAPE MEMORY EFFECT



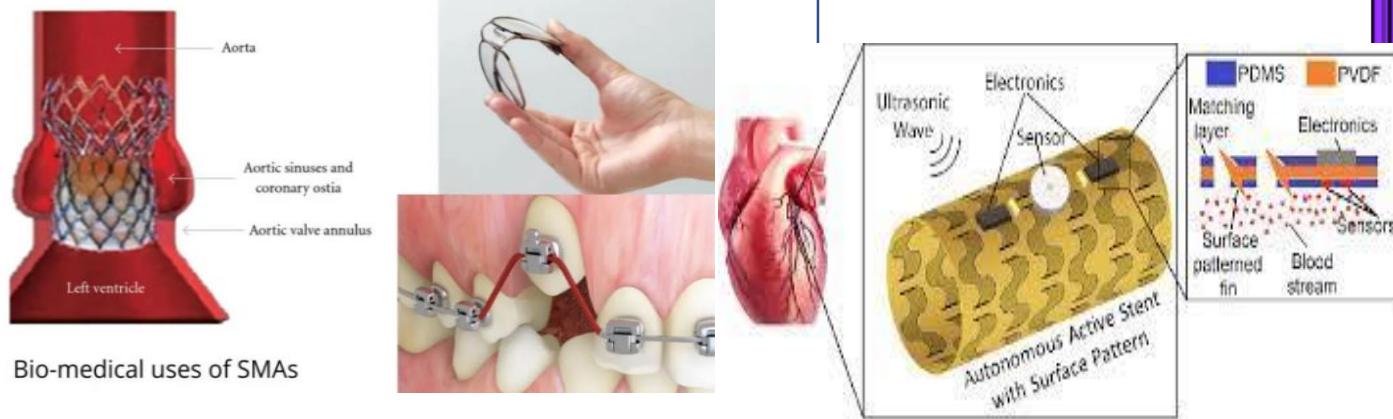


Engineering Applications

- Aerospace:** Deployable structures and adaptive wing components in aerospace applications.

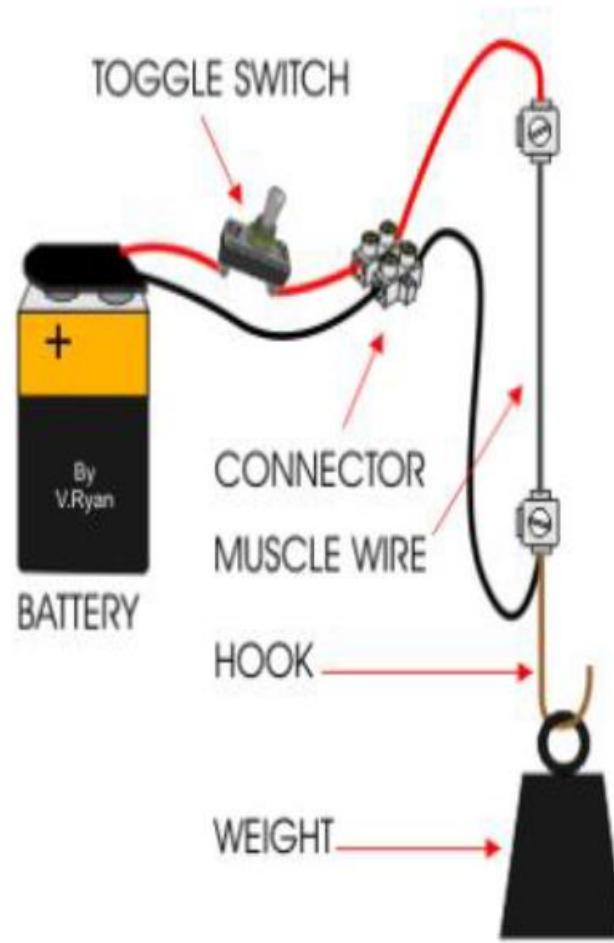


- Biomedical Devices:** Used in stents that can be compressed for insertion and then expand to their original shape within the body.



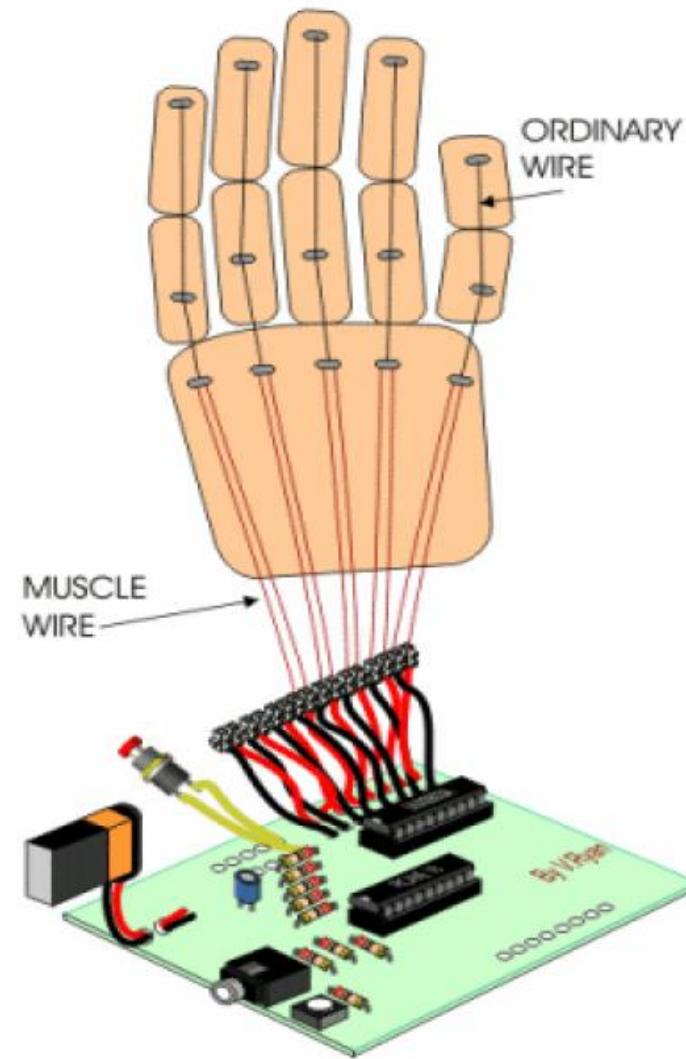
SMA in ROBOTICS- Muscle wire

- ▶ Muscle wire is NiTi alloy which can be stretched up to 8 % of its length and still recover. (at room temp 3 to 5 % stretch is possible)
- ▶ When a small current is passed through the wire it becomes much harder and returns to its original length with a reasonable force.
- ▶ A battery and switch are connected to muscle wire & a small weight stretches the muscle wire.
- ▶ The cycle of turning on and off the current has the effect of lifting and lowering of the weight.



