LECTURE NOTESON

ENGINEERING CHEMISTRY
ACADEMIC YEAR 2021-22

I B.Tech –II SEMESTER (R20)
CIVIL & MECH

E MINNIBABU, Assistant Professor

DEPARTMENT OF HUMANITIES AND BASIC SCIENCES

V S M COLLEGE OF ENGINEERING
RAMCHANDRAPURAM
E.G DISTRICT533255

JAWAHARLAL NEHRU TECHNOLOGICAL UNIVERSITY KAKINADA
KAKINADA – 533 003, Andhra Pradesh, India

DEPARTMENT OF CIVIL ENGINEERING

I Year - II Semester		L	T	P	C
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ENGINEERING CHEMISTRY (BS1202) ((Non-circuit branches)					

Knowledge of basic concepts of Chemistry for Engineering students will help them as professional engineers later in design and material selection, as well as utilizing the available resources.

COURSE OBJECTIVES

- ***Importance*** of usage of plastics in household appliances and composites (FRP) in aerospace and automotive industries.
- ***Outline*** the basics for the construction of electrochemical cells, batteries and fuel cells. Understand the mechanism of corrosion and how it can be prevented.
- ***Express*** the increases in demand as wide variety of advanced materials are introduced; which have excellent engineering properties. ***Classify and discuss*** the materials used in major industries like steel industry, metallurgical industries and construction industries and electrical equipment manufacturing industries. Lubrication is also ***summarized***.
- ***Relate*** the need of fuels as a source of energy to any industry, particularly industries like thermal power stations, steel industry, fertilizer industry etc., and hence introduced.
- ***Explain*** the importance and usage of water as basic material in almost all the industries; ***interpret*** drawbacks of steam boilers and also how portable water is supplied for drinking purposes.

UNIT I: POLYMER TECHNOLOGY 8 hrs

Polymerisation:- Introduction, methods of polymerization (emulsion and suspension), mechanical properties.

Plastics: Compounding, fabrication (compression, injection, blown film and extrusion), preparation, properties and applications (PVC, polycarbonates and Bakelite), mention some examples of plastic materials used in electronic gadgets, recycling of e-plastic waste (waste to wealth).

Elastomers:- Introduction, preparation, properties and applications (Buna S, thiokol and polyurethanes).

Composite materials: Fiber reinforced plastics, conducting polymers, biodegradable polymers, biopolymers, biomedical polymers.

Course Outcomes: *At the end of this unit, the students will be able to*

- ***Analyze*** the different types of composite plastic materials and ***interpret*** the mechanism of conduction in conducting polymers.

UNIT II: ELECTROCHEMICAL CELLS AND CORROSION 10 hrs

Single electrode potential, electrochemical series and uses of series, standard hydrogen electrode, calomel electrode, construction of glass electrode, batteries (Dry cell, Li ion battery and zinc air cells), fuel cells (H_2-O_2, CH_3OH-O_2, phosphoric acid and molten carbonate).

Corrosion:-Definition, theories of corrosion (chemical and electrochemical), galvanic corrosion, differential aeration corrosion, stress corrosion, galvanic series, factors influencing rate of corrosion, corrosion control (proper designing and cathodic protection), Protective coatings (surface preparation, cathodic coatings, anodic coatings, electroplating and electroless plating [nickel]), Paints (constituents, functions and special paints).

Course Outcomes: ***At the end of this unit, the students will be able to***

- ***Utilize*** the theory of construction of electrodes, batteries and fuel cells in redesigning new engineering products and c***ategorize*** the reasons for corrosion and study methods to control corrosion.

UNIT III: CHEMISTRY OF MATERIALS 10 hrs

Part- A:

Nano materials:- Introduction, sol-gel method, characterization by (Brunauer Emmet Teller [BET]), (scanning electron microscopy [SEM]) and (transmission electron microscopy [TEM]) with example (TiO_2), applications of graphene and fullerenes, carbon nanotubes (types, preparation and applications)

Thermal analysis techniques: Instrumentation and applications of thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC).

Part-B:

Refractories: - Definition, classification, properties (refractoriness, refractoriness under load, porosity and thermal spalling), failure of refractories.

Lubricants: - Definition, mechanism of lubricants, properties (definition and importance).

Cement: - Constituents, manufacturing, parameters to characterize the clinker formation: lime saturation factor (LSF), silica ratio (SR) and alumina ratio (AR), chemistry of setting and hardening, deterioration of cement.

Course Outcomes: ***At the end of this unit, the students will be able to***

- ***Synthesize*** nanomaterials for modern advances of engineering technology.
- ***Summarize*** the techniques that detect and measure changes of state of reaction.
- ***Illustrate*** the commonly used industrial materials.

UNIT IV: FUELS 10 hrs

Introduction, calorific value, higher calorific value, lower calorific values, problems using Dulong's formula, proximate and ultimate analysis of coal sample and their significance, numerical problems, petroleum (refining-cracking), synthetic petrol (Fischer Tropsch and Bergius), petrol knocking, diesel knocking, octane and cetane ratings, anti-knocking agents, Introduction to alternative fuels (Bio-diesel, ethanol, methanol, natural gas, liquefied petroleum gas, compressed natural gas), Flue gas analysis by Orsat apparatus, rocket fuels.

Course Outcomes: ***At the end of this unit, the students will be able to***

- ***Differentiate*** petroleum, petrol, synthetic petrol and have knowledge how they are produced.
- ***Study*** alternate fuels and a***nalyse*** flue gases.

UNIT V: WATER TECHNOLOGY 8 hrs

Hardness of water, determination of hardness by complexometric method, boiler troubles (priming and foaming, scale formation, boiler corrosion, caustic embrittlement), internal treatments, softening of hard water (zeolite process and related sums, ion exchange process), treatment of industrial waste water, potable water and its specifications, steps involved in purification of water, chlorination, break point chlorination-desalination (reverse osmosis and electro dialysis).

Course Outcomes: ***At the end of this unit, the students will be able to***

- ***Analyze*** the suitable methods for purification and treatment of hard water and brackish water.

Standard Books:

1. P.C. Jain and M. Jain "**Engineering Chemistry**", 15/e, Dhanpat Rai & Sons, Delhi, (Latest edition).
2. Shikha Agarwal, "**Engineering Chemistry**", Cambridge University Press, New Delhi, (2019).
3. S.S. Dara, "**A Textbook of Engineering Chemistry**", S.Chand & Co, (2010).
4. Shashi Chawla, "Engineering Chemistry", Dhanpat Rai Publicating Co. (Latest edition).

Reference:

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2. O.G. Palana, "**Engineering Chemistry**", Tata McGraw Hill Education Private Limited, (2009).
3. CNR Rao and JM Honig (Eds) "**Preparation and characterization of materials**" Academic press, New York (latest edition)
4. B. S. Murthy, P. Shankar and others, "**Textbook of Nanoscience and Nanotechnology**", University press (latest edition)

VSM COLLEGE OF ENGINEERING

RAMACHANDRAPURAM

DEPARTMENT OF BASIC SCIENCES AND HUMANITIES

Course Title	Year/Sem	Branch	Periods per Week
APPLIED CHEMISTRY	I/II	CSE BRANCH	5

Course Objectives

- Importance of usage of plastics in household appliances and composites (FRP) in aerospace and automotive industries.

- Outline the basics for the construction of electrochemical cells, batteries and fuel cells. Understand the mechanism of corrosion and how it can be prevented.

- Explain the preparation of semiconductors and nanomaterials, engineering applications of nanomaterials, superconductors and liquid crystals.

- Recall the increase in demand for power and hence alternative sources of power are studied due to depleting sources of fossil fuels. Advanced instrumental techniques are introduced.

- Outline the basics of computational chemistry and molecular switches

Unit No	Outcomes	Name of the Topic	No. of Periods required	Total Periods	Reference Book	Methodology to be adopted
		Unit-1				
I	CO 1, CO3, CO4 ***Polymerisation, Plastics, Elastomers***	Introduction, methods of polymerization	1	14	T1, T2 R20	Black Board
		Emulsion and suspension Polymerization	2			Black Board
		Mechanical properties of Polymers	1			Black Board
		Compounding, fabrication	1			E- CLASS ROOM
		compression, injection moulding	1			Black Board
		blown film and extrusion	1			E- CLASS ROOM
		preparation, properties and applications (PVC, polycarbonates and Bakelite)	2			Black Board
		plastic materials used in electronic gadgets	1			
		recycling of e-plastic waste	1			Black Board
		Introduction, preparation, properties and applications (Buna S, Thiokol and polyurethanes	1			Black Board
		Fiber reinforced plastics, conducting polymers	1			E- CLASS ROOM
		biodegradable polymers, biopolymers, biomedical polymers	1			Black Board

		Unit-2				
II	CO 1, CO3,CO4 Single electrode potential, ***Corrosion***	Single electrode potential, electrochemical series and uses of series	2	12	T1, T2 R20	Black Board
		standard hydrogen electrode, calomel electrode, construction of glass electrode	2			Black Board
		batteries (Dry cell, Li ion battery and zinc air cells), fuel cells (H_2-O_2, CH_3OH-O_2, phosphoric acid and molten carbonate)	2			E-CLASS ROOM
		Definition, theories of corrosion (chemical and electrochemical), galvanic corrosion, differential aeration corrosion, stress corrosion	2			Black Board
		galvanic series, factors influencing rate of corrosion, corrosion control (proper designing and cathodic protection	2			Black Board
		Protective coatings (surface preparation, cathodic coatings, anodic coatings, electroplating and electro less plating, Paints (constituents, functions and special paints).	2			Black Board
		Unit-3				
III	CO1, CO2, CO3 ***Nano materials, Thermal analysis techniques, Lubricants, Cement***	Introduction, sol-gel method	2	10	T1, T2 R20	Black Board
		characterization by (Brunauer Emmet Teller [BET])	1			Black Board
		applications of graphene and fullerenes, carbon nanotubes (types, preparation and applications)	1			E-CLASS ROOM
		Instrumentation and applications of thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC).	1			Black Board
		Definition, mechanism of lubricants, properties (definition and importance).	1			
		Constituents, manufacturing, parameters to characterize the clinker formation: lime saturation factor (LSF),	2			Black Board
		silica ratio (SR) and alumina ratio (AR),chemistry of setting and hardening, deterioration of cement..	1			E- CLASS ROOM
		deterioration of cement	1			Black Board

IV	CO 1, CO3, CO4 FUELS, Introduction, synthetic petrol (Fischer Tropsch and Bergius)	**Unit-4**		16		
		Introduction, calorific value, higher calorific value	2			Black Board
		lower calorific values, problems using Dulong’s formula, proximate and ultimate analysis of coal sample and their significance	2			Black Board
		numerical problems, petroleum (refining-cracking)	2			E-CLASS ROOM
		synthetic petrol (Fischer Tropsch and Bergius)	2			Black Board
		petrol knocking, diesel knocking,	1			Black Board
		anti-knocking agents	2			Black Board
		Introduction to alternative fuels (Bio-diesel, ethanol, , natural gas, liquefied petroleum gas, compressed natural gas)	2			Black Board
		Flue gas analysis by Orsat apparatus	1			Black Board
		rocket fuels	2			E-CLASS ROOM
		octane and cetane ratings	1			Black Board
		methanol.	1			Black Board

V	CO 1, CO2, CO3, CO4 Hardness of water, potable water and its specifications	**Unit-5**		12	T1, T2 R20	Black Board
		Hardness of water, determination of hardness by complexometric method	2			Black Board
		boiler troubles (priming and foaming, scale formation	2			Black Board
		boiler corrosion, caustic embrittlement)	2			E-CLASS ROOM
		internal treatments, softening of hard water (zeolite process and related sums, ion exchange process)	2			Black Board
		treatment of industrial waste water, potable water and its specifications	2			Black Board
		steps involved in purification of water, chlorination, break point chlorination-desalination (reverse osmosis and electro dialysis).	2			Black Board

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Faculty Member **Head of the Department** **Principal**

Applied chemistry

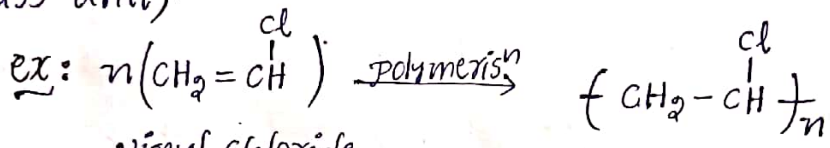
1. Polymer Technology

Introduction:

Polymer is a largest molecule formed by the repeated combination of small molecules (or) units called monomers.

⟹ In a polymer monomers are held together by covalent bonds.

⟹ Molecular weight of polymer lies between 5000 - 200 000 AMU (atomic mass unit).



ex: $n\left(CH_2=\overset{Cl}{\overset{|}{CH}}\right) \xrightarrow{\text{polymerisn}} \left[CH_2-\overset{Cl}{\overset{|}{CH}} \right]_n$

vinyl chloride PVC

where 'n' is degree of polymerisation.

Degree of polymerisation:

Number of repeating units in a polymer is known as degree of polymerisation.

Functionality:

Number of reactive sites in a monomer is called functionality of a monomer.

ex: ethene is bi functional monomer.

Polymerisation:

It is the chemical reaction at which two or more monomers combined together to form a polymer is known as polymerisation.

ex: $n(CH_2=CH_2) \xrightarrow{\text{polymerisation}} [CH_2-CH_2]_n$

monomer (ethene) polymer (polythene)

Types of polymerisation:

Based upon mechanism polymerisation is four types. They are

1. Addition polymerisation
2. condensation polymerisation
3. Co-polymerisation
4. co-ordination polymerisation (or) Zieglar-natta Polymerisation

Addition polymerisation:

It is the polymerisation reaction at which two or more monomers combined together without elimination of simple molecules is known as addition polymerisation.

ex: polythene, poly vinyl chloride (PVC), Teflon ... etc

⇒ Addition polymerisation is of three types of mechanism

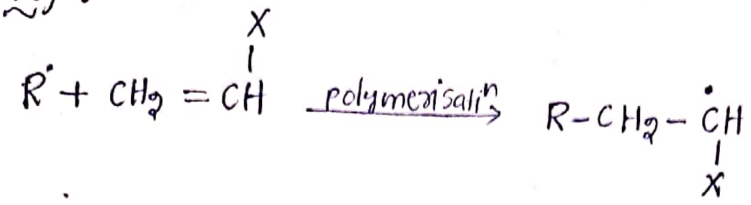
a) free radical mechanism
b) anionic mechanism
c) cationic mechanism.

a) **Free radical mechanism:** It undergoes homolytic clevage mean the bond is shifted towards both sides of the carbon elements.

$$R_2O_2 \xrightarrow[\text{ii) Light, iii) catalyst}]{\text{i) heat,}} 2R^{\cdot} + O_2\uparrow$$

→ It follows three steps. They are

Initiation step:

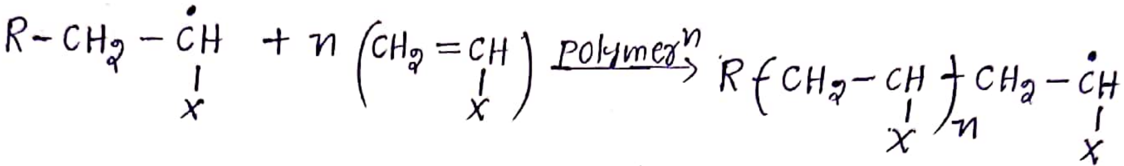


$$R^{\bullet} + CH_2 = \overset{X}{\overset{|}{CH}} \xrightarrow{\text{polymerisali}^{n}} R-CH_2-\underset{X}{\underset{|}{\dot{C}H}}$$

monomer radical

Propogation step:

In this step monomer radical reacts with another monomer for growth the chain.

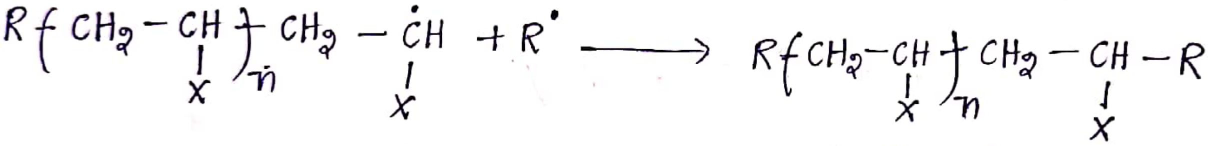


$$R-CH_2-\underset{X}{\underset{|}{\dot{C}H}} + n\left(CH_2=\underset{X}{\underset{|}{CH}}\right) \xrightarrow{\text{Polymer}^{n}} R\left(CH_2-\underset{X}{\underset{|}{CH}}\right)_n CH_2-\underset{X}{\underset{|}{\dot{C}H}}$$

"propogated monomer radical"

Termination step:

In this, The growth of chain is stopped with radical



$$R\left(CH_2-\underset{X}{\underset{|}{CH}}\right)_n CH_2-\underset{X}{\underset{|}{\dot{C}H}} + R^{\bullet} \longrightarrow R\left(CH_2-\underset{X}{\underset{|}{CH}}\right)_n CH_2-\underset{X}{\underset{|}{CH}}-R$$

dead polymer

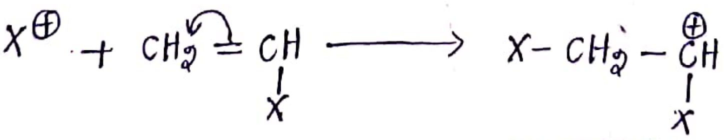
b) cationic mechanism:

Lewis acids are initiators. The electron pair acceptor (or) electron deficiency molecules acts as Lewis acid.

ex: $AlCl_3$, BF_3, $BeCl_2$, BCl_3 are positively charged metal ions.

⟹ Lewis acids are denoted as $X^{\oplus}$

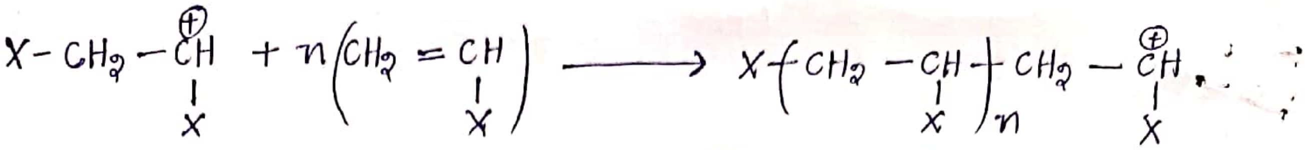
Initiation step:



$$X^{\oplus} + CH_2 = \underset{X}{\underset{|}{CH}} \longrightarrow X-CH_2-\underset{X}{\underset{|}{\overset{\oplus}{C}H}}$$

momer cation

Propogation step: In this step monomer cation reacts with another monomer for growth the chain.

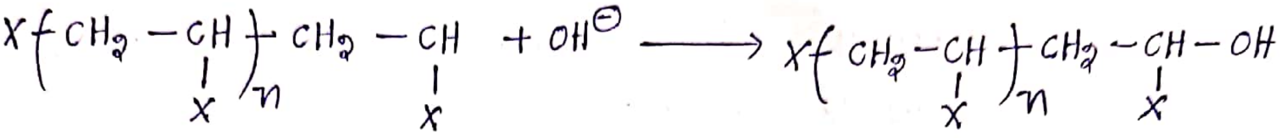


$X-CH_2-\overset{\oplus}{\underset{X}{CH}} + n\left(CH_2=\underset{X}{CH}\right) \longrightarrow X\left(CH_2-\underset{X}{CH}\right)_n CH_2-\overset{\oplus}{\underset{X}{CH}}$

Propagated monomer cation

Termination step:

In this step the growth of chain is stopped with OH^- ions.



$X\left(CH_2-\underset{X}{CH}\right)_n CH_2-\underset{X}{CH} + OH^\ominus \longrightarrow X\left(CH_2-\underset{X}{CH}\right)_n CH_2-\underset{X}{CH}-OH$

dead polymer.

c) Anionic mechanism:

Lewis bases are initiators. The electron pair donar (or) electron efficiency molecules acts as Lewis base.

ex: NH_3

⇒ Lewis bases are simple denoted as $Y^\ominus$

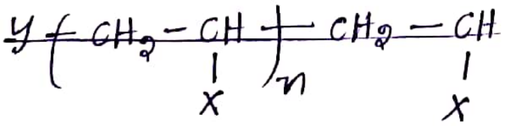
Initiation step:

$Y^\ominus + CH_2=\underset{X}{CH} \longrightarrow Y-CH_2-\overset{\ominus}{\underset{X}{CH}}$

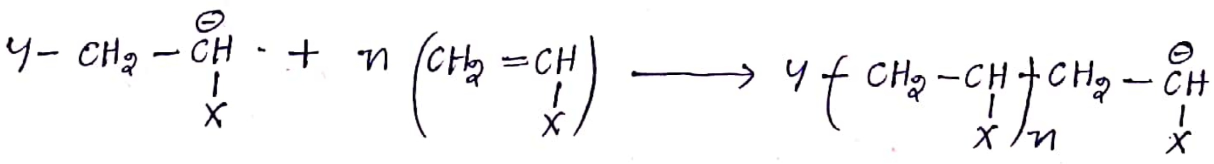
monomer anion

Propogation step:

In this step monomer anion reacts with another monomer for growth the chain.



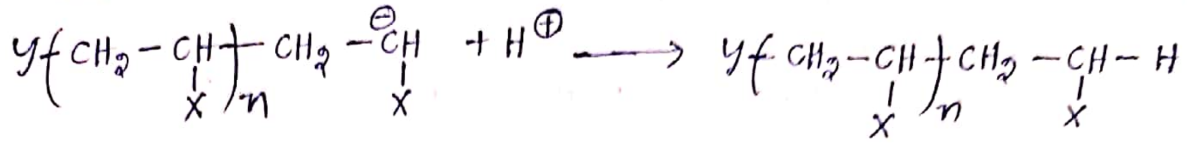
~~$Y\left(CH_2-\underset{X}{CH}\right)_n CH_2-\underset{X}{CH}$~~



$Y-CH_2-\overset{\ominus}{\underset{X}{CH}} + n\left(CH_2=\underset{X}{CH}\right) \longrightarrow Y\left(CH_2-\underset{X}{CH}\right)_n CH_2-\overset{\ominus}{\underset{X}{CH}}$

propogated monomer anion

Termination step:



$$Y\left(CH_2-\underset{X}{CH}\right)_n CH_2-\underset{X}{\overset{\ominus}{C}H} + H^{\oplus} \longrightarrow Y\left(CH_2-\underset{X}{CH}\right)_n CH_2-\underset{X}{CH}-H$$

dead polymer

2. Condensation polymerisation:

It is a polymerisation reaction at which two or more monomer combined together to form a polymer with elemination of simple molecules like alcohol, water, amonia is known as condensation polymerisation.

ex: bakelite (phenol formaldehye, resin, urea formaldehyde resin).

Flow chart:

Phenol + Formaldehyde

↓ (acid / alkali's)

Mono methylol phenol

↓ (conc H_2SO_4)

Novalac (Linear polymer)

$-nH_2O$ ↓ hexamine

bakelite [(cross-link), bulk polymer]

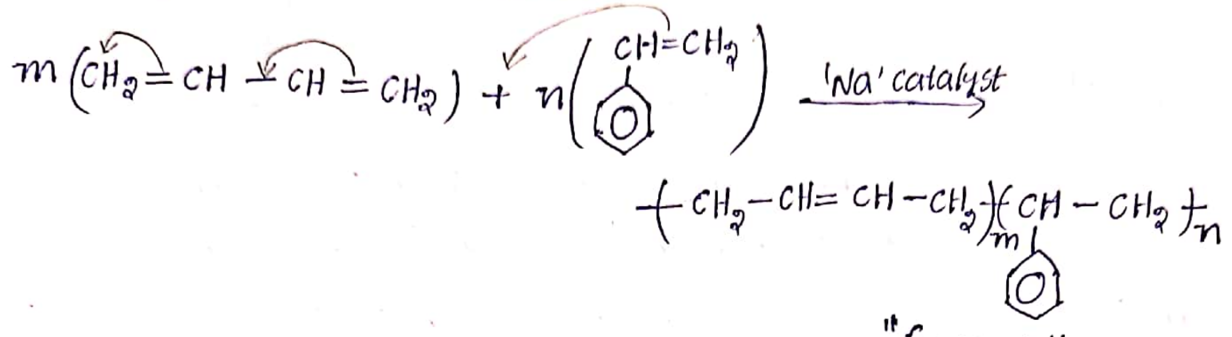
3. Co-polymerisation:

It is the polymerisation reaction at which two different monomers combined together to form entirely different polymer is known as co-polymer~~isation~~ and process is called co-polymerisation.

ex: buna-S, buna-N

Preperation of buna-s:

1,3- butadiene and styrene undergoes co-polymeri-sation to form buna-s rubber



"buna-s"

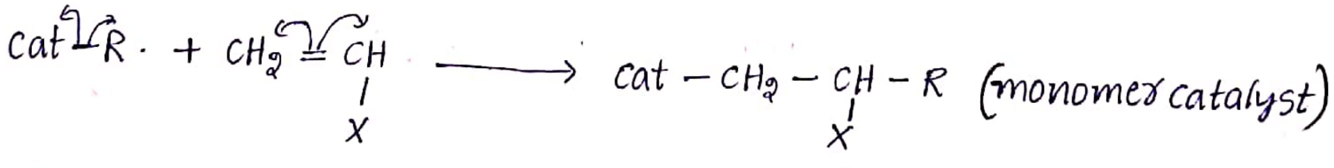
4. co-ordination polymerisation : ~~ze~~ (zieglar-natta) :

In this polymerisation two (or) more momers combined together to form a polymer in the presence of transition metal halide (catalyst) trialkylaluminium (co-~~plas~~ catalyst) is known as co-ordination polymerisation.

ex: $TiCl_3 + AlR_3$ (or) $TiCl_4 + AlR_3$

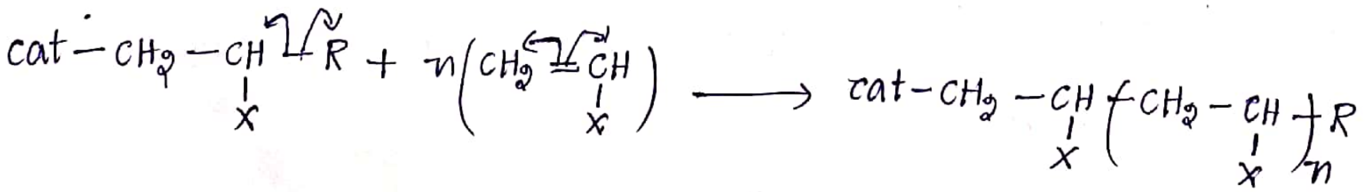
Mechanism:

Initiation step: catalyst reacts with monomer to form monomer catalyst.



$$\mathrm{cat-R} + \underset{\substack{|\\X}}{\mathrm{CH_2=CH}} \longrightarrow \mathrm{cat-CH_2-}\underset{\substack{|\\X}}{\mathrm{CH}}\mathrm{-R} \text{ (monomer catalyst)}$$

Propogation step: In this step monomer catalyst reacts with another monomer to growth the chain

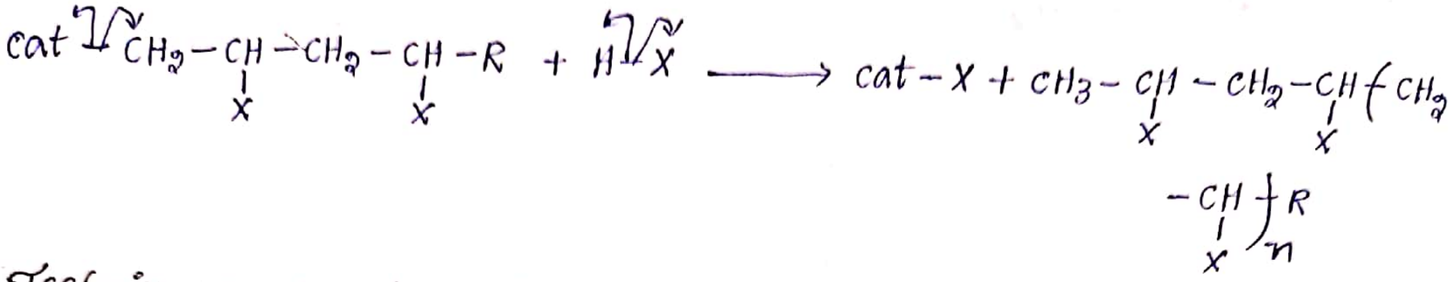


$$\mathrm{cat-CH_2-}\underset{\substack{|\\X}}{\mathrm{CH}}\mathrm{-R} + n\left(\mathrm{CH_2=}\underset{\substack{|\\X}}{\mathrm{CH}}\right) \longrightarrow \mathrm{cat-CH_2-}\underset{\substack{|\\X}}{\mathrm{CH}}\left(\mathrm{CH_2-}\underset{\substack{|\\X}}{\mathrm{CH}}\right)_n\mathrm{R}$$

"propogated monomer catalyst"

Termination step:

In this step the growth of chain is stopped with HX (hydrogen halides).

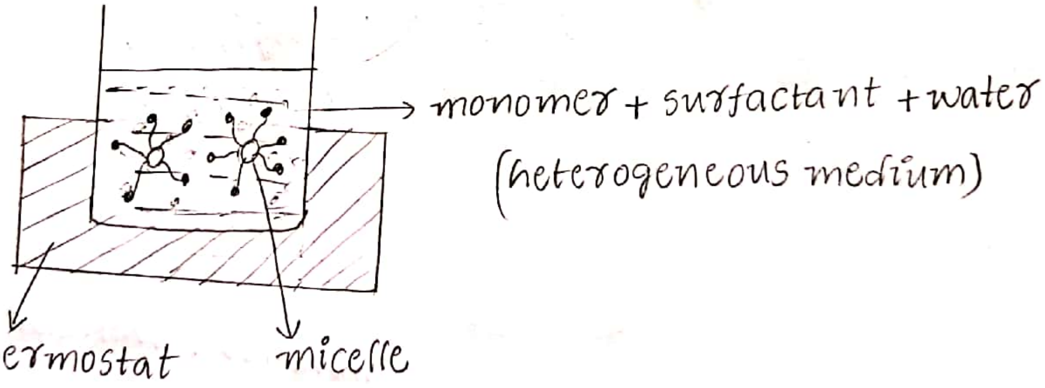


$$\text{cat}^{+}\,{}^{-}\text{CH}_2-\underset{X}{\text{CH}}-\text{CH}_2-\underset{X}{\text{CH}}-R + H^{+}X^{-} \longrightarrow \text{cat}-X + \text{CH}_3-\underset{X}{\text{CH}}-\text{CH}_2-\underset{X}{\text{CH}}\left(\text{CH}_2-\underset{X}{\text{CH}}\right)_n R$$

Techniques of polymerisation:

1. Emulsion polymerisation:

On the thermostat take a beaker contains water, monomer is heterogeneous medium, to this add surfactant means emulsifing agent and initiator in the presence of nitrogen at atmosphere, we get polymer. This process is known as emulsion polymerisation.



⇒ here,  : hydrophilic end

$$\Rightarrow \underbrace{\text{monomer} + H_2O}_{\text{heterogeneous medium}} + \text{surfactant} + \text{Initiator} \xrightarrow{N_2\ \text{atmosphere}} \text{polymer}$$

Advantages:

1. The rate of polymerisation is high.
2. Heat can be easily controlled and hence viscosity build up is low.

Disadvantages:

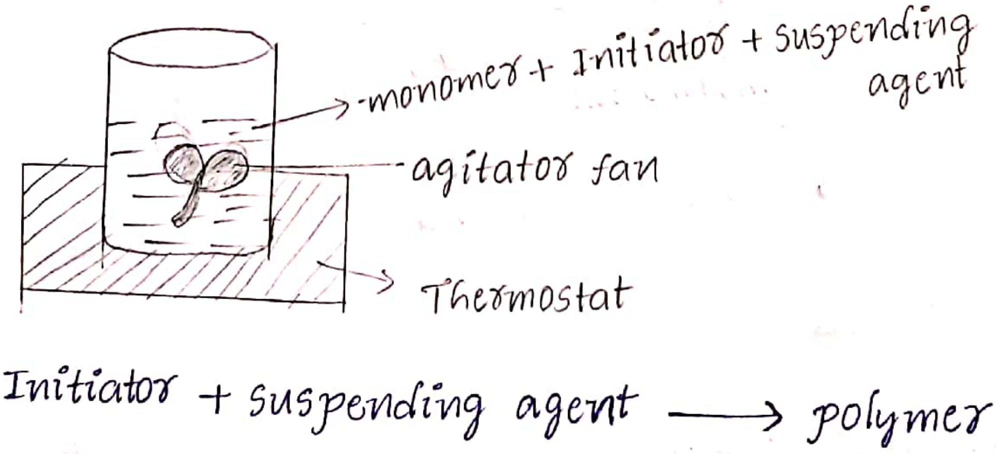
1. Polymer needs purification
2. It is difficult to remove entropped emulsifier and de emulsifier.

Application: emulsion polymerisation is used in largescale production like water based paints, adhesives, plastics etc.

2. Suspension polymerisation:

The monomer is water insoluble monomer to this add suspending agent is agitated at constant temperature in the presence of initiator we get polymer.

⇒ There is agitator fans to mix the suspension to get best polymer beads.



monomer + Initiator + suspending agent ⟶ polymer

Advantages:

1. Since water is used as a solvent. This method is economical.
2. Isolation of product is very easy and the product are very Pure.

Disadvantages:

1. This Method is applicable only for water insoluble monomers.
2. control of particle size is difficult.

Applications:

1. polystyrene beads are used as ion exchange resins.
2. ~~Pre~~posaration of thermacoal sheets for ceiling purpose.

Physical properties of polymers:

1. crystallinity: The polymers have 60% crystalline, 40% amorphous character, increasing of crystalline character automatically development of strength, hardness brittleness of a polymer.

   ex: 1. polythene have highly crystalline in a zig-zig confermation.

   2. Polythene have less crystalline in a bulky substituents.

2. Molecular weight:

   The strength and hardness will be depends upon molecular weight of polymer.

   ex: Less than 1000 – oily visous liquids

   1000–10,000 – soft, waxy solids.

greater than 10,000 – hard brittle solids
(or)
flexible solids.

3. Solubility:

The polymers are soluble in suitable organic solvents.

ex: eraser soluble in conc. H_2SO_4.

4. Effect of heat in polymer:

Polymers on heating gives rubbery state then visco-fluid state then degraded to monomer.

$$\text{Polymers} \xrightarrow{\Delta} \text{rubbery state} \xrightarrow{\Delta} \text{viscofluid state} \xrightarrow{\Delta} \text{degradation of monomer}$$

5. Permeability:

The polymers allows solvent molecules through it, i.e permeability property.

ex: In water, eraser absorbs water molecules and swell in size.

Mechanical properties of polymers:

1. elasticity:

This refers to the ability of material to recover to its initial shape and ~~diver~~ dimension when the applied stress removed.

2. plasticity:

The substances which are soften on heating and harden on cooling is known as plasticity.

ex: ~~rubber~~ plastic articles having plasticity nature.

3. **Hardness:** Refers to the ability of a material to surface deformation, indentation (or) abrasion.

4. **strength:** refers to the ability of a material to with stand a gradually applied stress without rupture.

5. **Ductility:** A ductile material undergoes large ~~in~~ irrecoverable deformation before rupture.

6. **brittleness:** A brittle material shatters suddenly without noticeable plastic deformation preceding failures.

Plastics: The substance are high molecular weight polymers which exhibits plasticity properties and can be moulded into desirable shape by applying, heat and pressure is called plastics.

ex: polythene, poly vinyl chloride (PVC), polystyrene ...etc.

Classification of plastics:

based upon heating the plastics are two types.

1. Thermo plastics (or) Thermo softening plastics
2. Thermo setting plastics (or) Thermo hardening plastics

Thermo plastics (or) Thermosoftening plastics:

The plastics which are soften on heating and harden on cooling is known as thermoplastics.

ex: polythene, polyvinyl chloride (PVC).

Thermo setting plastics (or) Thermohardening plastics:

The plastics which cannot converts into soft state by applying heat (or) pressure once they are in fixed state. ex: bakelite, nylon-6,6.

