

DEPARTMENT OF HUMANITIES AND SCIENCES

B.Tech I Year I&II Semester ENGINEERING CHEMISTRY

Subject Code: 23HBS9903

Regulation: HM23



ANNAMACHARYA INSTITUTE OF TECHNOLOGY AND SCIENCES

(Autonomous)

(Affiliated to J.N.T.U.A, Anantapur, Approved by A.I.C.T.E, New Delhi)

Utukur (P), C.K.Dinne (V&M), Kadapa-516003

Accredited by NAAC with 'A' Grade, Bangalore.



**ANNAMACHARYA INSTITUTE OF TECHNOLOGY & SCIENCES::KADAPA
(AUTONOMOUS)**

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**ENGINEERING CHEMISTRY
(Common to CIVIL, MECHANICAL ENGINEERING)**

Course Objectives:

- To familiarize engineering chemistry and its applications.
- To impart the concept of soft and hard waters, softening methods of hard water.
- To train the students on the principles and applications of electro chemistry, polymers , surface chemistry and cement.

Course Outcomes: At the end of the course, the students will be able to:

CO1: Demonstrate the corrosion prevention methods and factors affecting corrosion.

CO2: Explain the preparation, properties, and applications of plastics, elastomers & conducting polymers.

CO3: Explain calorific values, octane number, refining of petroleum and cracking of oils.

CO4: Explain the setting and hardening of cement.

CO5: Summarize the concepts of colloids, micelle and nanomaterials.

UNIT I Water Technology

Impurities in water, Hardness of water and its Units, Disadvantages of hard water, Estimation of hardness by EDTA method, Estimation of dissolved oxygen.

Boiler troubles –Priming, foaming, scale and sludge, Caustic embrittlement, Industrial water treatment – specifications for drinking water, Bureau of Indian Standards(BIS) and World health organization(WHO) standards, Ion-Exchange processes. desalination of brackish water, reverse osmosis (RO) and electrodialysis.

UNIT II Electrochemistry and Corrosion

Electrodes-Electro chemical cell, Nernst equation, Cell potential calculations.

Primary cells – Zinc-air battery, Fuel cells -hydrogen-oxygen, methanol-oxygen fuel cells – working of the cells. Secondary cells– Nickel-Cadmium (Ni-Cd) and lithium ion batteries-working of the batteries including cell reactions.

Science of Corrosion: Introduction to corrosion, Electro chemical theory of corrosion, differential aeration cell corrosion, galvanic corrosion, metal oxide formation by dry electro chemical corrosion, Factors affecting of corrosion, corrosion controlling methods: Sacrificial and impressed current cathodic protection. Electro plating (Nickel and Copper) .

UNIT III Polymers & Fuel Chemistry

Introduction to polymers, functionality of monomers, Mechanism of chain growth and step growth polymerization.

Plastics - Thermoplastics and Thermosetting. Preparation, Properties and applications of PVC, Teflon, Bakelite and Nylons.

Elastomers – Buna-S, Buna-N : preparation, properties and applications.

Fuels – Types of fuels, calorific value of fuels, numerical problems based on calorific value; Analysis of coal (Proximate and Ultimate analysis), Liquid Fuels, refining of petroleum, Octane and Cetane number- alternative fuels- propane, methanol, ethanol and bio fuel-biodiesel.

UNIT IV Modern Engineering Materials

Composites: Composites- Definition, Constituents, Classification- Particle, Fibre and Structural reinforced composites, properties and Engineering applications

Refractories- Classification, Properties, Factors affecting the refractory materials and Applications.

Lubricants- Classification, Functions of lubricants, Mechanism, Properties of lubricating oils – Viscosity, Viscosity Index, Flash point, Fire point, Cloud point, Pour point and Applications.

Building materials- Composition, preparation of Portland Cement, Setting and Hardening of cement.

UNIT V Surface Chemistry and Nanomaterials

Introduction to surface chemistry, colloids, nanometals and nanometal oxides, micelle formation, synthesis of colloids (Braggs Method), chemical and biological methods of preparation of nanometals and metal oxides, stabilization of colloids and nanomaterials by stabilizing agents. Adsorption isotherm (Freundlich and Langmuir), BET equation (no derivation), Applications of colloids and nanomaterials in catalysis, medicine and sensors.

Textbooks:

1. Engineering Chemistry, Jain and Jain, 16th Edition, 2013, Dhanpatrai.
2. Engineering Chemistry, K. N. Jayaveera, G. V. Subba Reddy and C. Ramachandraiah, First Edition, 2013, McGraw Hill Higher Education.
3. Peter Atkins, Julio de Paula and James Keeler, Atkins' Physical Chemistry, 10/e, Oxford University Press, 2010.

Reference Books:

1. H.F.W. Taylor, Cement Chemistry, 2/e, Thomas Telford Publications, 1997.
2. D.J. Shaw, Introduction to Colloids and Surface Chemistry, Butterworth-Heinemann, 1992.
3. Text book of Polymer Science, Fred W. Billmeyer Jr, 3rd Edition.

UNIT-I

1.1 Source of water:

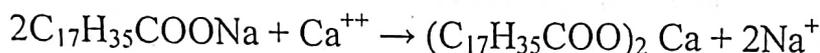
Surface water and ground water are the main sources of water. The surface water can be further classified into four major sources.

1. Rain water
2. River water
3. Lake water
4. Sea water

1.2 Hard water and Soft water:

1. Hard water :

Water, which does not produce lather with soap and produces white scum is called hard water. This is due to the presence of dissolved Ca and Mg salts.

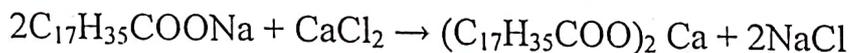


2. Soft water:

Water, which produces lather readily with soap solution is called soft water.

1.3 Hardness of water:

Hardness is the property or characteristics of water, which does not produce lather with soap. Hardness can be detected by treating water with soap.



1.3.1 Types of Hardness:

Hardness of water is two types:

- i) Temporary hardness
- ii) Permanent hardness

1.3.2 Temporary hardness (or) Carbonate hardness: This is due to the presence of bicarbonate of calcium and magnesium in water. This can be removed by boiling the water. When water is boiled the soluble bicarbonate of calcium and magnesium are decomposed to insoluble carbonates or hydroxide.



1.3.3 Permanent hardness of water (or) Non-Carbonate hardness : This is due to the presence of presence of sulphates and chlorides of calcium and magnesium. $CaCl_2$, $CaSO_4$, $MgCl_2$, $MgSO_4$, are responsible for permanent hardness of water.