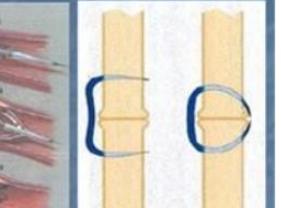
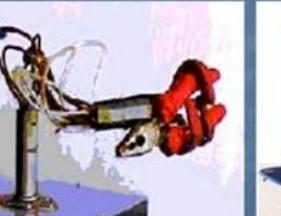
SMA in ROBOTICS- Robotic hand

- ▶ A clever use of muscle wire and a micro-controller circuit is a **robotic hand**.
- ▶ A robotic hand has ‘stretched muscle wires’ attached to the base of each finger
- ▶ When current is applied to the muscle wire it contracts to its ‘natural’ length by pulling on the ordinary wire.
- ▶ The micro-controller is programmed to give five of the outputs with switch on and off options.
- ▶ This makes the fingers of the hand move.



Other Applications

Applications of Shape Memory Alloys (SMAs)

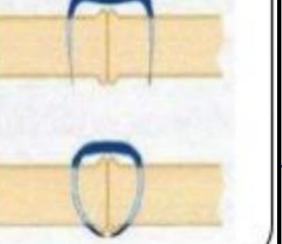
 F-14				
Aeronautic coupling & Solid-state actuator	Orthodontic archwire	Endodontic SMA tool	Self-expanding stent	SMA bone staple
				
Robotic application	SMA damper	Eyeglass frame	SMA thin film & MEMS	SMA art application

APPLICATIONS

- Medicine
- Optometry
- Engines
- Aerospace
- Robotics
- Automotive
- Pipings
- Civil structures
- Water spinkers
- Textile





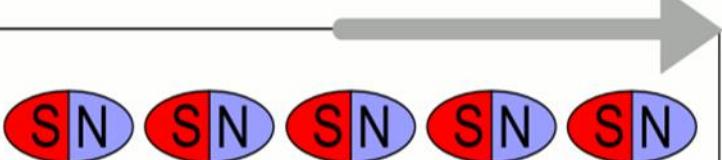



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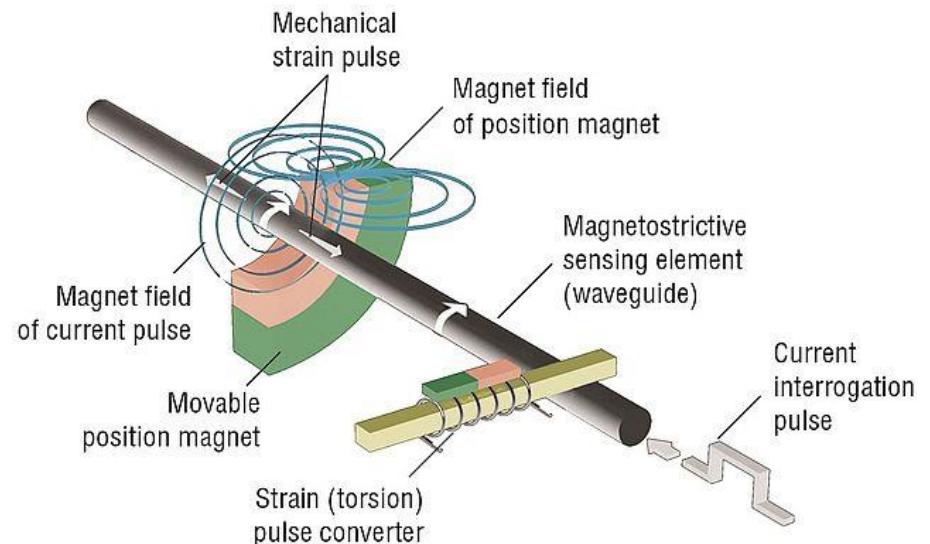
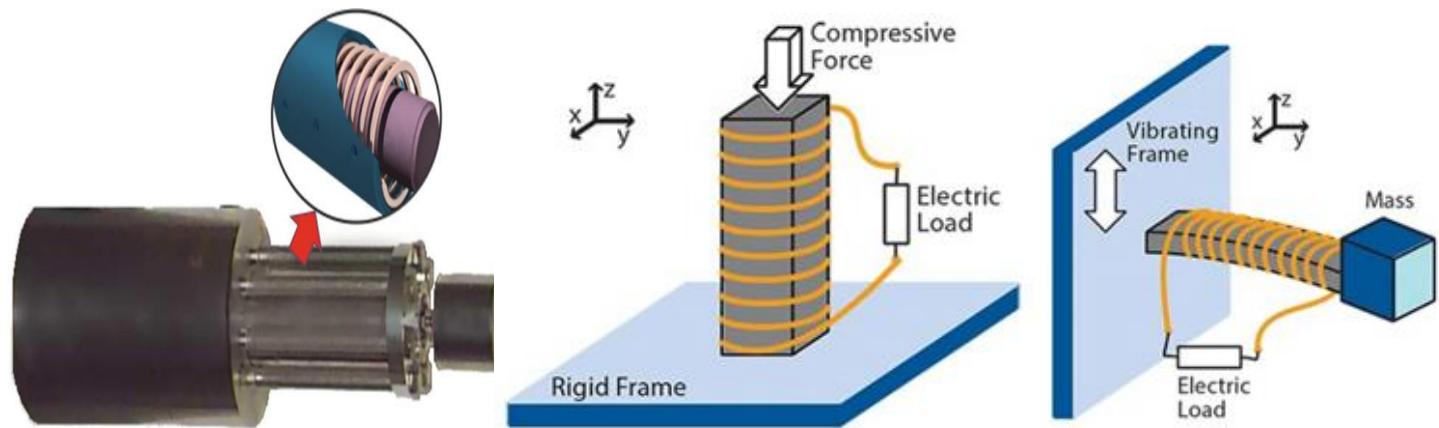
3. Magnetostrictive Materials:

- Magnetostrictive property of ferromagnetic materials that change their shape or dimensions during the process of magnetization
- This effect can be used to create sensors that measure a magnetic field or detect a force.
- These materials change their shape in response to an applied magnetic field.