Thermoplastics	Thermosetting plastics
1. The plastics which are soften on heating and harden on cooling is known as thermo plastics.	1. The plastics cannot converts into soft state by appyling heat (or) pressure once they are infixed state.
2. It undergoes additional polymerisation.	2. It undergoes condensation polymerisation.
3. These are reversible process.	3. These are irreversible process
4. These are linear shaped polymers.	4. These are cross-linked polymer
5. These are soluble in organic solvent	5. These are insoluble in organic solvent
6. These plastics have less vanderwaal's forces.	6. These plastics have strong ~~co~~ electrostatic force of attraction.
7. In this we ~~have~~ use same monomers.	7. In this we use different monomers.
ex: Polythene, Teflon, PVC	ex: bakelite, nylon-6,6.

Advantages of plastics over traditional materials:

1. Light in weight
2. Low cost
3. No corrosion
4. no damage by insects
5. easily maintenance
6. different colours
7. easy for transportation
8. wide range and shape

Disadvantages:

1. non-biodegrable
2. Increase pollution
3. Spoil the forest
4. Control the fertility of soil
5. risk for aquatic animals.
6. Plastics are soft
7. not suitable for cooking

Compounding of plastics :-

The process of mixing of raw plastics with special ingredients to develops special properties like tensile strength, colour, quantity ---etc. during moulding is known as compounding of plastics.

1, **Binders (or) Resins** :- Binder is the major ingredients present in plastic material. Binders hold the other ingredients together.

Ex:- Thermoplastic, Thermosetting plastics.

2, **fillers** :- fillers are cheap organic or inorganic compounds which are added to improve certain properties like hardness, strength, Quantity --etc.

Ex:- Asbestos, Mica, Silica, Nylon, polyester etc.

3, **Plasticisers** :- plasticisers are freely miscible with plastic material. It increase plasticity and reduce viscosity of plastics.

Ex:- Vegetable oils, camphor, Triphenyl phosphate etc.

4, **Catalysts (or) Accelerators** :- These are used to convert fusible resin into cross limited infusible resin during Moulding operation.

Ex:- H_2O_2, ZnO, ~~Ammonia~~, Benzoyl peroxide etc.

5, **Stabilizers** :- These are added to the plastics to improve thermal stability during Moulding.

Ex:- white lead, Lead silicate, cadmium and Barium Stearates ... etc.

C 6, fire Retardants :- These are added to plastics to prevent burnings.

Ex:- Mixture of Borax and Boric acid ... etc.

7, Colourants :- These are organic and inorganic pigments used to give colour to the plastic article.

Ex:- Barium Ef Titanium - white

Lead, Iron, Anthraquinones - Yellow

Carbon powder - Black

Azo dyes - Yellow, orange, Red.

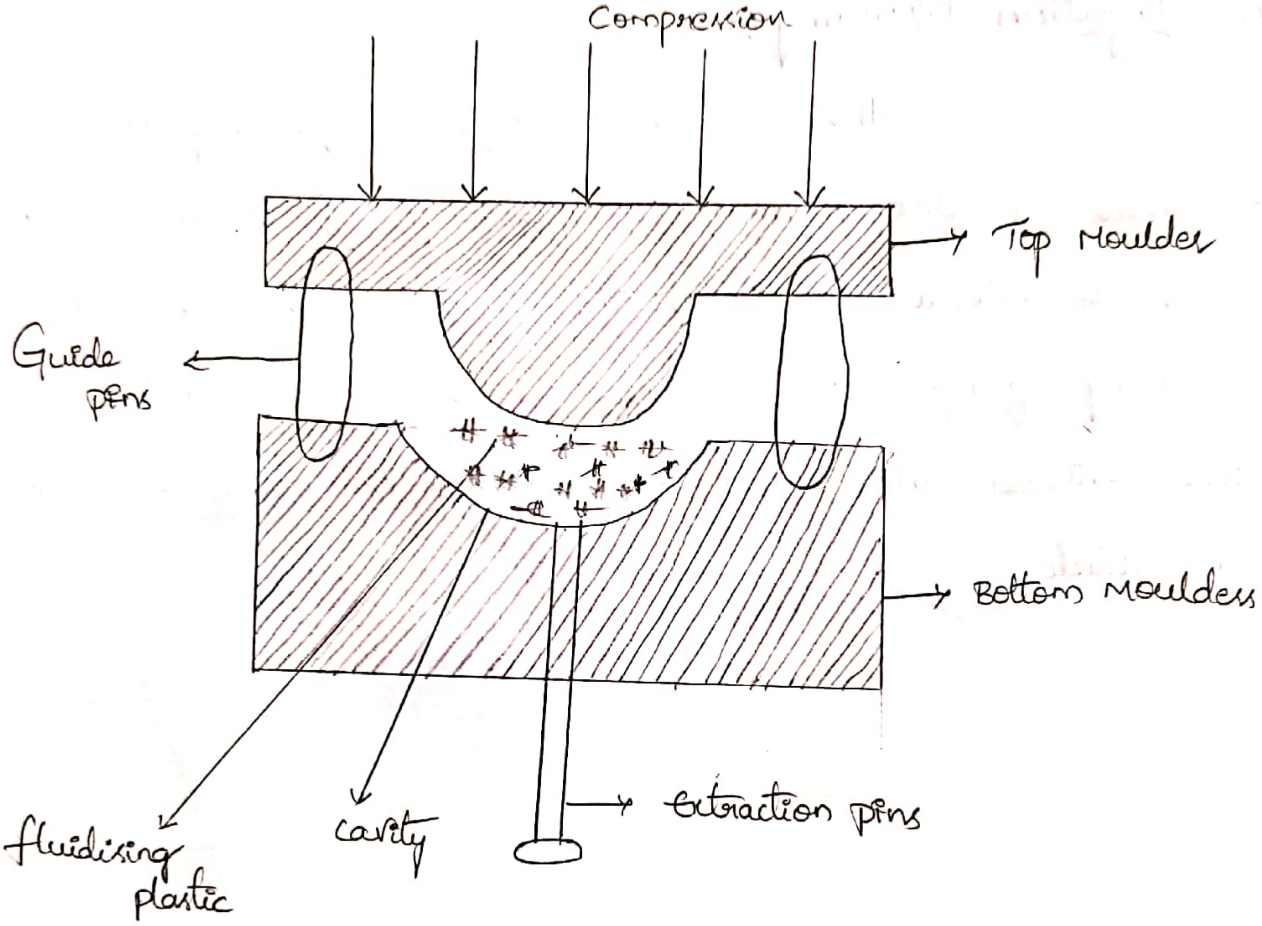
Fabrication of Plastics (or) Moulding :-

The Phenomenon of manufacturing of article from plastic material by applying heat and pressure in a cold moulder is called Moulding,

1, Compression Moulding
2, Injection Moulding
3, Extrusion Moulding
4, Blowing (or) Bubble casting Moulding.

1, Compression Moulding :-

Compression moulding is a method applied to both thermoplastics and thermosettings. It consists two half moulders moulders like Upper and Lower moulders. The lower moulder is filled with plastic powder. Then the lower moulder and upper moulder are closed and applied heat and pressure. After cooling the moulder, the plastic powder converted into fluidised plastic and to article, it is taken out from the moulder.



Advantages :-

1, The moulders and machine cost is very low when compared to other moulding methods.

2, In this method we should prepare shape controlled articles.

Disadvantages :-

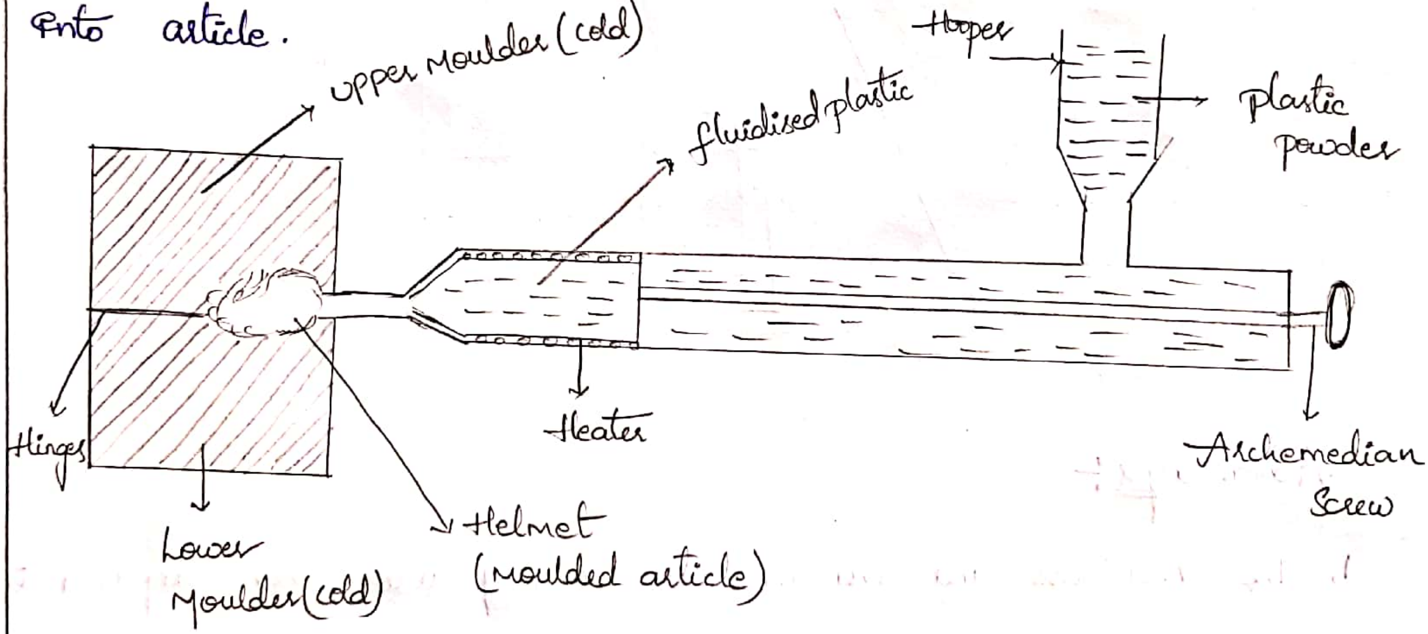
1, In this method we use hydraulic pumps for pressure. These are very high cost.

2, In this moulding maximum we should prepare thermosetting plastics. These are Irreversible Process.

Examples:- Cylindrical shape of articles, Switches, Switch Sockets, Mobile phones pouches, plastic tubs, Umbrella Handles, Burette stoppers.

2, Injection Moulding:-

This method is applicable for only thermoplastics. It consists a hooper in which plastic powder is taken. The powder is entered into a heated cylindrical chamber with the help of moving plunger, at nossel the powder is converted into fluidised plastic entered into a cool moulder. Then the plastic is converted into article.



Advantages:-

1, In this method we should prepare 90% of plastic articles.
2, It is also shape controlled moulding methods.

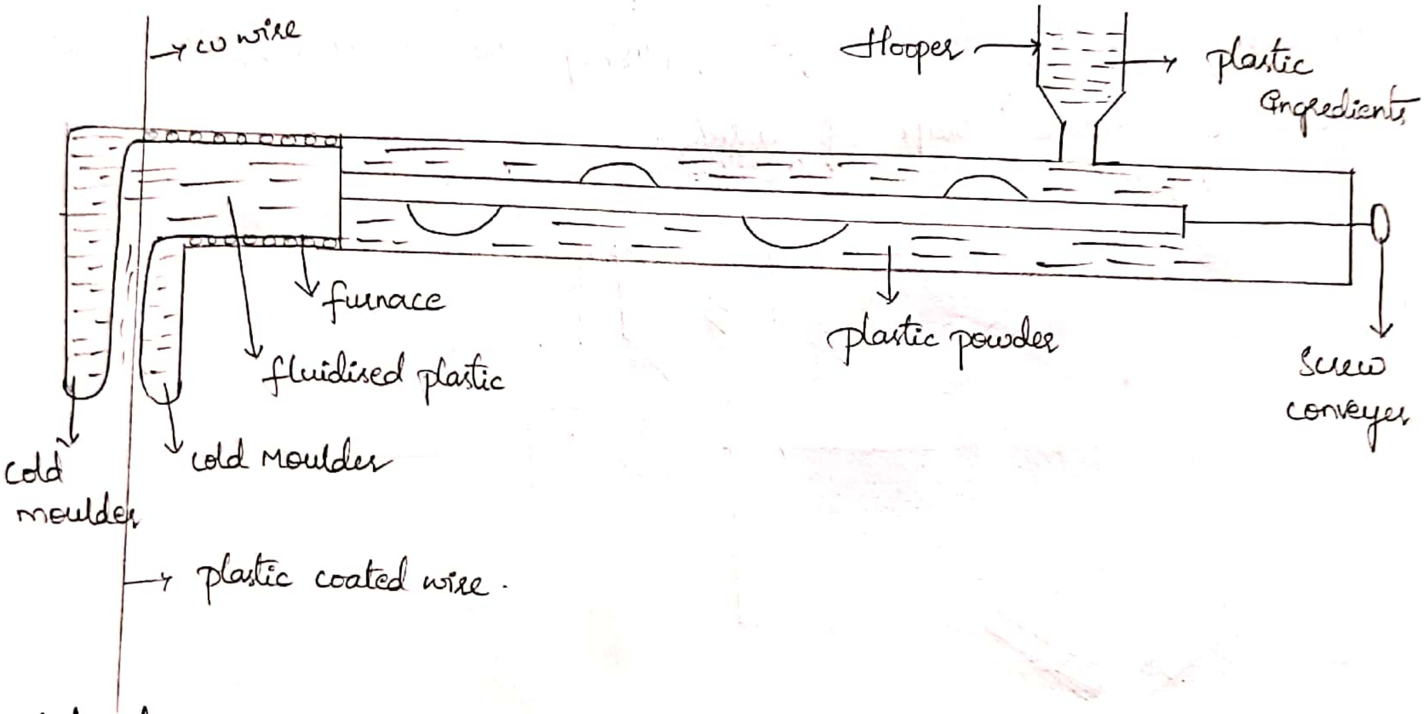
Disadvantages:-

Moulders and Moulding Machine is very high cost.

Examples:- Helmets, plastic buckets, plastic mugs, CPU exhausting fans.

5, Extrusion Moulding :-

This method is applicable for only thermoplastics. It consists a hooper in which plastic powder is taken. The Powdered is entered into a heated cylindrical chamber with the help of moving plunger, at nozzel the powder is converted into fluidised plastic. This fluidised plastic entered into a cool moulder. Then the plastic is converted into article.



Advantages :-

1, In this method we should prepare long range of articles.

2, The preparation articles have stiffness because of thermosetting character.

Disadvantages :-

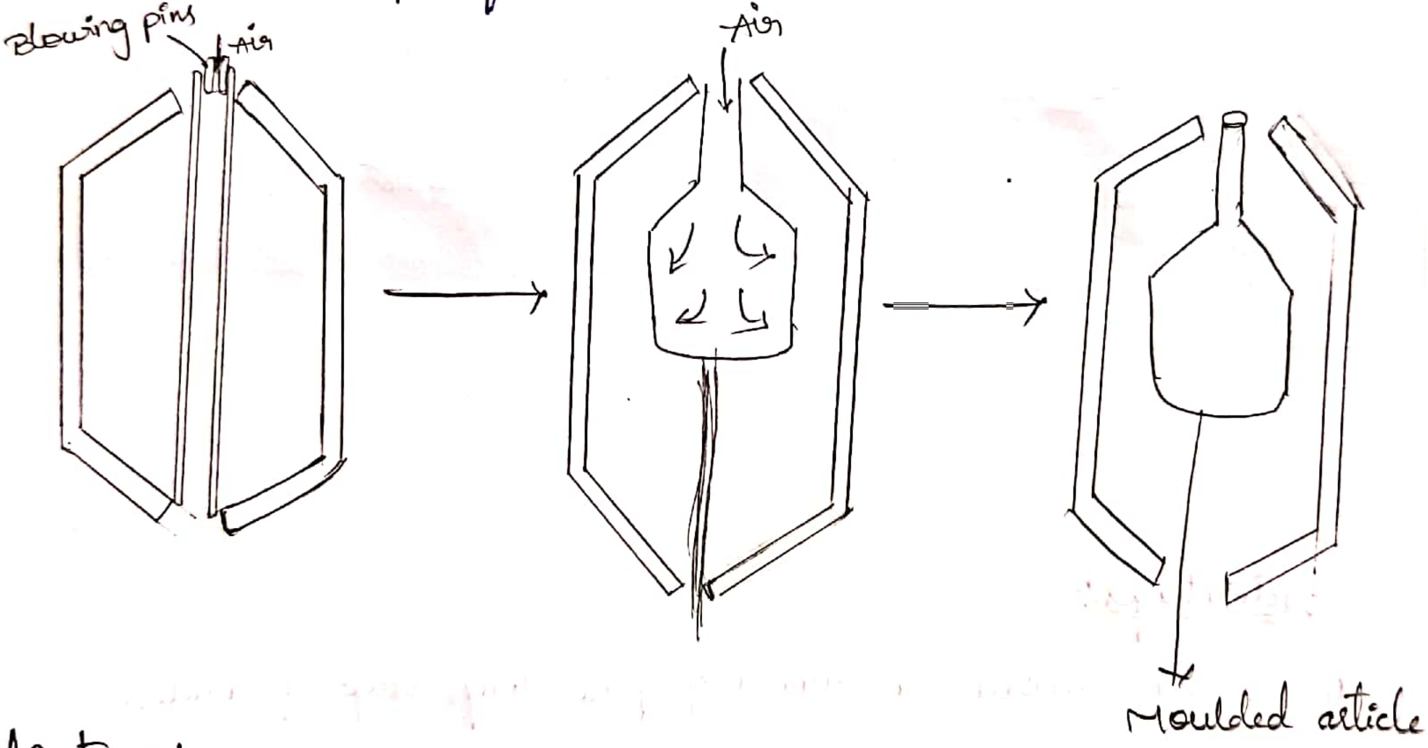
1, The plastic resin expanded to different directions.

2, Thermo-setting plastics are irreversible process.

Examples :- S-shaped chairs, cable wires, Motor tires, tubes, plastic pens, toothpaste tubes --etc.

4, Blowing (or) Bubble casting moulding:-

The moulding is applicable for thermoplastics, In this moulding hallow shaped articles like bottles, covers, balloons -- etc are fabricated parison is a hot and soft plastics is attached to blowing pins. The pins are placed in between the moulder. Then the moulder is closed and passing compressed air through blowing pins. The parison is expands like a balloon until it touches the Interior walls of the moulder. finally, the moulder is cooled and opendable desire shape of article.



Advantages:-

1, High durability, Tensile strength.
2, The moulding machine and moulders are low cost.
3, Electrical resistance property.

Disadvantages:-

The moulded some articles acts as thermoplastic nature and Some articles acts as thermo setting plastic nature.

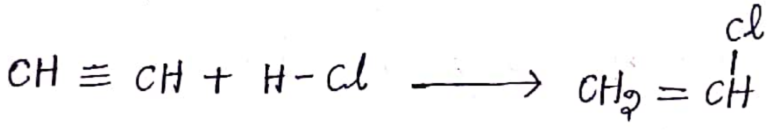
Example:- Hallospherical articles.

Plastics :- The polymeric material which have high molecular weight organic polymers which are moulded into desirable shape in the presence of temperature, pressure and catalyst is known as plastics.

1. **Poly vinyl chloride (PVC)** :- (koroseal) Poly vinyl chloride is Prepared by addition polymerisation of vinyl chloride monomer in the presence of benzoyl peroxide (or) hydrogen peroxide (H_2O_2) under pressure.

⇒ The acetylene molecule is treated with hydrogen chloride to form monomer. It is the internal rearrangement reaction.

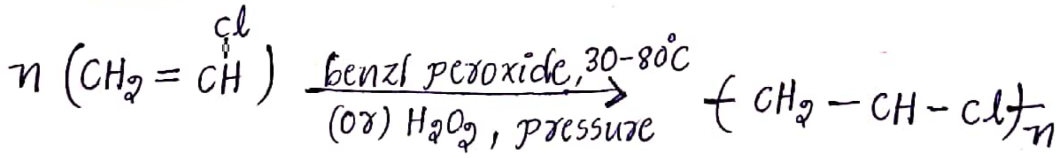
Monomer preperation :-



$$CH \equiv CH + H-Cl \longrightarrow CH_2 = \overset{Cl}{\overset{|}{C}}H$$

vinyl chloride

polymer preperation :-



$$n\,(CH_2 = \overset{Cl}{\overset{|}{C}}H) \xrightarrow[\text{(or) } H_2O_2\text{, pressure}]{\text{benzl peroxide, 30-80°C}} \{CH_2 - CH - Cl\}_n$$

PVC

Properties :-

⇒ PVC is a colourless, non-inflamable material.

⇒ Resistant to atmospheric conditions like O_2, CO_2 and moisture.

⇒ PVC is strong and brittle

⇒ PVC is not stable to heat and uv radiation.

Applications :-

1. Injection moulding articles like tool handles, radio, telephone components.

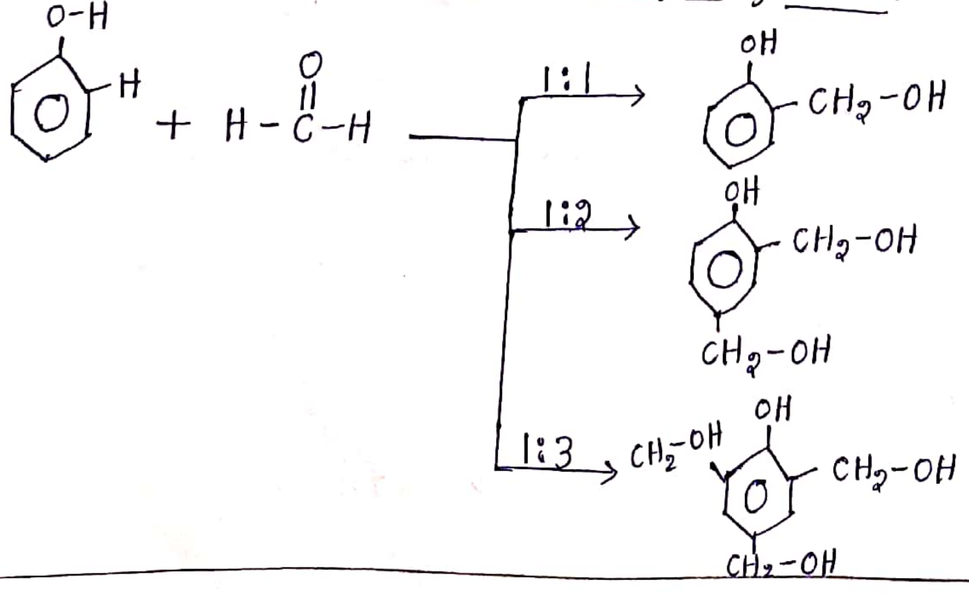
2. Chemical containers and foams used in buildings. camera's and air crafts.

3. Safety helmets, refrigrators components, tyres, cycle and motor cycle mudgaurds.

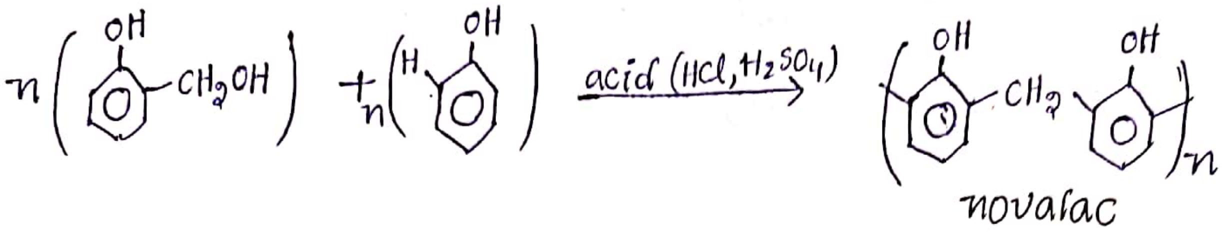
4. Agriculture sector bore pipes, water pipes.

2. Bakelite :- bakelite is prepared by condensation polymerisation of phenol and formaldehyde by the elimination of water molecules in the presence of acid, hexamine (hexamethylene tetra amine) in the mechanism novalac formed as a intermediate product which is linear shape thermoplastic polymer. Finally, novalac is converted into bakelite in the elimination of water molecules.

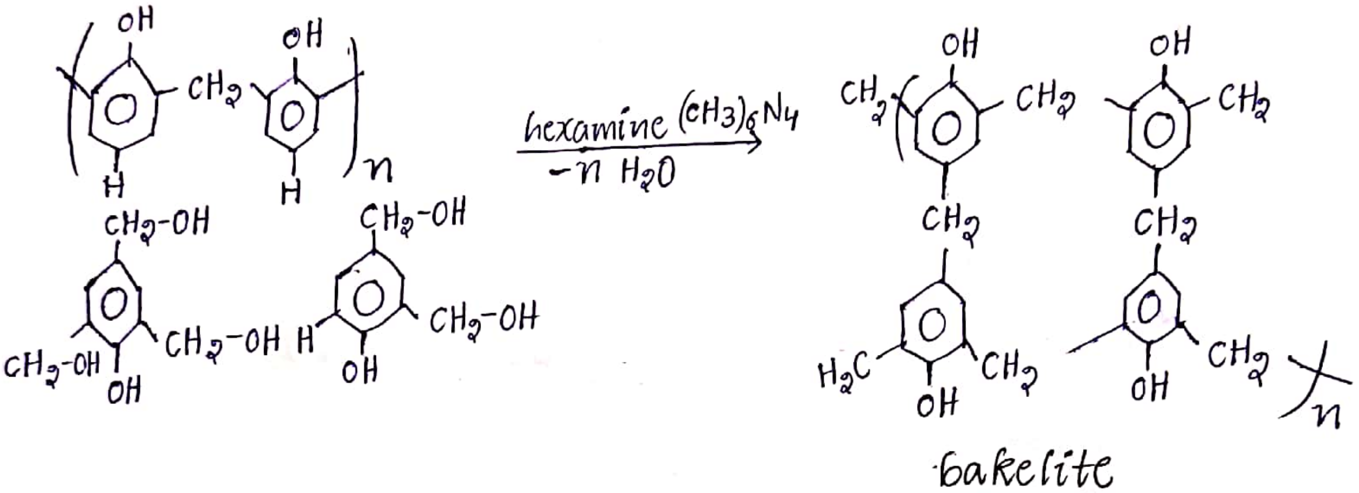
Step-1 : formation of methylol phenol



Step-2 : formation of novalac (linear polymer) :



Step-3 : formation of bakelite (pheno plastics) :-



Properties :-

1. bakelite is hard, rigid and strong.
2. It is a scratch, water resistant polymer.
3. Good anionic exchange resin.
4. Excellent electrical insulators
5. It is very good adhesive and corrosion resistance.

Applications :-

1. Electrical insulator parts like switches, switch boards, handles etc.
2. Moulded articles like telephone parts, cabinets for radio and television

3. In paints and varnishes.

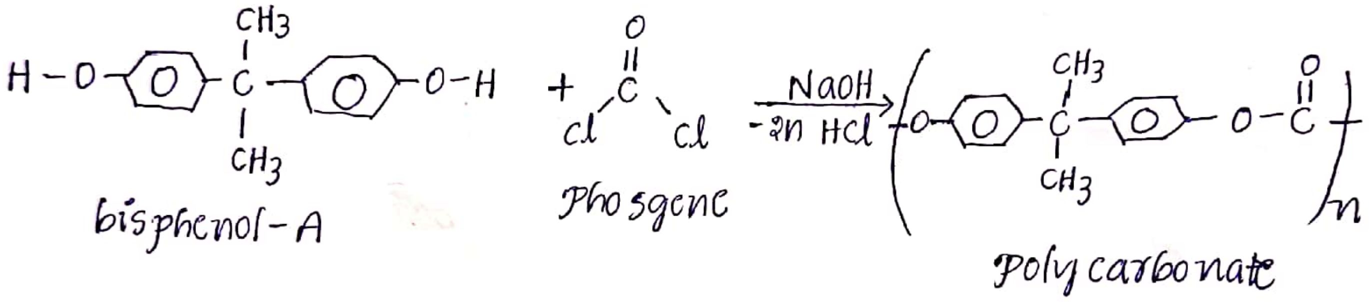
4. as an adhesive for grinding wheels etc.

5. used as anionic exchange resin.

3. Poly carbonates:-

It is prepared by condensation polymerisation of bisphenol-A and phosgene monomers in the Presence of NaOH as a catalyst.

⟹ Poly carbonate is thermoplastic.



Properties:-

1. It is durable material with impact resistance, low starch resistance.

2. high transperancy to visible light.

3. Good electrical insulators.

4. It undergo plastic deformation without cracking (or) breaking

Applications:-

1. electronic components:-

Electrical and telecomunications hard ware and also dielectric in high stability capacitors.

2. Construction materials:

Poly carbonates are used in industry for dome light, flat & curved glazing, sound walls.

3. storage devices like CD's, DVD's.

4. Laboratory safety goggles, sunglass, computer cases, name plates etc.

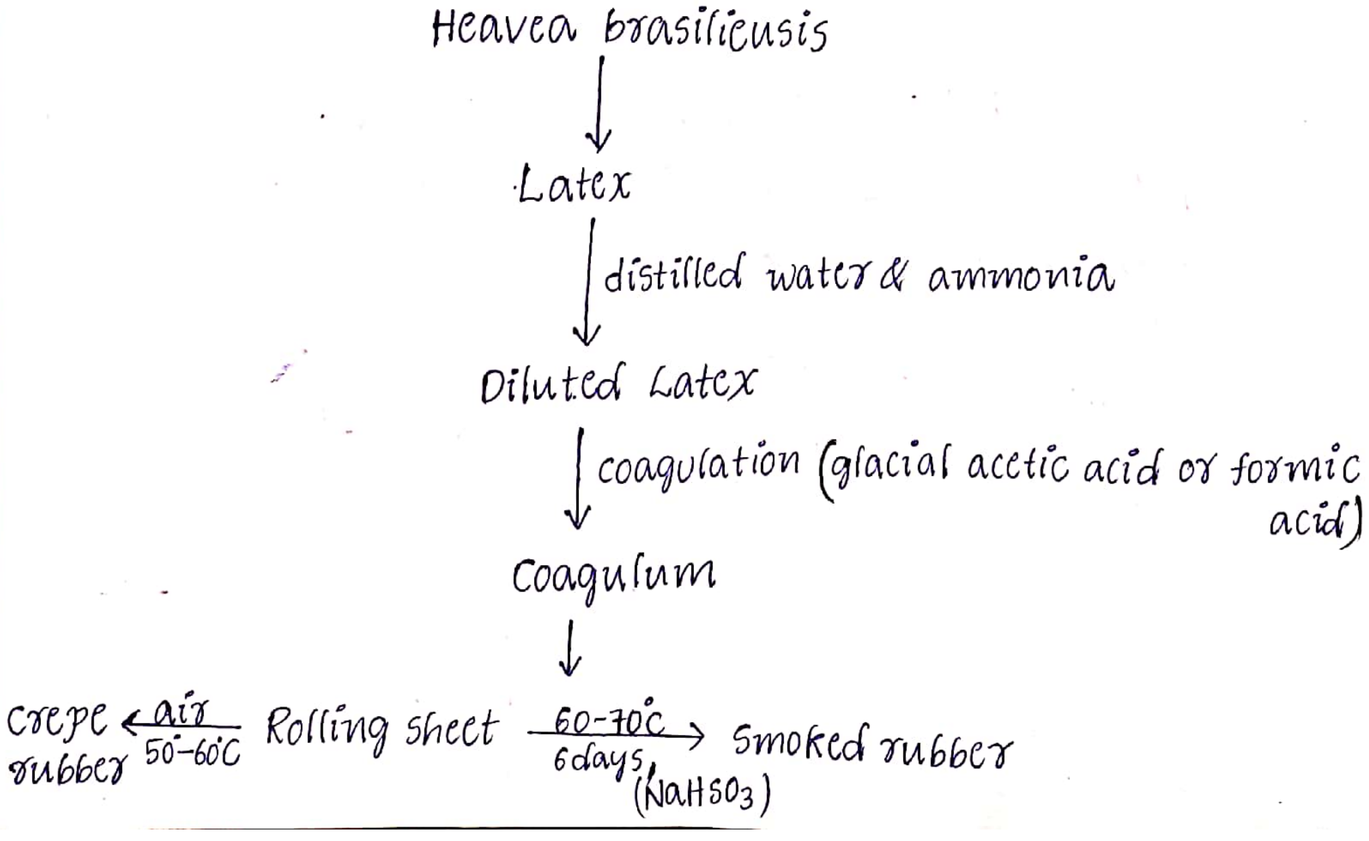
Rubbers: A polymeric material which is soft thermoplastic and flexibility is known as "rubber."

(OR)

The polymer having high molecular weight and the capable of regain its original length and shape after release of applied stress is called "rubbers."

Natural rubber: The rubber which is obtained from nature (plants) is known as natural rubber.

Extraction of natural rubber:

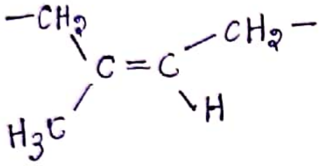


Preperation of natural rubber: It is prepared by addition Polymerisation of isoprene (or) 2-methyl 1,3-butadiene.

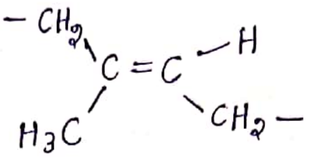
$$n\left(CH_2=\overset{CH_3}{\overset{|}{C}}-CH=CH_2\right)\xrightarrow[\text{polymerisation}]{\text{addition}}\left(CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2\right)_n$$

natural rubber (or)
cis-poly isoprene.

⇒ Cis-poly isoprene



⇒ Trans-poly isoprene (or) gutta percha rubber

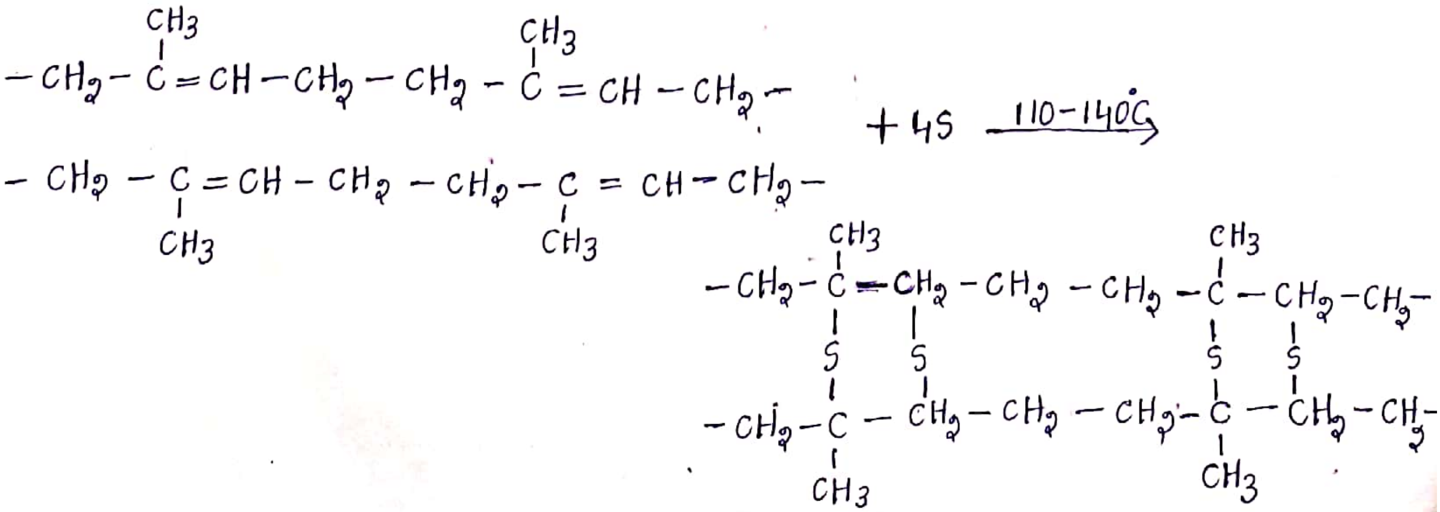


(came from palageum gutta & dichopsis purcha)

Properties of natural rubber:

1. Less tensile strength
2. Less durability
3. Low abrasion resistance
4. Less chemical resistance
5. Low load baring capacity
6. Less oil resistance

Vulcanisation: "charles good year" proposed vulcanisation process in 1839 to overcome the drawbacks of natural rubber with sulphur in the presence of 110-140°C temperature.



$$\begin{array}{l}
-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2-CH_2-\overset{CH_3}{\overset{|}{C}}=CH-CH_2- \\
-CH_2-\underset{CH_3}{\underset{|}{C}}=CH-CH_2-CH_2-\underset{CH_3}{\underset{|}{C}}=CH-CH_2-
\end{array} + 4S \xrightarrow{110-140°C}$$

$$\begin{array}{ccccccc}
 & CH_3 & & & CH_3 & & \\
 & | & & & | & & \\
-CH_2- & C & -CH_2- & -CH_2-CH_2- & C & -CH_2- & CH_2- \\
 & | & | & & | & | & \\
 & S & S & & S & S & \\
 & | & | & & | & | & \\
-CH_2- & C & -CH_2- & -CH_2-CH_2- & C & -CH_2- & CH_2- \\
 & | & & & | & & \\
 & CH_3 & & & CH_3 & &
\end{array}$$

Properties:

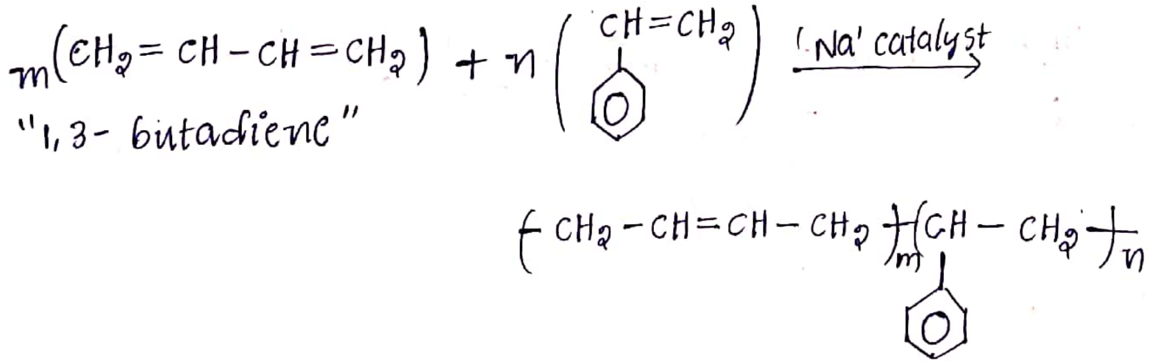
1. high tensile strength
2. high durability
3. high abrasion resistance
4. high chemical resistance
5. high load baring capacity
6. high oil resistance

Synthetic rubber or elastomers:

A polymeric material which can be stretched atleast twice its original shape but it returns to original position as soon as streatching forces are released.