1.3.4 Measurement of Hardness: The hardness is measured in milligram per litre. It is usually expressed in terms of $CaCO_3$ equivalents per litre. The reason for choosing $CaCO_3$ as

standard is because its molecular weight is 100 and equivalent weight is 50, which is easy for calculation and it is the most insoluble salt in water.

$$\begin{aligned} \text{CaCO}_3 \text{ equivalent} &= \frac{\text{Weight of the salt}}{\text{Molecular weight of the salt}} \times 100 \\ &= \frac{\text{Weight of the salt}}{\text{Equivalent weight of the salt}} \times 50 \end{aligned}$$

Temporary hardness = Hardness due to $\text{Ca}(\text{HCO}_3)_2$ + Hardness due to $\text{Mg}(\text{HCO}_3)_2$

Permanent hardness = Hardness due to CaCl_2 + Hardness due to CaSO_4 + Hardness due to MgCl_2 + Hardness due to MgSO_4

Total hardness = Temporary hardness + Permanent hardness

1.3.5 Units of hardness: The following are the common units used in hardness measurements.

1. Parts per million (ppm): It is the parts of calcium carbonate equivalent hardness per 10^6 parts of water

(or)

1 ppm = 1 part of CaCO_3 equivalent hardness in 10^6 parts of water.

2. Milligrams per litre (Mg/L): It is the number of CaCO_3 equivalent hardness in one litre of water

(or)

Mg/L = 1 mg of equivalent hardness per litre of water.

3. Degree clark: 1°Clark = 1 part of CaCO_3 equivalent hardness per 70,000 parts of water.

4. Degree French: 1°Fr = 1 part of CaCO_3 equivalent hardness in 10^5 parts of water

Table. 1 Molecular weight of some hardness producing salts

Hardness Producing salt	Molecular weight	Equivalent weight
$\text{Mg}(\text{HCO}_3)_2$	146	73
$\text{Ca}(\text{HCO}_3)_2$	162	81
MgCl_2	95	47.5

MgSO ₄	120	60
CaCl ₂	111	55.5
CaSO ₄	136	68
Mg(NO ₃) ₂	148	74

Exercise Problems:

1. Calculate temporary permanent and total hardness of a sample of water containing Ca(HCO₃)₂ = 32.4mgL⁻¹, Mg(HCO₃)₂ = 29.2mgL⁻¹, CaSO₄ = 13.5mgL⁻¹, CaCl₂ = 22.2mgL⁻¹.

Name of the hardness producing salt	Amount in Mgs/lit	Molecular weight	Amounts equivalent to CaCO ₃
Ca(HCO ₃) ₂	32.4	162	$\frac{32.4 \times 100}{162} = 20\text{mgs/lit.}$
Mg(HCO ₃) ₂	29.2	146	$\frac{29.2 \times 100}{146} = 20\text{mgs/lit.}$
CaSO ₄	13.6	136	$\frac{13.6 \times 100}{136} = 10\text{mgs/lit.}$
CaCl ₂	22.2	111	$\frac{22.2 \times 100}{111} = 20\text{mgs/lit.}$

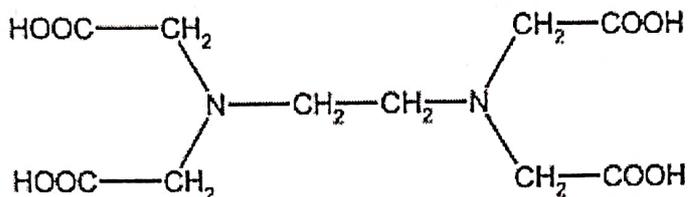
$$\begin{aligned} \text{Temporary hardness} &= \text{Hardness due to Ca(HCO}_3)_2 + \text{Hardness due to Mg(HCO}_3)_2 \\ &= 20 + 20 = 40 \text{ mgs/lit.} \end{aligned}$$

$$\begin{aligned} \text{Permanent hardness} &= \text{Hardness due to CaSO}_4 + \text{Hardness due to CaCl}_2 \\ &= 10 + 20 = 30 \text{ mgs/lit.} \end{aligned}$$

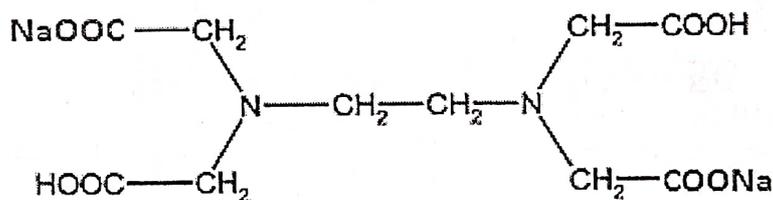
$$\begin{aligned} \text{Total hardness} &= \text{Temporary hardness} + \text{Permanent hardness} \\ &= 40 + 30 = 70 \text{ mgs/lit.} \end{aligned}$$

PRINCIPLE: The hardness of water is generally due to the presence of soluble salts of calcium and magnesium. EDTA (ethylene diamine tetra – acetic acid)used as complexing agent.

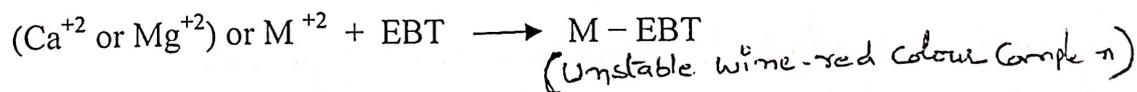
Structure of EDTA



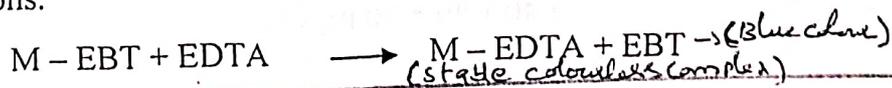
Since EDTA is insoluble in water, the disodium salt of EDTA is used as complexing agent with Ca^{+2} and Mg^{+2} ions.



When Erichrome Black- T (EBT) indicator is added to the hard water sample, it forms wine red colour, unstable complex with Ca^{+2} and Mg^{+2} ions.



When this solution is titrated against EDTA solution, the colour of the complex changes from wine red to deep blue which indicates the end point, i.e., EDTA formed stable complex with Ca^{+2} and Mg^{+2} ions.



Procedure:

Preparation of solutions:

EDTA Solution: It is prepared by dissolving 3.72 g of EDTA in 1000ml of distilled water.

Standard hardwater: 1gm of pure CaCO_3 is dissolved in small quantity of dil. HCl and made upto 1000ml using distilled water. 1ml of the solution contains 1mg CaCO_3 equivalent hardness.

Buffer solution: Add 67.5gms of NH_4Cl and 570 ml of NH_3 are dissolved and the solution is made upto 1000 ml using distilled water.

EBT indicator: 0.5 gms of EBT is dissolved in 100ml of alcohol.

Experimental procedure:

Standardisation of EDTA Solution: Pipette out 50 ml of standard hard water into a clean conical flask. Add 5ml of buffer solution and 2-3 drops of EBT indicators and titrate it against EDTA solution taken in the burette. The end point is the change of colour from wine red to steel blue.