Engineering Applications

- Sensors and Actuators:** Utilized in sensors for measuring magnetic fields and as actuators for precise control in robotics.



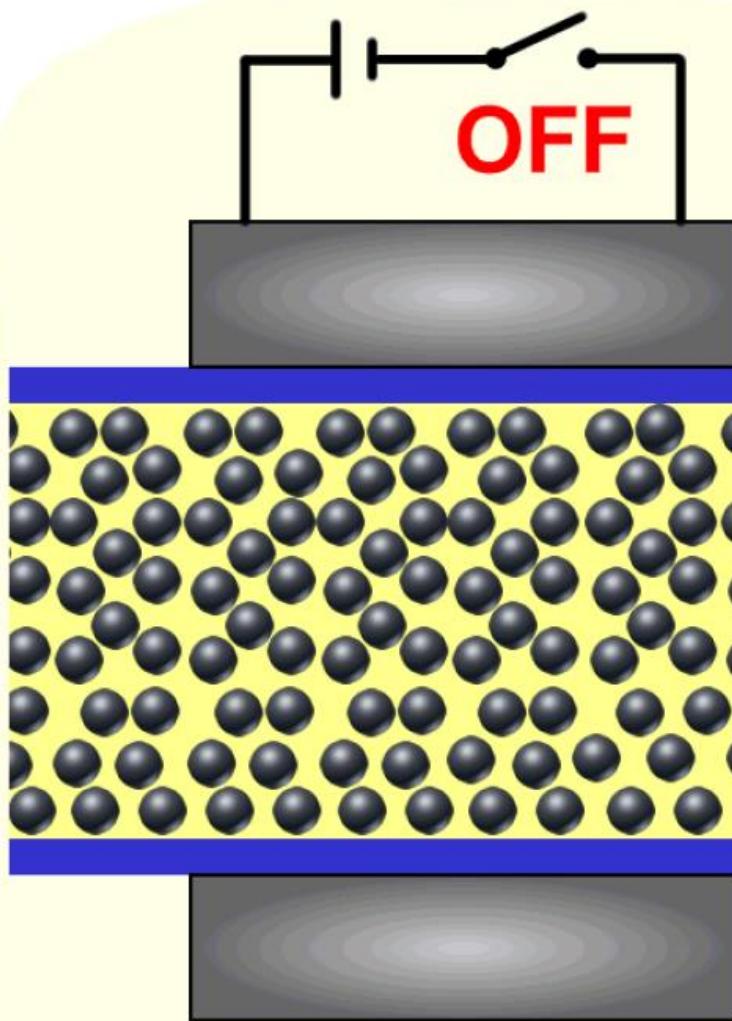


4. Electro rheological (ER) and Magneto rheological (MR) Fluids:

These are fluids whose viscosity can be change in character or composition by applying an electric or magnetic field.

- ▶ A MR fluid is a smart fluid which usually consists of 20–40 percent iron particles, suspended in mineral oil, synthetic oil, water or glycol.
- ▶ MRF also contains a substance which prevents the iron particles from setting.
- ▶ When subjected to a magnetic field, the magnetic particles inside increase the fluid's viscosity, rendering it viscoelastic solid.

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MRF solidifying and blocking a pipe in response to an external magnetic field.

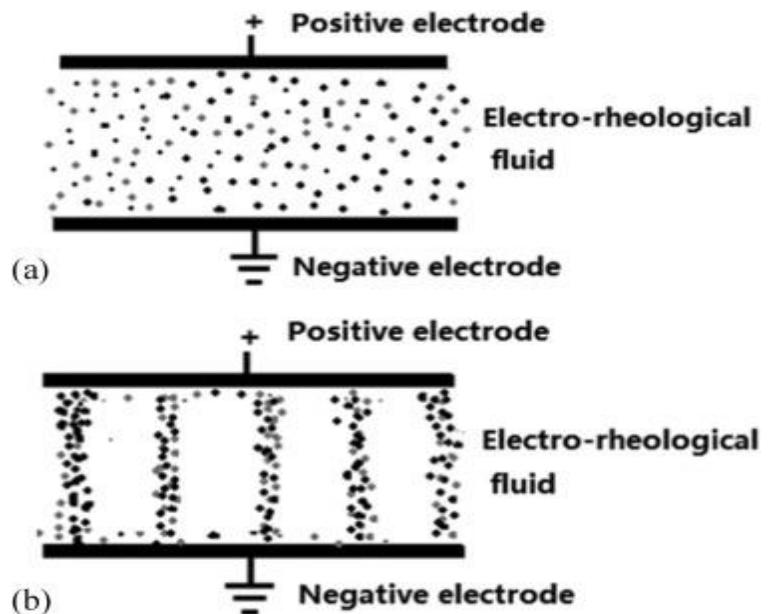
"OFF" position – the MR fluid is not magnetized & the particles inside, distributed randomly, allow the fluid to move freely, acting like a damper fluid.

"ON" position – the particles become energized and align into fibrous structures and restricts the movement of the fluid



Engineering Applications:

- **Dampers and Shock Absorbers:** Used in automotive and industrial applications to adjust suspension characteristics based on changing conditions.