⇒ Elastomers contains three types of rubbers. they are

1. **Buna-S:** It is prepared by co-polymerisation of 1,3-butadiene and styrene in the presence of sodium as a catalyst. It is also known as GRS (or) ameripole.



"buna-s rubber"

Properties:

1. It is strong and tough polymer.
2. It is vulcanised by sulphur mono chlorided (S_2Cl_2) or sulphur

3. Excellent abrasion resistance.

4. It traces of ozone present in atmosphere.

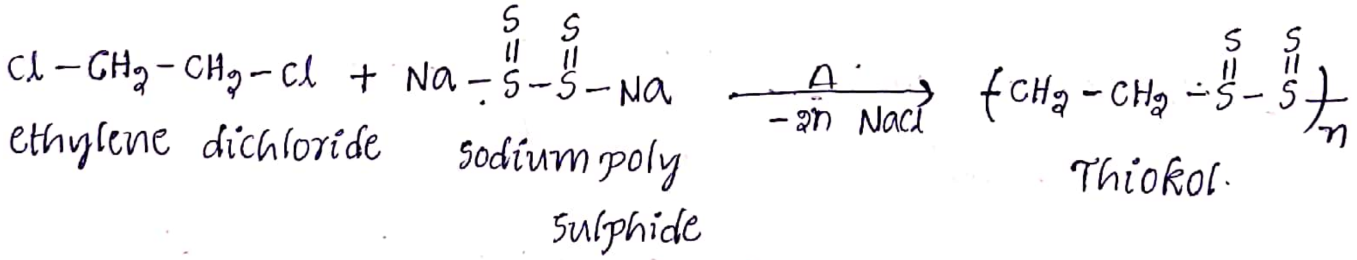
5. High load bearing capacity and resistance.

Applications:

1. Manufacture of tyres.
2. Foot wear industry for making shoe sales and foot wear component
3. Making wires & cable insulations.
4. Production of floor tiles, tank limings in chemical industries and as adhesive.

2. Thiokol Rubber: (government rubber of polysulphide): It is the co-polymerisation reaction with elemination of simple molecules like Nacl.

⇒ It does not undergoes vulcanisation because of it has excess number of sulphur elements.



$$Cl-CH_2-CH_2-Cl + Na-\overset{S}{\overset{\|}{S}}-\overset{S}{\overset{\|}{S}}-Na \xrightarrow[-2n\ NaCl]{\Delta} \left[CH_2-CH_2-\overset{S}{\overset{\|}{S}}-\overset{S}{\overset{\|}{S}}\right]_n$$

Properties:

1. It posses strength & impermeability to gases.
2. This rubber cannot be vulcanised & It cannot form hard rubber.
3. Good resistance to mineral oils, fuels, abrasion, oxygen, solvents, ozone & sunlight.

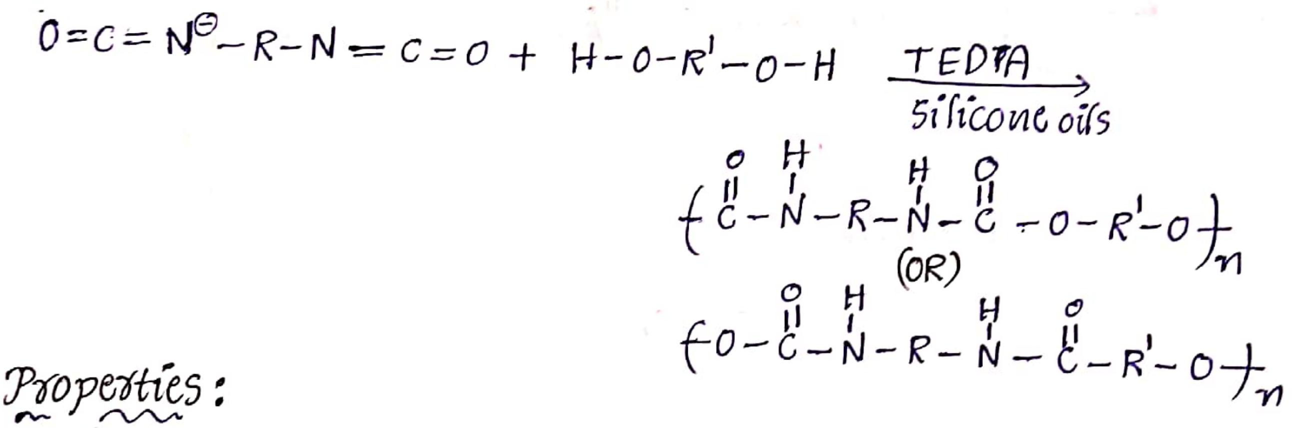
Applications :

1. used for barrage balloons, life rafts and Jacket which are inflated by CO_2.

2. Living hoses for conveying gesolin and oil.

3. Making gaskets and seals for printing rolls

3. Poly urethanes : (Poly iso cyanide rubber) : It is prepared by rearrangement of co-polymerisation reaction. Momomers are di-iso cyanide and di-ol in the presence of catalyst (tri ethylene di amine) and surfactant (silicone oils)



$$O=C=N^{\ominus}-R-N=C=O + H-O-R'-O-H \xrightarrow[\text{silicone oils}]{\text{TEDA}}$$

$$\left(\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-O-R'-O\right)_n$$

(OR)

$$\left(O-\overset{O}{\overset{\|}{C}}-\overset{H}{\overset{|}{N}}-R-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-R'-O\right)_n$$

Properties :

1. It posses excellent hardness, tensile strength, impact resistance, abrasion and tear resistance

2. Resistance to heat, moisture, gases, chemicals, oils, solvents etc.,

3. Adsorption of heavy metals and colouring agents.

4. It possess high load bearing capacity & flexibility.

Application:

1. Refrigeration, freezers, furniture and bedding.

2. Foot wear, automotives, coatings and adhesives.

3. Elastomer and sealants.

4. Purification of water and sevage water for adsorption of colouring matter & heavy metals.

Fibre rein forced plastics (FRP's):

The reinforcing of plastic matrix with high strength of fibre materials like sand, silica, lime stone, glass, carbon etc is known as "fibre reinforced plastics".

Components of ~~P~~ FRP's:

1. Plastic matrix
2. Fibre material

Plastic matrix:

⇒ The plastic material used in FRP's is called "matrix"

⇒ The purpose of plastic matrix is to form body and state of the FRP's.

ex: Thermo plastic matrix (polythene, PVC)

Thermo setting matrix (bakelite, urea formaldehyde resin, nylon-6,6)

Fiber material:

The purpose of fiber materials to develops special properties like tensile strength, durability, ductility all resistance is known as fiber material.

ex: sand, silica, limestone, folic acid, carbonfiber.

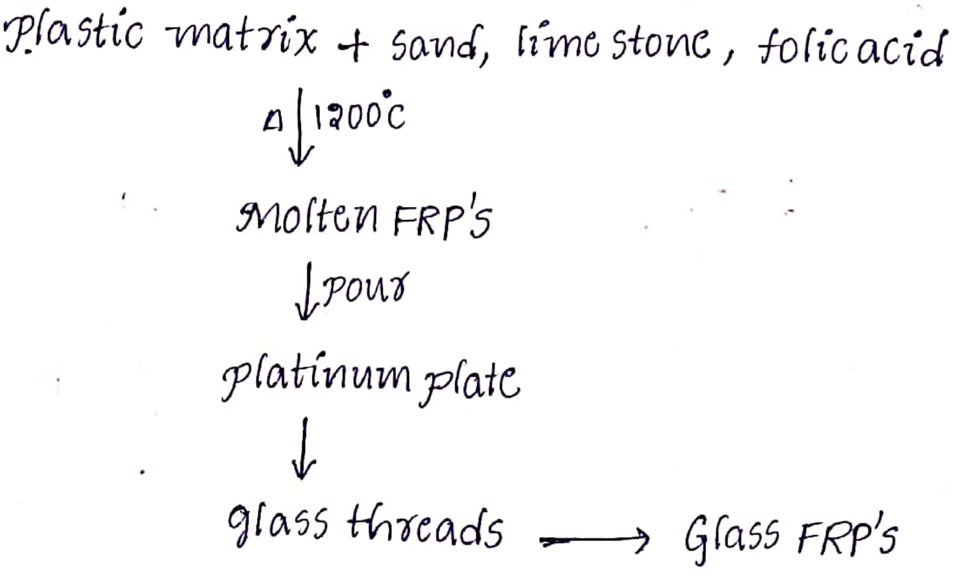
Classification of FRP's:

FRP's is classified into three types based on mixing of fiber material.

1. Glass FRP's
2. aramide (or) bullet proof FRP's
3. carbon FRP's

Glass FRP's:

Glass FRP's is prepared by mixing of sand, limestone folic acid and minior ~~io~~ ingredients. The mixture is heated it melts about 1200°C. The molten glass is passed through fine holes in a platinum plate. Glass threads (or) needles are obtained these are cooled, gathered and finally we get FRP's.



Properties :

1. It has high tensile strength
2. Long durability
3. corrosion resistant
4. electrical resistant

Applications :

⇒ These are used in making of automobiles glasses, storage tanks, fuel tanks ... etc.

Aramide (or) bullet proof FRP's :

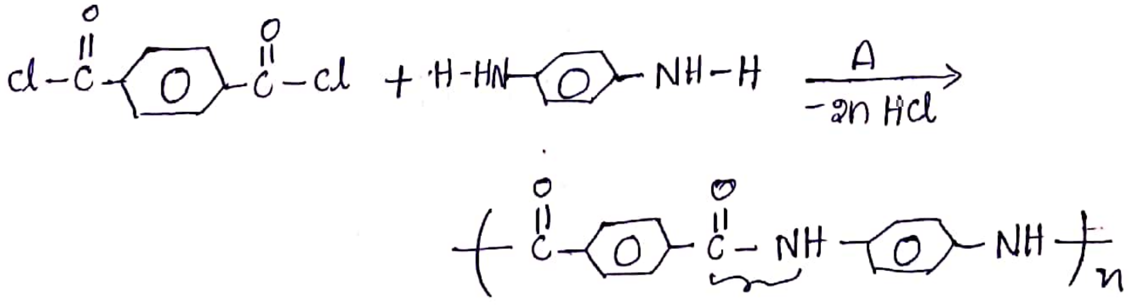
Aramide means aromatic poly amide.

⇒ These are two types

1. kevlar FRP's
2. Nomax FRP's

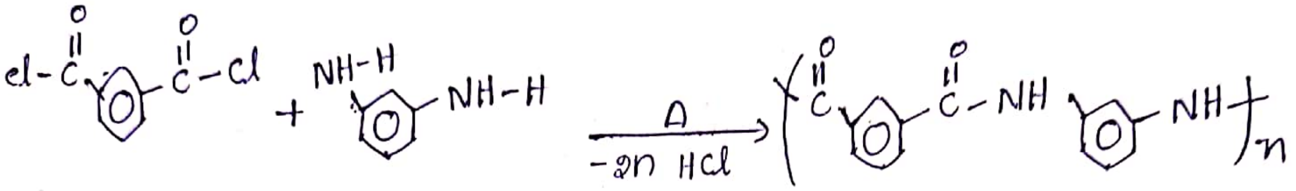
kevlar FRP's :

It is prepared by condensation polymerisation of Para pthalallyl chloride and para phenylene diamine in the presence of temperature, our elimination molecule is HCl.



kevlar FRP's

Nomax FRP'S: It is prepared by condensation polymerisation of meta thalallyl chloride and meta phenylene diamine in the presence of temperature, our elimination is HCl.



nomax FRP'S

Properties:

1. It is very strong
2. It has high heat stability and flexibility
3. chemical resistance
4. corrosion resistance
5. Thermal resistance

Applications:

1. It is used in space crafts, aeroplanes and circuit industry.
2. It is used to make car parts (tyres, break)
3. It is used to make helmets, bullet proof, glasses.
4. It is used in gaskets.

Carbon FRP's: The plastic matrix combined with carbon fibre to form carbon FRP's.

ex: decorative articles, roof designing of houses

Properties:

1. high strength and stiffness
2. Good mechanical strength & chemical resistance.

Applications :

1. used in vehicles, satellites.
2. used in industrial machinary.

Bio degradable polymers :

Generally polymers are non-biodegradable but some of the polymers are degraded in the presence of micro organisms is known as bio degradable polymers.

Controlling factors of degradation :

1. Percentage of crystalinity in polymers.
2. Molecular weight of polymer.
3. Hydrophobicity of polymer.
4. environment surrounding of polymer.

⇒ There are two types of biodegradable polymer.

1. naturally occuring bio-degradable polymer.
2. Synthasised bio-degradable polymer.

Naturally occuring bio-degradable polymer :

There are 4 types of natural biodegradable polymers.

1. Poly sacharides:

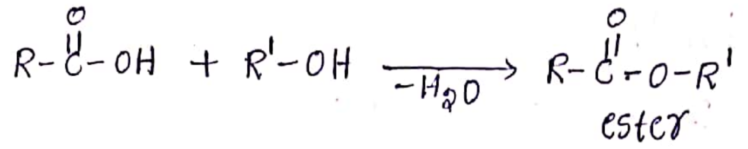
ex: starch, cellulose (green plants)

2. protiens :

ex:- Gelatin, casien (cheese protien)

3. Polyesters:

ex: Poly hydroxy alkanoids

⇒ 

$R-\overset{O}{\overset{\|}{C}}-OH + R'-OH \xrightarrow[-H_2O]{} \underset{ester}{R-\overset{O}{\overset{\|}{C}}-O-R'}$

4. others:

ex: Liquine, shellac, naturalrubber

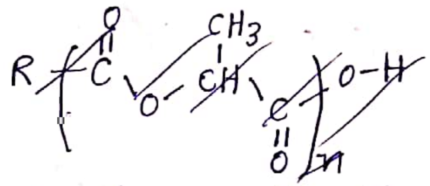
Synthetic biodegrable polymer:

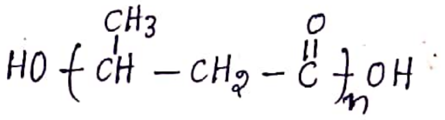
These are many polymers prepared by biological process and these are bio-degradable.

ex: alcohol from molasis, poly latic acids etc.

1. Poly hydroxy alkanoates (PHA): BIOPOL.

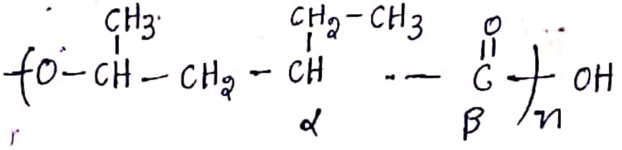
It is used in orthopedic surgeries



1. 

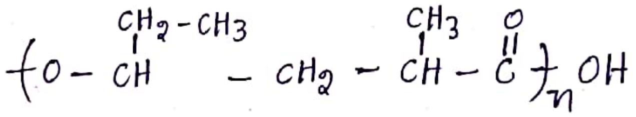
$HO\{\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{O}{\overset{\|}{C}}\}_n OH$

Poly 3 hydroxy butyrate.

2. 

$\{O-\overset{CH_3}{\overset{|}{CH}}-CH_2-\underset{\alpha}{\overset{CH_2-CH_3}{\overset{|}{CH}}}--\underset{\beta}{\overset{O}{\overset{\|}{C}}}\}_n OH$

poly β-hydroxy valrianate.

3. 

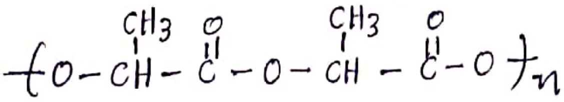
$\{O-\overset{CH_2-CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}\}_n OH$

poly - hydroxy valarianate

2. Poly Latic acid: (Tapioca)

The fermentation of tapioca (or) starch in aerobic condition we get poly Latic acid. (food packing & dippers).

⇒ Tapioca - root part of cassava plant (brazil).



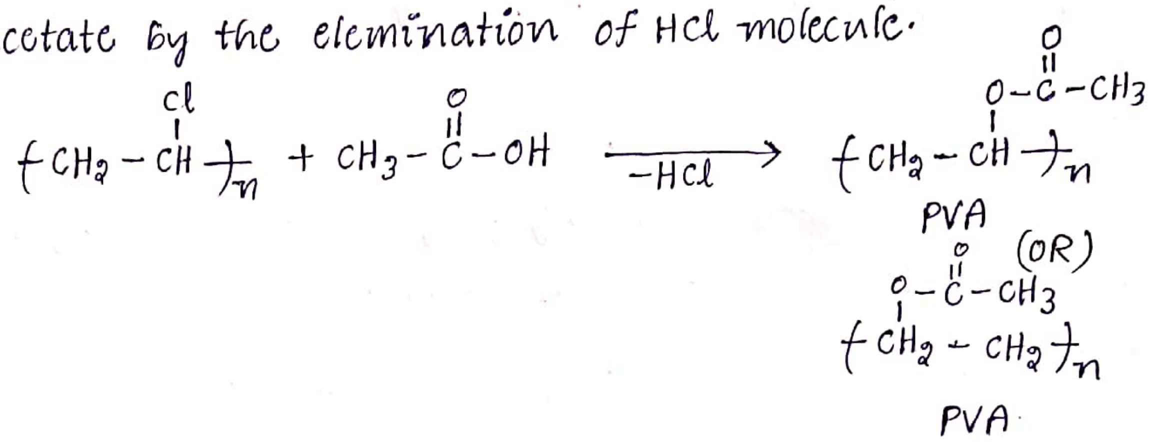
$$-\!\!\left[O-\overset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-O-\overset{CH_3}{\underset{|}{CH}}-\overset{O}{\overset{||}{C}}-O\right]\!\!-_n$$

Poly Lactide

3. Poly vinyl acetate (PVA):

Fermentation of malasis (or) starch.

⇒ poly vinyl chloride treated with acetic acid to form poly vinyl acetate by the elemination of HCl molecule.



$$-\!\!\left[CH_2-\overset{Cl}{\overset{|}{CH}}\right]\!\!-_n + CH_3-\overset{O}{\overset{||}{C}}-OH \xrightarrow[-HCl]{} -\!\!\left[CH_2-\overset{O-\overset{O}{\overset{||}{C}}-CH_3}{\overset{|}{CH}}\right]\!\!-_n$$

PVA

(OR)

$$-\!\!\left[\overset{O-\overset{O}{\overset{||}{C}}-CH_3}{\overset{|}{CH_2}}-CH_2\right]\!\!-_n$$

PVA.

Applications of biodegradable polymer:

1. These are prepared from natural materials.

2. compostable bats help in the disposcale of the vegetable matter.

3. These are environmentry friendly.

4. The polymers of Land fill by solid waste can be reduced.

Conducting polymer:

Generally polymers are insulators but some of the polymers exhibits slightly conducting property because of conjugated double bonds & doped material is known as conducting polymer.

There are two types of conducting polymers.

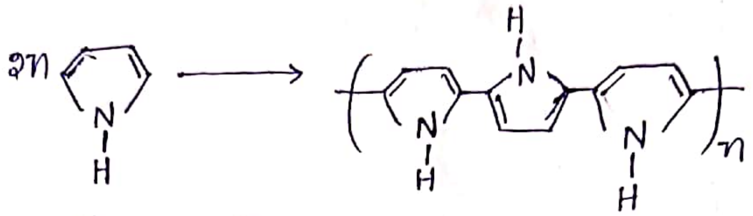
1. Conjugated conducting polymer

2. Doped conducting polymer

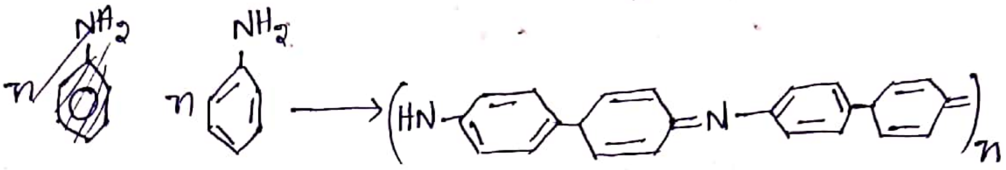
1. Conjugated conducting polymers:

Poly acetylene: $n(CH \equiv CH) \longrightarrow -[CH=CH]-_n$.

Poly pyrrole:



Poly aniline :



Poly aniline (or) emraldine

2. Doped conduction polymer:

It contains two types of doping.

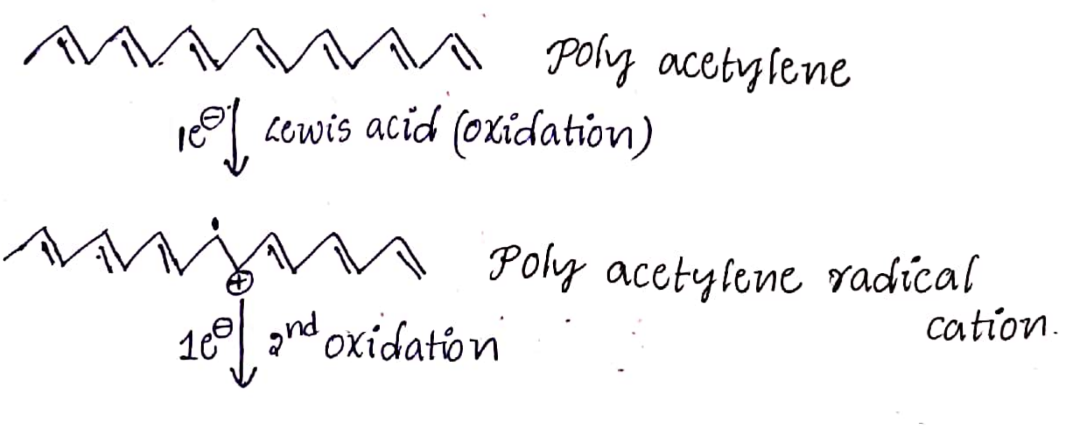
1. P-type doping (or) oxidative doping
2. N-type doping (or) reductive doping

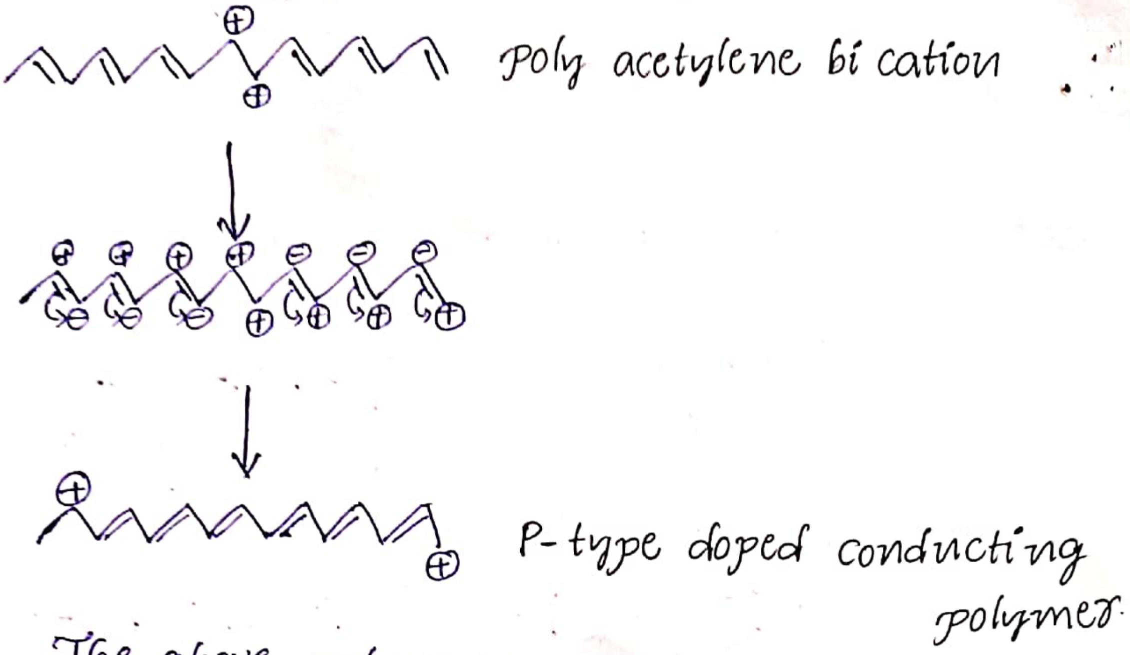
P-type conducting polymer:

In P-type doping, our doped material is lewis acid. The nature of lewis acid is electron pair acceptor means electron deficiency molecules.

ex: $AlCl_3$, $FeCl_3$, BF_3, BCl_3 ...

Mechanism:





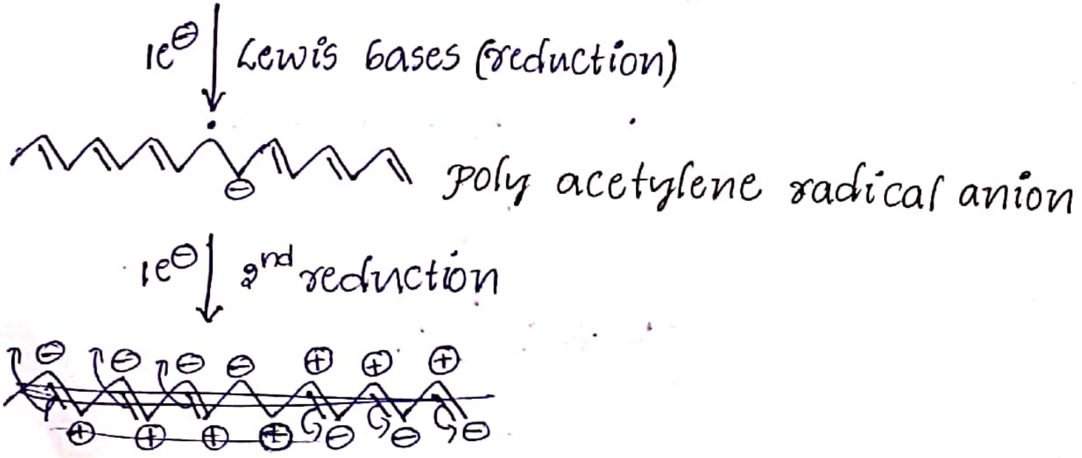
The above polymer the positive charge is moves entire polymer to break the old bonds to forms the new bonds. In which the conducting is due to positive charge. Hence these are called P-type conductivity polymer.

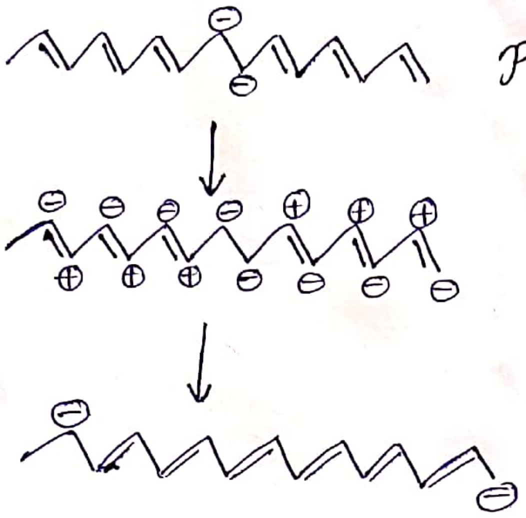
N-type conducting Polymers:

In N-type dopping our doped material is Lewis bases. The nature of Lewis base is electron pair donar mean electron deficiency molecules.

ex: NH_3, H_2O, CN^-, ClO_4^- .....

Mechanism:





Poly acetylene bi anion

N- type doped conducting polymer

The above polymer the negative charge moves entire the polymer to break the old bonds to form new bonds, in which the conductivity is due to negative charge. Hence these are called N-type conducting polymer.

prepared by

Sarvepalli. Venkata Rao

M.Sc. B.Ed

E- Waste and Control methods ÷

* Introduction ÷

Plastics ÷

The Polymeric Materials which have high Molecular weight Organic Polymers which Are Moulded into desirable State In the Presence of temperature, Pressure and Catalyst is known As Plastics.

E- Waste ÷

E-waste (or) electronic waste is created when an electronic Product is discarded AFter the end of Its useful life. The rapid Expansion of technology and the Consumption driven Society results in the creation of a very large Amt of e-Waste In every Minute.

we Can Simply Said that

$$\boxed{\text{Technology} \propto \text{E Plastic waste Consumption}}$$

In 2006, the united State Estimated the Amt of World wide Electronic waste discarded each year to be 50 Million Metric tons

E Plastic waste is not An national Issue. It is an International (or) global Issue.

* Source of E- Waste ÷

The E- waste Can be generated by the All sectors like govt Sector, house hold sector, Private sector

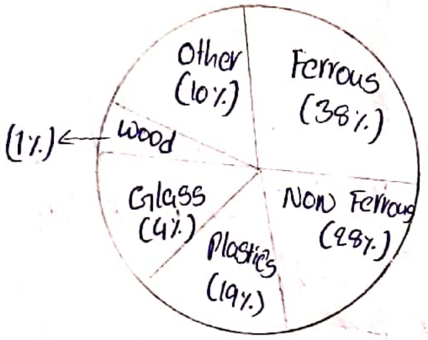
In the Form of
(i) Computers
(ii) Moniters
(iii) Televisions
(iv) Printers
etc

Todays Electronic Gadgets Tomorrow's Electronic waste.

* Reasons For E-waste ÷

- * Advancement to technology
- * changes in Fashion, Style & Status
- * Nearing end of their useful life

* Components OF E-waste ÷



* EFFects due to components OF E-waste

Sl.No	Component	Extract	EFFects
1	Lead	CRT (Cathode Ray tube)	Anaemia, damage to nervous System
2	Mercury	Flat screen monitors,	muscle weakness.
3	Pvc (Poly vinyl chloride)	Insulation of wires	respiratory diseases
4	Bisphenol A	Plastic components	heart Problems
5	Poly chlorinated Biphenols	Plastic components.	Damage to the liver

* E- Plastic DISPOSal ÷

→ Plastic waste ÷

From key boards, casing, plastic hardware components.

→ Printed circuit Board waste ÷

From the circutory boards like Mother board, TV - Internal circuits etc.

*Control Methods (Recycling of E-waste)

- Dis Assembly / dismantling ÷

Disassembly is the systematic removal of components, parts, a group of parts or a subassembly from a product which is in E-waste.

- Upgrading ÷

It Includes comminuting and separation of materials using mechanical / physical and/or metallurgical processing. Methods to recover materials include refining and other.

- Material Recovery ÷

The materials are recovered by recycling facilities. The plastics, glass, metals can be recovered by sorting them before mixing with other waste.

* Advantages of Recycling E-waste

- Asset recovery
- Reduction of need for land fills
- Reduction of Junks
- Resale and Reuse
- creation of Jobs

* Conclusion ÷

→ e-waste is one of the Fastest growing problem In the world. Hence we Aware of that.

→ Product design by using safe and most emerging technologies and raw materials, which are environment friendly.

→ Implementing 3R principle
Reduce - Reuse - Recycle.

Bio polymer

Definition: It is a polymer that is developed from living beings. It is a biodegradable chemical compound that is regarded as the most organic compound in the ecosphere.

The mame "Biopolymer" indicates that it is a biodegradable polymer.

Biopolymer History:

This polymer has been present on earth for billions of years. It is older than synthetic polymers such as plastics.

Ex: 1. protiens 2. Carbohydrates 3. DNA 4. RNA 5. lipids 6. Nucleic acids 7. peptides 8. polysaccharides.

→ DNA biopolymer is the most important of humans

→ The most common biopolymer is Cellulose. It is also the most abundant organic compound on this planet.

→ It comprises 33% of all planet component on earth.

Bio polymer classification:

Sugar based Biopolymers:

starch or sucrose is used as input for manufacturing poly hydroxi butyrate. sugar based polymers can be produced by blowing, injection, vaccum forming and extrusion. Lactic acid polymers are created from milk sugar that is extracted from potatoes. Maize, wheat and sugar beet.

Starch based Biopolymers:

Starch acts as a natural polymer and can be obtained from wheat, topica, maize and potatoes. The materials is stored in tissues of plants as one way carbohydrates. It is not present in Animal tissues.

Biopolymers based on synthetic materials:

Synthetic compounds that are obtained from Potroleum can also be used for making biodegradable polymers such as aliphatic aromatic copolyesters.

Cellulose based polymers:

These are used for packing cigarettes, CDs and confectionary. It is obtained from natural resources like cotton, wood, wheat and corn.

The production of biopolymer may be done either from animal products or agricultural plants.

Biopolymer types:

Thes are prilimarily two types of Biopolymer, one that is obtained from living organisms and another that is produced from renewable resources but require polymerization

Biopolymer uses:

1. Biopolymers based on synthetic are used to manufacture substrate mats.
2. Cellulose based Biopolymers, such as cellphone are used as packaging material.
3. These polymers can reduce carbon dioxide levels in the atmospher and also decrease carbon emission.

Bio Material:- The substances that has been engineered to interact with biological systems for medical purpose. directly with living cells of our body.

Bio Medical polymers:- The polymers that have been used for medical including preventive medicine, and surgical treatment of diseases.

Properties:-

* Non-toxic
* light weight
* Resistance to biochemical attack
* fexibility
* It can be fabricable into desired shape without affecting properties.

Types of Bio-Medical polymers.

Natural:- These are divived from naturally occuring materials (or) organisms.

These are divided into 3 types on based of chemical structure.

1) Polysacharides:- These monosachaides combine together to form a polysacharide.

Ex:- Cellulose, chitin, collagen.

* Cellulose formation:-

Glucose combines to form cellulose

*It is used for Drug delivery, blood purification, wound dressing.

2) Protein → collagen

collagen → protein made of amino acids.

*It is used in cosmetic surgical treatment.

3) Bacterial polyesters → production of medical devices.

Ex:- screws, base fixation, tissue repairs

Properties of Natural Bio-Medical polymers.

- *Cheap to manufacture
- * Non-toxic
- * Highly porous
- * Bio degradable

Biodegradable:- It is carried not through thermal oxidation, photolysis (or) radiolysis but through enzymatic or non-enzymatic hydrolysis.

⇒ Degradation time must match the time required

⇒ should be Metabolised in the body after fulfilling its purpose.

⇒ Remain sufficiently strong untill the surrounding tissue has healed.

Synthetic:- These are artificially prepared ② in Industry.

According to properties ~~of~~ these are four types

- * Biostable
- * Bio eradible
- * water soluble
- * others.

Biostable:- polymers which are used for long time in place of organs i.e, artificial organs.

Ex:- polyurethane.

Bio erodiable:- which serve short term purpose in body and decompose to small molecules that can be metabolized (or) excreted.