Let the volume of EDTA consumed be V_1 ml

Estimation of total hardness of water sample: Pipette out 50 ml of the given hard water sample into a clean conical flask and titrate it against EDTA as before. Let the volume of EDTA consumed be V_2 ml

Estimation of permanent hardness of water sample: Take 100 ml of the same hard water sample in a 250ml beaker. Boil it for 15 min. During boiling temporary hardness gets removed. Cool and filter the solution and make upto 100ml in a standard flask by adding distilled water.

Pipette out 20 ml of the made up solution into a clean conical flask and titrate it against EDTA as before.

Let the volume of EDTA consumed be V_3 ml

Calculations:

V_1 ml of EDTA consumed by 50 ml standard hard water

$$V_1 \text{ ml of EDTA} = 50 \text{ mg of CaCO}_3$$

$$1 \text{ ml of EDTA} = \frac{50}{V_1} \text{ mg of CaCO}_3$$

Estimation of Total hardness:

V_2 ml of EDTA consumed by 50 ml standard hard water

$$1 \text{ ml of EDTA consumed} = \frac{50}{V_1} \text{ mg of CaCO}_3$$

$$V_2 \text{ ml of EDTA} = V_2 \times \frac{50}{V_1} \text{ mg of CaCO}_3$$

$$\therefore 50 \text{ ml of sample hard water contains} = \frac{50}{V_1} \times V_2 \text{ mg of CaCO}_3$$

$$\therefore 1000 \text{ ml of sample hard water contains} = \frac{50}{V_1} \times \frac{V_2}{50} \times 1000 \text{ mg/L}$$

$$\boxed{\text{Total hardness} = \frac{V_2}{V_1} \times 1000 \text{ mg/L}} \quad - \textcircled{1}$$

Estimation of Permanent hardness:

$$50 \text{ ml of boiled water} = V_3 \text{ ml of EDTA}$$

$$1 \text{ ml of EDTA consumed} = \frac{50}{V_1} \text{ mg of CaCO}_3$$

$$V_3 \text{ ml of EDTA} = V_3 \times \frac{50}{V_1} \text{ mg of CaCO}_3$$

$$\therefore 50 \text{ ml of boiled hard water contains} = \frac{50}{V_1} \times V_3 \text{ mg of CaCO}_3$$

$$\therefore 1000 \text{ ml of sample hard water contains} = \frac{50}{V_1} \times \frac{V_3}{50} \times 1000 \text{ mg/L}$$

$$\boxed{\text{Permanent hardness} = \frac{V_3}{V_1} \times 1000 \text{ mg/L}} \quad - \textcircled{2}$$

$$\text{Temporary hardness} = \text{Total hardness} - \text{Permanent hardness}$$

$$= \frac{V_2}{V_1} - \frac{V_3}{V_1} \times 1000$$

$$= 1000 \left[\frac{V_2 - V_3}{V_1} \right] \text{ ppm}$$

1.5 Boiler Troubles:

Boilers are used for steam generation. The troubles that arise in the boilers in the boilers due to presence of impurities in the boiler feed water are called boiler troubles.

The major boiler troubles are (1) Priming and foaming (2) Boiler corrosion (3) Caustic embrittlement (4) Sludge and scale formation.

1.(a) Priming:- Priming is the process of production of wet steam. During steam production certain water droplets also get into the steam due to dissolved solid impurities in water, high level water, sudden rise of temperature, poor boiler design.

Priming can be avoided by (i) using soft water (ii) Low level water in boiler (iii) good boiler design

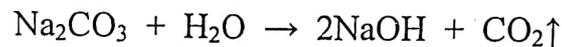
(b) Foaming:- Foaming is the formation of stable bubbles above the surface of water. It is mainly due to presence of oil and alkali in the boiler feed water.

Foaming can be avoided by (i) adding anti foaming agents like synthetic polyamides. (ii) adding coagulants like sodium aluminate, aluminium hydroxide.

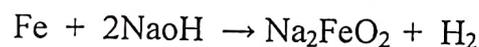
2. Caustic embrittlement:-

Caustic embrittlement is the phenomenon during which the boiler material becomes brittle due to the accumulation of NaOH in boiler.

Source of formation of NaOH are generally by using highly alkaline water (or) Na_2CO_3 present in water.



This NaOH moves into the minute hair cracks present in the inner side of boiler by capillary action and attacks the surrounding area, thereby dissolving iron of boiler as sodium ferroate (Na_2FeO_2).



This causes the embrittlement of boiler parts particularly at bends, reverts, joints etc. Causing failure of boilers.

3. Scale and sludge :-

a) Sludge : A loose and slimy precipitate formed within boiler is called Sludge. Salts like CaCl_2 , CaSO_4 , MgCl_2 , MgSO_4 , etc., are responsible for sludge formation in boilers.

Disadvantages: (i) Sludge is a bad conductor of heat. (ii) Excess of sludge formation decreases the efficiency of boiler.

Prevention: (i) using soft water (ii) Frequent blow-down operation should be carried out.

b) Scale: A hard, adhering coating on the inner walls of boilers is called scale. Salts like CaSO_4 , $\text{Ca}(\text{HCO}_3)_2$, etc., are responsible for scale formation in boilers.

Disadvantages: (i) Scale acts as a bad conductor of heat (ii) Wastage of (or) energy (iii) leading to explosion.

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Removal of scale: (i) Scale can be removed by thermal shocks (ii) using wire brush (or) scarper (iii) carbonate scale can be removal by 5-10% HCl.

PREVENTION:-

There is two treatment methods to prevent scale formation. 1) Internal treatment method 2) External treatment method.

1.6 Characteristics of drinking water:

As per the WHO and by Indian council of medical research (ICMR) the followings are the important characteristics of potable water.

1. It should be clear, colorless and odorless
2. It should be cool, pleasant to taste
3. It should be free from harmful bacteria and suspended impurities.
4. It should be free from dissolved gases like CO_2 , H_2S , NH_3 , etc., and poisonous minerals like lead, arsenic, Manganese etc.
5. Hardness should be less than 500ppm.
6. Chloride content should be less than 250ppm.
7. Fluoride content should be less than 1.5ppm.
8. Total dissolved solids (TDS) content should be less than 500ppm.
9. pH of the potable water should be 6.5 to 8.5.

1.7 Specification for drinking Water:

Water used for drinking should have certain quality. The following summaries several quality criteria and their standards for drinking water.

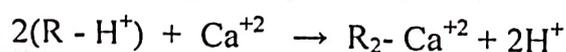
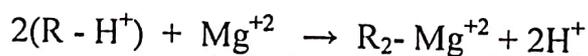
S.No	Parameter	WHO Standard in Mg/liter	ISI (or) BIS Standard in mg/liter
1	Colour, Odour & Taste.	Colourless, Odourless & Tasteless.	Colourless, Odourless & Tasteless.
2	p ^H	6.9	6.9
3	Total dissolved solids(TDS)	1500	-----
4	Dissoved Oxygen	-----	3.0
5	Chloride	250	600
6	Sulphate	400	1000
7	Nitrate	45	-----
8	Cyanide	0.02	0.01
9	Fluoride	1.5	3.0
10	Chromium	0.05	0.05
11	Lead	0.05	0.1
12	Arsenic	0.05	0.2

1.9 Ion – Exchange Process

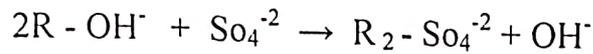
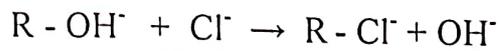
Ion – exchange resins are insoluble cross- linked long chain organic polymers.