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5. Smart Polymers:

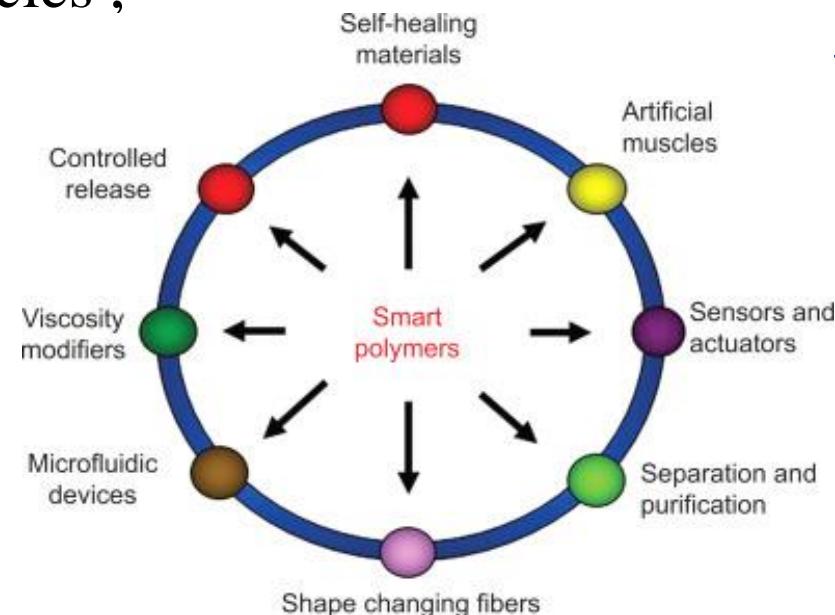
- Polymers that undergo reversible changes in their properties in response to external stimuli.
- A significant change in structure and properties can be induced by a very small stimulus that makes them unique and effective.



Engineering Applications:

They are used for **sensors** and **actuators** such as artificial muscles , the **production of hydrogels**, **biodegradable packaging**.

- **Biomedical Devices:** Used in drug delivery systems and as responsive coatings for medical implants.
- **Textiles:** Responsive fabrics for applications like moisture management or color-changing textiles.



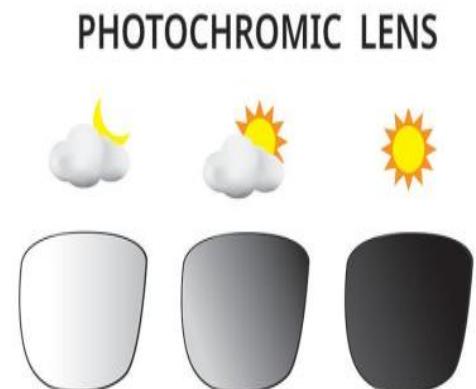


6. Thermochromic and Photo chromic Materials:

- Photochromic materials are able to change color when irradiated with visible or UV light.
- Thermochromic materials undergo a color change when heated above or below a threshold temperature.

Engineering Applications:

- **Smart Windows:** Windows that automatically adjust their tint based on sunlight intensity.
- **Packaging:** Indicators for temperature-sensitive products.



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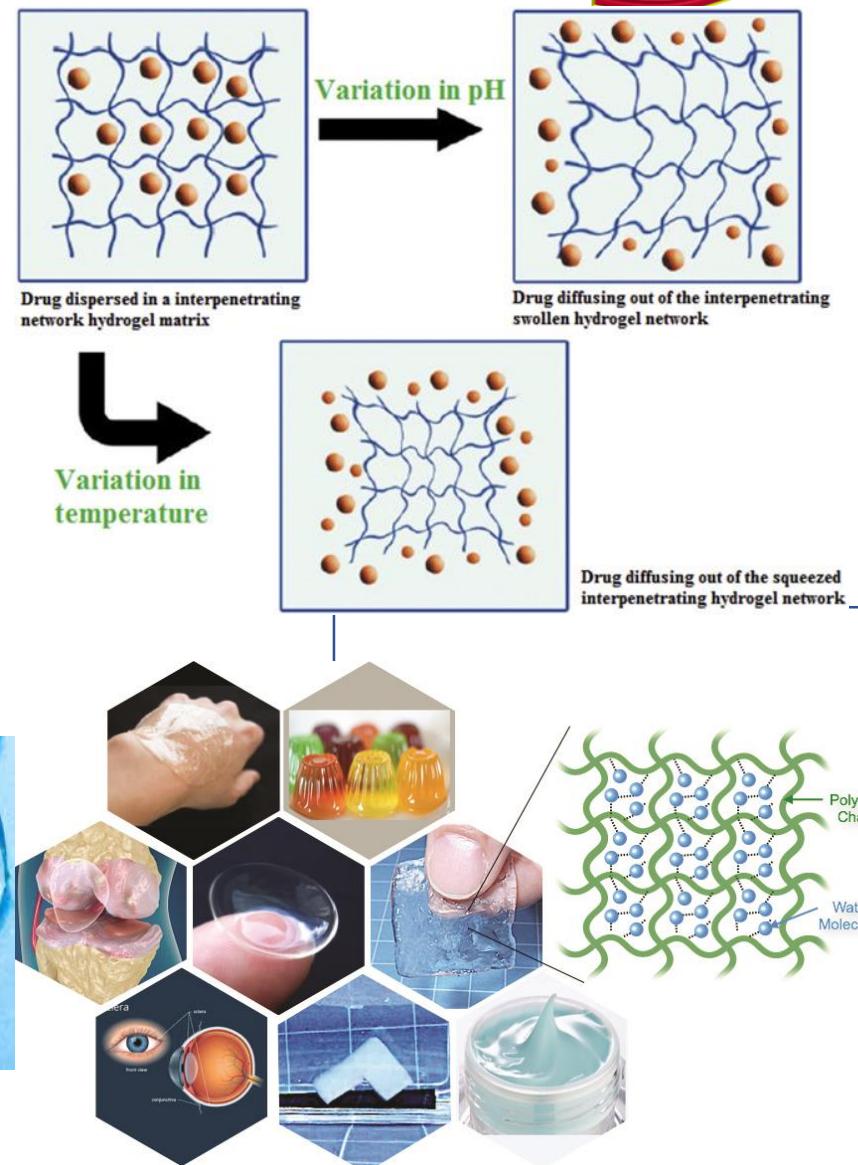
7. Hydrogels:

- Hydrogels are a unique class of three dimensional cross-linked polymeric networks that can hold a large fraction of aqueous solvents and biological fluids within their structures.
- Water-absorbing polymers that can change their size and shape in response to environmental conditions.

Engineering Applications:

Biomedical: Used in drug delivery, wound care, and tissue engineering due to their high water content and biocompatibility.