Water Soluble polymers:- that forms part of plasma or) which functions as macromolecular drug.

Applications:- Most widely used are is silicone rubber (Poly dimethyl siloxane)

- * Desirable fexibility
- * inertness to body fluids.
- * non-toxicity

Poly urethane is used in Biostable polymers.

- * Blood filtration.
- * Heart valves
- * vascular tubing

Artificial Heart:-

In the year 1982, Scientist Robert Jarvik is a person who developed a artifical heath by using Smooth polyurethane.

Nane:- Jarvik 7

1st patient to have artificial heart Barney clock.

* Artifical kidney transplantation by willem kolff.

ABIO Heart:-

Made of titanium and a plastic to which the blood doesnot stick to its walls.

* walls are fexible made of silicons.
* lifespan is about 5 years
* polyvinyl chloride (PVC) $\left[CH_2-\overset{Cl}{CH}\right]_n$
  Manufacture of disposable syringes.
* Polyproplene:- Heart valves; blood filteration.
* Polyalkylsophane:- Membrane oxygenater.
* Poly Methyl meta acrylale:- (PMMC)
  Contact lense; dental restoratives
  Facture fixation.

Advantages:-

- less cost effective.
- Great no.of choice for treatment of diseases

Disadvantages:-

- shows various problems if used as permanent for body.
- low effectiveness.

Conclusion:-

Now-a days the medical field is developing rapidly by its wonderful discoveries. as biomedical Polymers is also are of the great discoveries by the great ~~scilints~~ scitiests. and still many scitiests are working to make the Biomedical polymers without any dis advantage and as these plays a major role in medicine. So everyone should be aware of its usage and may use in a Proper ways.

prepared by

Sarvepalli. Venkata Rao

M.Sc B.Ed

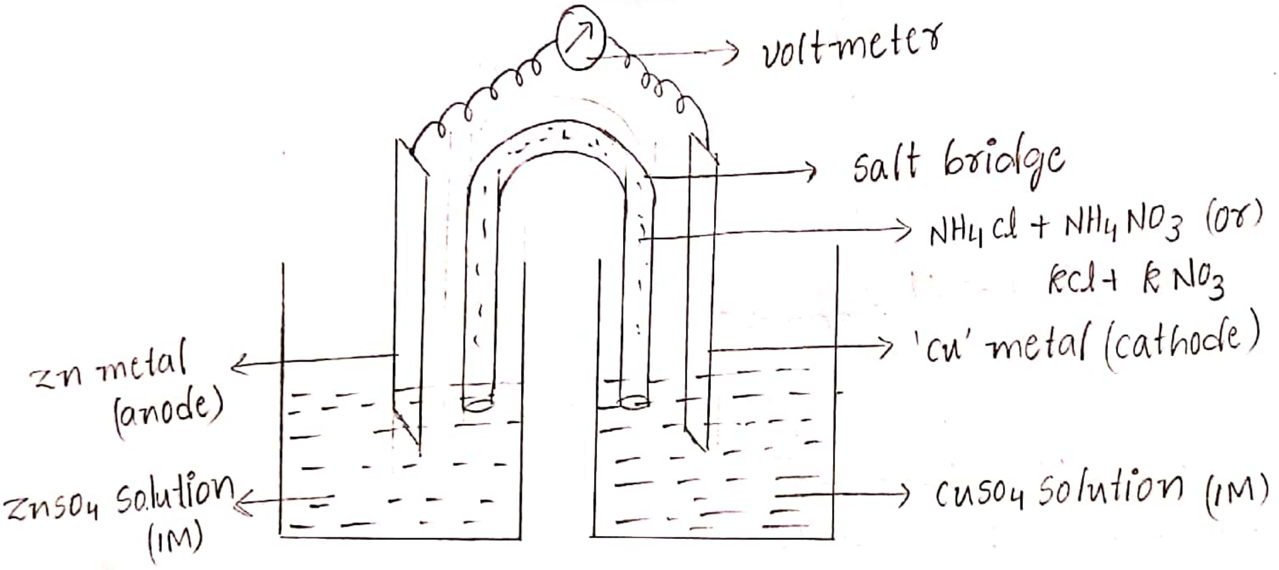
UNIT-II

ELECTROCHEMICAL CELLS AND CORROSION

Introduction: Electro chemistry is the branch of physical chemistry which explains electricity and chemical reaction.

Electro chemical cells:

A device which converts chemical energy into electrical energy by spontaneous redox reaction is known as electro chemical cell (or) voltaic cell (or) galvanic cell (or) Daniel cell.



It consists of two half cells the half cell on the left side consists a 'zinc metal electrode' dipped in '$ZnSO_4$' solution. The half cell on the right side consists a 'cu' electrode dipped in $CuSO_4$ solution. These two half cells are joined by salt bridge. In which zn and cu electrodes are connected to voltmeter and electrolytes ($ZnSO_4$, $CuSO_4$) connected by salt bridge.

Cell Representation:

⟹ Anode half cell is written on left hand side and cathode half cell is written on right hand side.

⟹ Anode is represented by first metal electron and then electrolyte. These two are seperated by vertical line (or) semi colon.

$$Zn / ZnSO_4 \quad (or) \quad Zn ; ZnSO_4$$

⟹ cathode is represented by first metal electron and then electrolyte. These two are seperated by vertical (or) semi colon

$$CuSO_4 / Cu \quad (or) \quad CuSO_4 ; Cu$$

⟹ These two ~~cell~~ are seperated by salt bridge which is indicated by double vertical line.

Cell reaction – $Zn / \underset{(1M)}{ZnSO_4} // \underset{(1M)}{CuSO_4} / Cu$

Oxidation half cell reaction: 'zinc metal' acts as anode undergoes oxidation reaction by losing of electrons to form 'Zn^{+2}'.

At anode: $Zn \longrightarrow Zn^{+2} + 2e^-$ (oxidation)

Reduction half cell reaction: 'copper metal' acts as cathode undergoes reduction reaction by gainning of electrons to form 'Cu'.

At cathode: $Cu^{+2} + 2e^- \longrightarrow Cu$ (reduction)

Net Reaction:

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

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

$$Zn + Cu^{+2} \longrightarrow Zn^{+2} + Cu$$

Role of salt bridge: salt bridge is inverted U-shaped tube which have KCl, KNO_3 and gelatin (or) NH_4Cl, NH_4NO_3 and gelatin. is gel state is known as "agar agar gel"

⟹ It prevents accumulation charge of liquid junction potential

⟹ It allows electrons from anode to cathode.

⟹ It does not allows electrolyte substance from anode to cathode.

Single electrode potential:

when a metal rod dipped in its salt solution The metal atom tends either to lose electrons (oxidation) or to accept electrons (reduction) the process of oxidation (or) reduction depends on the nature of metal. In this process there develops a potential between the metal atoms and its corresponding ions called the electrode potential. There is a between metal and metal ion and the potential value of electrolyte is zero and hence is called single electrode potential. It is measured in volts.

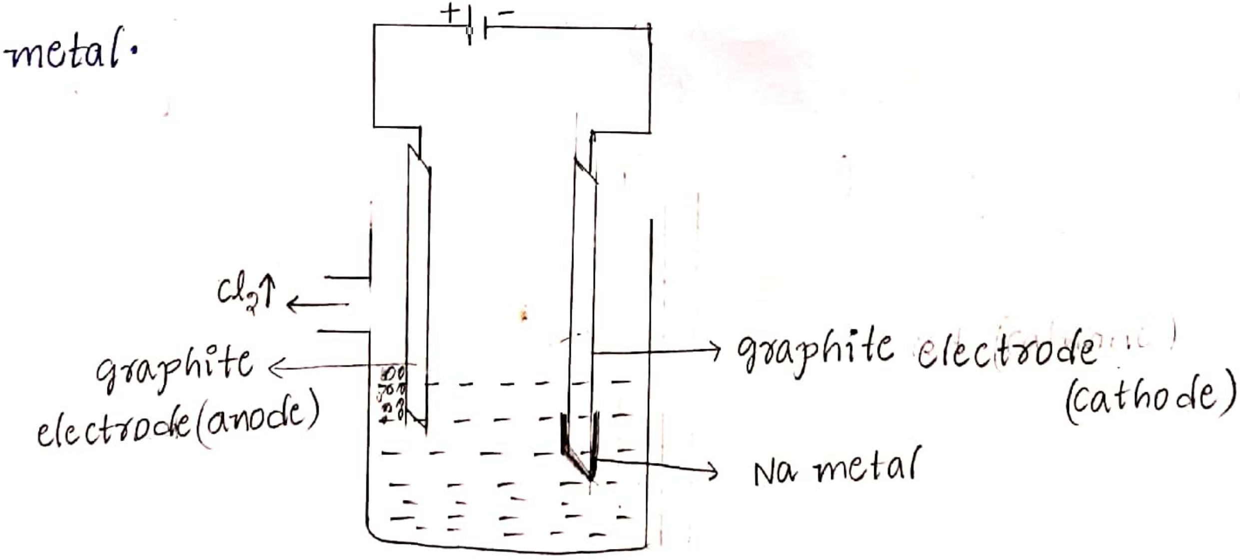
Electrolytic cell (or) irreversible cell:

A device which converts electrical energy into chemical energy by spontaneous redox reaction is called electrolytic cell (or) irreversible cell.

Electrolysis of fused Nacl:

In this process two platinum electrodes are immersed into fused Nacl electrolyte solution, in this two platinum electrodes are connected to battery. positive cell terminal connected platinum electrode acts as anode and undergoes oxidation, negative cell terminal acts as cathode and undergoes reduction.

At anode position chloride irons combine to release Cl_2 gas, at cathode position sodium ions gains electrons to form sodium metal.



Ionisation reaction: $2NaCl \rightleftharpoons 2Na^+ + 2Cl^-$

At anode: $2Cl^- \longrightarrow Cl_2\uparrow + 2e^-$ (oxidation)

At cathode: $2Na^+ + 2e^- \longrightarrow 2Na$ (reduction)

∴ Net reaction:

$$2Cl^- \longrightarrow Cl_2\uparrow + \cancel{2e^-}$$

$$2Na^+ + \cancel{2e^-} \longrightarrow 2Na$$

$$2Na^+ + 2Cl^- \longrightarrow 2Na + Cl_2\uparrow$$

Electro chemical series (galvanic series):

A series of metals arranged in increasing order of standard reduction potential and decreasing order of standard oxidation potential is known as "electro chemical series"

$$Li \longrightarrow Li^{+1} + 1e^{\ominus}$$

$$K \longrightarrow K^{+1} + 1e^{\ominus}$$

$$Ca \longrightarrow Ca^{+2} + 2e^{\ominus}$$

$$Na \longrightarrow Na^{+1} + 1e^{\ominus}$$

$$Mg \longrightarrow Mg^{+2} + 2e^{\ominus}$$

$$Al \longrightarrow Al^{+3} + 3e^{\ominus}$$

$$Zn \longrightarrow Zn^{+2} + 2e^{\ominus}$$

$$Cr \longrightarrow Cr^{+3} + 3e^{\ominus}$$

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

$$Sn \longrightarrow Sn^{+2} + 2e^{\ominus}$$

$$Pb \longrightarrow Pb^{+2} + 2e^{\ominus}$$

} ANODE

$$H_2 \longrightarrow 2H^{\oplus} + 2e^{\ominus}$$

} BOTH ANODE AND CATHODE

$$Cu \longrightarrow Cu^{+2} + 2e^{\ominus}$$

$$Ag \longrightarrow Ag^{+1} + 1e^{\ominus}$$

$$Fe \longrightarrow Fe^{+3} + 3e^{\ominus}$$

$$Pt \longrightarrow Pt^{+3} + 3e^{\ominus}$$

} CATHODE

Significance:

1. we understood reactivity of the metals

2. Hydrogen acts as both anode and cathode because of which undergoes oxidation, reduction reaction.

3. Above the hydrogen element the metals acts as anode undergoe oxidation reaction which have negative electrode potential value.

4. below the hydrogen element the metals acts as cathode undergoes reduction reaction which have positive electrode potential value.

5. we should calculate electro motive force EMF using electro chemical series

$$\boxed{EMF = E_{cathode} - E_{anode}}$$

6. In metallurgy concept we should seperate metals from ore.

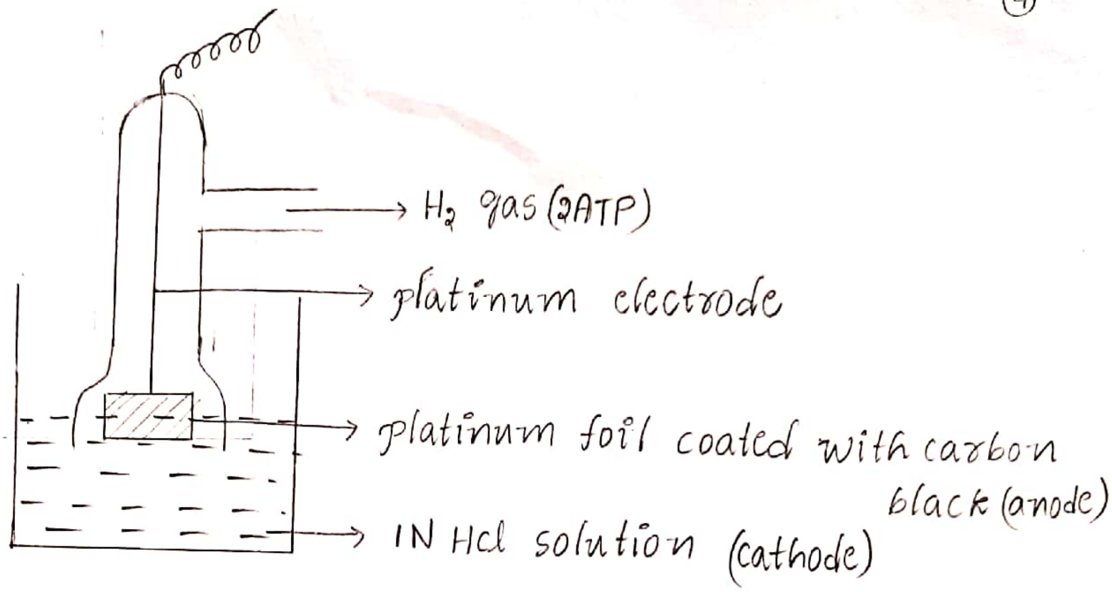
7. Above the hydrogen element which acts as anode undergoes rapid corrosion when compared to lower position of metals.

Standard hydrogen electrode (or) normal hydrogen electrode:

Placing platinum foil into 1N of Hcl solution. The foil is coated with carbon black powder which absorbs hydrogen gas. The foil is closed with open bell like glass tube which have inlead for the supplying of hydrogen gas at 2ATP. The platinum foil absorbs hydrogen gas then converted into hydrogen electrode.

1. Here, hydrogen electrode acts as anode.

2. The electrolyte solution acts as cathode.

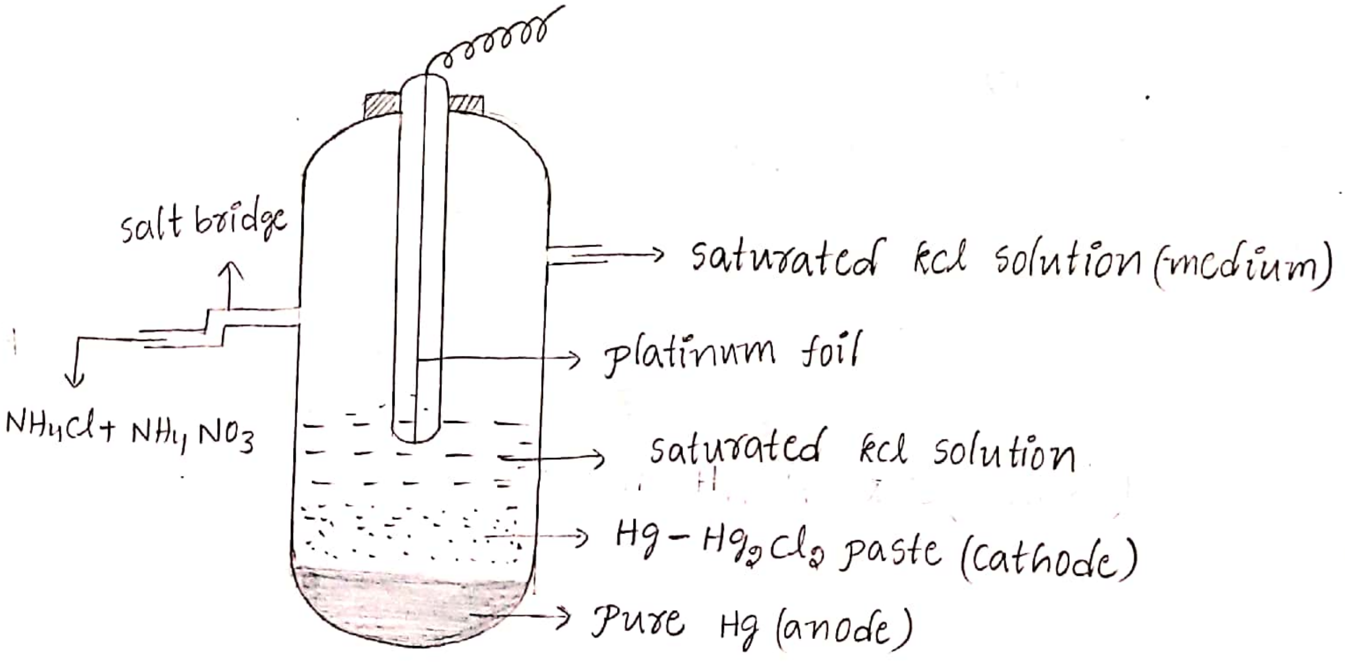


At anode: $H_2 \longrightarrow 2H^+ + 2e^-$ (oxidation)

At cathode: ~~$2H^+$~~ $2H^+ + 2e^- \longrightarrow H_2 \uparrow$ (reduction)

⟹ Here, net reaction is 'zero', the electrode potential also zero.

Calomel electrode (or) Hg – Hg_2Cl_2 electrode:



Construction:

It consists along glass tube the bottom to the glass is filled with pure 'Hg' above the pure Hg mecury-mercurous Chloride electrode. The remaining portion of the tube is filled with saturated kcl solution. The glass having two inlets, one is used for filled saturated kcl and another one is acts as salt bridge. The platinum electrode immersed in the tube upto the paste.

⟹ The potential calomel electrode is depends on concentration of kcl solution.

⟹ If we take saturated kcl solution then the E° value is '0'v.

working:

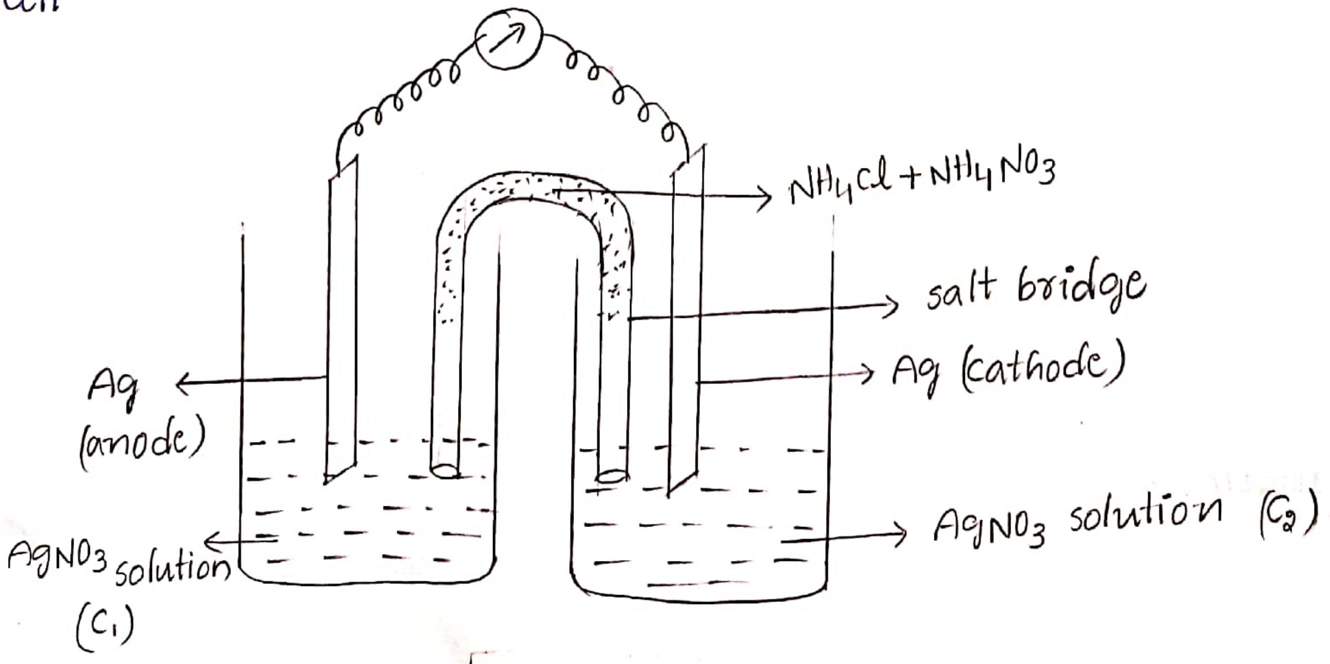
At anode: $2Hg \longrightarrow Hg_2^{+2} + 2e^-$ (oxidation)

At cathode: $Hg_2^{+2} + 2e^- \longrightarrow 2Hg$ (reduction)

⟹ The net reaction is zero. so, electrode potential is zero.

Concentration cell:

A device which converts chemical energy into electrical energy by spontaneous redox reaction. Here, the Concentration of electrolyte is different is known as concentration cell.



⟹ $C_2 > C_1$

operator: In which electrodes are same and electrons are also same but concentrations are different c_1 and c_2. In which $c_2 > c_1$.

At anode: $Ag_{(c_1)} \longrightarrow Ag^{+1}_{(c_1)} + 1e^-$ (oxidation)

At cathode: $Ag^{+1}_{(c_2)} + 1e^- \longrightarrow Ag_{(c_2)}$ (reduction)

net reaction:

$$\begin{array}{l} Ag(c_1) \longrightarrow Ag^{+1}_{(c_1)} + 1e^- \\ Ag^{+1}_{(c_2)} + 1e^- \longrightarrow Ag(c_2) \\ \hline Ag(c_1) + Ag^{+1}_{(c_2)} \longrightarrow Ag^{+1}_{(c_1)} + Ag_{(c_2)} \\ \hline \end{array}$$

According to "nernest equation"

$$\Longrightarrow EMF = E^\circ + \frac{0.0592}{n} \log(k)$$

$$\Longrightarrow EMF = E_R - E_L$$

Cell representation: $Ag(c_1) / AgNO_3(c_1) // AgNO_3(c_2) / Ag_{(c_2)}$

$$E_R = E^\circ + \frac{0.0592}{n} \log(c_2)$$

$$E_L = E^\circ + \frac{0.0592}{n} \log(c_1)$$

$$EMF = E_R - E_L$$

$$= \cancel{E^\circ} + \frac{0.0592}{n} \log(c_2) - \cancel{E^\circ} - \frac{0.0592}{n} \log(c_1)$$

$$= \frac{0.0592}{n} [\log(c_2) - \log(c_1)]$$

$$\boxed{EMF = \frac{0.0592}{n} \log\left(\frac{c_2}{c_1}\right)}$$

Battery : A device which converts chemical energy into electrical energy is known as battery. Battery principle is same to electrochemical cell.

The batteries are two types ~~p~~, they are

1. Primary battery
2. Secondary battery

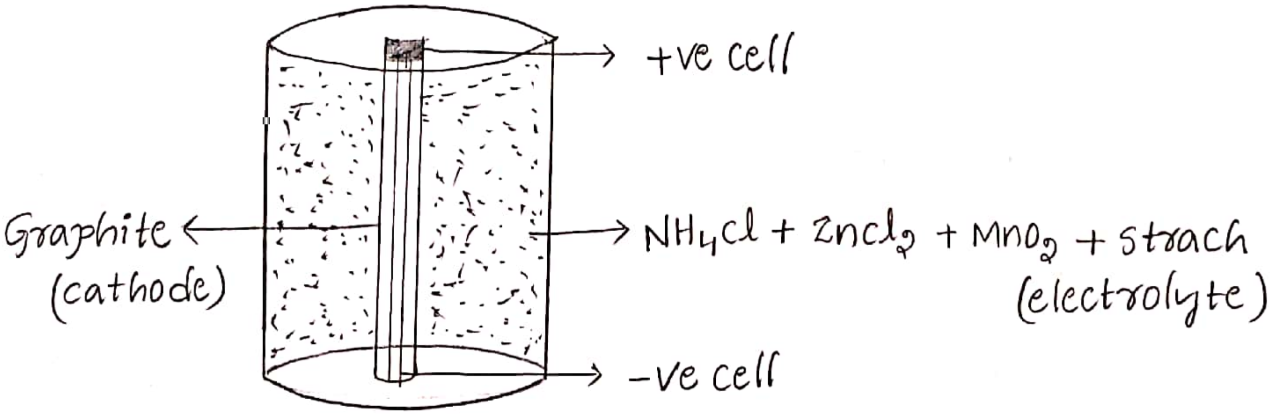
1. **Primary battery**: The starting stage of batteries (or) non-rechargable batteries is known as primary batteries

ex: dry cell Lechlance cell, zinc air cell

2. **Secondary battery**: Present using batteries (or) rechargable batteries is known as secondary batteries.

ex: nickel - cadmium cell, nickel metal hydride cell

Dry cell (or) Lechlanche cells:



Zinc can acts as anode undergoes oxidation. Graphite rod acts as cathode but it does not undergoes reduction reaction because of it is a non-metallic element.

The mixture of NH_4Cl, $ZnCl_2$, MnO_2 and small amount of starch powder acts as electrolyte which undergoes reduction reaction.

At anode: $Zn \longrightarrow Zn^{+2} + 2e^-$ (oxidation)

At cathode: $2NH_4^+ + 2MnO_2 + 2e^- \longrightarrow Mn_2O_3 + 2NH_3 + H_2O$ (reduction)

Net Reaction:

$$Zn \longrightarrow Zn^{+2} + \cancel{2e^-}$$

$$2NH_4^+ + 2MnO_2 + \cancel{2e^-} \longrightarrow Mn_2O_3 + 2NH_3 + H_2O$$

$$Zn + 2NH_4^+ + 2MnO_2 \longrightarrow Zn^{+2} + Mn_2O_3 + 2NH_3 + H_2O \ (1.6V)$$

Advantages:

1. It is low price.
2. It given 1.5 volt of voltage.
3. These are nontoxic batteries.

uses: It is used in electronic devices like calculator radios, wall locks, vacmens ..etc.

Nickel cadmium cells (Ni-CD):

It is an example of example of secondary cell (or) battery. In this cell cadium metal acts as anode undergoes oxidation and nickel oxi hydroxide

$NiO(OH)_2$ acts as cathode undergoes reduction and alkaline potassium hydroxide (KOH) acts as electrolyte.

The power out for these batteries is 1.4V

At anode: $Cd + 2OH^- \longrightarrow Cd(OH)_2 + 2e^-$ (oxidation)

At cathode: $2NiO(OH)_2 + 2H_2O + 2e^- \longrightarrow 2Ni(OH)_2 + 2OH^-$ (reduction)

Net reaction: $Cd + \cancel{2OH^-} \longrightarrow Cd(OH)_2 + \cancel{2e^-}$

$2NiO(OH)_2 + 2H_2O + \cancel{2e^-} \longrightarrow 2Ni(OH)_2 + \cancel{2OH^-}$

$Cd + 2NiO(OH)_2 + 2H_2O \longrightarrow Cd(OH)_2 + 2Ni(OH)_2$ [1.4V]

Uses:

1. These are used in medical applications.
2. These are used in research equipment.
3. These are used in high quality Lab equipments.

Nickel-metal hydrides cell ($Ni-MH_2$):

In this cell MH_2 acts as anode undergoes oxidation and nickel oxihydroxide [$NiO(OH)_2$] acts as cathode undergoes reduction and electrolyte solution is alkaline KOH solution. These batteries are recharging power is 1.2V

At anode: $MH + OH^- \longrightarrow M + H_2O + 1e^-$ (oxidation)

At cathode: $NiO(OH) + H_2O + 1e^- \longrightarrow Ni(OH)_2 + OH^-$ (reduction) net reaction:

$$MH + OH^- \longrightarrow M + H_2O + 1e^-$$
$$NiO(OH) + H_2O + 1e^- \longrightarrow Ni(OH)_2 + OH^-$$

$$MH + NiO(OH) \longrightarrow M + Ni(OH)_2 \quad (1.2V)$$

uses:

1. It is used in electronic devices like computers.
2. It also used in electrical vehicles.

Lithium ion cell ($Li-MnO_2$ cell): In this cell Lithium metal acts as anode and undergoes oxidation and MnO_2 acts as cathode undergoes reduction and Lithium metal is organic solvent in electrolyte.

The power output for this cell is [1.3V]

At anode: $Li \longrightarrow Li^{+1} + 1e^-$ (oxidation)

At cathode: $MnO_2 + Li^{+1} + 1e^- \longrightarrow Li-MnO_2$ (reduction)

Net reaction: $Li \longrightarrow \cancel{Li^{+1}} \cancel{+1e^-}$

$$MnO_2 + \cancel{Li^{+1}} \cancel{+1e^-} \longrightarrow Li-MnO_2$$

$$Li + MnO_2 \longrightarrow Li-MnO_2 \quad (1.3V)$$

Applications:

1. These are used in automatic cameras.
2. conic types of lithium cells are used in rist watches and calculators.

Zinc air cells: In the type of primary cell, the cell of zinc metal acts as anode undergoes oxidation and porous carbon plate acts as cathode undergoes reduction and alkaline KOH acts as electrolyte.

At anode: $Zn + 2OH^- \longrightarrow ZnO + H_2O + 2e^-$ (oxidation)

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

Net reaction:

$$Zn + \cancel{2OH^-} \longrightarrow ZnO + \cancel{H_2O} + \cancel{2e^-}$$

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

$$Zn + \frac{1}{2}O_2 \longrightarrow ZnO \quad (1.5V)$$

⇒ The power output for this cell is - 1.5V

Applications:

1. These are used in milaitary voice transmitters.
2. It is also used in electronic pagers.

Fuel cells:

A fuel cell is an electrochemical cell which converts chemical energy into electrical energy by using fuel in the presence of oxygen and hydrogen gases respectively.

The basic principles of fuel cells are identical to those of the electro-chemical cells.

The fuel and the oxidising agents are continuously and seperately supplied to the electrodes of cell, at which they undergo reactions. Fuel cells are capable of supplying current as long as the reactants are supplied.

∴ Fuel cells are characterised by

1. high energy efficiency.
2. Low noice Level
3. no thermal pollution

Hydrogen - oxygen fuel cells ($H_2 - O_2$) :

In this fuel cell, 2 porous graphite electrodes coated with platinum particles acts as anode and cathode. The electrolyte solution is 2.5% of KOH solution means 2.5g KOH present in 100ml of water.

At anode: $2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$ (oxidation)

At cathode: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$ (reduction)

net reaction:

$$\begin{array}{l} 2H_2 + \cancel{4OH^-} \longrightarrow 4H_2O + \cancel{4e^-} \\ O_2 + 2H_2O + \cancel{4e^-} \longrightarrow \cancel{4OH^-} \\ \hline 2H_2 + O_2 \longrightarrow 2H_2O \quad (1.23V) \\ \hline \end{array}$$

⟹ The power output is 1.23V

Applications:

1. As an auxiliary energy source in space vehicle, submarines... ..etc.
2. Because of light weight, these are preferred for space craft. and product H_2O is a valuable fresh water for astronauts.

Advantages:

1. Energy conversion is very high.
2. Noise & thermal pollution are low.

3. Maintanance cost is Low.

4. Product H_2O, is a drinking water source for astronouts.

Limitations:

1. The lifetime of fuel cell is not accurately known.
2. This initial cost is high.

Methyl alcohol oxygen fuel cell (CH_3OH-O_2): [alkaline fuel cell]

Materials: 2 porous nickel plate, one porous nickel plate is coated impregnated with platinum particle which acts as anode, another porous nickel plate is coated with silver particles acts as cathode. The electrolyte solution is saturated KOH solution.

At anode:

$$CH_3OH + 6OH^- \longrightarrow CO_2 + 5H_2O + 6e^- \text{ (oxidation)}$$

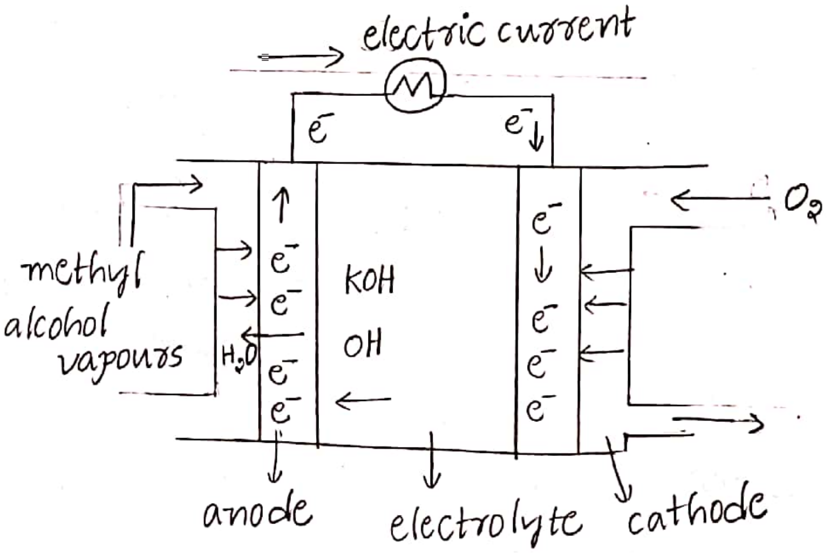
At cathode: $\frac{3}{2}O_2 + 3H_2O + 6e^- \longrightarrow 6OH^-$ (reduction)

net reaction:

$$CH_3OH + \cancel{6OH^-} \longrightarrow CO_2 + 5H_2O + \cancel{6e^-}$$

$$\frac{3}{2}O_2 + 3H_2O + \cancel{6e^-} \longrightarrow \cancel{6OH^-}$$

$$CH_3OH + \frac{3}{2}O_2 \longrightarrow CO_2 + 2H_2O$$



Advantages:

1. These cells are stable at all environmentmental conditions.
2. Easy to transport.
3. Less risk to aquatic plants, animals ...etc.
4. Because methanol possess lower inflamability limit than gasoline it posses less fire risk than gasoline.
5. B'co$_2$ of high hydrogen concentration in methanol it is an excellent fuel.

Phosphoric Acid fuel cells (PAFC):

In phosphoric acid fuel cell, 2porous carbon plates coated with platinum particles acts as anode & cathode. The electrolyte solution is a mixture of phosphoric acid & silica carbide matrix (SiC_2). The power output is 100 - 400 kw. Power output is very high due to it is strong acid acts as a electrolyte.

At anode: $2H_2 \longrightarrow 4H^+ + 4e^-$ (oxidation)

At cathode: $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ (reduction)

net reaction:

$$2H_2 \longrightarrow \cancel{4H^+} + \cancel{4e^-}$$

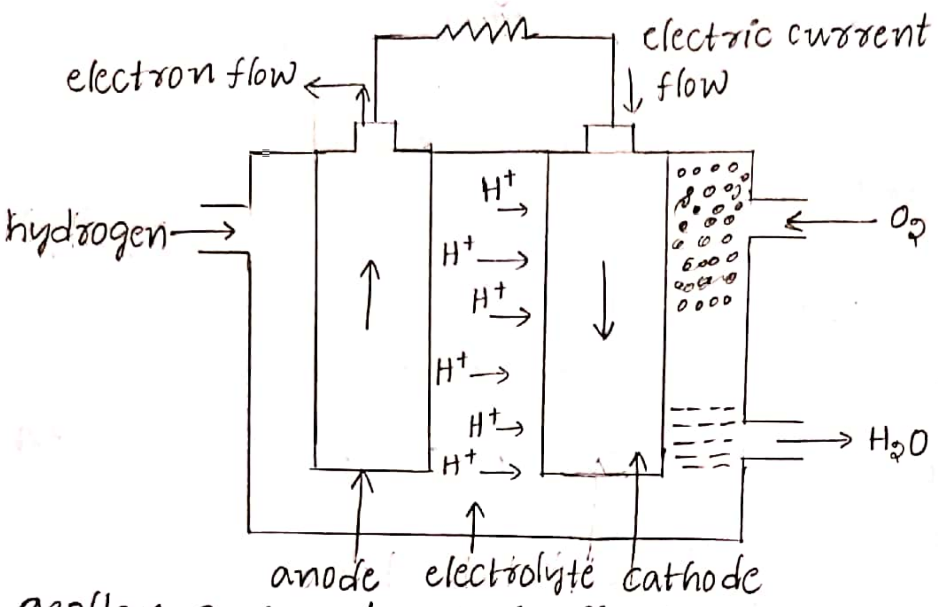
$$O_2 + \cancel{4H^+} + \cancel{4e^-} \longrightarrow 2H_2O$$

$$2H_2 + O_2 \longrightarrow 2H_2O \text{ (100-400Kw)}$$

Applications:

1. Phosphoric acid fuel cells are used for stationary power generation with output 100kw to 400kw

2. used for Large vehicles as buses.