Process : The process involves the following the following steps.

The first chamber is packed with cation exchange resin. When hard water passed through a bed of cation –exchange resin it exchange hydrogen(H⁺) ions with Ca⁺², Mg⁺², K⁺, Na⁺ etc. of hardwater.

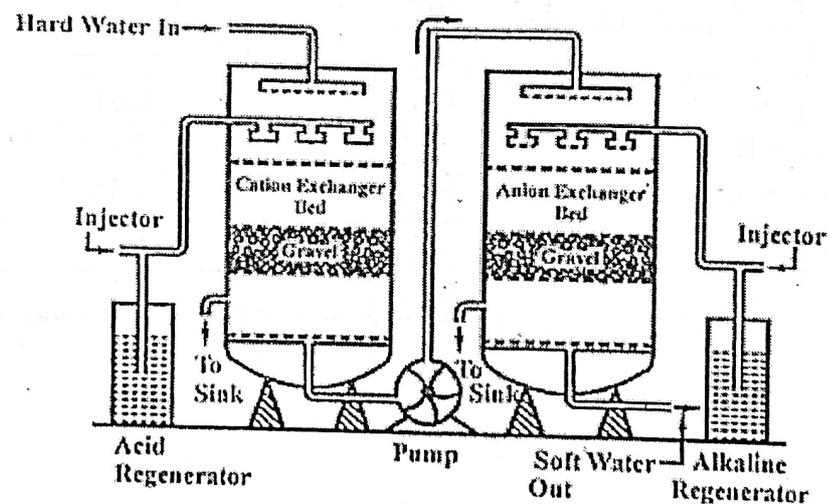


The second chamber is packed with anion exchange resin. The water coming out from first chamber contains H^+ , Cl^- , SO_4^{-2} and CO_3^{-2} ions. It is now passed through second chamber. Here it exchange OH^- ions with anions like Cl^- , SO_4^{-2} , CO_3^{-2} , HCO_3^- .



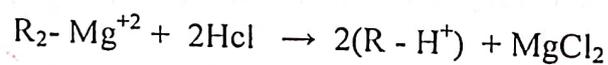
Thus hardness producing cations and anions are removed.

The H^+ ions from first chamber combines with OH^- produced from second chamber to form water.

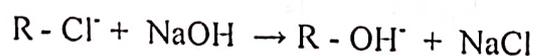


Regeneration of resins

- (i) The cation exchange resins can be regenerated by passing Dil.Hcl.



- (ii) The anion exchange resins can be regenerated by passing NaOH.



Advantages: (i) The softened water by this method completely free from salts.

(ii) Highly acidic (or) highly alkaline water also can be softened.

Dis - Advantages: (i) The experiment is very costly. (ii) Turbid water decreases the efficiency of resins.

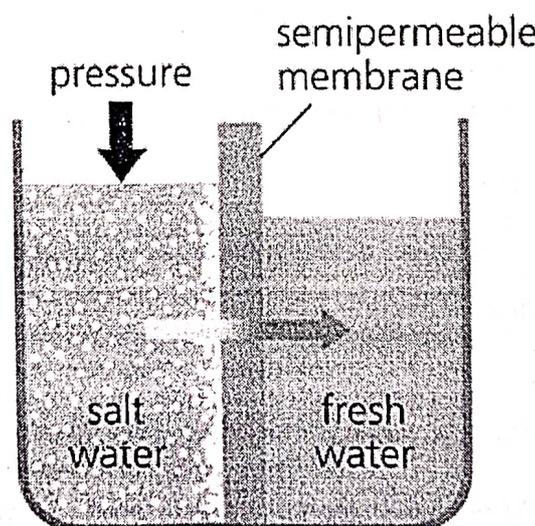
1.10 Desalination of Brackish water:

The water containing dissolved salts with a peculiar salty or brackish taste is called brackish water. The process of removing the salts from the water is known as desalination of brackish water.

1.10.1 Reverse Osmosis

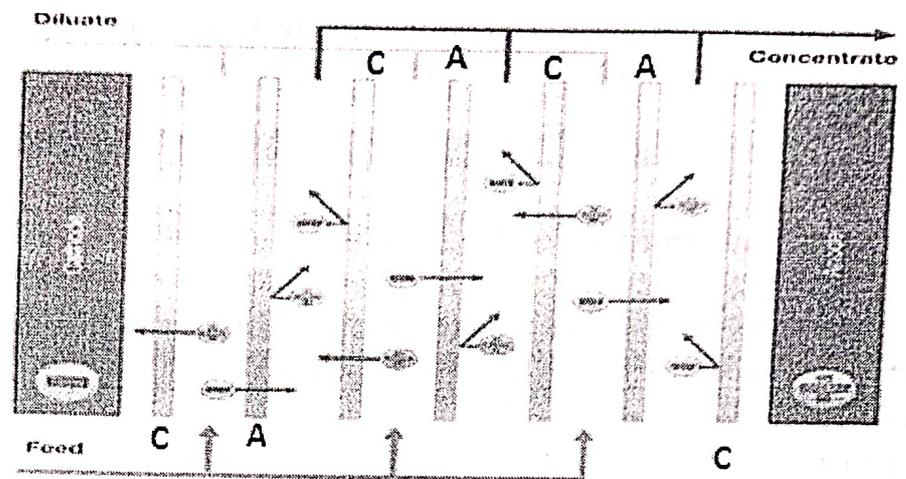
If pressure in excess of osmotic pressure is applied on the higher concentration side, the solvent flow is reversed i.e., solvent flows from higher concentration to lower concentration. This process is called reverse osmosis.

Salt water is taken as higher concentration and water is taken as solvent. If pressure is applied on the salt water, the water flows from salt water to water side.



1.10.2 Electro-dialysis:

The process of decreasing the concentration of salts in saline water using in selective membranes under the influence of direct current is called electro-dialysis.



The electro-dialysis cell consists of a series of cation permeable membrane 'C' and anion permeable membrane 'A'. Saline water is passed under pressure about $5-6 \text{ kg m}^{-2}$ between membrane pairs and electric field is applied across the two electrodes immersed in saline water. The cations ions move through 'C', while anions move through 'A'. Then fresh water produced in 'CA' is collected and the concentrated brackish water from 'AC' compartment is discharged.

1.11 Descriptive type questions

1. What is meant by carbonate and non-carbonate hardness of water? Explain with examples.
2. What is the principle of EDTA method? Describe the estimation of hardness of water by EDTA method?
3. Explain scale and sludge formation in boiler. How are they removed.
4. What are ion exchange resins? How will you purify water by resins and explain the advantages over the methods.
5. Describe the Reverse Osmosis method for desalination of water.
6. What is desalination? Describe the Electro dialysis method for desalination of water?