➤ The engineering applications of smart materials continue to expand as researchers and engineers explore new ways to leverage their unique properties for innovative solutions across various industries.



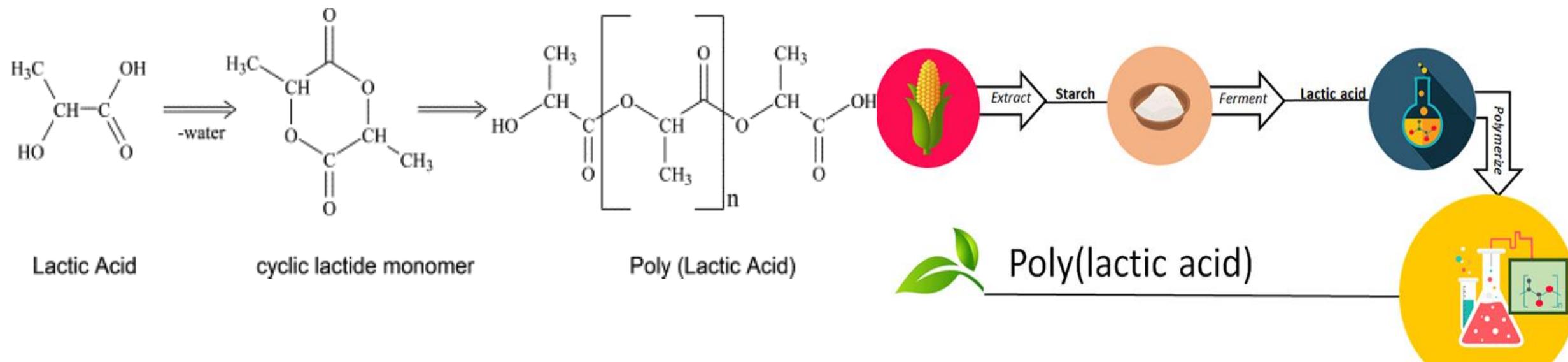


Poly L-Lactic Acid (PLLA):

- Polylactic acid (PLA) is chosen as the polymer with shape-memory properties.
- PLLA is a biodegradable and bioactive thermoplastic made from renewable resources such as starch, sugarcane, etc.

Preparation:- It is prepared by the catalytic dimerisation of lactic acid resulting in the formation of lactide monomer .

polymerisation of lactide monomer, in presence of stannous octate($C_{16}H_{30}O_4Sn$) to give poly lactic acid.





Properties of Polylactic Acid (PLA):

PLA exhibits a range of properties that make it suitable for various applications:

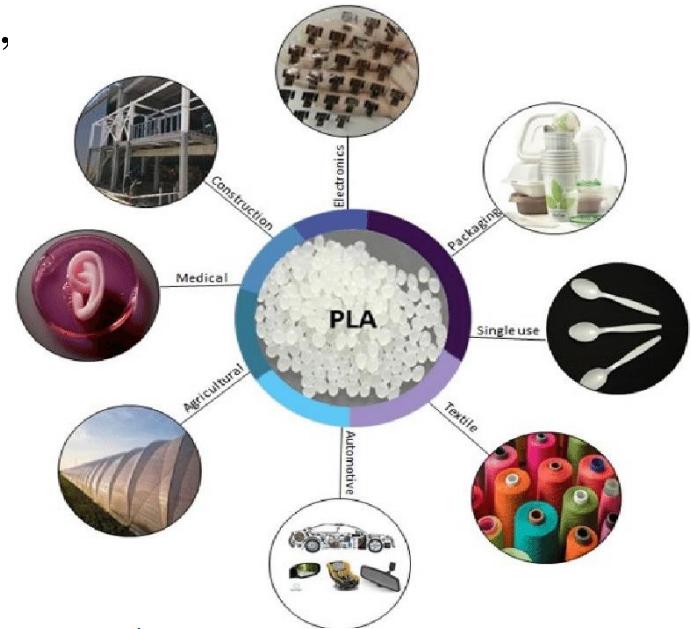
- 1. Biodegradability:** PLA is biodegradable under the right conditions, making it an environmentally friendly material.
- 2. Biocompatibility:** It is safe for use in medical and food-contact applications due to its biocompatibility.
- 3. Transparency:** PLA is transparent and can be made into clear, glossy products.
- 4. Renewable Source:** PLA is derived from renewable resources, such as corn starch or sugarcane.
- 5. Rigidity:** It offers good rigidity and can be engineered to be similar in strength to conventional plastics.
- 6. Heat Resistance:** PLA has moderate heat resistance, but it may deform at relatively low temperatures, limiting its use in high-temperature applications.
- 7. Brittleness:** PLA can be somewhat brittle, which can affect its use in applications requiring impact resistance.
- 8. Barrier Properties:** It has reasonable barrier properties against moisture and gases.