Molten carbonate fuel cells (MCFC): In this fuel cell, one porous nickel plate is imprignated with platinum particles acts as anode, another porous nickel plate is coated with Lithinated nickel oxide acts as cathode. The electrolyte solution is sodium potassium carbonate and ciramic cell ($LiAlO_2$).

At anode: $H_2 + CO_3^{-2} \longrightarrow H_2O + CO_2 + 2e^-$ (oxidation)

At cathode: $\frac{1}{2}O_2 + CO_2 + 2e^- \longrightarrow CO_3^{-2}$ (reduction)

Net reaction:

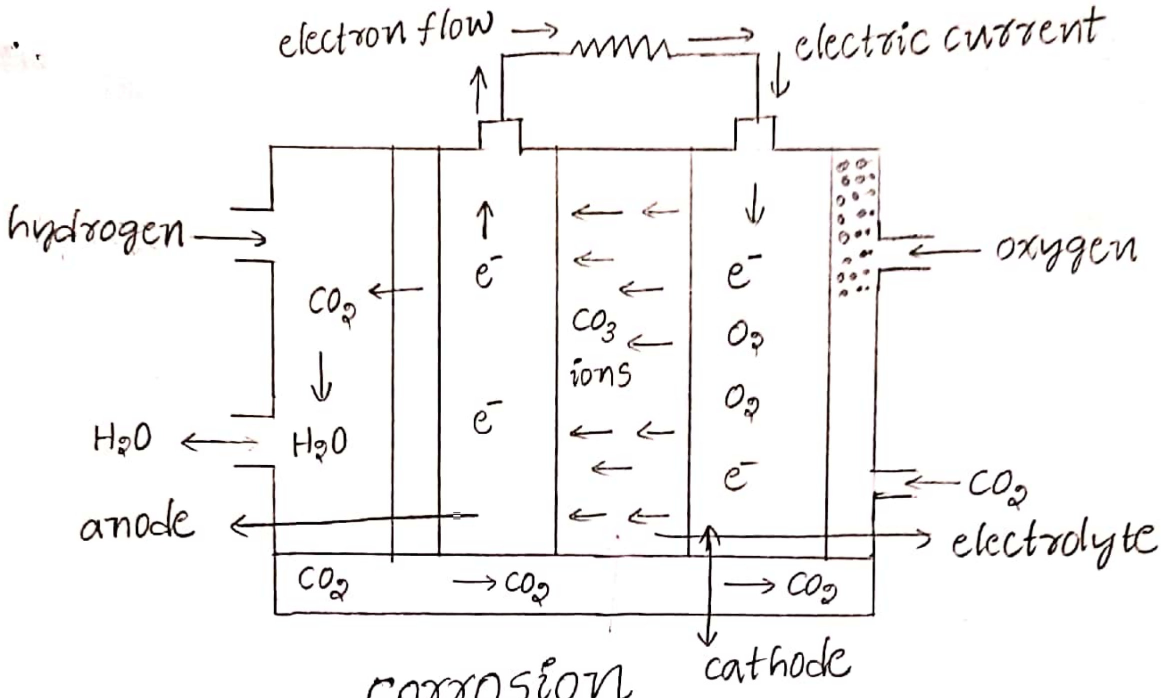
$$H_2 + \cancel{CO_3^{-2}} \longrightarrow H_2O + \cancel{CO_2} + \cancel{2e^-}$$

$$\frac{1}{2}O_2 + \cancel{CO_2} + \cancel{2e^-} \longrightarrow \cancel{CO_3^{-2}}$$

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$$

Applications:

Molten carbonate fuel cells are used in many industries to produce electric power via steam turbines.



Corrosion

Corrosion: The process of destruction (or) deteriation of metals quantity by the action of environment is known as corrosion

ex: 1. Iron form reddish brown colour precipitate in its surface is known as rusting of iron $[Fe_2O_3 \cdot x \cdot H_2O]$.

2. copper forms greenish colour layer in its surface is known as rusting of copper (Cu_2O)

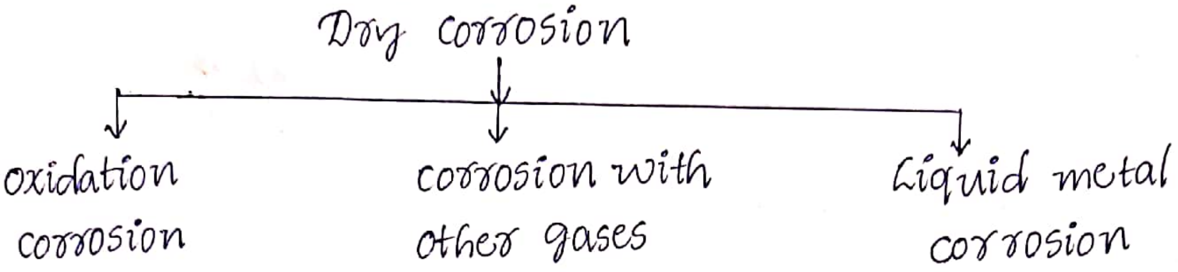
Theories of corrosion:

1. **Acid - theorey corrosion:** The metals interacts with atmosphere gases like carbon dioxide, water vapour and oxygen gas to form metallic carbonic acids. Furthur ;carbonic acid generates corrosion to the metal.

ex: $Fe + H_2O + 2CO_2 + \frac{1}{2} O_2 \longrightarrow Fe(HCO_3)_2$

Iron carbonic acid.

Dry theory (or) Direct chemical attack theorey of corrosion:



1. oxidation corrosion: Metals reacts with dry atmospheric oxygen to form a metal oxide layer on it's surface.

At anode: $M \longrightarrow M^{+n} + ne^{-}$ (oxidation)

At cathode: $\frac{1}{2} O_2 + ne^{-} \longrightarrow O^{-2}$ (reduction)

$$M + \frac{1}{2} O_2 \longrightarrow M^{+n} + O^{-2} \longrightarrow M_2O_3$$

metal oxide layer

Nature of M_2O Layer:

1. Stable, non-porous: If the M_2O Layer is stable and non-porous which is protective and acts as a barier between metal and environment, that means M_2O Layer prevents the further corrosic of metal.

ex: copper, aluminium

2. unstable M_2O Layer:

If the M_2O Layer is unstable then it is immediately decomposer does not takes place oxygen. In this metal corrosion does not take place.

ex: gold, platinum

3. **volatile nature:** If the metal oxide Layer is volatile in nature rapid corrosion takes place.

ex: MO

4. **stable porous:** If the M_2O 8 Layer is stable and porous which increase the further corrosion of the metal.

ex: chromium

2. **Corrosion with other gases:** In this concept metals interacts with other gases like chlorine, flourine, CO_2, sulphur dioxide, NOX to form protective and non-protective Layer.

ex: $2Ag + Cl_2 \longrightarrow 2AgCl$ (protective)

$Sn + Cl_2 \longrightarrow SnCl_2$ (non- protective)

In above two example silver metal interacts with chlorine gas to form protective layer but interacts with stanum metal to form non-protective Layer.

3. **Liquid metal corrosion:**

All the metals are solids at room temperature except of mercury. The mercury interact with ~~Layer~~ other metals to form amalgam except of iron, platinum is known Liquid metal corrosion.

⟹ This amalgum is useful in dental treatment to full fill cavity present in teeth.

wet theorey (or) electrochemical attack theory:

In electrochemical theorey metals acts as anode undergoes oxidation and environment it acts as cathode undergoes reduction reaction in two cases those are acidic environment, basic (or) neutral environment.

At anode: $M \longrightarrow M^{+n} + ne^{\ominus}$ (oxidation)

At cathode:

case-i : $2H^+ + 2e^- \longrightarrow H_2 \uparrow$ (reduction)

case-ii : $\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$ (reduction)

Rusting of iron:

The iron metal interacts with basic (or) neutral environment to form yellow colour ferrous hydroxide. Immediately it loses water molecules to get reddish brown colour precipitate ~~tio~~ as a rust $(Fe_2O_3 \cdot xH_2O)$

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

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

net reaction:

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

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

$$Fe + \frac{1}{2}O_2 + H_2O \longrightarrow Fe^{+2} + 2OH^- \longrightarrow \underbrace{Fe(OH)_2}_{\text{yellow colour}}$$

$$\Longrightarrow 2Fe(OH)_2 \xrightarrow[-H_2O]{} \underbrace{Fe_2O_3 \cdot xH_2O}_{\text{reddish brown colour.}}$$

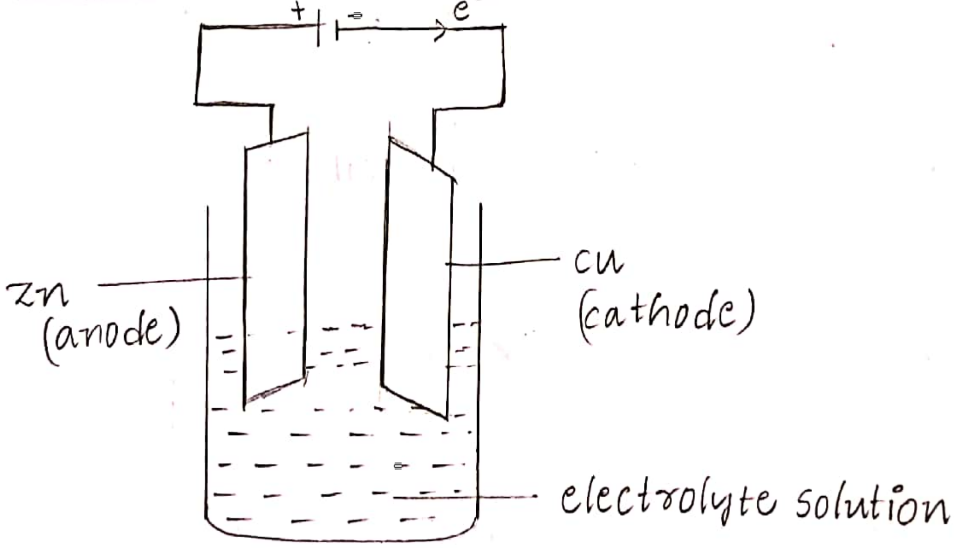
Formation of different types of cells during corrosion: ⑰

There are four types of cells.

1. Different metal corrosion.
2. Different aeration (or) concentration cell corrosion.
3. water line corrosion.
4. stress corrosion.

1. Different metal corrosion:

Whenever two different metals placed in electrolyte solution connected with electrically. According to electrochemical series out of these two metals one metal acts as anode (zinc) undergoes corrosion, another metal acts as cathode (copper) does not undergoes corrosion is known as "different metal ~~coroco~~ corrosion"

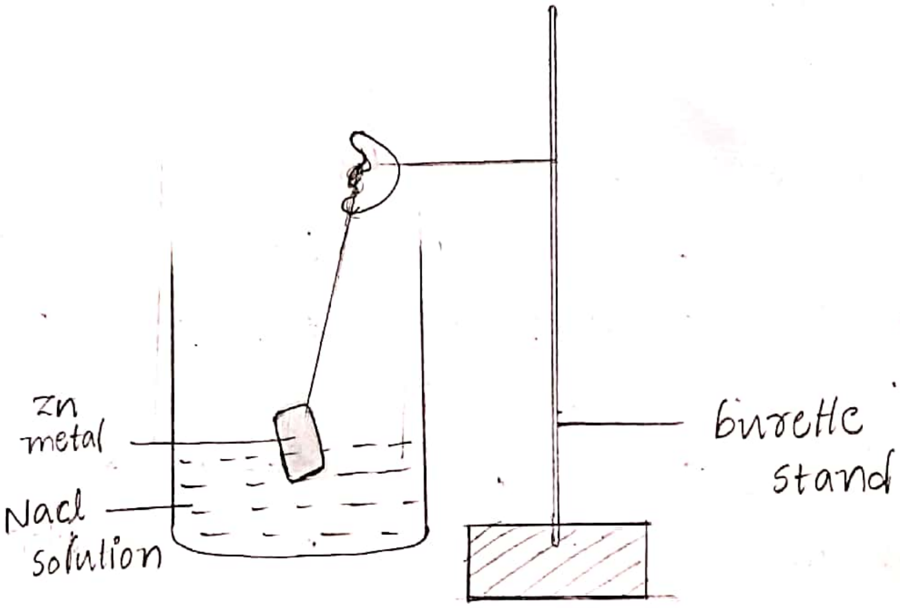


At anode: $Zn \longrightarrow Zn^{+2} + 2e^{-}$ (oxidation)

At cathode: $Cu + 2e^{-} \longrightarrow Cu$ (reduction)

2. Different aeration (or) concentration cell corrosion:

In this cell is prepared by the concentration of electrolyte solution. Zinc metal dipped in Nacl solution is partially here ~~un~~dipped portion of zinc metal acts as anode undergoes corrosion and undipped portion of zinc metal acts as cathode does not undergoes corrosion.

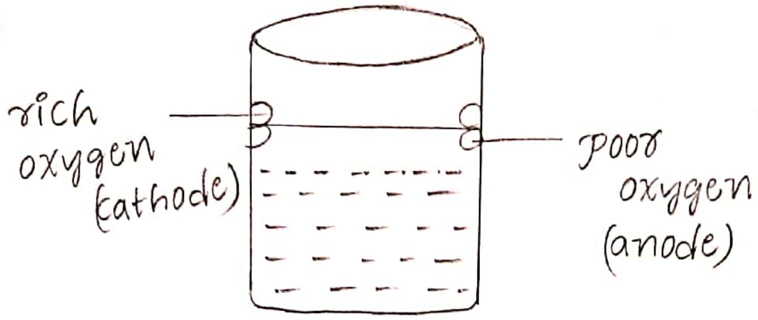


At anode: $Zn \longrightarrow Zn^{+2} + 2e^-$ (oxidation)

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

3. Water Line corrosion: In this cell is prepared by concentration of oxygen Level

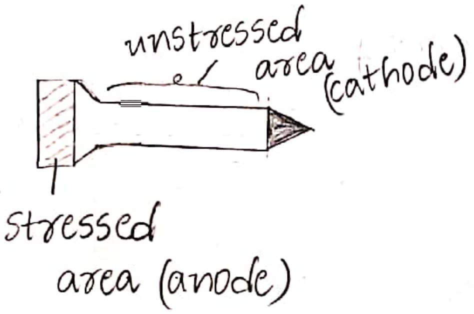
example: Take a water container which is filled with water below the water Level is poor oxygenated part acts as anode undergoes corrosion and above the water Level is rich oxygen part acts as cathode does-not undergoes corroison.

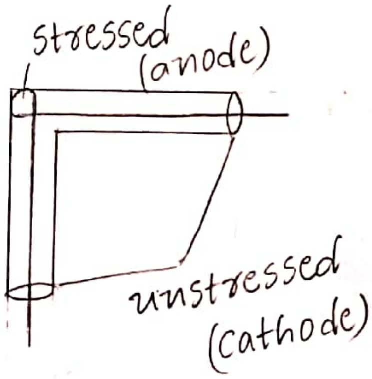


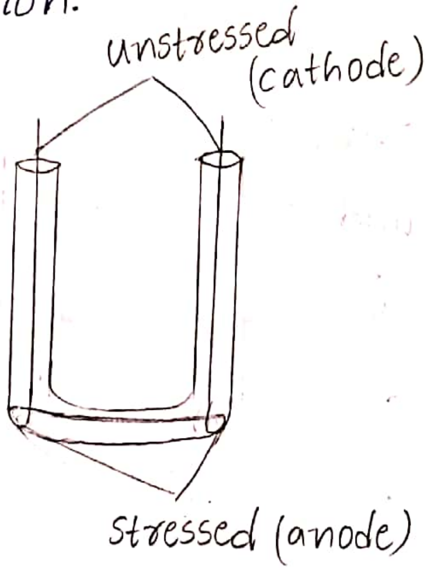
4. Stress corrosion:

Stress cells are prepared by stressing

example: In a nail, head and tail part is stressed area acts as anode undergoes corrosion. The remaining body is unstressed area acts as cathode does not undergoes corrosion.







Passivity of metals:

The process in which a metal exhibits higher corrosion resistance is called "passivity of metal."

When a stable, non-porous and higher protective M_2O layer is formed on the surface of it is called "Passivity". This metal M_2O layer is formed a barrier between metal and environment and protective the metal form corrosion. This property is called "passivity."

Factors influencing rate of corrosion:

1. Nature of metal
2. Nature of environment

Nature of metal:

a) Physical state of metals:

The rate of corrosion is informed by grain due to stress, Smaller the size of metal greated the rate of corrosion.

b) Position of metal on galvanic series:

when two metals are in contact with electrolyte. The metal above the series acts as anode and undergoes corrosion. The metal below the series acts as cathode and does not undergoes corrosion.

c) Surface of metal: A rough surface of metal rapidly corrodes as it collects more dust. A smooth surface does not corroded easily.

d) Purity of metal: Generally pure metals does not undergoes corrosion if impurities are added undergoes corrosion.

e) Nature of M_2O Layer:

If the M_2O Layer is stable, non-porous which protects the metals but M_2O Layer is stable, porous which increases the corrosion.

Nature of environment :

⑭

a) effect of temperature: Corrosion rate is proportional to temperature, increases the temperation rate of corrosion also increases.

b) humidity (or) moisture: Moisture in the atmosphere acts as electrolyte and causes electro chemical corrosion (or) wett corrosion.

c) Amount of oxygen in atmosphere:

oxygen in atmosphere causes differential areation types of corrosion less oxygenated part acts as anode and more oxygenated part acts as cathode. corrosion take place at anode.

d) presence of impurities in atmosphere:

Impurities like H_2S, SO_2 ... etc. present in the atmosphere metal undergoes rapidly corrosion.

e) Effects of pH: In acidic environment metal undergoes rapid corrosion.

Corrosion control:

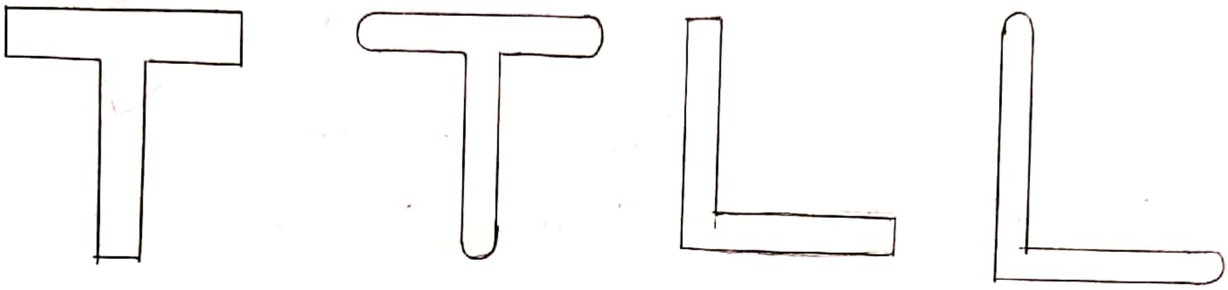
1. Proper designing:

⟹ when anode and cathode materials are used to gather then the area of anodic material is Large.

⟹ The anodic part should not be painted (or) coated because any cracks in coating causes rapid corrosion

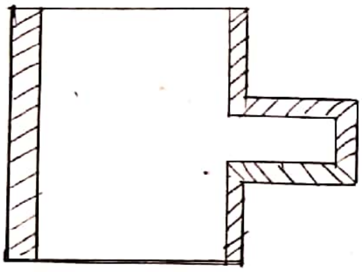
⇒ Avoiding alloys

⇒ Angles, corners, edges should be avoided in a structure.

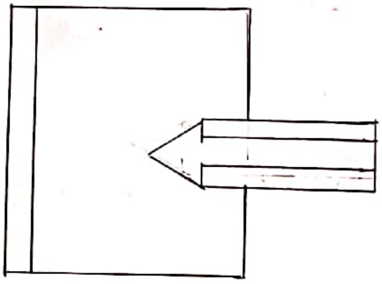


⇒ The materials should not have sharp corners and revises. They help in store of impurities.

⇒ The proper design should avoid the presence revises between the adjacent parts of the structure.



Poor



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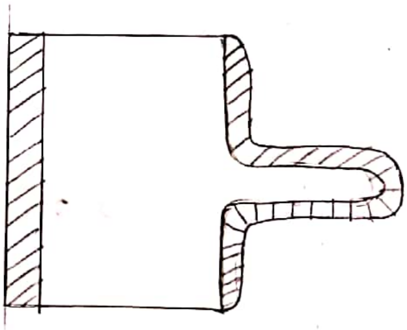

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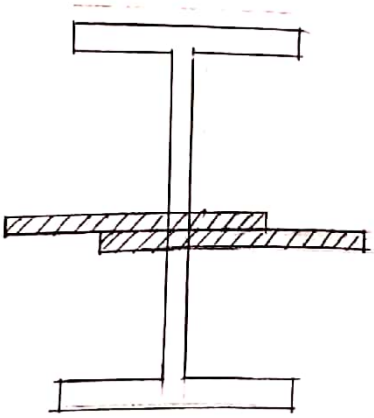

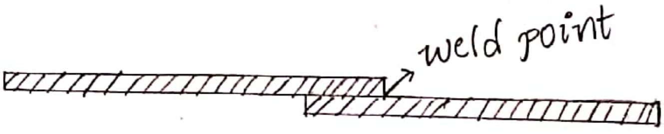

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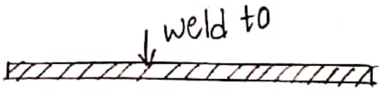
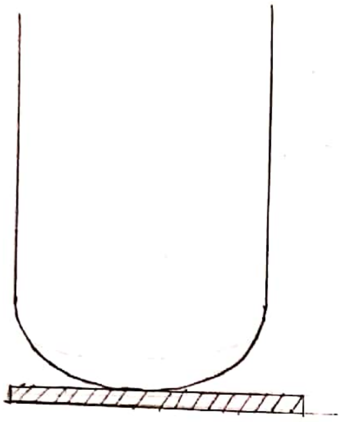
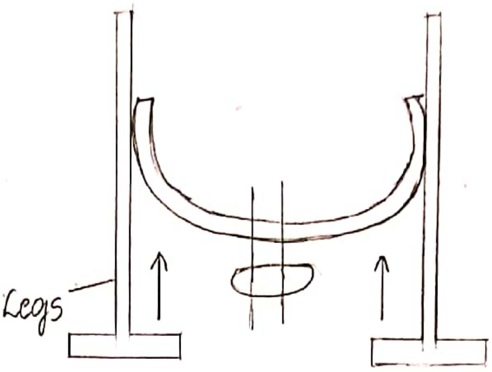


best

when ever possible the equipment should be supported is on legs free air circulation.



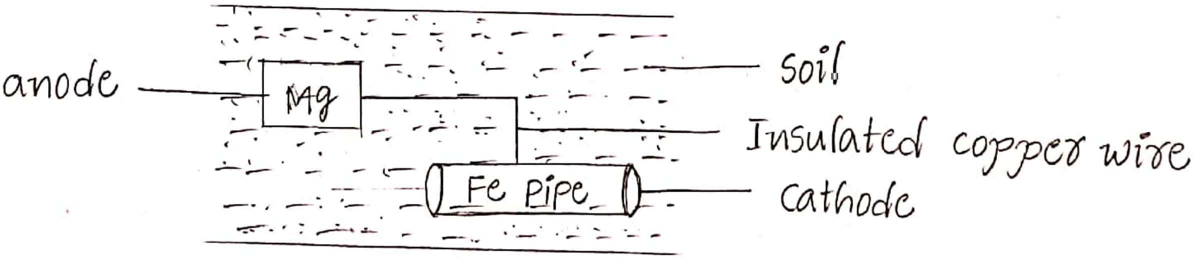


2. Cathodic protection:

The principle involved in this metal is to force the metal to be protected like a cathode they by corrosion does not occurs. It is two types

1. Sacrifical anodic protection
2. Impressed current cathode protection

1. sacrifical anodic protection:



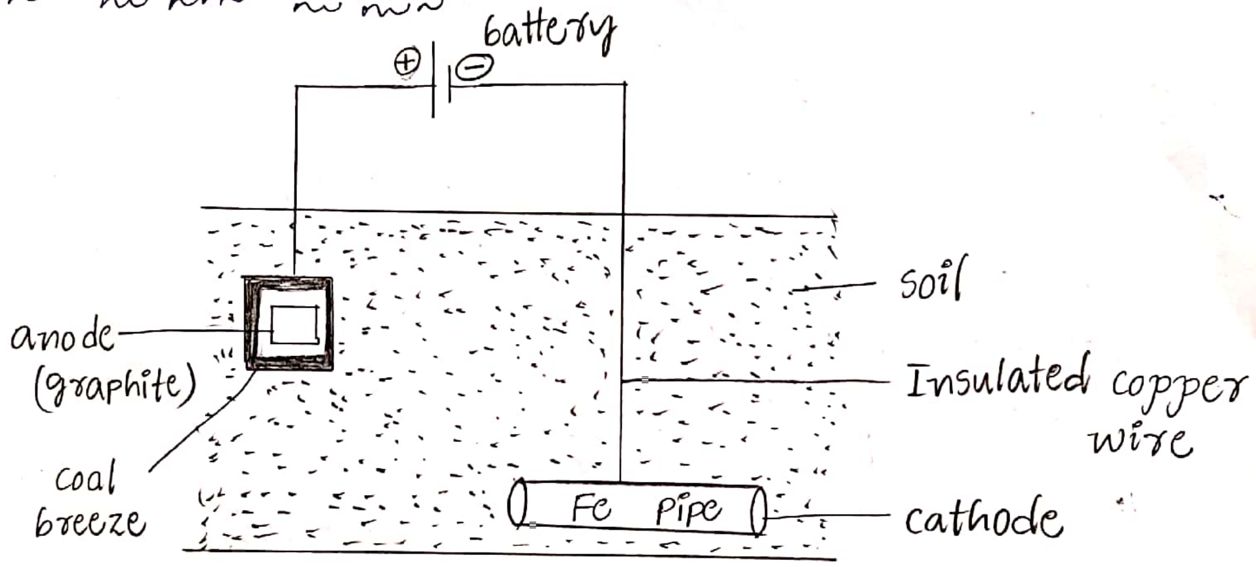
In this method a more anode metal is ~~connecte~~ connected to base metal for protection from corrosion the more anode metal itself corrode slowly, while the base is protected.

The more anode metal is called sacrifical anode. the corrode the sacrifical anode is replaced by fresh one general all used sacrifical anode Mg-Zn, Al, ...etc.

Application:

1. To prevent corrosion of understand iron pipes, cable wires ...etc
2. To prevent corrosion of shiphulls.

2. Impressed voltage method:



In this method an impressed current is applied in opposite direction then the base metal changes from anode to cathode.

In this method the base metal is connected to negative terminal of D.C. Hence the base metal acts as cathode and protected from corrosion. The positive terminal of D.C. connected to graphite and acts as ~~cathode~~ anode undergoes corrosion. This type of protection is used in burried oil pipes, water pipes.

Applications:

1. To prevent rust formation of Laid upships.
2. To prevent rust formation in transmission line towers.

Protectective coatings:

Metallic coating: The surface of base metal is coated with an other metal is called metallic coating. It is of two types.

i) anodic coating
ii) cathodic coating

i) **anodic coating:** The base metal is coated with more anode metal is called "anode coating". Generally used anode metals are zn, Mg, Al.

If any holes breaks (or) cracks are formed on the anode coating. A galvanic cell is formed between the coat metal and exposed part of base metal zinc is more anodic than iron.

Hence zinc acts as anode and undergoes corrosion; Fe acts as cathode and protected from corrosion.

Base metal iron is coated with more anode zinc (coated metal).

ii) **cathodic coating:** Generally used cathode are tin (Sn). Cathode coating provide effective protection the base metal only when the Layer is continuous and does not form any hole (or) break. If any hole (or) crack are formed on the coated Layer. The base metal undergoes more corrosion.

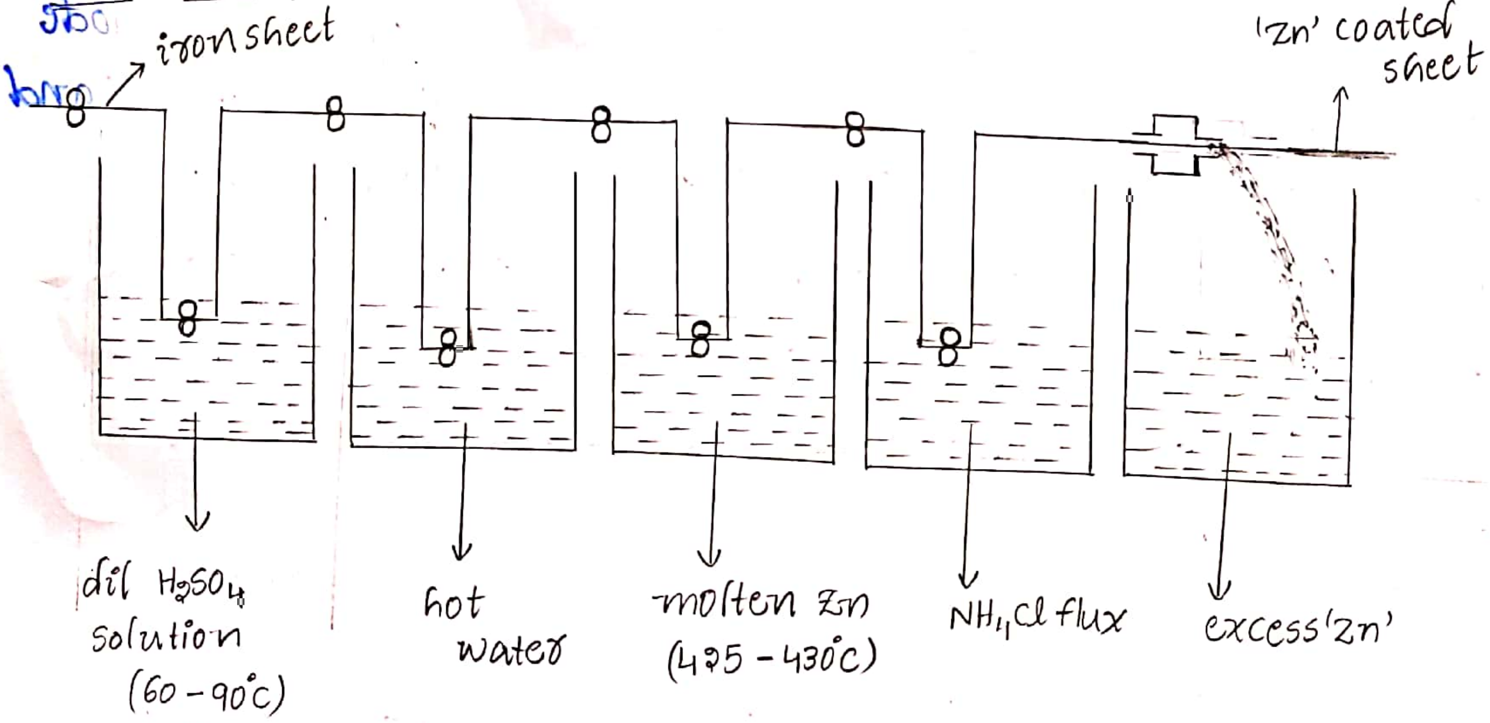
Example:

Tin coating on the surface of iron provides protection and as long as the surface of metal is covered but if any hole (or) crack fromed tin layer.

Application methods of corrosion:

1. Galvanising }
2. Tinning } "Hot dipping process"
3. Electroplating
4. Electroless plating
5. Metal cladding

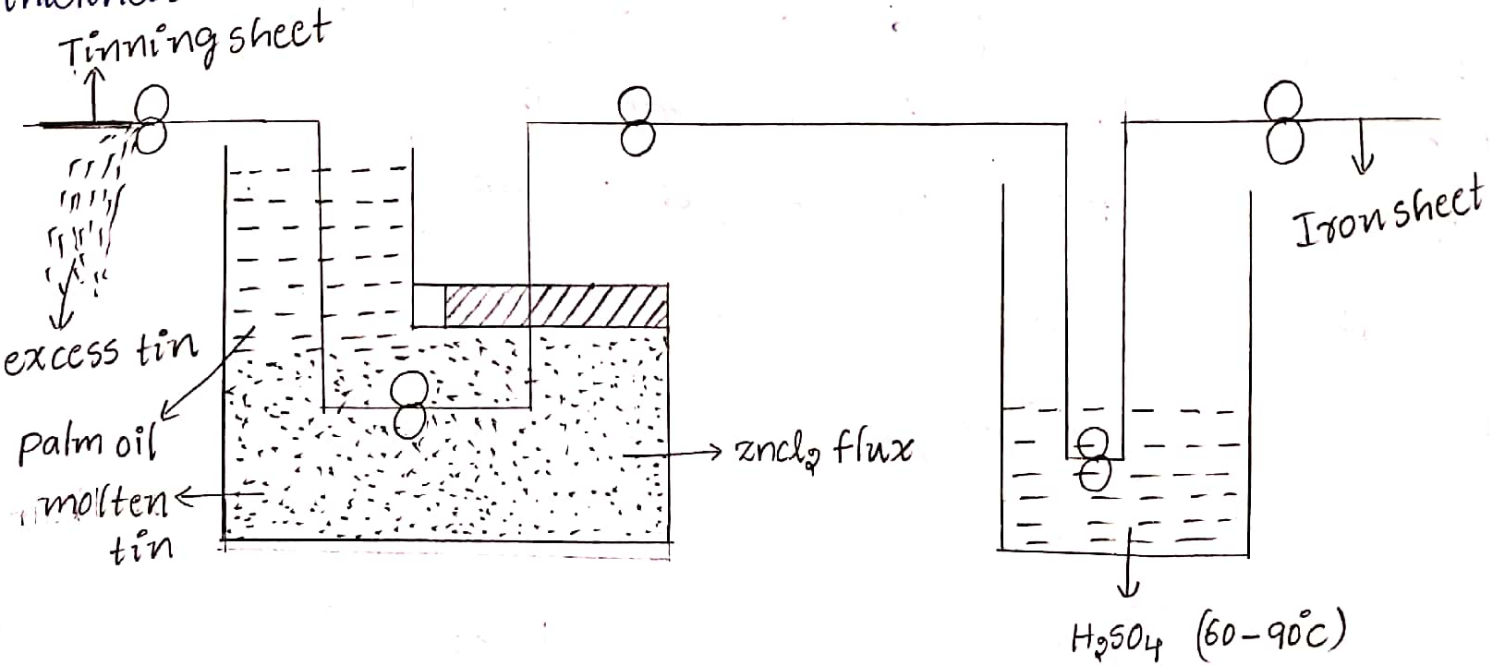
1. Galvanising:



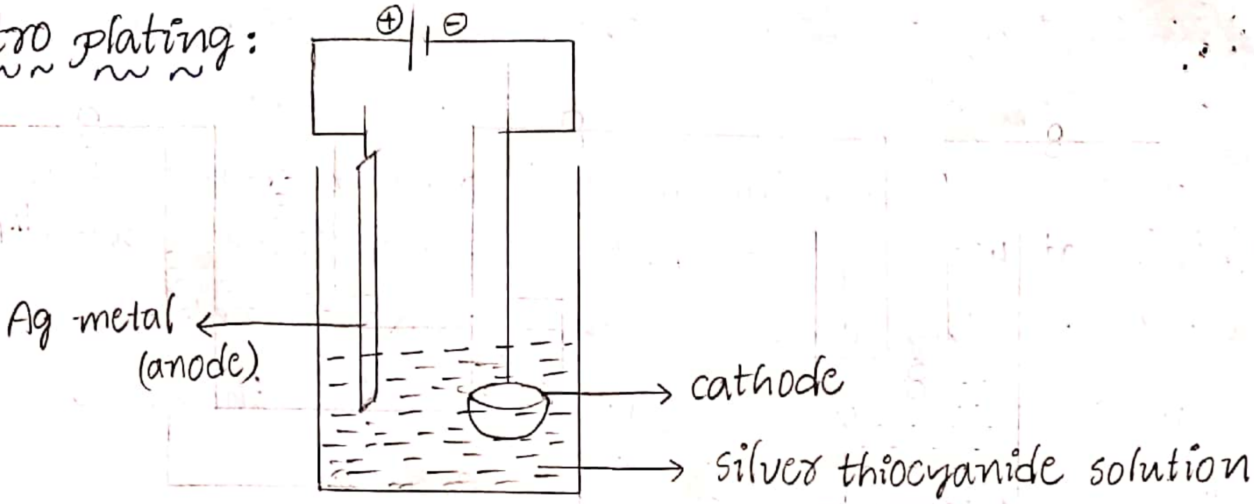
∴ Galvanising is the process. The iron sheet is coated with Zinc. The iron article is first dipped in dilute H_2SO_4 to remove rust and dust. Then, this metal is dipped in molten zinc bar maintain at 430°C. The surface of bar is covered with NH_4Cl flux. For sticking on the surface of molten 'zn'. The coated base metal is passed through. uniform ~~tic~~ thickness of coat metal. Finally we get galvanising article.