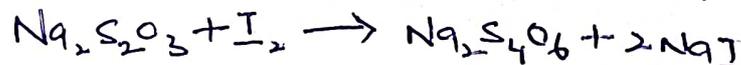
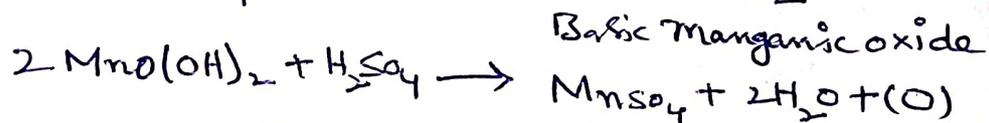
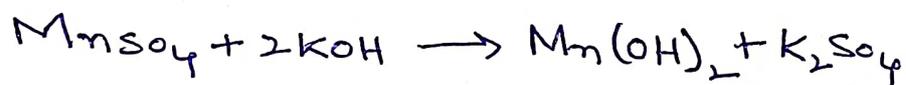
1.12 Short answer questions

1. Define Hard water and Soft water?
2. What is carbonate hardness and non- carbonate hardness?
3. What are the units expressed to hardness of water?

4. What is permanent hardness of water? mention the salts caused for the permanent hardness?
5. What is Temporary hardness of water? mention the salts caused for the temporary hardness?
6. Why Expression of hardness in terms of equivalents of CaCO_3 ?
7. What are scale and sludge?
8. What is meant by priming and foaming?
9. What is caustic embrittlement? Cause of caustic embrittlement? How it is prevented?
10. What is meant by Reverse osmosis? (Or) write the principle involved in desalination of water?
11. Define Brackish water?
12. Distinguish between soft water and (DM) demineralised water.
13. What is Electro dialysis?

Estimation of Dissolved Oxygen: (Winkler's method)

Principle: The determination of dissolved oxygen is based on the oxidation of potassium iodide by dissolved oxygen.



Procedure: 2 ml of MnSO_4 solution and 2 ml of alkaline KI solution are added to 250 ml of water sample. The bottle is shaken well for 10-15 minutes and allowed to stand for few minutes to settle precipitate. Then 2-3 ml con. H_2SO_4 is added and shaken to dissolve the precipitate. 100 ml of the solution is pipetted out from the bottle into a clean ~~dry~~ clinical flask and titrated against standard hypo solution using starch as a

Indicator. End point is disappearance blue colour

Calculation

$$\text{Volume of hypo Consumed} = V_1 \text{ ml}$$

$$\text{Normality of hypo sol.} = N_1$$

$$\text{Normality of the dissolved oxygen} = \frac{V_1 N_1}{100}$$

$$\text{Weight of dissolved oxygen per litre of water} = \frac{V_1 N_1 \times 8}{100} \text{ g}$$

$$= \frac{V_1 \times N_1 \times 8 \times 10}{100 \times 1000} \text{ ppm}$$

UNIT-II

ELECTROCHEMISTRYIntroduction

Electrochemistry is a branch of chemistry, which deals with the chemical applications of electricity. Electrochemistry deals with the chemical reactions produced by passing electric current through an electrolyte (or) the production of electric current through chemical reactions.

Cell Terminology:-

Current: Current is the flow of electrons through a wire or any conductor.

Electrode: Electrode is a material (or) a metallic rod/bar/strip which conducts electrons.

Anode: Anode is the electrode at which oxidation occurs.

Cathode: Cathode is the electrode at which reduction occurs.

Electrolyte: Electrolyte is a water soluble substance forming ions in solution, and conduct electric current.

Anode Compartment: It is the compartment of the cell in which oxidation half-reactions occurs. It contains the anode.

Cathode Compartment: It contains the cathode. It is the compartment of the cell in which reduction half-reaction occurs.

Half-cell:- Half cell is a part of cell, containing electrode and electrolytic solution. If oxidation occurs at the electrode that is called oxidation half cell. If reduction occurs at the electrode that is called reduction half cell.

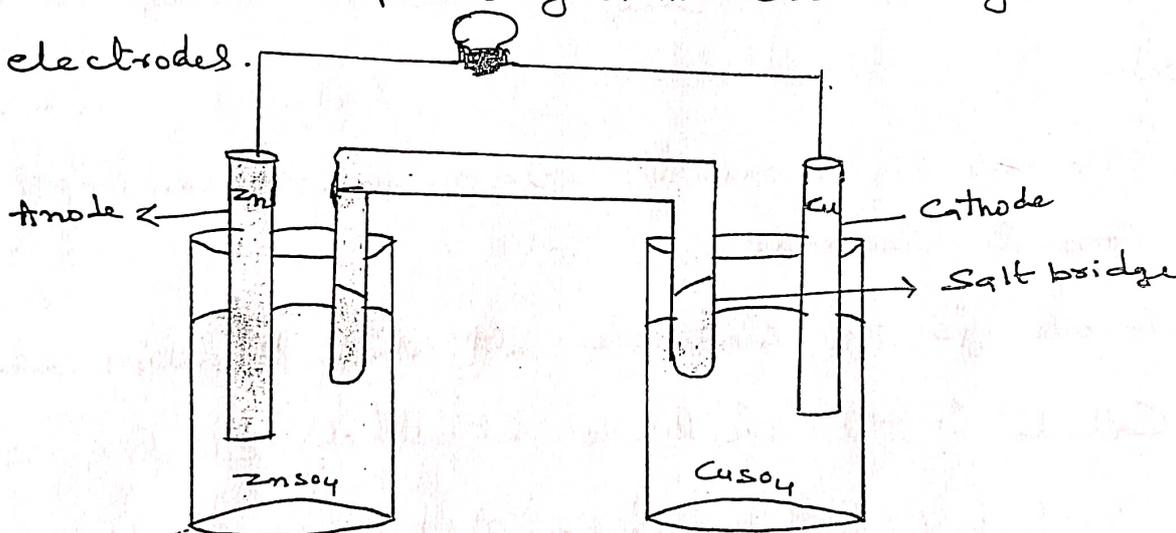
Cell: Cell is a device consisting two half cell. The two half cells are connected through one wire.

Electrochemical cell (Galvanic cell):

Electrochemical cell (or) galvanic cell is a device which converts free energy of a chemical process into electrical energy.

It is made up of two half cells. One is oxidation (or) anodic half cell and the other is reduction (or) cathodic half cell.

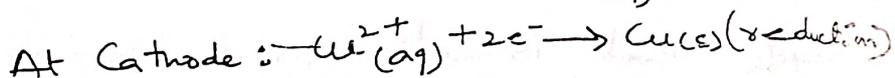
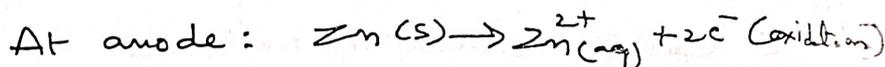
Daniel Cell is an example of galvanic cell having zinc and copper electrodes.