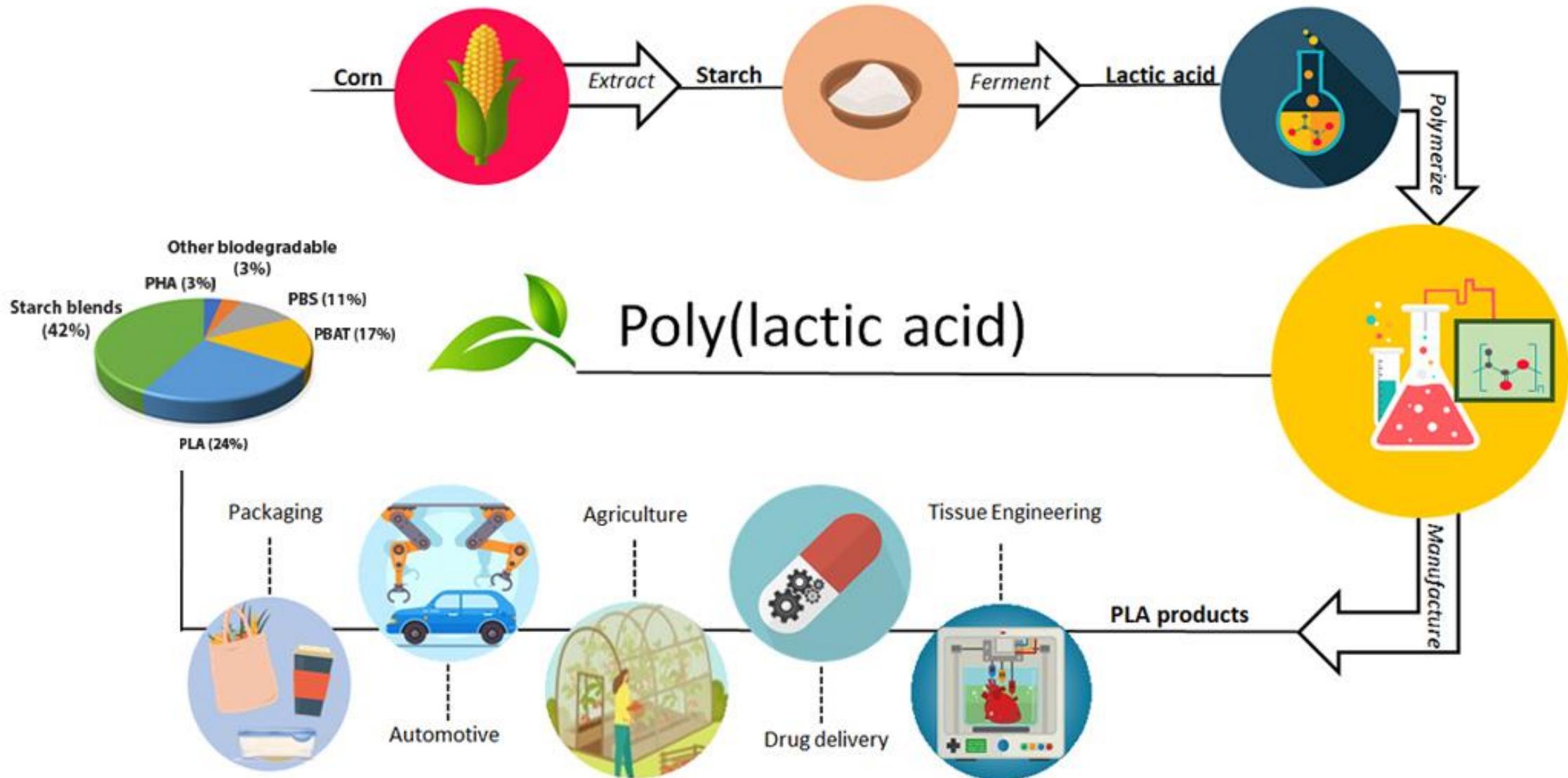
Uses of Polylactic Acid (PLA):

PLA finds applications in various industries due to its unique properties:

- Packaging:** For producing biodegradable and compostable packaging materials, such as disposable cups, food containers, and films.
- Textiles:** PLA fibers are used in the textile industry to produce biodegradable and sustainable fabrics.
- Medical and Healthcare:** Used in medical devices, such as sutures, tissue engineering scaffolds, and drug delivery systems, due to its biocompatibility.
- 3D Printing:** It is a popular material for 3D printing due to its ease of use, biodegradability, and availability in various colors.
- Filaments:** It is used in the manufacture of filaments for fused deposition modeling (FDM) 3D printers.
- Biodegradable Films:** PLA films are used for agricultural applications, such as mulch films, as they can be plowed into the soil after use.
- Disposable Tableware:** PLA is used to produce disposable plates, bowls, and utensils for single-use applications.
- Consumer Goods:** PLA can be found in consumer goods like toys, cutlery, and cosmetic packaging.



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Applications of Smart Materials

- ▶ Smart switches & actuators(NiTi -long life)
- ▶ Safety device, fuse, alarms (CuZnAl –reliability)
- ▶ Artificial limbs, blood vessels & muscles
(SM Polyurethane –bio compatibility)
- ▶ Adhesive tapes/bands (time bound adhesive property /painless removal/healing property)
- ▶ Food packaging industry–wrappers(adoptability)
- ▶ Smart spoons (Temperature sensitive polymers)
- ▶ Smart nose & tongue (recognition characteristics)
- ▶ Smart clothes (Adaptive to temperature changes)



TOPICS:

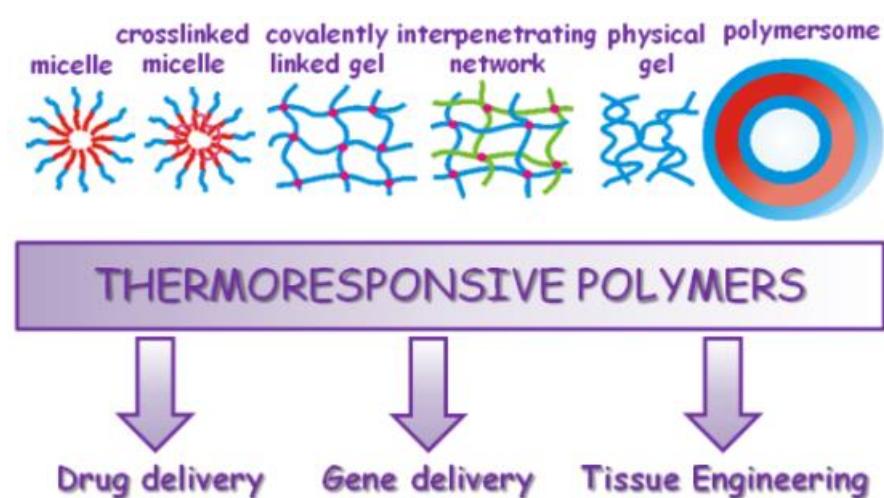
- Thermo response materials
- Polyacryl amides, Poly vinyl amides

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Thermo-responsive materials:(Temperature-responsive polymers)

- These are the polymers that exhibit drastic and discontinuous changes in their physical properties with temperature.
- Thermo responsive polymers are a class of “smart” materials that have the ability to respond to a change in temperature; a property that makes them useful materials in a wide range of applications and consequently attracts much scientific interest.