2. Tinning:

Tinning is coated tin over the iron or steel articles. The process consists in first treating steel sheet indilute sulphuric acid to remove any oxide film. After this, it is passed through a bath of zinc chloride flux. The flux helps the molten metal to add here to the metal sheet. Next, the sheet passes through a tank of molten tin and finally through a series of rollers from under neath the surface of a layer palm oil. The palm oil protects the hot tin-coated surface aganist oxidation. The rollers remove any excess of tin and produce a thin film of uniform thickness.



3. Electro plating:



Electroplating is a process in which the coated metal is deposited on the base. Metal by passing D.C through an electrolyte solution.

In this process the cleaned base metal is made as cathode to be connected negative to terminals of D.C and the coat metal is taken electrolyte. The electrodes are connected to battery and D.C. current is passed. Now electrolysis is takes place and the coats metal is deposited over the base metal.

example: The ~~coat~~ s coast silver on a copper spoon where spoon acts as cathode and silver acts as anode and silver thio sulphur (or) cynate is electrolyte. when the electrodes are connected D.C, Ag is deposited on the spoon.

S.NO	Name of the anode	Electrolyte solution
1.	silver	silver thio cyanide
2.	Arrum	$AuCl_2$
3.	nickel	$NiCl_2$

4.	platinum	$PtCl_2$
5.	cadmium	$CdSO_4$

Electroless plating:

A techinque of deposition of coat metal and a catalystical active surface of base metal by as suitable reducing agents without using electrical energy is known as "electroless plating."

Electroless plating process:

In this process electrons release from the oxidation of reducing agents, reduce the metal ions at catalytically active surface to metal atoms and deposited to coat metal.

Electroless plating of nickel:

1. Bathing solution (or) electrolitic bathing solution — $NiCl_2$ solution
2. Reducing agent — sodium hypophosphate
3. buffer solution — sodium acetate
4. Medium solution (or) complexing agent — sodium succinate
5. pH — 4-5
6. temperature - 93°C

at anode : $H_2PO_2^{\ominus} + H_2O \longrightarrow H_2PO_3^{\ominus} + 2H^{\oplus} + 2e^{\ominus}$ (oxidation)

at cathode: $Ni^{+2} + 2e^{-} \longrightarrow Ni$ (reduction)

Electroless plating of copper:

1. Bathing solution (or) electrolitic bathing solution — $CuSO_4$
2. Reducing agent — formaldehyde
3. buffer solution — Rochelle salt (Sodium potassium tatrate)
4. Medium solution (or) complexing agent — EDTA solution
5. pH — 11 to 12
6. Temperature — 25°C

At anode:

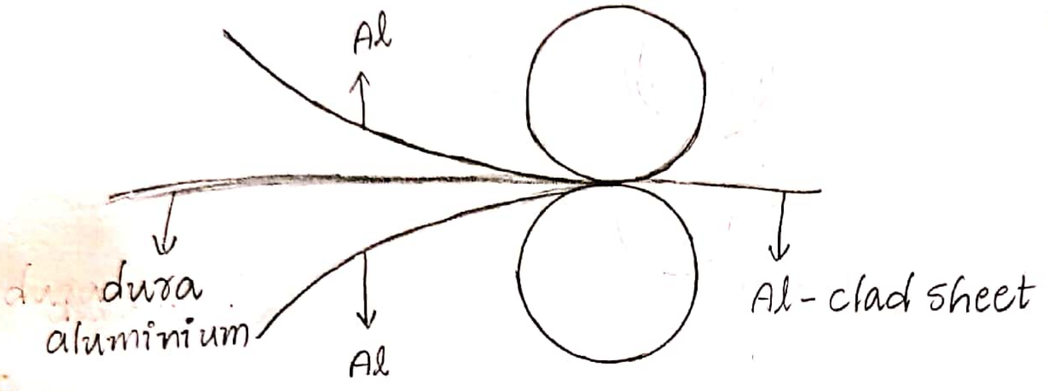
$$2HCHO + 4OH^{\ominus} \longrightarrow 2HCOO^{\ominus} + 2H_2O + H_2 + 2e^{\ominus}$$

At cathode: $Cu^{+2} + 2e^{\ominus} \longrightarrow Cu$

Metal clading (or) Metal sandwitching:

In this process base metal is coated with two homogeneous metals to form cladding sheet like sandwitch manne.

example: Dura aluminium is coated with two 'Al' metals in the presence of electric rollers by applying temperature and pressure to form Al-clad sheet.



Paints (OR) organic coating:

Paint is a dispersion of a pigment in a medium oil paint contain the following indgridients.

1. Binders: These are added to paints to hold together all the ingridients with pigments.
   ex: wax

2. Fillers: These are added to paints to reduce the cost & to improve the special property like durabilised hardness, strength
   ex: Talc, silica, gypsum.

3. Pigments: These are added to paints for different colours
   ex: carbon - black
   ZnO - white.

4. Drying oil: The liquid position of paints in which the pigment is dissolved is called medium (or) drying oil.

ex: soyabeen oil, fish oil

5. Tinners: These are added to paint to reduce the thin so that, they can easily applied on the surface.

ex: kerosene, vitamin-C

6. Plasticizers: These are added to paints to give the plasticity and flexibility to the paint.

ex: Triphenyl amine.

7. Antioxidants:

These are added to paints to prevent oxidation of paints.

8. Anti skinning: These are added to paints to prevent skinning of paints.

ex: polyhydroxy phenyl.

prepared by

Sarvepalli. VenkataRao
M.Sc. B.Ed

UNIT-III

PART-A

NON-Elemental Semi Conducting materials.

The materials which behave as insulator at absoulte zero and conduct electricity at normal temperatures are called semi conductors.

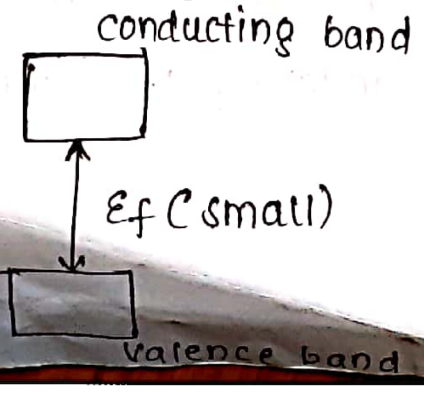
→ This property of semiconductivity explained based on band theory.

Types of semiconductors.

* Semiconductors are two types.

1. Intrinsic semiconductors
2. Extrinsic Semi conductors

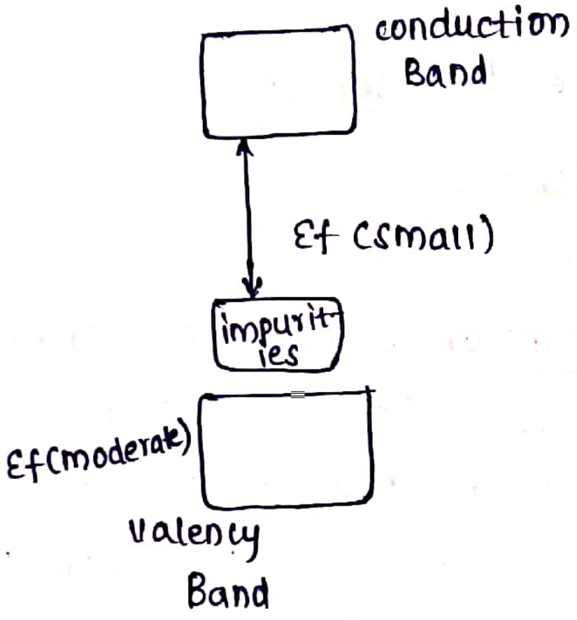
1. Intrinsic Semi conductors :- In the fermi energy gap is small b/w the valence band and conduction band, so that the electron from valence band is excited to conduction band, it is called intrinsic semiconductor both the hole left in valence band and the excited electron to the conduction band contributes towards conductivity. As the temperature rises, the no.of electrons promoted to the conduction band increases contributing to the increase in conductivity of semi conductor.



2. **Extrinsic semiconductors :-**

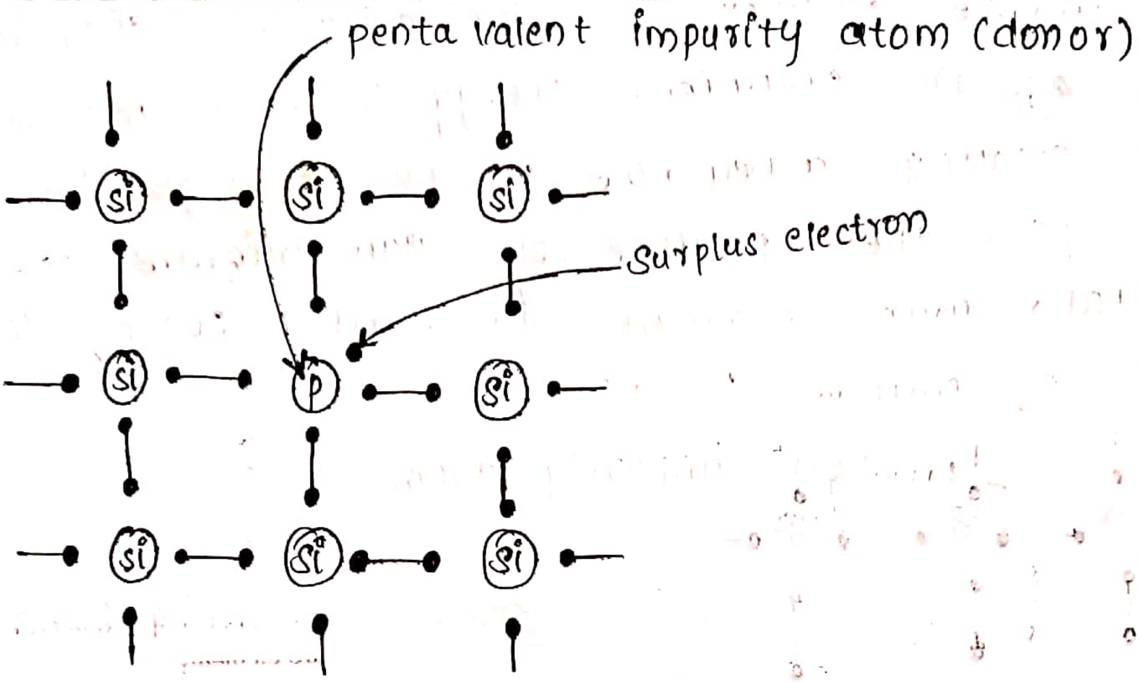
The fermi energy gap between valency band and conduction band is moderate in semi conductors is known as Extrinsic semi conductors.

* This gap is full-filled with impurities is known as doping.

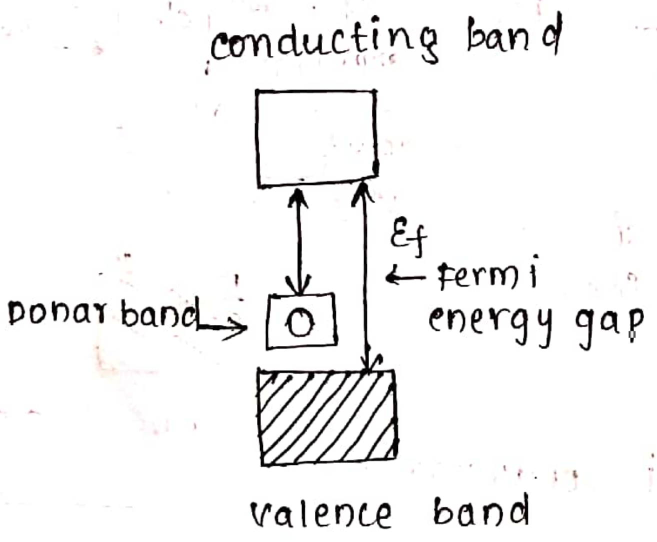


N-type semi conductors :- The pentavalent impurities like P, Ar, to the silicon (or) Germanium semi conductors is known as N-type semi conductor.

* penta valent impurities have five electrons out of these four electrons bonded with si (or) Ge, one surplus electron is waandering in semi conductors.



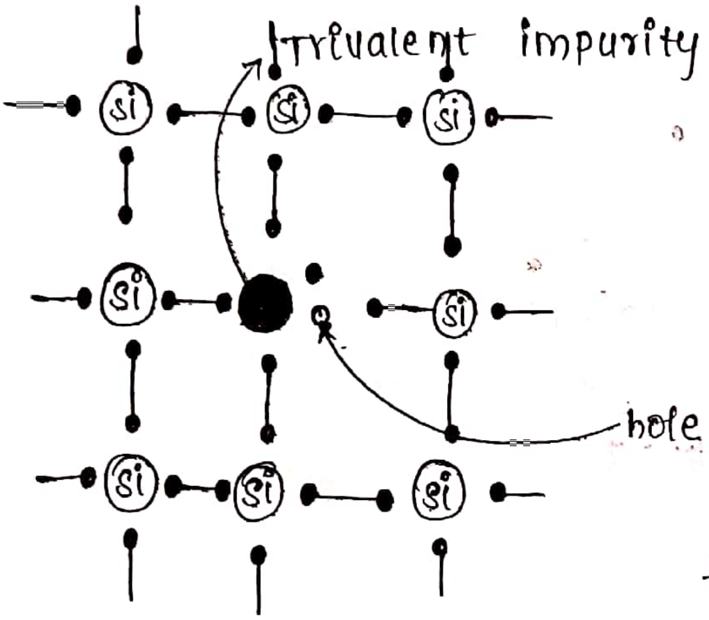
a) Doping of impurity



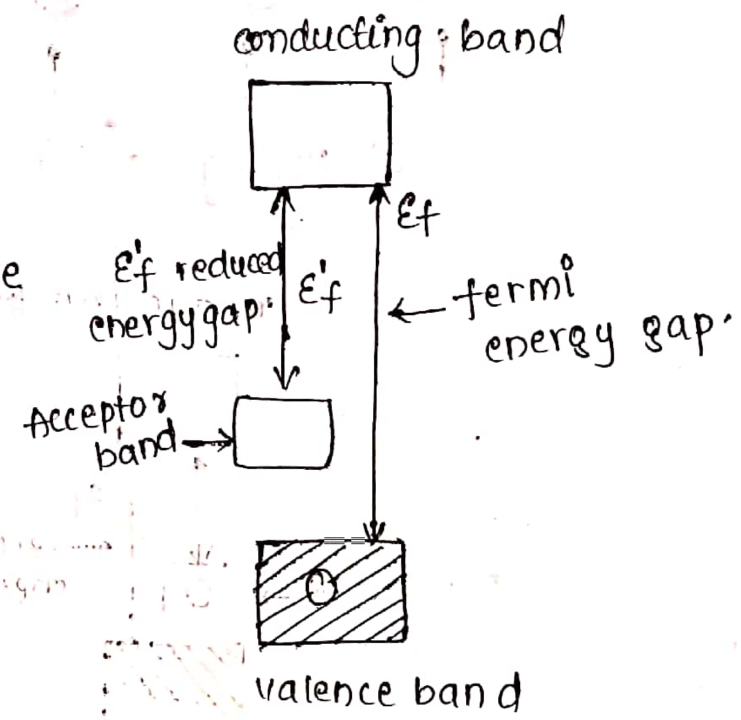
A dopant with more electrons form a narrow band.

<u>P- type semiconductors</u> :- By introducing a trivalent impurity atom like Al, B, Ga into Si or Ge, the replacement of these Si or Ge atoms by impurity produces an incomplete bond in the structure producing a positive hole. The positive holes are localized around trivalent impurity atom at low temperatures or absolute zero. At Normal temperatures

the valence electrons on the adjacent si or Ge atom may again sufficient energy to move into the hole, thus creating a new hole on the si or Ge. By a series of hops, the positive hole can migrate across the crystal, thus current is carried out by the migration of positive centres.



a) positive hole on si caystal lattice.



Stoichiometric semi conductors:-

The crystal structures and band structures similar to that of silicon (si) and Germanium (Ge) are developed by the combination of group Ⅲ and group Ⅴ elemants and group-Ⅱ and group Ⅵ elements named as stoichiometric semiconductors.

Ex:-

Ex:-

Group III & V combination		Group II & VI combination	
Semi conductor	fermi energy gap (E_f) (ev)	semiconductor	fermi energy gap(E_f) (ev)
Gap	2.24	cds	2.42
GaAs	1.35	cdse	1.74
Gasb	0.67	pbs	0.37
InAs	0.36		

characteristics of stoichiometric semi conductors:

1. stiochiometric semi conductors have wide energy gap, which leads to broad exhaustion zone with high conductivities. Hence they can be used at wider range of temperatures.
2. They can be doped to n or p-type semiconductors.

Non-stoichiometric semi conductors: The transition metal attached with chalcogen elements like oxygen to form two (or) more different semi conductor materials is known as non-stoichiometric semi conductors.

* In this type of semiconductor does not obey Arhenius theory of electrolytic dissassociation means the total no.of anions is not equal to total no.of cations.

Ex:- Fe + O - FeO, Fe_2O_3.

Cu + O - CuO, Cu_2O, Cu_3O

Ti + O - TiO_2, TiO_3, TiO

Mn + O - MnO, Mn_2O_3, MnO_4, Mn_2O_7.

Controlled valency semiconductors.

$Ni^{2+}_{0.7}\ Ni^{3+}_{0.2}O$ is a hopping semiconductor producing hopping semiconductivity by hopping of electrons from Ni^{2+} to Ni^{3+} ions. the concentration and conductivity of Ni^{3+} is controlled by the addition of small amount of Li^+ ions.

$$LiO + NiO + O_2 \longrightarrow Li_x\ Ni^{2+}_{1-2x}\ Ni^{3+}_x\ O$$

The semiconductor shows conductivities depending on temperatures and find applications as thermistors. (thermally sensitive resistors). These semiconductors can be used over a wide range of temperature upto 200°c. The compound containing the composition $Li^+_{0.05}\ Ni^{2+}_{0.9}\ N^{3+}_{0.05}$ is electroneutral semiconductor which is shown as below.

Positive charge	Negative charge
$Li^+_{0.05} = 0.05 \times 1 = 0.05$	$O^2 = 2$
$Ni^{2+}_{0.9} = 0.9 \times 2 = 1.8$	
$Ni^{3+}_{0.05} = 0.05 \times 3 = 0.15$	
2.0	2

Thus $Li^+_{0.05}\ Ni^{2+}_{0.9}\ N^{3+}_{0.05}$ is neutral semiconductor.

Chalcogen photo semiconductors

oxygen (o), sulpher (s), selenium (se) and Tellurium (Te) are collectievly called chalcogens or ore forming elements because a large no. of metal ores are oxides or sulphides.

The characteristics of chalcogens are:

1. They behave as semiconductors or photo conductors either alone or by combining with other elements.
2. They rapidly form glass on cooling and viscous liquids on melting.
3. selenium is an excellent photo conductor. Its conductivity increases enormously on exposing to light, hence it is used in photo copying process (xerox)

preparation of semi conductors

1. preparation of ultra pure Ge → Distillation, → Zone Refining

2. preparation of single crystals — czochralski crystal pulling technique.

3. Doping
   - Epitary
   - Diffusion
   - Ion implantation technique

1. preparation of ultra pure Ge.

a) Distillation :-

Ge + layer of HCl

↓ Cl_2 gas

Ge Cl_4 (intermediate substance)

↓

Fractionating column

↓

Ice Bath

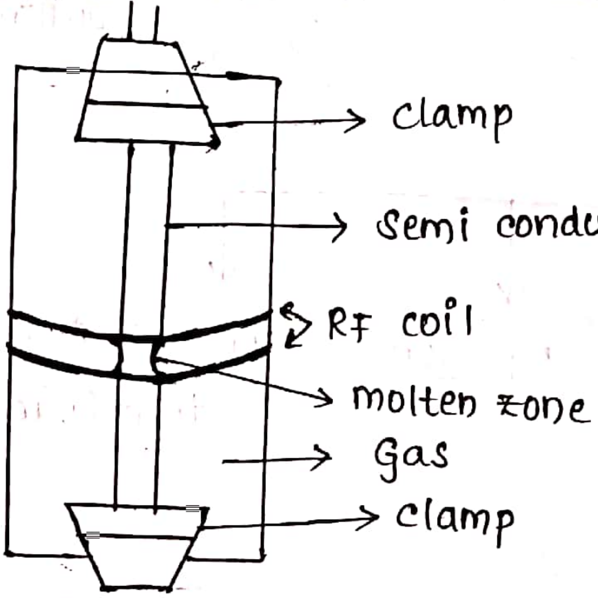
↓ N_2 atp

Ge (o)

↓

Zone Refining

b) Zone Refining :- zone Refining is a metallurgical process which is based on the principle that the impurities present in a metal are more soluble in molten metal than in solid metal. for the purification of Ge vertical zone refiner is used.



Vertical zone Refiner

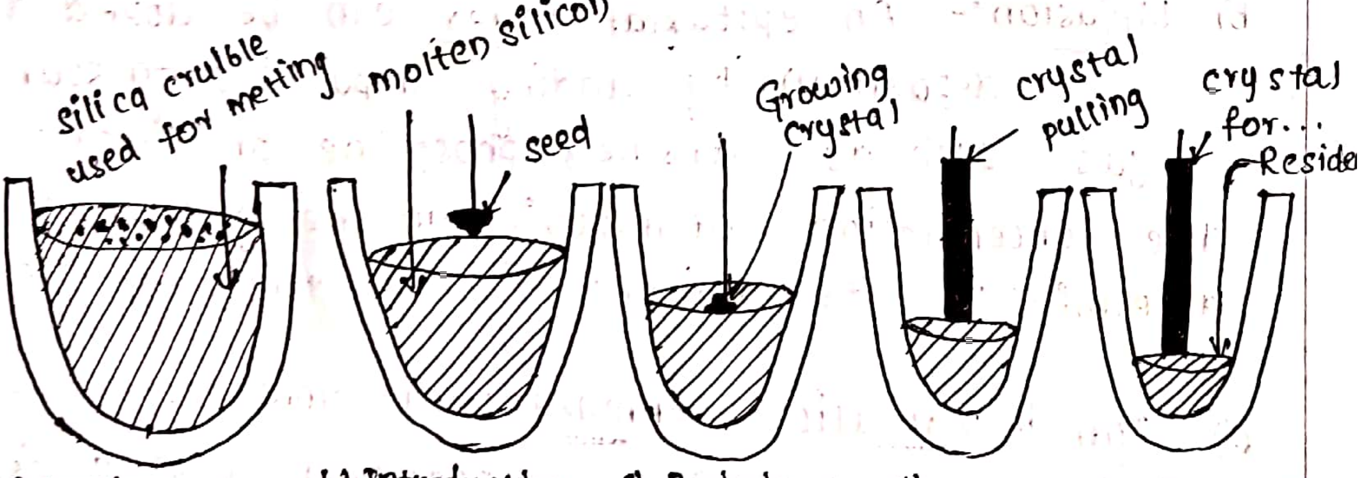
2. preparation of single crystals of si or Ge :-

The basic requirement for the fabrication of a semiconductor device is that the semi conductor used must be a single crystal. Hence single crystal of si and Ge are produced by Czochralski crystal pulling technique.

Czochralski crystal pulling technique.

This process was named after the polist scientist Jan Czochralski who invented the method in 1916 by accident while studying crystalization methods.

In this method single crystals are grown in such a way that during crystal growth atoms reproduce the same atomic arrangement as that of the seed crystal.



a) melting of poly silicon

b) Introduction of seed crystal

c) Beginning the crystal growth

d) crystal pulling

e) Formed crystal with a residence of silicon.

Czochralski process.

3) **Doping** :- Introducing an impurity into the semiconducting crystal is called doping.

* one Boron (or) Arsenic atom added to 100 millions of Germanium (or) silicon.

a) **Epitaxy** :- The word 'Epitaxy' is derived from Greek, 'Epi' means several, 'taxy' means several manner. The deposition of a crystalline substance over the crystalline substrate. Epitaxy refers to the deposition of a crystalline over layer on a crystalline substrate which acts as seed crystal. The following are some of the technique molecular beam epitaxy (MBE).

b) **Diffusion** :- An epitaxial layer can be doped during deposition by adding impurities to source gas such as arsine, phosphine or diborane. The concentration of impurity in the gas phase determines its concentration in the deposited film.

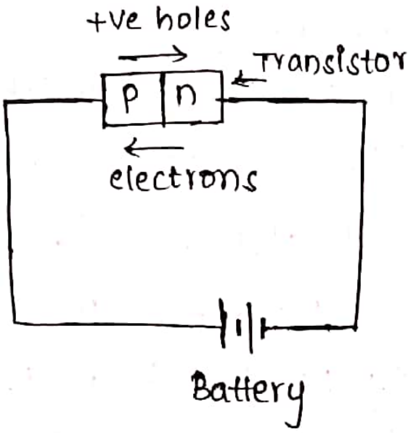
c) **Ion implantation tehnique** :- In this technique a semiconductor material is bombarded with an electrically controlled beam having higher energy of 10kev containing impurity ions like boron or phosphorous. Ion implantation method is extensively used in the fabrication of high frequency devices.

P-n Junction

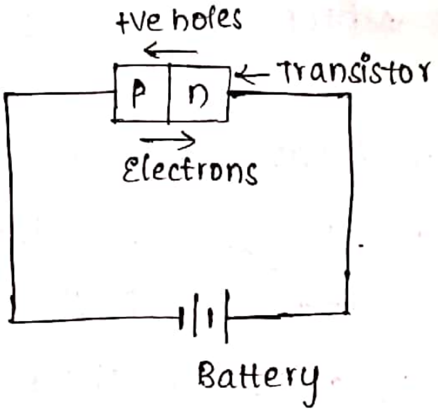
When a single crystal of si or Ge is doped with Indium at one end arsenic at the other end which constitutes one part p-type semiconductor and the other n-type semiconductor with middle boundary region where the two sides meet. This is known as p-n Junction. The group III elements B, Al, Ga or In and group V element like p or As are mostly used because of their low melting point, which is useful for high temperature diffusion of the appropriate dopant element.

p-n Junction as a Rectifier:

current from an outside source is allowed to flow through a rectifier only in one direction and this is very useful because it helps in converting alternate current (AC) to direct current (DC). The function of p-n Junction as rectifier is discussed below. A transistor with two zones, one p-type and the other n-type with p,n-Junction in between is known diode. If p-type semiconductor region is connected to the positive terminal of battery and n-type region is connected to the negative terminal of the same battery. From n-type region electrons with migrate towards the p,n-junction, where as holes will migrate towards the p-n junction. At the p-n junction of diode, the migrating electrons from the n-type region move into the vacant holes in the valence band of the p-type region. This migration of electrons and holes can continue and a current flows as long as the external voltage than a battery is supplied.



a) conducts

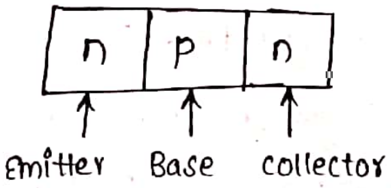


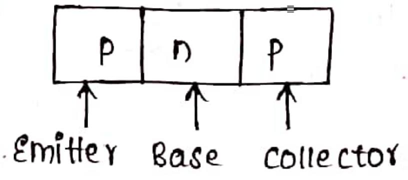
b) does not conduct.

When the connection is reversed p-type region is connecting to the negative terminal of the battery and n-type region is connecting to the positive terminal of the battery the positive holes move away from p-n Junction in p-type region and the electrons migrate away from p-n Junction in the n-type region. The current does not flow at the junction as there are no electrons or positive holes.

→ Junction transistors

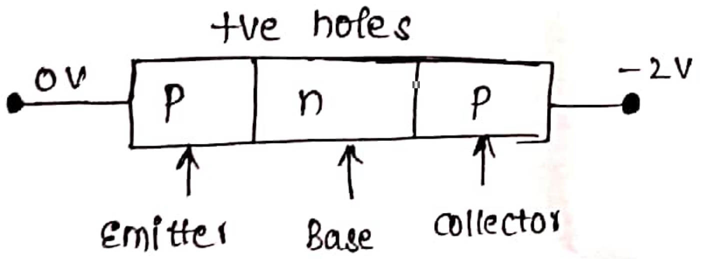
Transistors are single crystals of silicon which have been doped to give three zones, either p-n-p or n-p-n as shown below

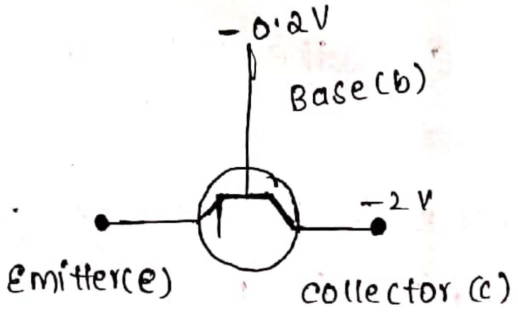




Different voltages must be applied to the three regions of the transistor to make it work with respect to the emitter, the base is typically -0.2 V and the collector is typically -2 volts.

In the p-n-p transistor, the charge carriers in the emitter are positive holes, which migrate from the Emitter at 0 volts to the base at -0.2 volts. The positive holes cross the emitter/base p-n junction. In the n-type base region some holes combine with electrons and are destroyed. Electrons flow in the reverse direction from the base to the emitter. There is thus a small base current. Since the collector has much greater negative voltage and the base is very thin, most of the positive holes pass through the base to collector, where they combine with electrons from the circuit. At the emitter, electrons leave the p-type semi conductor and enter the circuit by producing more positive holes. Typically if the emitter current is 1mA, the base current is 0.02 mA and the collector current is 0.98 mA. The n-p-n transistor work in a similar way, except the polarity of the base voltage is reversed. Thus the collector and base are positive w.r.to the emitter.





Typical bias voltages for p-n-p transistor.

~~A~~**Applications of transistors**:- Transistors are most widely used as.

1) Amplifiers and oscillators in radio, T.V, computers and hi-fi circuits, photo transistors, solar cells, detectors for ionizing ~~radiantions~~ radiations, thermisters and tunnel diodes.

-.o—

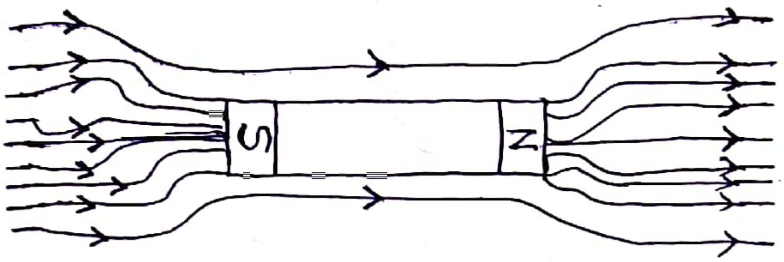
* MAGNETIC MATERIALS *

(1) Ferro magnetism:-

Ferromagnetic substances are those substances which are strongly attaracted by a magnet.

Eg:- Iron, cobalt, Nickel, Gadolinium etc.

* The lines of force tend to crowd into the specimen.



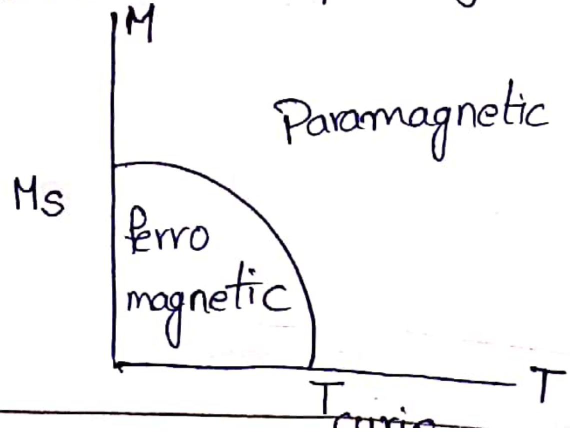
* It have spin (or) magnetic moment (or) dipole aligment. and also parallel and orderly alignment.

* It's behavior is heavy attraction of lines of force towards the centre.

* This magnetism having same magnetic direction as the External magnetic field.

* The permiability is very high.

* High positive susceptibility.



When temperature of the material is Greater than it curve temperature it is converted into paramagnet.

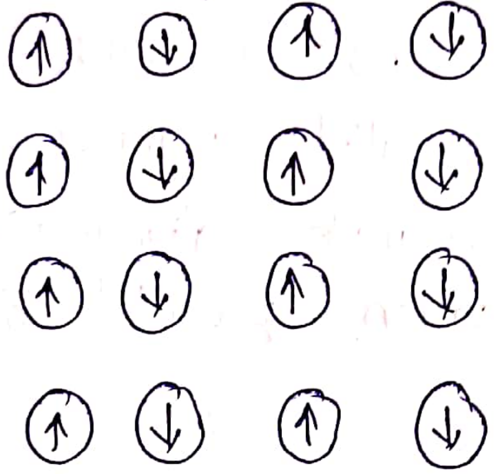
Application:-

A common Application for ferro magnetic materials is in the usage of data storage systems.

2) Ferri magnetism:-

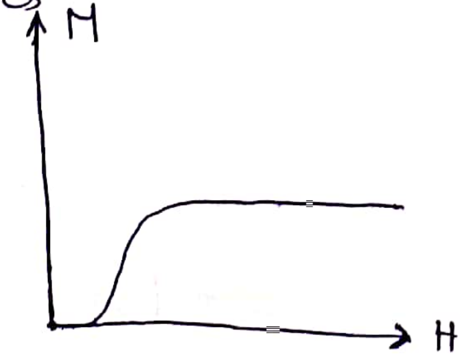
Ferri magnetic compounds observed in which have more complex crystal structure than pure elements. like gold, silver, hydrogen, iron.

Atoms have mixed parallel and anti-parallel aligned magnetic ~~[illegible]~~. moments.



Ferrimagnetic material are weakly attracked to magnetic materials compared to ferro magnetic material.

Magnetic material can also classified as ferri magnetism although these are not observed in any pure elements. But these are found in mixed oxides like ferrites.



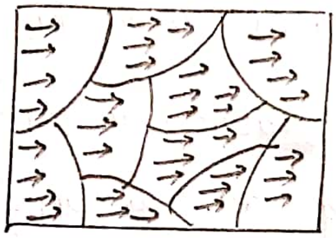
M → Magnetisation.

H → Influence on any applied field.

Example:- In Barium ferrite $[(2BaO \cdot 6Fe_2O_3)_2]$ have 64 ions. out of these Barium and oxygen doesn't have magnetic moment. In this, we have $24Fe^{+3}$ ions in this $16Fe^{+3}$ ions are undergoes parallel alignment and $8Fe^{+3}$ ions are anti-parallel alignement. and Gives a net magnetisation parallel to the applied field.

Ferro Magnetic Materials :- In some materials the permanent atomic magnetic moments have strong tendency to align them selves even without any external field. These materials are called ferro magnetic materials.

Before applying external field



After applying external field.

→ Ferro magnetic materials are permanent magnets. means the material that can be magnetized by an external field and remain magnetized after the external field is removed.

→ This is due to presence of domains, (domains are nothing but a group of atoms in that material). The domains have different direction of magnetic moments. So these, moments shows magnetic property after removing external field (or) before applying the magnetic field.

→ However, when we placed these material in external field domains are align in the direction of magnetic field. materials shows large magnetic property even the small magnetic field is applied due to domains.