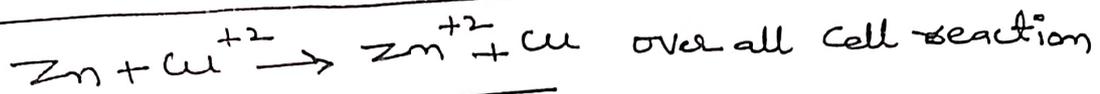
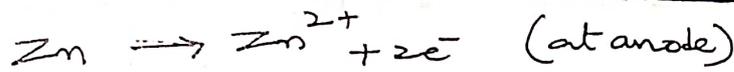
The oxidation half cell consists of Zn rod dipped in $ZnSO_4$ solution and the reduction half cell consists of Cu rod dipped in $CuSO_4$ solution.

Both the half cells connected externally by metallic conductor (wire) and internally by a bent glass tube having strong electrolyte (KCl) called salt bridge (it allows the flow of the current by completing the circuit and maintains electrically neutrality).

The flow of electrons will be externally from anode to cathode. The flow of current is due to the difference in electrode potentials of both electrodes. The EMF of the cell is measured in Volts with the help of potentiometer.



The cell reactions are



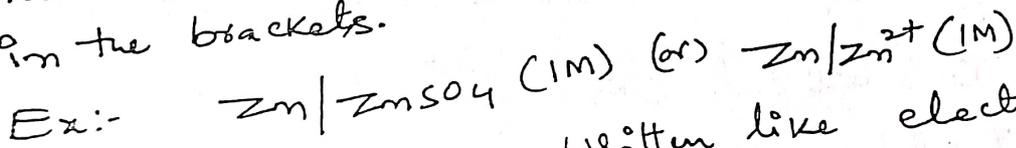
Use of Salt bridge: - It is a U-shaped tube containing saturated solution of KCl (or) NH_4NO_3 in agar-agar gel. Connects the two half cells of the galvanic cells.

- functions: -
- 1) It permits the flow of ions between the two half cells.
 - 2) It prevents mixing of the two solutions of the half cells.

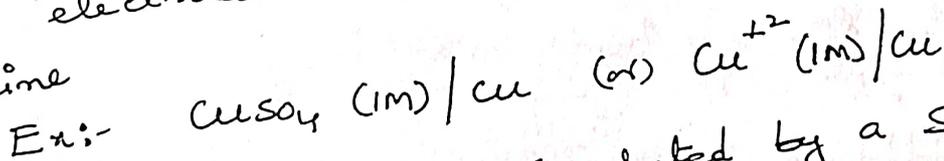
Presentation of a galvanic cell:-

A galvanic cell consists of two electrodes anode and cathode. The Anode is written on the left hand side while cathode is written on the right hand side.

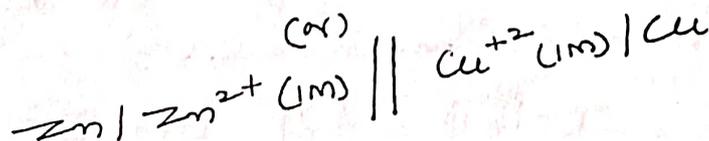
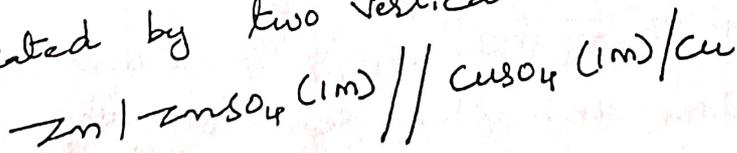
The anode must be written like electrode metal first and then electrolyte; concentration of electrolyte is indicated in the brackets.



The cathode must be written like electrolyte is first and then electrode metal. These two are separated by a vertical line.

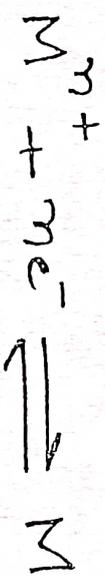


The two half cells are separated by a salt bridge which is indicated by two vertical lines.



Nernst Equation (for electrode potential)

Consider the following redox reaction



For such a redox reversible reaction, the free energy change (ΔG) and its equilibrium constant (K) are inter related as

$$\Delta G = -RT \ln K + RT \ln \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$= \Delta G^\circ + RT \ln \frac{[\text{Products}]}{[\text{Reactants}]} \quad \text{--- (1)}$$

G° = standard free energy change

The above equation (1) is known as Van't Hoff isotherm.

A decrease in free energy ($-\Delta G$) in the above reaction will produce electrical energy. In the cell, if the reaction involves transfer of 'n' number of electrons, then 'nF' Faraday of electricity will flow. If 'E' is the emf of the cell, then the total electrical energy (nEF) produced in the cell is

$$-\Delta G_1 = nEF \text{ or } -\Delta G^\circ = nE^\circ F \quad \text{--- (2)}$$

Comparing equation (1) and (2), it becomes

$$-nEF = -nE^\circ F + RT \ln \frac{[M]}{[M^{n+}]} \quad \text{--- (3)}$$

Dividing the above equation (3) by $-nF$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]} \quad \left[\begin{array}{l} \text{activity of solid metal} \\ [M] = 1 \end{array} \right]$$

In general,
$$E = E^\circ - \frac{RT}{nF} \ln \frac{[\text{Products}]}{[\text{Reactants}]}$$

(4)

$$E = E^\circ + \frac{RT}{nF} \ln [M^{n+}]$$

(5)

$$E = E^\circ + \frac{2.303RT}{nF} \log [M^{n+}] \rightarrow (4)$$

When, $R = 8.314 \text{ J/mole}^\circ\text{C}$
 $F = 96500 \text{ coulombs}$
 $T = 298 \text{ K (25}^\circ\text{C)}$
 Then equation (4) becomes

$$E = E^\circ_{red} + \frac{0.0591}{n} \log [M^{n+}] \rightarrow (5)$$

In general
$$E = E^\circ_{red} + \frac{0.0591}{n} \log C$$

For oxidation potential,
$$E = E^\circ_{oxi} - \frac{0.0591}{n} \log [M^{n+}] \rightarrow (6)$$

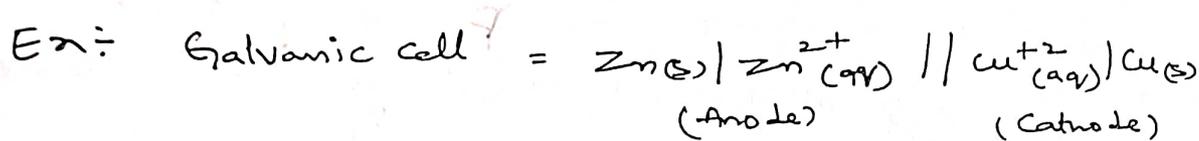
The above equations 5 & 6 are known as "Nernst equation for electrode potential".