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There are two main types of Thermo responsive polymers:

- 1. Lower critical solution temperature (LCST)**

- 2. Upper critical solution temperature (UCST)**

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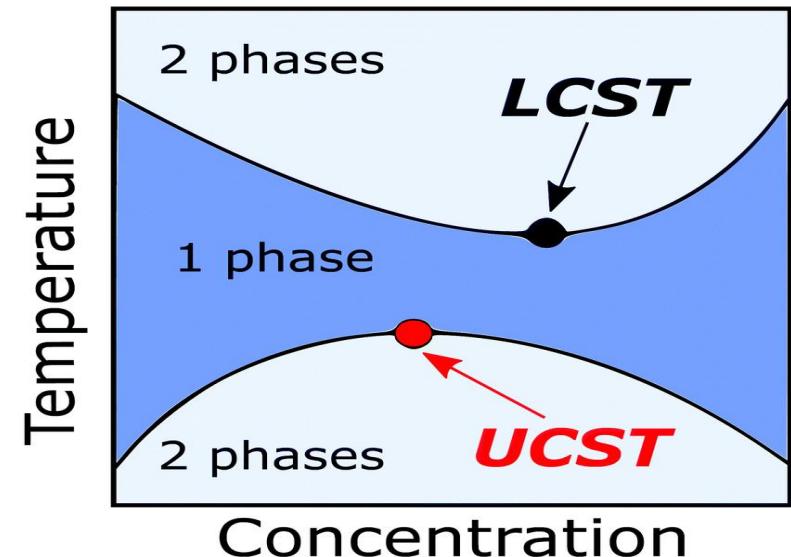


1. Lower critical solution temperature (LCST) :

The lower critical solution temperature (LCST) or lower consolute temperature is the critical temperature below which the components of a mixture are miscible in all proportions.

2. Upper critical solution temperature (UCST):

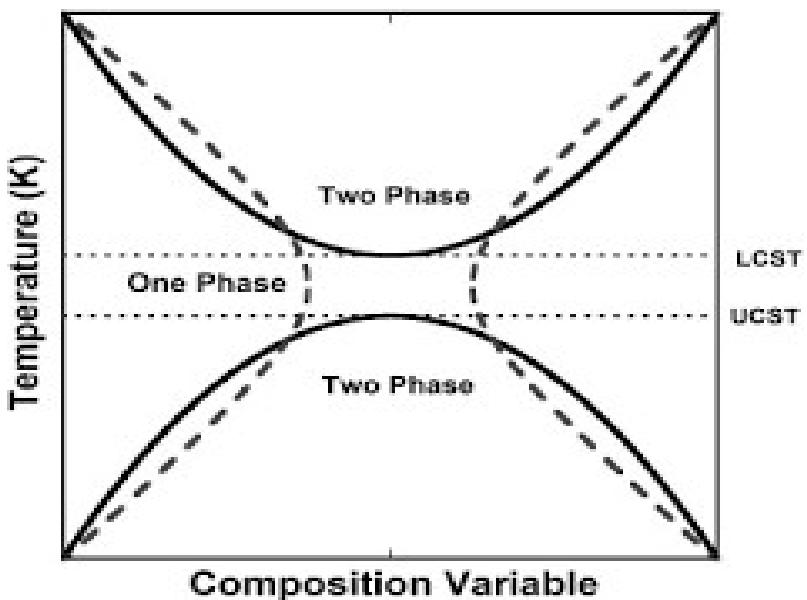
The upper critical solution temperature (UCST) or upper consolute temperature is the critical temperature above which the components of a mixture are miscible in all proportions.



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- LCST and UCST are the respective critical temperature points below and above which the polymer and solvent are completely miscible.

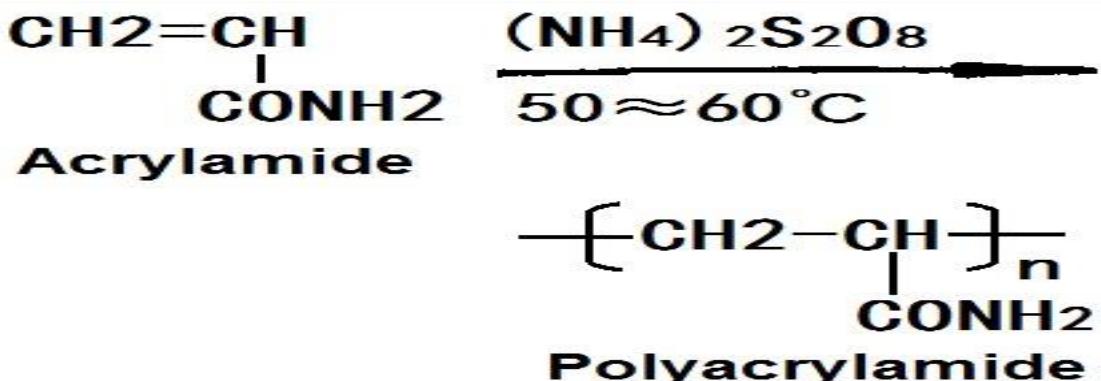


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Polyacrylamide:

- also briefly referred as PAM, is commonly a polymer with acrylamide monomers bonded connected by end to end configuration.
- It is formed by the polymerization of free acrylamide monomer radical.
- it is a hard glassy solid at room temperature.



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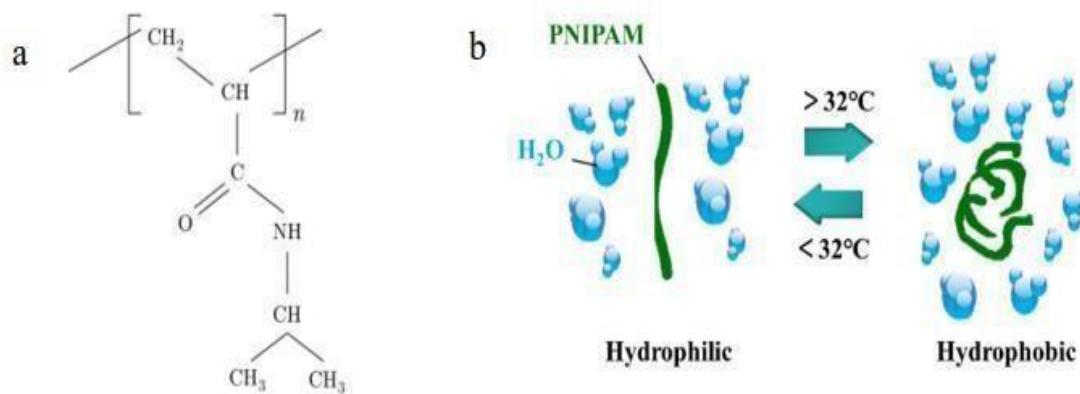
- PAM has both hydrophilic amido groups and hydrophobic alkylene groups.
- When the temperature is low, there is a strong hydrogen bond between the amide groups and the external water molecules.
- PAM is hydrophilic, macroscopically swelling occurs for the volume.