Retentivity :- The value of magnetic Induction $\vec{B}$ left in the material, when the small magnetising force H is removed. this is known as "Rentivity (or) remanence"

→ Retentivity become zero. By applying two methods.

i) co ericivity

ii) curie temperature

co ericivity :- TO reduce the retentivity to zero, we have to apply a magnetising force in opposite direction this value in magnetising force is called co ericivity.

curie temperature :- Temperature is inversly proportional to the magnetising force. we apply the temperature (or) heating the material at a certain temperature retentivity become zero. That temperature is called curie temperature.

Every substance has its specific curie constant c.

→ magnetic suspectibility is inversly proportional to absolute temperature.

$$x = \frac{c}{T-T_c}$$

x = magnetic suspectiblity

c = material specific curie constant

T = absolute temperature

T_c = curie temperature.

Hysterisis curve :- The curve represent the relation between intensity of magnetization (I) of a ferro magnetic material with magnetic intensity (H) is called hysterisis curve.

Electrical insulators

Insulators :-

The Substance which are capable of oppes or resists the flow of heat (or) electricity (or) sound through them are known as "insulators"

Insulators can be classified into 3 types

(1) Thermal insulators
(2) Sound insulators
(3) Electrical insulators

Electrical insulators :-

The materials which are capables of oppes/resists the flow of electricity through them are known as "Electrical insulators"

$$\boxed{\epsilon = C/C_0}$$

C = capacitence system in material inserted
C_0 = capacitance of system with vaccum between the capacitor plates.

Charcterstics of electrical insulators :-

A good electrical insulators should posses

→ low electrical conductivity and high resisitivity
→ low dielectric constant
→ low porocity
→ Chemical inertness towards Acids, Alkalis, Solvents

These insulators ~~afm~~ Electrical can be classified into the three types

* Gaseous insulators

* Liquid insulators

* Solid insulators

Gaseous insulators:-

The best Examples of gaseous insulators Air, Nitrogen, Hydrogen etc.,

Air:-

Properties:-

-> Most important of all dielectric gases

-> It acts as a realible insulating materials when Voltage are not very high

Applications:-

-> It provides insulation between over head transmission lines without any cause.

Nitrogen:-

Properties:-

-> It is chemically inert dielectric

Application:-

-> used in transforms and Capacitors

Liquid insulators:-

(1) Mineral oils:-

Properties:-

→ These are obtained from crued petroleum

→ These are used tempaiture range of 50°c to 110°c

Application:-

→ These are used in capacitors, switch gases atc.,

(2) Askarles:-

→ These are highly inflammble synthetic insulating liquids used in tempaiture range 50°c to 110°c

Application:-

→ These are used as transformer liquid

Solid insulators:-

Paper & press boards:-

Property:-

→ Thes are strong and more heat resistant

Application:-

→ These are used for winedings and cable oil insulator

Polystyrene:-

Property:- It posses Excellent di-electric properties

Application:- It is used insulators in high-frequency capacitors, telephones atc.,

B. CHEMISTRY OF ADVANCED MATERIALS

NANO MATERIALS:

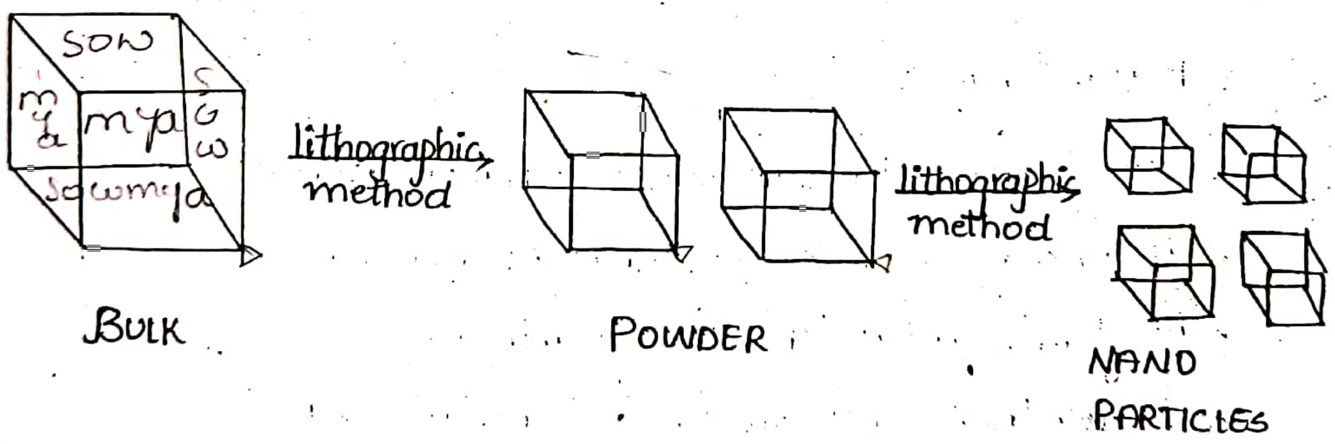
①

The materials like metals, ceramics, polymeric materials or composite materials with dimensions and tolerances in the range of 1nm to 100nm are called the Nano materials. They exhibit unique properties like melting point reactivity, reaction rates, electrical conductivity, colour, transparency etc.

GENERAL METHOD FOR PREPARATION OF NANO MATERIALS:

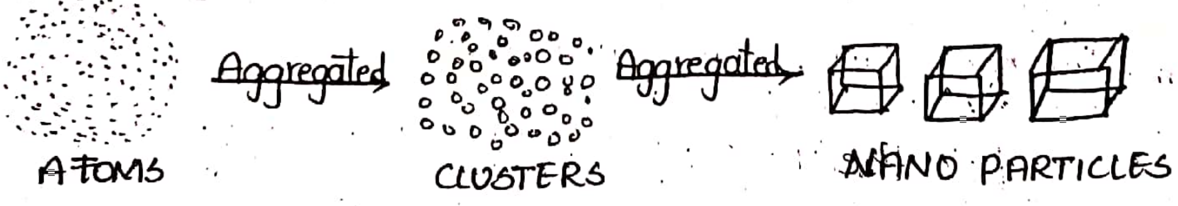
1. TOP-DOWN APPROACH METHOD:

In this method bulk materials are converted to powder and then to nanoparticles by making use of lithographic methods. This method is used in the microelectronic industry.



2. BOTTOM-UP APPORACH METHOD:

In this method very small particles like atoms are assembled to get clusters which in turn are ~~arrego~~ aggregated to get nanoparticles. Fullerenes and polymer nano composites are prepared by this method.



PREPARATION OF NANO MATERIALS BY INDUSTRIAL METHOD.

1. SOL-GEL METHOD:

Sol-gel preparation is bottom-up approach for the synthesis of nanomaterials. Sol-gel processing is wet chemical technique that uses a sol to produce an integrated network i.e., gel. Metal oxides or metal chlorides undergoes hydrolysis and poly-condensation reactions to form a colloid which is a system composed of nano particles dispersed in a solvent. The solvent evolves toward the formation of an inorganic continous network containing a liquid phase (gel). Formation of a metal oxide involves connecting the metal centres with oxo (M-OM) (or) hydroxo ~~polymers~~ (M-OH-M) bridges generating metal-oxo (or) metal-hydroxo polymers in the solution. After drying process, liquid phase is removed from gel and calcination is performed. Alcohol is used as solvent.

Advantages:

→ It forms similar size of nanomaterials

→ It undergoes low temperature reactions

→ It forms microstructure particles

→ It controls any stage of the reactions.

2. CHEMICAL REDUCTION METHOD:

This method belongs to bottom-up approach. Metal nanoparticles particularly silver nanoparticles are prepared by this method.

Preparation of silver nanoparticles:

For the preparation of silver nanoparticles silver nitrate solution and 8% w/w sodium dodecylsulphate (SDS) are used as metal salt precursor and metal stabilizing agent respectively. Hydrazine hydrate and citrate solution are used as reducing agents. The transparent colourless solution will be ② converted to pale yellow and pale red colour which indicates the formation of silver nanoparticles. The nanoparticles are purified by centrifugation.

Applications:

→ Nanoparticles like silver, gold, platinum etc., are prepared by this method.

3. BEUNAR EMMET TELLER METHOD (BET):

Nano crystalline particles of "$Co_xFe_{(3-x)}O_4$" are synthesised by combustion reaction method using iron nitrate, cobalt nitrates and urea with Asa's fuel without template and subsequent heat treatment. The maximum reaction temperature range is 850-1010°c and combustion lasts for 30 sec. for all system. The materials are washed with deionised water and the byproducts are rinsed off producing pure nanoparticles.

4. TRANSMISSION ELECTRON MICROSCOPIC METHOD (TEM):

This is a shape controlled method for the synthesis of colloidal platinum nanoparticles which is potentially important in the field of catalysis. A solution of potassium platinum chloride solution (0.00001M) is prepared in water and treated with 0.2ml of 0.1M sodium polyacrylate. The resulting solution is bubbled with Ar gas for 20 min. The pt ions are reduced by bubbling hydrogen gas for 5 min. The reaction vessel is sealed and left overnight. The solution turns light golden and nanoparticle are purified and separated.

PROPERTIES OF NANOMATERIALS:

→ The magnetic properties increases with decrease in size of materials.

→ Melting point of the nanomaterials increases when compared with other material depending on size of particles

→ Solubility of nanomaterials is more than other materials due to decreased size.

→ Colour : The physical property colour is again size dependant.

→ Transparency : Transparency of nanomaterials is more than other materials.

→ Catalytic Behavious: Due to increased surface area, the catalytic activity of the nanomaterials is more than other materials.

→ Collodial properties : The collodial nanoparticles are called coercing colloids.

→ Chemical Reactivity : Nanoparticles posses high chemical reactivity

→ Reaction Rates: High reaction rates were observed with nanomaterial.

→ The nano materials exhibit good dispersibility

→ The nanomaterials can be used as good conducting, semi-conducting and insulating materials.

FULLERENES:

A fullerene is any molecule composed entirely of carbon in the form of a hallow sphere, ellipsoid or tube.

The first fullerene molecule was prepared in 1985 by "Richard Smalley etal" at Rice University, USA. They were awarded Nobel Prize in 1996 for their work.

③

TYPES OF FULLERENE:

1. BUCKYBALL CLUSTERS:

The smallest is C_{20} (unsaturated version of dodecahe-drane) and most common is C_{60}.

2. CARBON NANOTUBES:

Hollow tubes of very small dimensions having single or multiple walls.

3. MEGATUBES:

Larger in diameter than nanotubes and prepared with walls of different thickness.

4. POLYMERS:

Chain, two dimensional and three dimensional polymers are formed under high-pressure, high temperature.

5. NANO ONIONS:

Spherical particles based on multiple layers surrounding a buckybal core proposed for lubricants.

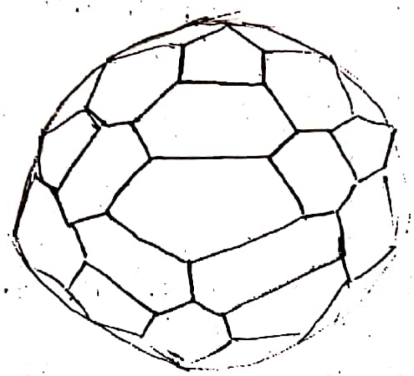
6. LINKED BALL AND CHAIN DIMERS:

Two buckballs linked by a carbon chain.

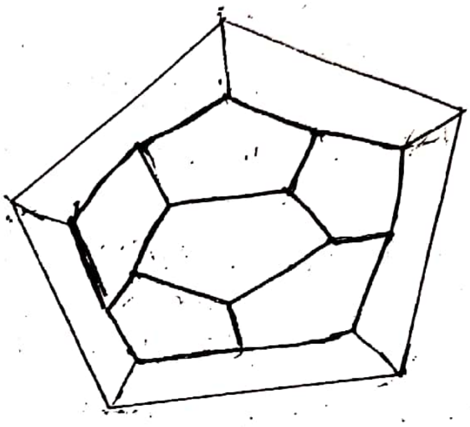
The different individual fullerenes based on composition is listed below.

BUCKMINSTER FULLERENE:

It is the smallest fullerene molecule. The structur of C_{60} is called "Truncated Icosahéprone" containing 20 hexagon and 12 pentagons with carbon atom at the vertices of each polygon. The vanderwaals diameter of C_{60} is 1.1 nm and average bond length is 1.4 A°



C_{60} fullerence



C_{20} fullerence

b, BORON BUCKYBALLS:

A type of buckyball which uses boron atoms instead of a carbon atom is Boron fullerene.

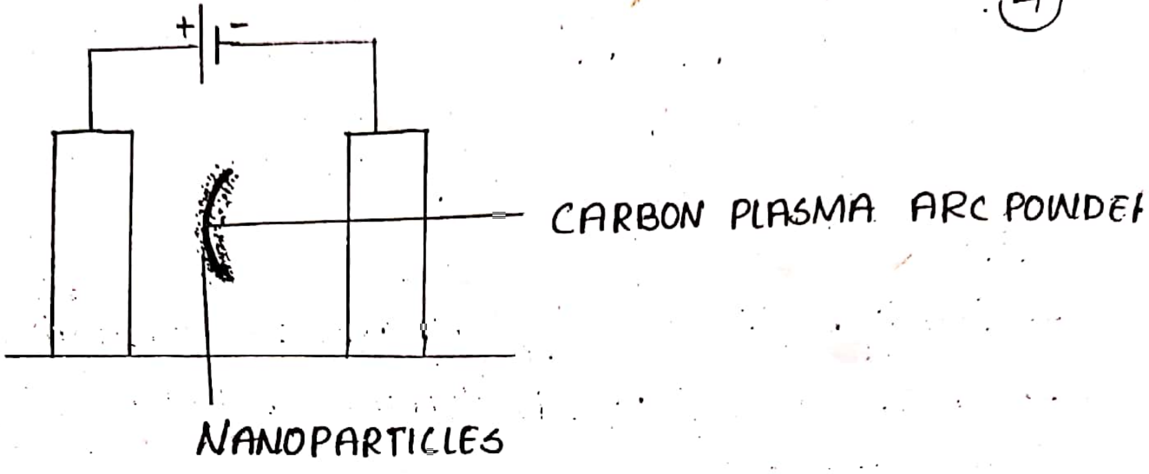
c, METALLO FULLERENES:

These are a class of novel nanoparticles, comprises 80 carbon atom (C_{80}) forming a sphere which encloses a complex of three metal atoms and one nitrogen atom.

PREPARATION OF FULLERENES:

A common method used to produce fullerenes is to send a large current between two nearby graphite electrodes in an innert atmosphere. The resulting carbon plasma arc between the electrodes cools into sooty residue from which many fullerenes can be isolated. The fullerenes are extracted from soot using multi step procedure.

④



PROPERTIES OF FULLERENES:

→ Endohedral Fullerenes:

When other atoms tapped inside fullerenes to form inclusion compounds is known as endohedral fullerenes.

Eg: Tb_3NeC_{84} (Egg shaped fullerene).

→ Solubility:

Fullerenes are sparingly soluble in many solvents, common solvents for fullerenes are toulene, CS_2

→ Ceramic sculptures:

Several sculptures symbolizing wave particle duality are created.

→ Chirality:

Some fullerenes are inherently chiral because they are D_2-symmetric and have been successfully resolved.

→ Hydrogenation:

C_{60} exhibits a small degree of aromatic character, underg addition with hydrogen to polyhydrofullerenes.

→ Halogenation:

Addition of F, Cl and Br occur for C_{60} under various conditions, produces a vast no: of halogenated derivatives.

→ Addition of oxygen:

C_{60} can be oxygenated to epoxide $C_{60}O$.

Applications:

→ Buckyballs are efficient medium to make hydrogen fuel.

→ In medical field, buckminister fullerene is used to inhibi the HIV virus

→ It is used in preparation of solarenergy.

CARBON NANOTUBES (CNT):

Carbon nanotubes are sheets of graphite about 0.4nm in diameter. Carbon nanotubes are otherwise called bucky tubes

There are two types of carbon nanotubes

1. Single Wall nanotubes
2. Multi Wall nanotubes

PREPARATION METHODS OF CARBON NANOTUBES

i, ARC DISCHARGE METHOD:

By arc discharge of graphite electrodes in presence of ionised gas to reach high temperature and by using a current of 100 amps CNT was produced. The yield is 30% and produces both single and multi-walled nanotube with lengths of upto 50 micrometers.

ii, LASER ABLATION:

In this process a pulsed laser vapourises a graphite target, in a high temperature reactor. While an innert gas is bled into the chamber, nanotube develops on the cooler ⑤ surface of the reactor as the vapourised carbon condenses. To improve the yield a composite of graphite, metal catalyst particles (co and Ni mixture) was used to synthesis single walled CNT.

iii, PLASMA TORCH METHOD:

Single walled CNT was prepared by this method. In thermal plasma torch method high frequency oscillating currents in a coil in flowing innert gas was fed with feedstock of carbon black and catalyst particles and then cooled down to get single walled ~~nanotubes~~. This method produces 2gms of CNT per mintue.

iv, CHEMICAL VAPOUR DEPOSITION (CVD):

During chemical vapour deposition process a substrate was prepared with a layer of metal catalyst nanoparticles (Ni or co). The substrate is heated to 700°c and a mixture of nitrogen and carbon containing acetylene or ethylene or ethanol or methane was passed. The carbon containing gas is broken and carbon is transported to the edges of the particle where it form CNT. Fluidised bed red reactor is most widely used for CNT production.

PROPERTIES OF CNT:

→ Strength:

CNT possess strength upto 100 gigapascals (GPa)

→ Hardness:

Standard single walled CNT withstands a pressure upto 25 GPa without deformation

→ Kinetic Properties:

Multiwalled CNT exhibit a striking telescoping property

→ Electrical properties:

CNT is semiconducting with a very small band gap between valence band and conducting band.

→ Electromagnetic wave absorption:

CNT possess microwave absorption characterstic

→ Thermal properties:

CNT are very good thermal conductor, CNT at room temperature has thermal conductivity 3500 $WM^{-1}K^{-1}$. The temperature stability of CNT is 2800°c in vaccum & 750°c in air.

→ Toxicity:

CNT possess toxicity.

Applications of CNT:

→ CNT's are used to make space elevators, stab-proof, bullet-proof clothing

→ CNT is used in paper batteries

→ Used in digital switching devices, electromagnetic wave detectors.

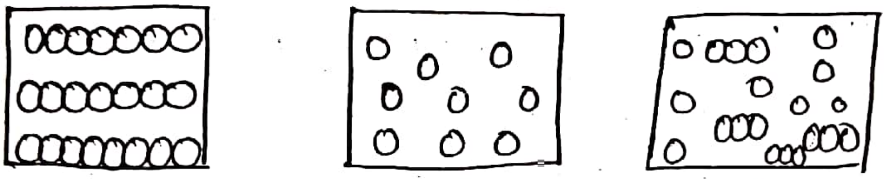
→ CNT can store hydrogen

→ Single walled CNT is inserted around cancerous cell, hence used in medical field.

⑥

LIQUID CRYSTALS (LCs):

The substances which exhibits conventional liquid properties as well as crystalline solid property is called liquid crystals.



SOLID LIQUID LIQUID CRYSTALS

Types of liquid crystals:

1, Thermotropic LCs
2, Lyotropic LCs
3, Metallotropic LCs

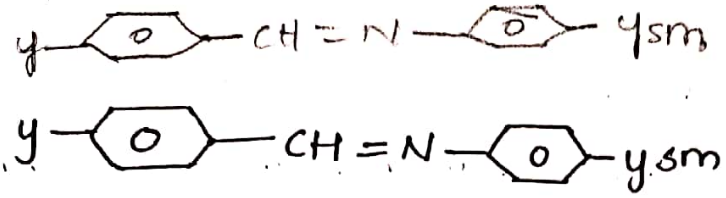
→ Thermotropic LCs:

Thermotropic phases are those that occur in a certai temperature range. Examples of thermotropic liquid crystalline substances are cholesteryl benzoate, exhibit liquid crystalline state 145.5 - 178.5°C, P- azoxyanisole at 116 - 135 °C, and P-azoxyphenetole at 137 - 167°C.

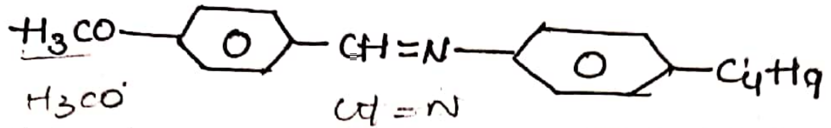
There are three distinct phases in which thermotropic LCs exists.

a, Nematic liquid phases:

Nematic in Greek means thread like simple structures



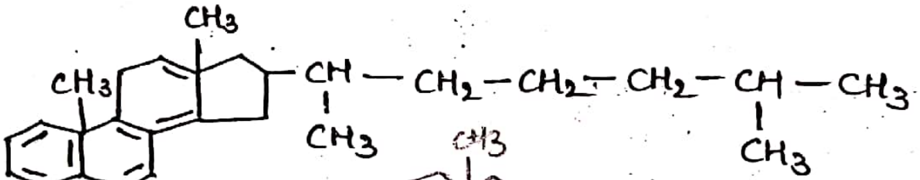
Example:

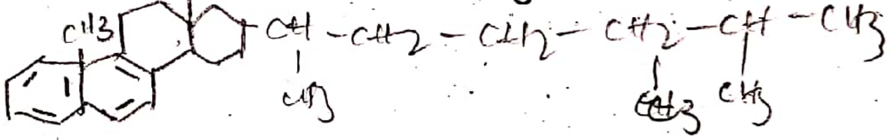


b, Cholestric LCs:

The molecules are aligned parallel to a preferred direction as in nematic phase. When proceeding in a direction normal to the plane, the preferred direction rotates continuously, the result is helical structure.

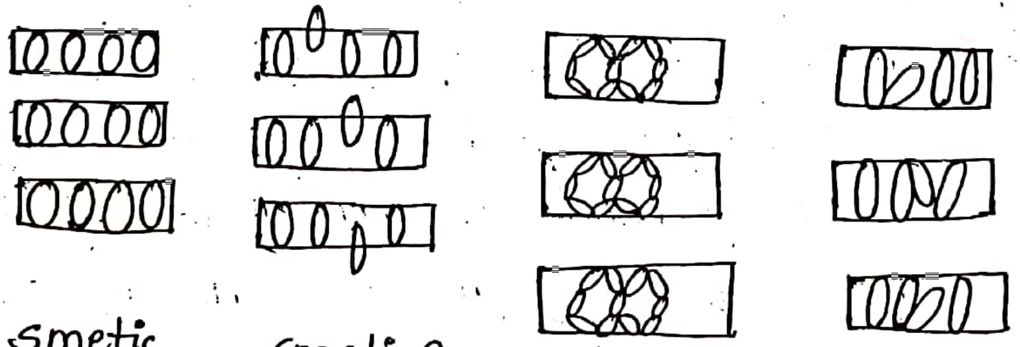
Example:





c, Smetic LCs:

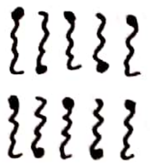
In greek smetic means soap. There are three types of smetic phases based on orientation of the director.



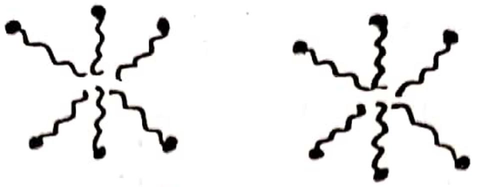
smetic smetic A smetic B smetic C

Lyotropic LCs:

Whenever the substance is added to liquid crystals it will increase the concentration of liquid crystal phase is called lyotropic LCs.



LAMELLAR LYOTROPIC LCS



HEXAGONAL LYOTROPIC LCS

APPLICATIONS:

- → Preparation of LCD TV's, laptops, computer monitors
- → It is used in inhibition of cancer cells, tumour cells
- → Used in aquariums
- → Used in electromagnetic wave detectors.

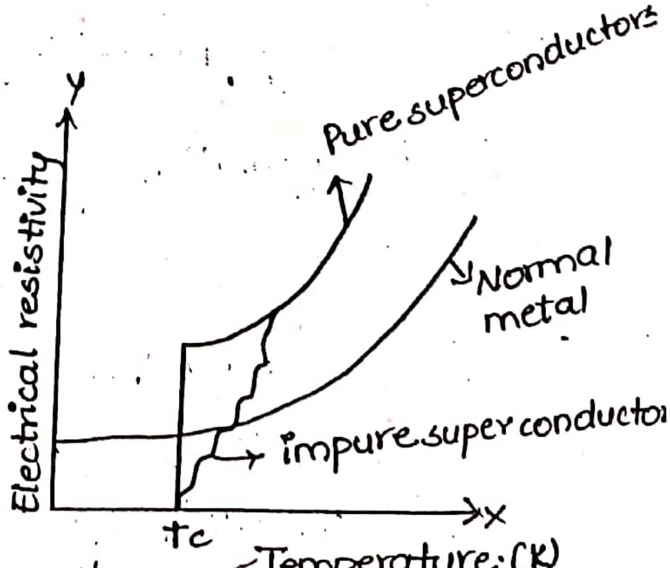
SUPER CONDUCTORS:

The scientist Dutch physicist "Kammerlingh Onnes" in 1911 proposed super conductors.

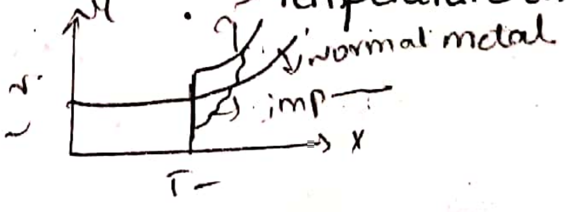
A solid which offers no resistance to passage of electricity through it is called super conductors.

Types of superconductors:

i, Type-I superconductor (or) Ideal superconductor:



- → In this superconductor, it exhibits diamagnetic property and also meissner effect.
- → The critical temperature (Tc) is high when compared to normal temperature (T)



Super critical fluid extraction method :-

1. SFE is the presence of seperating of one component from another component using super critical fluid as the extracting solvent extraction is usually from a solid matrix. but can also be from liquids

2. SFE method is used for analytical purpose on a large scale to either unwanted material from a product (de-caffination) or collect a desired product (essential oils)

3. These essential oils can include limonene ($C_{10}H_{10}$) (terpene type of hydro carbon) and other straight solvents

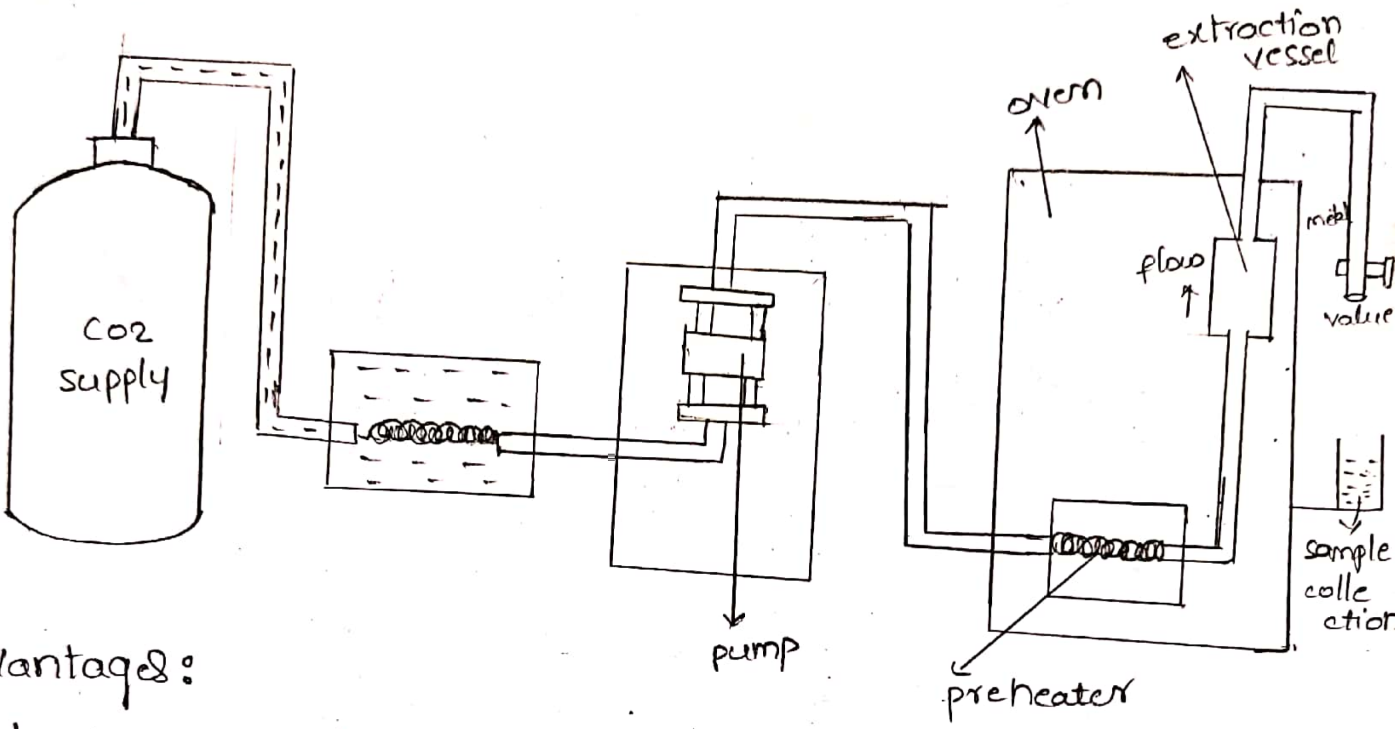
4. Carbondioxide (CO_2) is the most used super critical fluid some time co-solvents such as methanol and ethanol

conditions of SFE :-

1. In SFE method, we use CO_2 undergoes critical temperature above of 31°c and critical (temperature) pressure is 74 bar $\boxed{1 \text{ bar} = 10^5 \text{ pascal}}$

procedure :-

The system must contain a pump for the CO_2 a pressure cell contain sample. we apply a pressure cell contain sample. we apply pressure in the system and a collecting vessel. The Liquid is pumped to a heating zone where it is heated it is heated to super critical condition. it then passes into extraction vessel where it rapidly. diffuses into solid matrix and dissolve the material to be extracted



advantages:

1. selectivity:- In SFE method we apply selected temperature and pressure

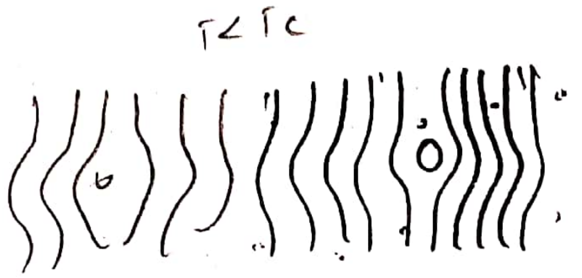
2. speed:- In SFE method speed depends upon diffusion of matrix and extracted materials

Limitations:-

In SFE method, we supply high pressure it increase the cost compared to conventional liquid extraction.

* Super critical fluid extraction method:-

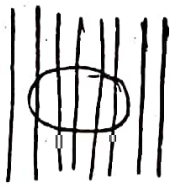
In theis method the extraction of food, coffine, sugar, polymers, peterochemi



Type-II Super conductor (or) Hard superconductor:

→ In this super conductor, it exhibits magnetisation, value is zero from lesser magnetic field to higher magnetic field.

→ The critical temperature (T_c) is less when compared to normal temperature (T)



$Y Ba_2 Cu_3 O_{7-x}$

$Y Ba_2 Cu_3 O_{7-x}$

Example for superconductor:

Yittrium Barium Cuprate ($YBa_2Cu_3O_{7-x}$)

It contains yittrium oxide, barium carbonate, cuprous oxide in stichiometric ratio (1:2:3) and hence is called 1:2:3 molar super conductor and $T_c = 90°K$

Synthesis of 1:2:3 superconductor by ceramic method:

Step 1: Preparation of a homogenous mixture of there oxides (Y_2O_3, $BaCO_3$ and CuO) in their molar ratios

Step 2: Heating them to obtain oxygen deficient superconductor in a muffle furnace.

Step 3: Annealing the above compound to room temperature to retain its composition, structure and superconducting properties

CLASSES OF SUPERCONDUCTORS:

1. Elements Eg: Hg, Nb, La
2. Alloys Eg: La_3In, Nb_3Ge
3. Simple compounds Eg: NbN
4. Molecular Crystals Eg: $C_{60}K_x$
5. Ceramics Eg: Mixed metal oxides
6. Inorganic Polymers Eg: $(SN)_x$
7. Organic compounds

E — Hg, La
Alloys — La_3In.
simplecom — NbN
molecul crystal — $C_{60}K_x$
ceram — mixed

Elem - Hg, La, Nb ⑧
Alloys — La_3In
Sim — NbN
MO — $C_{60}K_x$
Ceramics - mixed metal oxides
In - SN_x
or —

PROPERTIES OF SUPERCONDUCTORS:

→ Sc are brittle, so used in preparation of electronic wires

→ Themoelectric property is zero

→ The magnetisation property is zero

→ When current is passed through the superconducting materials, the heating loss I^2R is zero.

APPLICATIONS OF SUPERCONDUCTORS:

→ Used in MRI scanners

→ $(YBa_2CO_3O_{7-x})$ is used in industrial catalyst like hydrogenatio oxidation etc.,

→ Used as a alcohol sensor to prevent road accidents $(La_3Sr_xO_3-x)$

→ It is also used in preparation of electronic devices like cellular telephones.

prepared by
Sarvepalli Venkata Rao
M.Sc B.Ed

Contents

Introduction

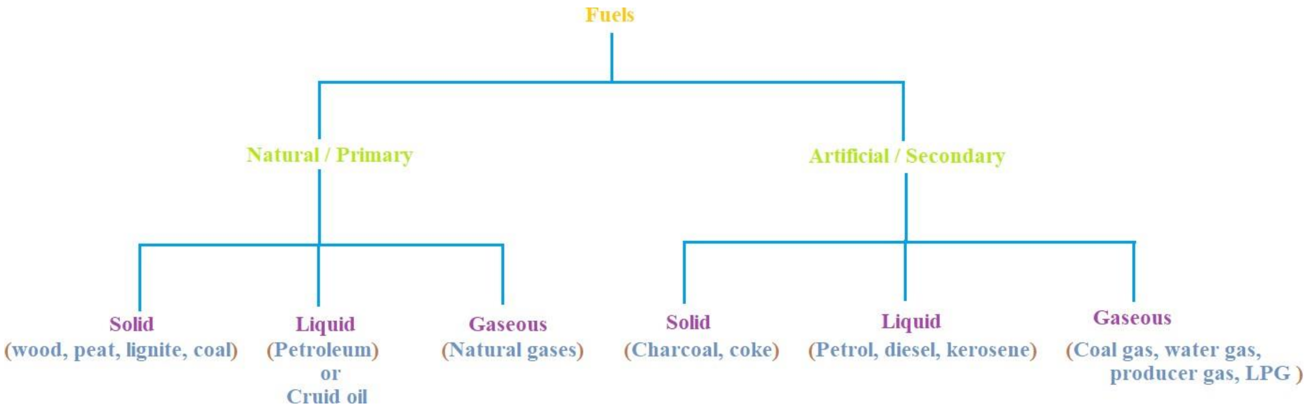
A fuel is a substance that contains carbon and hydrogen undergoes combustion in presence of oxygen to gives large amount of energy.

$$\text{Fuel} + O_2 \longrightarrow CO_2 + H_2O + \text{Energy}$$

Classification of Fuel

On the basis of occurrence fuel is classified into two categories; natural or primary fuels and artificial or secondary fuels.

i) **Natural/primary fuels**: These fuels are naturally present.
ii) **Artificial/ secondary fuels**: They are synthesized by primary fuels.



Characteristics of Good Fuel

i) Fuel should have high calorific value.
ii) Must have moderate ignition temperature.
iii) Fuel should have low moisture content.
iv) Available in bulk at low cost.
v) Should not burn spontaneously.
vi) Fuel should burn efficiently, without releasing hazardous pollutants.
vii) Handling, storage and transportation should be easy.

Unit of heat

i) **Calorie**: it is the amount of heat required to raise the temperature of 1 gram of water through one degree centigrade.

ii) **British Thermal Unit (BTU):** it is the amount of heat required to raise the temperature of 1 pond of water to one degree Fahrenheit.
1 B.T.U. = 252 cal = 0.252 kcal
1 kcal = 3.968 B.T.U.

iii) **Centigrade Heat Unit (CHU):** it is define as the amount of heat required to raise the temperature of 1 pond of water to one degree centigrade.

1 kcal = 3.968 B.T.U. = 2.2 C.H.U.