Cell Potential (or) EMF (Electromotive force)

Electromotive force (or) Cell potential is defined as
"The potential difference between two electrodes of a cell."

EMF of a cell = Standard reduction potential of right hand side
- Standard reduction potential of left hand side electrode

$$E_{\text{cell}}^{\circ} = E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ} \quad (\text{or}) \quad E_{\text{R.H.S}}^{\circ} - E_{\text{L.H.S}}^{\circ}$$



$$E_{\text{cell}}^{\circ} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{Zn}/\text{Zn}^{2+}}^{\circ} \quad (\text{or}) \quad E_{\text{Cathode}}^{\circ} - E_{\text{Anode}}^{\circ}$$

Calculation of Cell Potential :-

Calculation of cell potential at standard conditions at 1M concentration and 1 atm pressure at 25°C is carried out under the following steps.

Procedure: Step 1 :- Write the oxidation and reduction half-reactions for the cell

Step 2 :- Look up the reduction potential $[E_{\text{red}}^{\circ}]$ for the reduction half reaction.

Step 3 :- Look up the reduction potential (or) oxidation potential for the oxidation half reaction. The oxidation potential = $E_{\text{oxi}}^{\circ} = -E_{\text{red}}^{\circ}$

Step 4 :- Add the two half-cell potentials to get the overall cell standard cell potential $\Rightarrow E_{\text{cell}}^{\circ} = E_{\text{Cathode}}^{\circ} - E_{\text{Anode}}^{\circ}$

$$E_{\text{cell}}^{\circ} = E_{\text{reduction}}^{\circ} - E_{\text{oxidation}}^{\circ}$$

$$\begin{aligned} \Rightarrow \text{only for Cell Potential} &= E_{\text{cell}} = E_{\text{red}} + [E_{\text{oxi}}] \quad (\text{or}) \quad E_{\text{cell}} = E_{\text{red}} - E_{\text{red}} \\ &= E_{\text{Cathode}} - E_{\text{Anode}} \quad (\text{or}) \\ &= E_{\text{Anode}} + E_{\text{Cathode}} \end{aligned}$$

Battery (or) Cells

A Cell :- Contains only one anode and Cathode

A Battery :- Contains several anode and Cathode

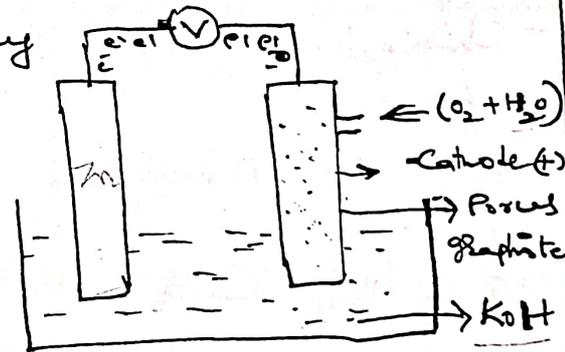
Types of Battery :-

1. Primary Battery (or) Primary cells :- [Non-Rechargeable Battery]
 These cells are not designed to be recharged. (or) Electrode reactions cannot be reversed by passing external electrical energy. Therefore these are used only once, after they become dry (or) dead Ex:- Zinc-Air Battery.

Zinc-Air Battery :-

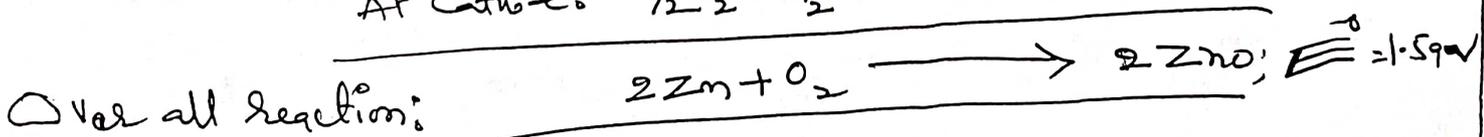
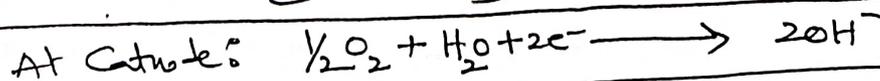
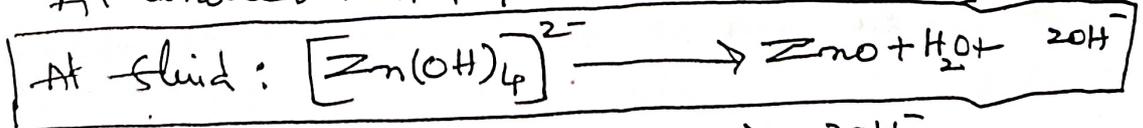
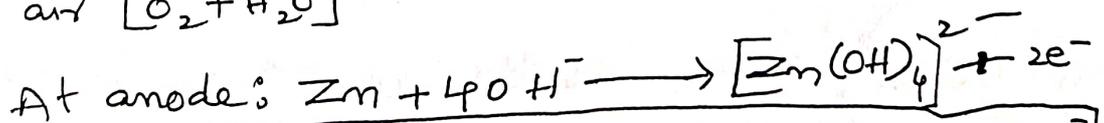
Zinc-Air Battery is an example of non-rechargeable battery and also called metal-Air battery

Construction :- Granulated zinc and with an electrolyte KOH to form a porous mass. Porous graphite acts as a Cathode.



Working :- At anode oxidation takes place in the zinc electrode by the liberation of electrons. These are transferred to Cathode. At Cathode, reduction takes place in the porous nature of electrode by passing of air $[O_2 + H_2O]$

Reactions :-



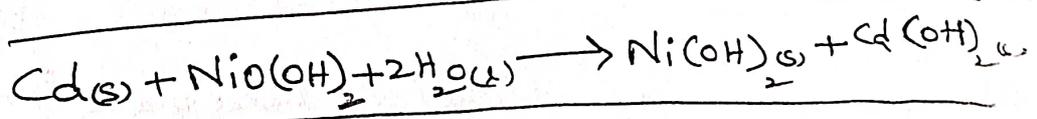
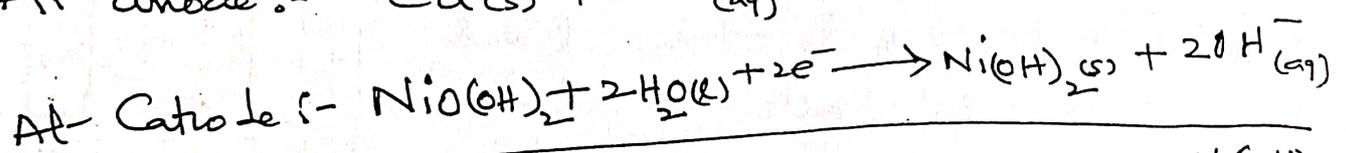
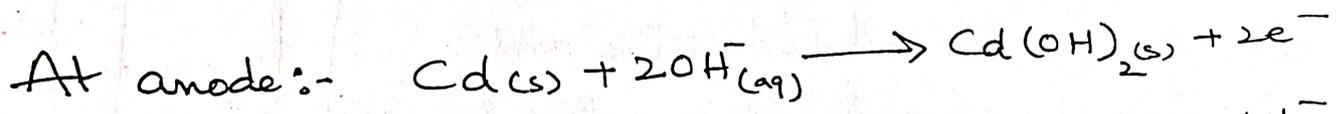
Secondary Cell (or) Battery

In Secondary batteries, the chemical reactions are reversed by passing direct electric current in opposite direction. The cells are designed for repeated use and they are able to be rechargeable.