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- When the temperature reaches the low critical dissolution temperature (LCST), the hydrogen bond between the amide group and the water molecule is destroyed, the hydrophobicity of the alkyl group in the structure plays a leading role, and PAM becomes hydrophobic and gradually shrinks.
- Many studies have shown that the LCST of PAM is about 32°C, which is close to physiological temperature and easy to adjust, so it has been developed for biomedical, e.g., drug delivery systems, cardiovascular repair, sensing analysis, medical imaging and so on.



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Properties of poly acrylamide

- **Polyacrylamide (PAM)** is a water-soluble synthetic polymer which possesses useful properties such as good adhesiveness, proper hygroscopicity, high hydrophilicity, and non-toxicity.
- It has good thermal stability and is soluble in water.
- its aqueous solution is clear and transparent with its viscosity increasing with increased molecular weight of the polymer, and also having a logarithmic relationship with the change in concentration of the polymer.
- Except for a few solvent such as acetic acid, acrylic acid, ethylene glycol, glycerol and formamide, it is generally insoluble in organic solvents.

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Thermoresponsive Property:

- PAM is a well-known thermo responsive poly acrylamide. It has a lower critical solution temperature (LCST) around 32°C. Below this temperature, PAM is water-soluble and hydrophilic.
- Above the LCST, it becomes hydrophobic and undergoes a phase transition, precipitating out of solution.

Applications:

- PAM and other polyacrylamides with similar thermoresponsive properties have applications in drug delivery, tissue engineering, and as components in smart materials.
- Serum proteins must be adequately removed to prevent inhibition of the trypsin. If phenol present in cell media, the poly acrylamide gels should change from a pink color to almost clear, indicating the cells are ready to be trypsinized.



Other uses of PAM

1. It is used as a flocculants in water treatment industry.
2. It can be used as setting agent in sugar industry settling agent
3. It can be used as a soil conditioner, flocculants, and can be used in textile
4. It can be used at coal field, oil field
5. It can also be used as sewage treatment agent

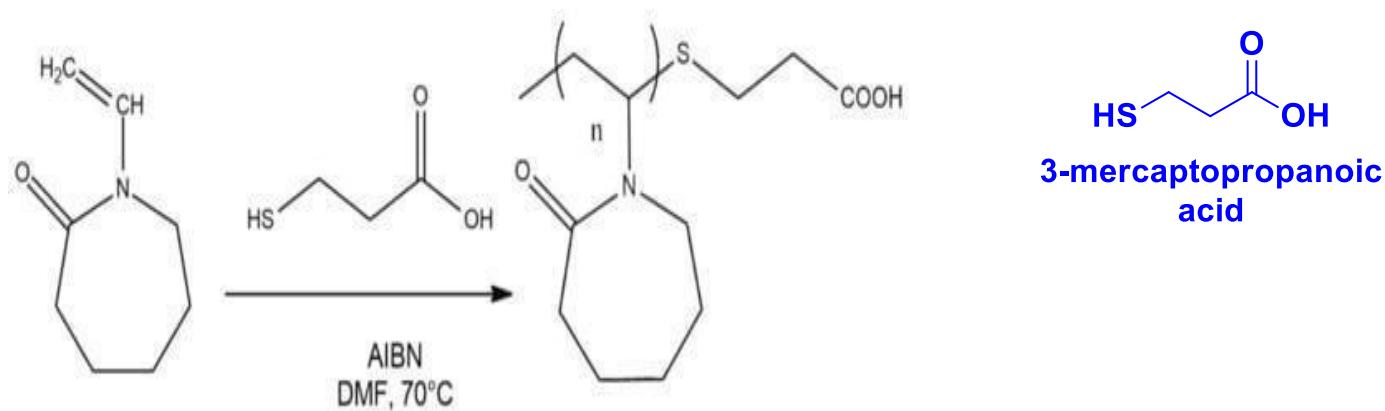
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Poly vinylamides (PVAm):

Amongst thermoresponsive polyvinyl amides, Poly(N-vinylcaprolactam) (PNVCL) is a well-studied temperature-responsive polymer, second only to poly(Nisopropylacrylamide) (PNIPAAm) the most popular temperature-responsive polymer.

The polymers show similar LCST behavior in water between 30-32 °C.



Synthesis of PNVCL-COOH polymers by free radical polymerization by using a modified version of the protocol.

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Properties of PVAm

- **Able to thicken across a wide range of pH.**
- **Able to thicken high salt concentration solutions.**
- **Resistance to acids and alkalis.**
- **Water-soluble.**
- **Adhesion and pressure sensitive adhesion.**
- **Resistant to heat.**
- **PVA properties like strength, thermostability, chemical resistance, transparency, lightweight, and moldability.**



Poly vinylamides (PVAm):

Thermo responsive Property:

- Poly(N-vinylcaprolactam) (PNVCL) is an example of a polyvinylamide with thermoresponsive behavior.
- It exhibits a similar LCST as PNIPAAm, making it soluble in water below the LCST and insoluble above it.

Applications:

- Poly vinylamides are used in various applications, including drug delivery, as flocculants, and in the formulation of responsive coatings.

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- In both cases, the thermo responsive behavior of these polymers allows for controlled changes in their solubility, which is advantageous for applications where temperature-dependent properties are desired.
- These properties can be harnessed in drug delivery systems, where the polymer can act as a carrier that releases its payload in response to temperature changes, or in other smart material applications.
- Additionally, the LCST of these polymers is often close to body temperature, making them particularly suitable for biomedical applications.

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A black and gold fountain pen is positioned diagonally across a white surface, pointing towards the top left. It has written the words "Thank you" in a large, elegant, black cursive script.

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