Calorific value

Calorific value of fuel can be define as the amount of heat evolved when one unit mass or volume of the fuel undergoes completely combustion in presence of oxygen.

i) **High or gross calorific value (HCV or GCV)**: it is defined as amount of heat evolve when one unit mass or volume of the fuel is completely burnt and combustible products are cooled to room temperature (25ºC or 77ºF).

ii) **Low or net calorific value (LCV or NCV)**: it is defined as amount of heat evolve when one unit mass or volume of the fuel is completely burnt and combustible products are permitted to escape. Therefore net calorific value is lower than gross calorific value.

LCV = HCV – latent heat of water vapour
LCV = HCV – mass of hydrogen × 9 × latent heat of steam (587 kcal/kg)

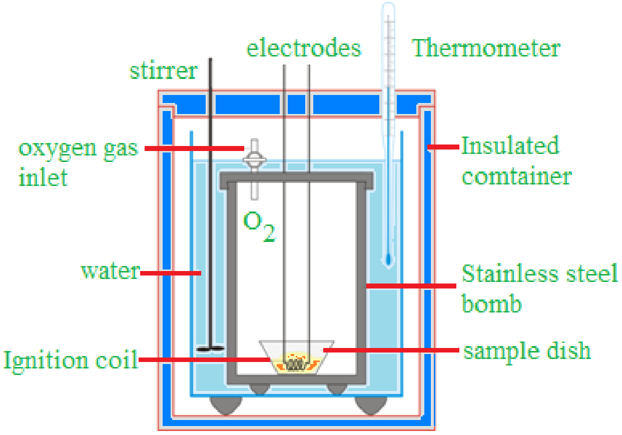
One part by mass of hydrogen produced nine parts by mass of water molecule. Therefore,

LCV = HCV – H/100 × 9 × 587 kcal/kg
H = percentage of hydrogen in fuel

Determination of calorific value

i) Bomb calorimeter

Bomb calorimeter is used to determine calorific value of solid and liquid fuels experimentally. A bomb calorimeter contains a cylindrical bomb made by stainless steel. Combustion takes place in this cylinder. The lid contains two stainless steel electrodes. Oxygen is supplied through oxygen valve for combustion. The electrode is attached with a small ring which supports nickel or stainless steel made crucible. The bomb is taken in a copper calorimeter which is surrounded by air and water jacket in order to prevent heat loss by radiation. The copper calorimeter also contains electrically operated stirrer and Beckmann’s thermometer (take reading with temperature difference up to 0.01ºC.



Working: In a crucible, a known amount of the fuel is placed in the nickel or stainless steel crucible which is supported by a ring. A fine magnesium wire touches the fuel sample, which is already connected to the electrodes. The bomb lid is lightly screwed and filled with oxygen at about 25 atm pressure, is placed in copper calorimeter containing a known amount of water. The electrically operated stirrer is driven and notes the initial temperature of water (T_1). After that both the electrodes are connected to a battery to complete the circuit. The fuel sample is burn and heat is liberated. To maintain the uniform temperature, water is continuously stirred and the final temperature (T_2) of water is noted.

Calculation:

Mass of fuel (solid or liquid)= x g

Mass of water taken = W g

Water equivalent of calorimeter = w g

Initial temperature of water in calorimeter = T_1 K

Final temperature of water in calorimeter = T_2 K

High or gross calorific value = $\frac{(W+w)(T2-T1)}{x}$ **cal/g**

LCV = HCV – H/100 × 9 × 587 kcal/kg

H = percentage of hydrogen in fuel

Corrections:

$$\textbf{HCV or GCV} = \frac{(W+w)(T2-T1-Tc)-(Cs+Cn+Cf+Cc)}{x}$$

Where

T_c = cooling corrections

Cs = Corrections for sulphuric acid (H_2SO_4)

Cn = Corrections for nitric acid (HNO_3)

Cf = Corrections for fuse wire

Cc = Corrections for cotton thread

ii) Theoretical calculation by Dulong's formula:

The theoretical calculation of calorific value of a fuel can be approximately calculated by Dulong's formula, based on the percentage of the constituents (C, H, O and S) present in the fuel.

As per Dulong's formula

$$\textbf{HCV} = \frac{1}{100}\left[8080\,C + 34500\left(H - \frac{O}{8}\right) + 2240\,S\right] \textbf{ kcal/kg}$$

Where, C, H, O and S are percentage of carbon, hydrogen, oxygen and sulphur present in fuel. In above formula the oxygen is assumed to be present in combined form with hydrogen or in form of water (H_2O).

$$\mathbf{H_2 + 1/2O_2 \longrightarrow H_2O}$$

2g 16g 18g

1g 8g 9g

Total mass of hydrogen in fuel – fixed hydrogen

Total mass of hydrogen in fuel – (1/8) mass of oxygen in the fuel

∴ 8 part of oxygen combine with 1 part of hydrogen to form H_2O.

$$\text{Fixed hydrogen} = \frac{\text{Mass of oxygen in the fuel}}{8}$$

Then the amount of hydrogen available for combustion

= total mass of hydrogen in fuel – fixed hydrogen

= [H-O/8]

LCV = HCV – H/100 × 9 × 587 kcal/kg

Analysis of Coal

The quality of coal can be analyzed by two analysis; proximate and ultimate analysis.

Proximate analysis:

In this analysis moisture, volatile matter, ash and fixed carbon can be determined.

Moisture: A known amount of finely powdered air-dried coal sample is taken in crucible. The crucible is placed inside an electric hot air-oven, at 105° to 110°C for 1 hour. The crucible is then taken out, cooled in desiccators and weighed. Difference in the weight of sample gives the information about the weight loss due to removal of moisture.

$$\textbf{\% of moisture} = \frac{\textbf{loss of weight}}{\textbf{weight of coal taken}} \times \mathbf{100}$$

Lesser the amount of moisture content, better the quality of fuel.

Volatile matter: The moisture free coal sample is taken in a crucible, covered with a lid and placed in muffle furnace (electric furnace) at 950°C for 7 minutes and then remove the crucible from the oven and cooled first in air, then cooled in a desiccator and weighed again. Loss in weight is due to presence of volatile matter in coal sample.

$$\textbf{\% of volatile matter} = \frac{\textbf{loss of weight}}{\textbf{weight of coal taken}} \times \mathbf{100}$$

Low quantity of volatile matter, better the quality of a coal.

Ash: The residual coal sample taken in a crucible and then heated without lid in a muffle furnace at 700-750°C for an hour. The crucible is then taken out, cooled first in air, then in desiccators and weighed again. The process of heating, cooling and weighing are repeated until a constant weight is not obtained. The residue is reported as ash on percentage-basis.

$$\textbf{\% of ash} = \frac{\textbf{weight of residue left}}{\textbf{weight of dry coal taken}} \times \mathbf{100}$$

Ash is non-combustible substance which reduces the calorific value of a coal. Therefore, low quantity of ash contents, better the quality of a coal.

Fixed carbon: The fixed carbon percentage is determined by following equation

% of fixed carbon = 100 – (% of moisture + % of volatile matter + % of ash)

Greater the calorific value, higher the % of fixed carbon.

Ultimate analysis:

Ultimate analysis is involving the measurement of C, H, N, S, and O.

Carbon and hydrogen: In a combustion apparatus, about 1-2 gram of coal sample is burnt in a current of oxygen to convert C and H into CO_2 and H_2O respectively. The gaseous products CO_2 and H_2O are absorbed in KOH and $CaCl_2$ tubes of known weights, respectively. The increase in weights of these (KOH and $CaCl_2$) are then determined.

Calculation:

$$\begin{array}{lcl} C + O_2 & \longrightarrow & CO_2 \\ 12 \quad 32 & & 44 \end{array}$$

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

$$\begin{array}{lcl} H_2 + 1/2O_2 & \longrightarrow & H_2O \\ 2 \qquad 16 & & 18 \end{array}$$

$$CaCl_2 + 7H_2O \longrightarrow CaCl_2.7H_2O$$

$$\text{\% of carbon} = \frac{\text{Increase in weight of KOH} \times 12}{\text{weight of coal sample taken} \times 44} \times 100$$

$$\text{\% of hydrogen} = \frac{\text{Increase in weight of CaCl2} \times 2}{\text{weight of coal sample taken} \times 18} \times 100$$

Nitrogen: In Kjeldahl's flask add accurately weighed powdered coal and heated with concentrated H_2SO_4 and K_2SO_4 as a catalyst. The solution becomes clear when all the nitrogen is converted into ammonium sulphate then it is treated with excess of NaOH which convert ammonium sulphate into ammonia; the liberated ammonia is distilled over and absorbed in a known volume of standard (N/10) H_2SO_4 solution. From the volume of H_2SO_4 used by liberated ammonia, the percentage of Nitrogen in coal, calculated as follows:

$$N_2 + H_2SO_4 \longrightarrow (NH_4)_2SO_4 \xrightarrow{NaOH} 2Na_2SO_4 + 2NH_3 + 2H_2O$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

The volume of unused H_2SO_4 is then determined by titrating against standard NaOH solution (N/10)

Calculation:

The amount of H_2SO_4 required to neutralize ammonia evolve from coal is calculated as follows:

Amount of acid **= N/10 V_1 – N/10 V_2**

= 0.1 (V_1 – V_2) mili equivalents

$$= \frac{0.1\ (V1 - V2)}{1000} \text{ equivalents}$$

Thus,

$$\textbf{Weight of N} = \frac{0.1\ (V1 - V2)}{1000} \times 14$$

V_1 = Volume of standard H_2SO_4 (N/10) solution
V_2 = Volume of standard NaOH (N/10) solution
Thus,

$$\textbf{\% of nitrogen} = \frac{\text{weight of nitrogen}}{\text{weight of coal sample}} \times 100$$

$$= \frac{0.1\frac{(V1 - V2)}{1000}}{1} \times 14 \times 100$$

$$\textbf{\% of nitrogen} = 0.1\ (V_1 - V_2) \times 1.4$$

Sulphur: A known amount of coal sample is burnt in bomb calorimeter in presence of oxygen. After that, sulphur present in coal is converted into SO_2 and SO_3. The ash obtained from the bomb calorimeter, is extracted with dil. HCl. The washings (acid extracts) are treated with Barium chloride solution and the sulphates are precipitate as Barium sulphate. This precipitate is filtered, washed, dried and heated to obtain constant weight.

Calculation:

$$\underset{32}{S} \longrightarrow SO_4^{2-} \longrightarrow \underset{233}{BaSO_4}$$

$$\frac{\text{weight of sulphur}}{\text{weight of BaSO4}} = \frac{\text{atomic weight of sulphur}}{\text{molecular weight of BaSO4}}$$

$$\textbf{Weight of sulphur} = \frac{32}{233} \times \text{weight of } BaSO_4$$

Thus,

$$\textbf{\% of sulphur} = \frac{\text{weight of BaSO4 obtained} \times 32}{\text{weight of coal taken in bomb calorimeter} \times 233} \times 100$$

Ash: Percentage of ash calculated by method given in proximate analysis.

Oxygen: It is calculated by subtracting the sum of total % of carbon, hydrogen, nitrogen, sulphur and ash from 100.

Calculation:

% of oxygen = 100 – [% carbon + % hydrogen + % nitrogen + % sulphur + % ash]

Biogas

It is formed by the bacterial degradation of biomass under anaerobic condition (airtight digesters). Biogas mainly contains methane (50-70%), carbon dioxide and trace amount of water, sulfur and hydrogen sulphide.

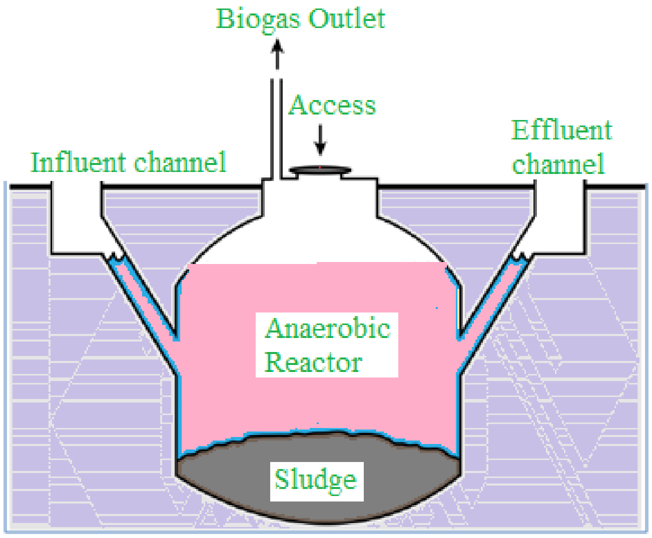
Biogas generation

The biogas generated by anaerobic digestion of organic waste (animal waste, plant residue, crops) in biogas plant, mainly involve three steps: hydrolysis, acid formation and gas production.

Hydrolysis: In this step, macromolecule like fats, proteins, carbohydrates are broken down through hydrolysis into fatty acids, amino acids and sugars respectively.

Acid formation: in this step, fatty acids, amino acids and sugars are fermented by acid producing bacteria under anaerobic condition into acetic acid, carbon dioxide and hydrogen.

Gas production: In this step, methanogenic bacteria produce methane either by fermenting acetic acid to form methane and carbon dioxide or by reduction of carbon dioxide into methane.



Advantage of biogas

i) Produce organic waste
ii) Burn without smoke
iii) Renewable
iv) Help to reduce waste.

Disadvantage of biogas

i) Methane is health hazardous.
ii) Not efficient like fossil fuel.

Content

1. Hardness of water

Water which does not produce lather with soap is termed as hard water. The hardness is usually expressed in terms of Ca & Mg salts like bicarbonate, carbonate, sulphate, chloride etc.

Formation of Hard water:

Hard water is formed due to presence of minerals like Ca and Mg. they are not removed or separated by sedimentation or filtration. When hard water reacts with soap (sodium salt of stearic acid or pametic acid) gives curdy precipitate.

$$2C_{17}H_{35}COONa + CaCl_2 \rightarrow Ca(C_{17}H_{35}COO)_2\downarrow + NaCl$$

$$2\,C_{17}H_{35}COONa + MgSO_4 \rightarrow (C_{17}H_{35}COO)_2Mg\downarrow + Na_2SO_4$$

In above reaction hard water react with sodium salt of stearic acid to form calcium stearate or magnesium stearate which being insoluble and separate out without producing lather.

2. Types of hardness

a) **Temporary hardness:**

Temporary hardness of water is caused by Ca and Mg bicarbonate. This can be removed by simply boiling of water. Due to boiling bicarbonate is converted into carbonate (insoluble precipitate)

$$Ca(HCO_3)_2 \rightarrow CaCO_3\downarrow + H_2O + CO_2\uparrow$$

$$Mg(HCO_3)_2 \rightarrow Mg(OH)_2\downarrow + 2CO_2\uparrow$$

Temporary hardness can also be removed by adding hydrated lime to precipitate insoluble carbonate.

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2CaCO_3\downarrow + 2H_2O$$
$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow Mg(OH)_2\downarrow + 2CaCO_3\downarrow + 2H_2O$$

b) **Permanent hardness:**

Permanent hardness is caused by the presence of soluble salt of Ca and Mg other than bicarbonate such as chloride and sulphate. Permanent hardness cannot be removed by boiling of water or hydrated lime. It can be eliminate by water softening techniques like Lime-soda process, Zeolite, Ion-exchange resin, reverese osmosis etc.

3. Degree of hardness

The unit in which hardness is usually expressed, known as degree of hardness. Degree of hardness is expressed in terms of calcium carbonate ($CaCO_3$) equivalent because $CaCO_3$ have molecular weight 100 and it is easily precipitate. Degree of hardness may be expressed as follows-

$$\text{Equivalent of } CaCO_3 = \frac{[\mathit{strength\ of\ substance\ producing\ hardness}\ (\frac{mg}{lit})] \times [\mathit{chemical\ equvalent\ of}\ \mathrm{CaCO3}] \times 2}{[\mathit{chemical\ equivalent\ of\ hardness\ producing\ substance}] \times 2}$$

OR

$$\text{Equivalent of } CaCO_3 = \frac{[\mathit{strength\ of\ substance\ producing\ hardness}\ (\frac{mg}{lit})] \times 100}{[\mathit{hemical\ equivalent\ of\ hardness\ producing\ substance}] \times 2}$$

Unit of hardness:

i) **Parts per million (ppm):** it is the number of equivalent part $CaCO_3$ present per million (10^6) part of water by weight.

ii) **Milligram per litre (mg/lit):** it is the number of milligram of $CaCO_3$ present in one litre of water.

iii) **Degree Clarke (ºCl):** it is the number of equivalent part of $CaCO_3$ present per 70,000 part of water.

iv) **Degree French (ºFr):** it is the number of equivalent part of $CaCO_3$ present per 10^5 part of water.

Correlation between ppm, mg/lit, ºCl and ºFr:

[1ppm= 1mg/lit=0.07 ºCl= 0.1 ºFr]

4. Boiler Trouble

Boilers are used in industries and power station to generate steam. During conversion of water into steam in boiler, the dissolve and suspended solids are not removed. All the impurities are deposited in form of **scale** and **sludge** within the boiler and causes boiler troubles.

a) **Scales formation:**

Scales are hard deposits, which stick on the inner wall of the boiler. These are formed by $CaCO_3$, $CaSO_4$, $Ca(HCO_3)_2$, $Mg(OH)_2$ etc. in hot portion of boiler.

b) **Sludge formation:**

Sludge form loose, slimy and soft precipitate in the colder area of the boiler. The sludge formed by the $CaCl_2$, $MgCl_2$, $MgCO_3$, $MgSO_4$ etc.

Problems caused in boilers:

i) Scales and sludge is poor conductor of heat & therefore prevent effective transfer of heat to water.

ii) In this condition excessive heat is required which increase fuel consumption.

iii) Scale often crack due to their uneven expansion allowing the water to come immediately in contact with overheated metal. This suddenly result in the formation of large quantity of steam which in turn leads to excess pressure and then to explosion.

5. Boiler trouble removal by internal treatment

Internal treatment:

i) Sludge formation can be removed by blow down operation. In this case impurities can be removed by an outlet present at the bottom of boiler.

ii) Scale formation can be prevented by internal treatment that involve addition of chemical to the boiler water either to ppt the scale forming impurities in the form of sludge so that they can be removed by blow down method or to convert them into soluble compounds.

a) **Calgon treatment:**

Calgon is sodium meta hexa phoaphate, which can be used to covert CaSO4 into soluble complex.

$$\underset{\textbf{Calgon}}{Na_2[Na_4(PO_3)_6]} + 2CaSO_4 \longrightarrow \underset{\textbf{soluble}}{Na_2[Ca_2(PO_3)_6]} + 2Na_2SO_4$$

b) **Phosphate treatment:**

Scale formation can be removed by adding sodium phosphate, which reacts with hardness of water and form soft sludge of Ca and Mg phosphates which can be removed by blow-down operation.

$$3CaCl_2 + 2Na_3PO_4 \longrightarrow Ca_3(PO_4)_2\downarrow + 6NaCl$$

$$MgSO_4 + 2Na_3PO_4 \longrightarrow Mg_3(PO_4)_2\downarrow + 3Na_2SO_4$$

6. Techniques for water softening (External treatment)

a) Zeolite process

Zeolite is a three-dimensional silicate. The chemical formula of zeolite is hydrated sodium aluminum silicate represented as $Na_2OAl_2O_3.xSiO_2.yH_2O$ (x = 2-10 & y = 2-6). Zeolites are capable exchanging ions with sodium ions. So it is capable of exchanging hardness producing icons present in water. This process also called as permutit process. Zeolite can be written as Na_2Ze The two Na^+ icons is replaced by one Ca^{2+} or Mg^{2+} ions.

$$Na_2Ze + Ca^{2+} \longrightarrow CaZe + 2Na^+$$

Process:-

The apparatus is made of cylindrical metallic vessel several beds are made inside it where zeolite salt is kept. Raw water is poured inside the apparatus through inlet that passes through beds and thus chemical ion exchange reactions are takes place. After the use of this process for a certain time, Zeolite is exhausted i.e all Na^+ ions are replaced by Ca^{2+} or Mg^{2+} and therefore this will not be used for soften the water.

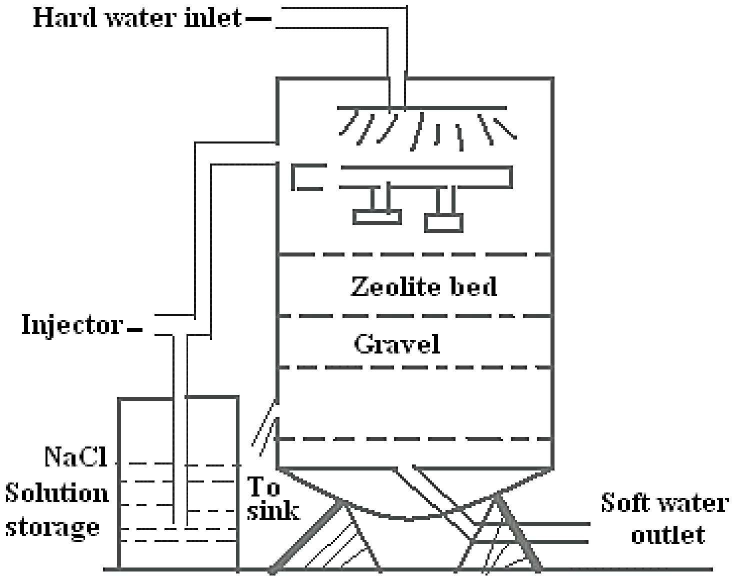
$$Na_2Ze + CaCl_2/CaSO_4/\ Ca(HCO_3)_2 \longrightarrow CaZe + 2NaCl/Na_2SO_4/2NaHCO_3$$

Regeneration:

Exhausted zeolite can be regenerated by treating it with brine solution (10% NaCl solution)

$$(Ca^{2+}/Mg^{2+})\ Ze + NaCl \longrightarrow Na_2Ze + CaCl_2\ (or)\ MgCl_2$$

Exhausted Zeolite on washing with cold water, $CaCl_2$ & $MgCl_2$ can be removed and regenerated zeolite is this ready to be reused.



b) Ion-exchange resin:

In this process cations and anions are completely removed by passing impure water into two different columns. First column contain sulphuric acid resin with acidic group $-SO_3H$. This column is known as cation exchange resin because it exchange only cations like Ca^{2+}, Mg^{2+}, Na^+ etc.

$$\text{Resin–}SO_3H + Na^+ \longrightarrow \text{resin-}SO_3^-Na^+ + H^+$$

$$2\text{Resin–}SO_3H + Ca^{2+} \longrightarrow (\text{resin-}SO_3)_2Ca + 2H^+$$

$$2\text{Resin–}SO_3H + Mg^{2+} \longrightarrow (\text{resin-}SO_3)_2Mg + 2H^+$$

Whereas, second column contain resin with basic group like $-NR_3^+OH^-$. It is known as anion exchange resin because it exchanges anions like Cl^-, SO_4^{2-} etc.

$$\text{resin–}NR_3^+OH^- + Cl^- \longrightarrow \text{resin–}NR_3^+Cl^- + OH^-$$

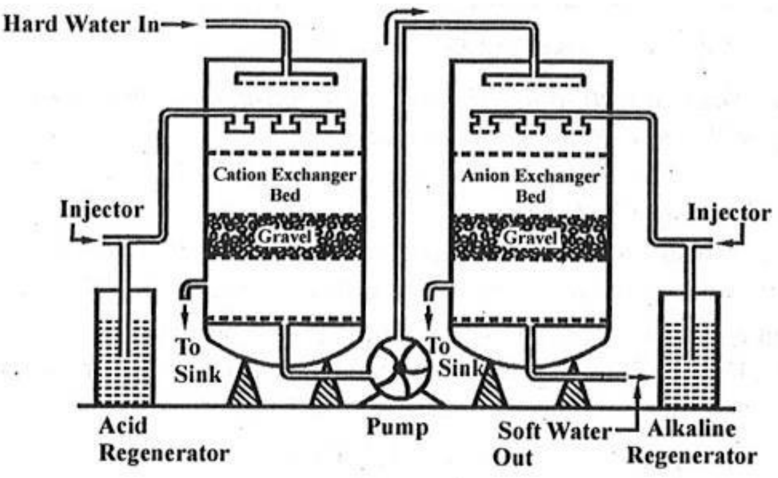
The removal of H^+ ions from the first column and OH^- ions from the second column react to form water.

Regeneration:

when both the column are exhausted, then first and second column are treated with dilute sulphuric acid or HCl (generate H^+ ions) and aqueous NaOH (generate OH^- ions) respectively. So, they have to be regenerated.

$$(\text{resin-}SO_3)_2Ca + 2H^+ \longrightarrow 2\text{Resin–}SO_3H + Ca^{2+}$$

$$(\text{resin-}SO_3)_2Mg + 2H^+ \longrightarrow 2\text{Resin–}SO_3H + Mg^{2+}$$



c) Lime-soda process:

In this process, hydrated lime & sada ash use to remove hardness from water.

i) Hydrated lime:

Hydrated lime is used to remove temporary hardness of water. It react with $Ca(HCO_3)_2$ & $Mg(CO_3)_2$ to form insoluble precipitate of calcium carbonate and magnesium hydroxide respectively.

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$$

$$Mg(HCO_3)_2 + 2Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + 2CaCO_3\downarrow + 2H_2O$$

Hydrated lime is also used to remove permanent hardness (magnesium salt impurities only) from water. It reacts with $MgSO_4$ & $MgCl_2$ to form insoluble precipitate of magnesium hydroxide.

$$MgCl_2 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + CaCl_2$$

$$MgSO_4 + Ca(OH)_2 \longrightarrow Mg(OH)_2\downarrow + CaSO_4$$

In above reaction calcium based impurities like $CaCl_2$ & $CaSO_4$ also form, which are soluble in water. Therefore calcium based impurities ($CaCl_2$ & $CaSO_4$) are not removed by lime treatment.

ii) Soda ash:

Sodium carbonate (Na_2CO_3) is used to remove permanent hardness of water which caused by $MgSO_4$ & $MgCl_2$ or $CaCl_2$ & $CaSO_4$.

$CaCl_2 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + 2NaCl$

$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + Na_2SO_4$

$MgCl_2 + Na_2CO_3 \longrightarrow MgCO_3\downarrow + 2NaCl$

$MgSO_4 + Na_2CO_3 \longrightarrow MgCO_3\downarrow + Na_2SO_4$

The amount of lime-sada required for the softening of hard water can be calculated by following formula-

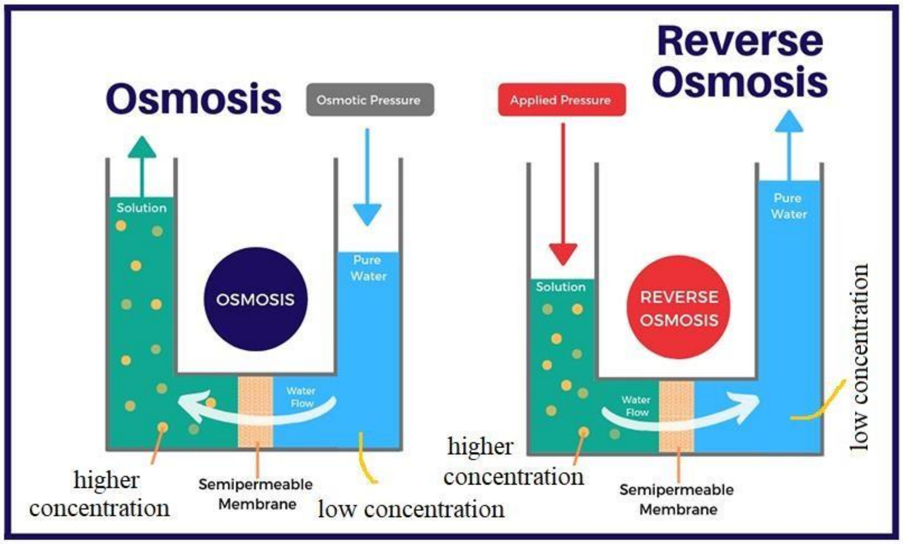
$$\text{Lime requirement} = \frac{74}{100}[\text{temporary hardness of Ca} + 2 \times \text{temporary hardness of Mg} + \text{permanent hardness of Mg in terms of } CaCO_3 \text{ equivalents}]$$

Soda requirement = $\frac{106}{100}$[permanent hardness of $CaCl_2$ + $CaSO_4$ + $MgCl_2$ + $MgSO_4$

in terms of $CaCO_3$ equivalents]

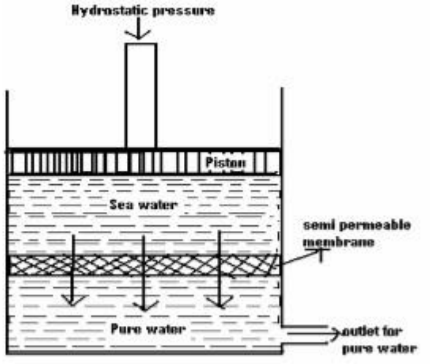
d) Reverse osmosis:

The minimum excess pressure yhat has to be applied on the solution to prevent the entry of the solvent molecule (pure water) into solution through semi permeable membrane is known as osmotic pressure (lower concentration to higher concentration).



If a pressure higher than the osmotic pressure is applied on the solution, the solvent (pure water) will flow reverse, higher concentration solution to low concentration solution, the process is known as reverse osmosis.

Reverse osmosis process can also be used in purification of sea water, for this purpose sea water is delivered under pressure through the semi-permeable membrane where water permeate the minute pores of the membrane & is delivered as purified water.



Advantages:

1) Reverse osmosis system have low maintenance requirement.
2) It removes colloidal silica, which is not removed by demineralization.
3) RO system required less energy as compare to other technology.
4) The reverse osmosis is gaining ground at present for converting sea water into drinking water and for obtaining water for very high pressure boilers.

7. Phase rule

Phase rule (Willard Gibbs in 1874), play an important role to know the behavior of heterogeneous system whereas as law of mass action is apply to know the behavior of homogenous system. If the equilibrium between any numbers of phases is not influenced by gravitational/electrical/magnetic forces but is influenced by pressure, temperature and concentration, then the number of degrees of freedom (F) is related to the number of components (C) and the number of phases (P) as:

$$F = C - P + 2$$

Explanation of terms used in phase rule:

1) **Phase (P):**

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

a) **Gaseous phase:**

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

b) **Liquid phase:**

The number of liquid phase depends upon the number of liquid present and their miscibility. If two liquid are miscible then they form single phase eg. Alcohol in water. If two liquids are immiscible then they form two separate phase eg. Benzene in water, oil in water etc.

c) **Solid phase:**

All the solid phase constitutes the separate phase.

$$CaCO_3\,(s) \longleftrightarrow CaO\,(s) + CO_2\,(g) \qquad (C=3)$$

2) **Component (P):**

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

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

3) Degree of freedom (F):

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

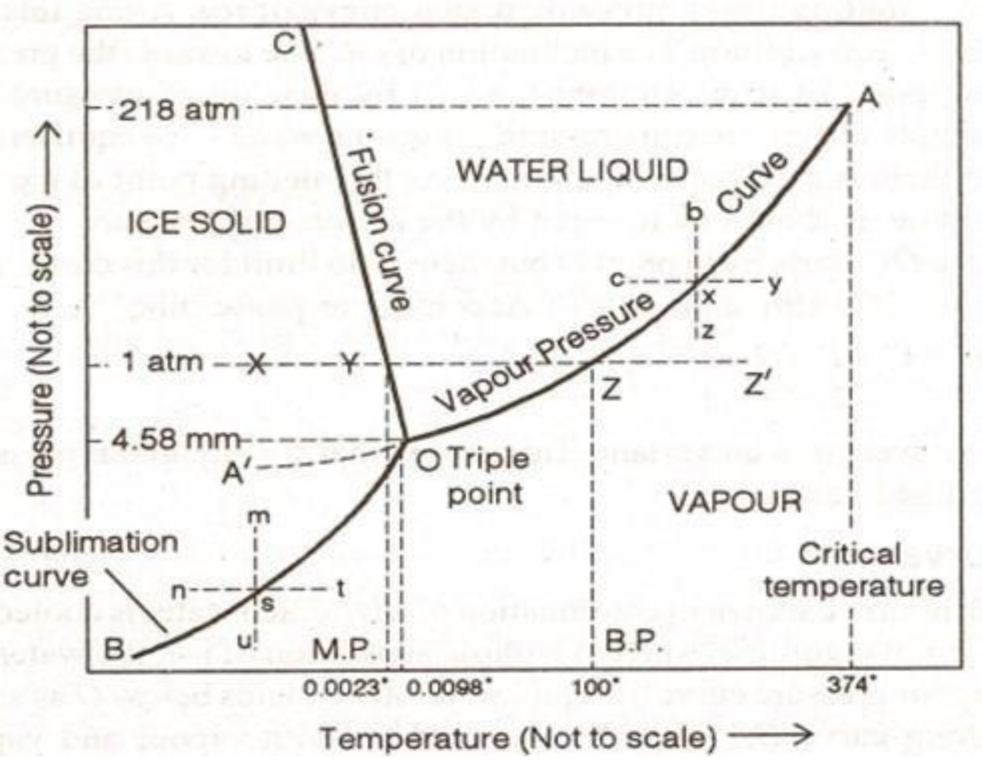
$$F=C-P+2$$

Where,
F=0 (Invarient)
F=1 (Univarient)
F=2 (Bivarient)………& so on

$$F \; a \; C$$

$$F \; a \; \frac{1}{P}$$

8. Application of phase rule one component water system



Water exists in 3 possible phases, namely solid ice, liquid water and water-vapour. Hence, there can be three forms of equilibria, each involving two phases such as.

Solid Ice ⟷ Liquid Water
Liquid Water ⟷ Water-vapour
Solid Ice ⟷ Water-vapour

The phase diagram for the water system is as follows and it contains curves, areas, and triple point.

Curve OA

The curve OA is called vapourisation curve, it represents the equilibrium between water and vapour. At any point on the curve the following equilibrium will exist.

Liquid Water ⟷ Water- vapour

This equilibrium (i.e. line OA) will extend upto the critical temperature (374°C). Beyond the critical temperature the equilibrium will disappear and only water vapour will exist

Curve OB

The curve OB is called sublimation curve of ice, it represents the equilibrium between solid ice and water-vapour. At any point on the curve the following equilibrium will exist.

Solid Ice ⟷ Water- vapour

This equilibrium (i.e.line OB) will extend up to the absolute zero (− 273°C). Beyond absolute zero only solid ice will exist and no water-vapour.

Curve OC

The curve OC is called melting point curve of ice, it represents the equilibrium between ice and water. At any point on the curve the following equilibrium will exist.

Solid Ice ⟷ Liquid Water

The curve OC is slightly inclined towards pressure axis. This shows that melting point of ice decreases with increase of pressure.

Curve OB′(Metastable Equilibrium)

The curve OB′ is called vapour pressure curve of the super-cooled water (or) metastable equilibrium where the following equilibrium will exist.

Super- cooled water ⟷ Water- vapour

Sometimes water can be cooled below it‟s freezing point (0°C) without the formation of ice, this water is called super-cooled water. Super cooled water is unstable and it can be converted into solid ice by “seeding” (or) by slight disturbance.

Along the curves OA,OB,OC and OB′

The no. of phases(P) is 2 ,component(C) is 1 and the degree of freedom of the system is one i.e., univariant. This is predicted by the phase rule:

$$\mathbf{F = C - P + 2;\ F = 1 - 2 + 2;\ F = 1}$$

Therefore, either temperature (or) pressure must be fixed to define the system.

Point ‘O’ (Triple point)

The three curves OA, OB and OC meet at a point „O‟, where three phases namely solid ice, liquid water and water-vapour are simultaneously at equilibrium. This point is called triple point, at this point the following equilibrium will exist

$$\textbf{Ice(s)} \leftrightarrow \textbf{Water(l)} \leftrightarrow \textbf{Vapour(g)}$$

At this point the no. of phases (P) is 3, component(C) is 1 and the degree of freedom of the system is zero i.e., nonvariant. This is predicted by the phase rule:

$$\mathbf{F = C - P + 2;\ F = 1 - 3 + 2;\ F = 0}$$

This takes place only at a constant temperature (0.0075°C) and pressure (4.58 mm of Hg).

Areas

Areas AOC, BOC, AOB represent liquid water, solid ice and water-vapour respectively where the no. of phases (P) and component(C) are one. Hence the degree of freedom of the system is two i.e., bivariant. This is predicted by the phase rule:

$$\mathbf{F = C - P + 2;\ F = 1 - 1 + 2;\ F = 2}$$

Therefore, both temperature and pressure must be fixed to define the system at any point in the areas.