Nickel-Cadmium Cell :-

The Nickel-Cadmium Cell (or) Ni-Cad battery is a secondary cell that produces a potential of about 1.4V which is slightly lower than that of Zn-Carbon cell.

It consists of Cadmium anode and a cathode of a plate of Ni(OH)_2 . The electrode reactions in the cell during discharge are



The cell reactions can be readily reversed since the reaction products Ni(OH)_2 and Cd(OH)_2 adhere to the electrode surface.

Application :- This battery used in (i) Portable power tools
(ii) Flash lights
(iii) CD players
(iv) electronic calculators
(v) electronic cars
(vi) Cordless electronic shavers

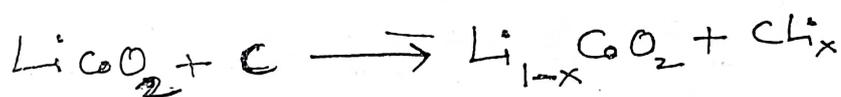
Lithium-ion batteries (or) Lithium-ion Cell :-

The movement of Lithium ions are responsible for charging & discharging.

Construction:- The positive electrode is typically made from a layer of chemical compound called Lithium-Cobalt oxide (LiCoO_2)

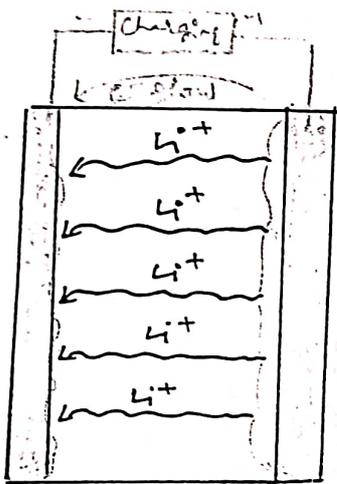
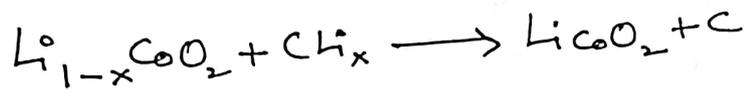
The negative electrode is made from layers of Porous Carbon (Graphite). Both the electrodes are dipped in a polymer gel electrolyte and separated by a separator, which allows the Li^+ ions to pass through.

Working: (i) Charging:- During charging Li^+ ions flow from the positive electrode (LiCoO_2) to the negative electrode (graphite) through the electrolyte.



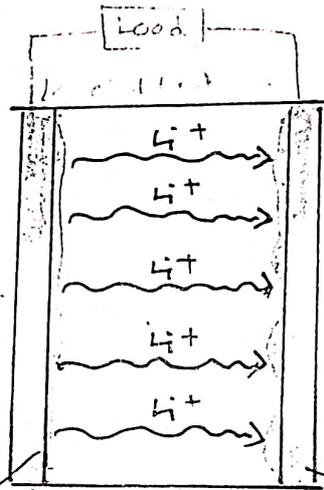
Discharging:-

During discharging, the Li^+ ions flow back through the electrolyte from negative electrode to the positive electrode. Electrons flow from the negative electrode to the positive electrode. The Li^+ ions and electrons combine at the positive electrode and deposit there as Li.



Graphite

LiCoO_2



Graphite

$\text{Li}_{1-x}\text{CoO}_2$

Advantages:- (i) These are high voltage and light weight batteries

(ii) These are smaller in size

(iii) These produce high voltage than Ni-Cd batteries

Uses:- (i) The Lithium Ion batteries are used in cell phones.

(ii) These are used in laptops,

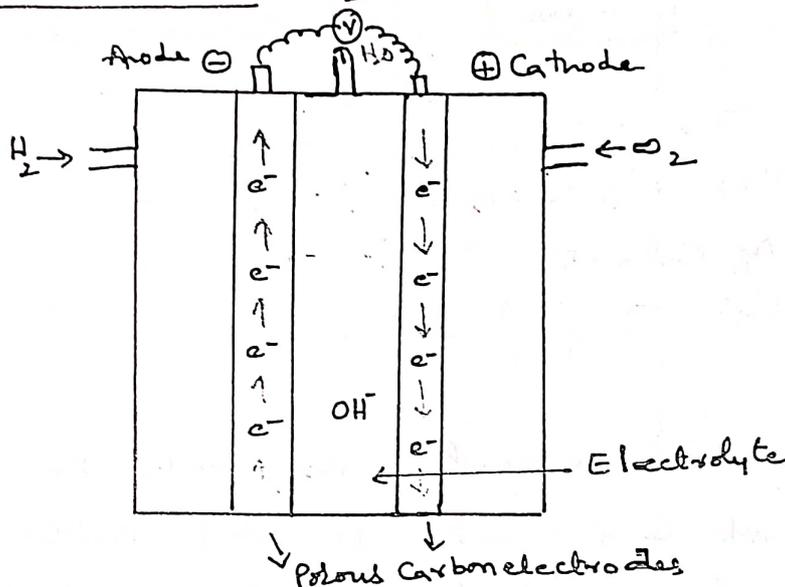
(iii) These are used in electric vehicles etc.

Fuel Cells

Definition:- Fuel cell is a voltaic cell, which converts the chemical energy of the fuels directly into electricity without combustion.

Ex:- ① Hydrogen-oxygen fuel cell ② methanol-oxygen fuel cell

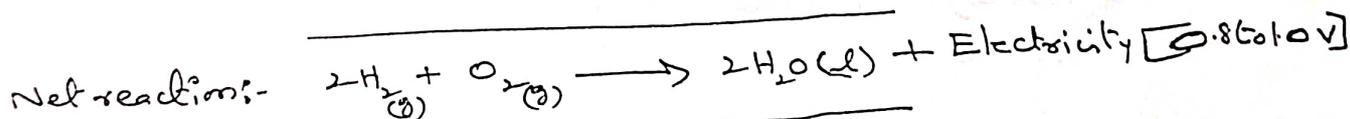
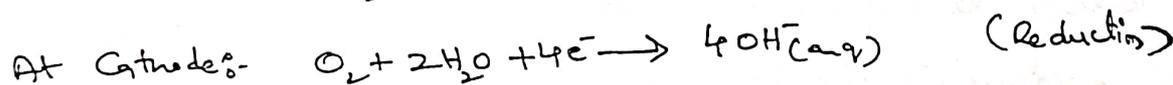
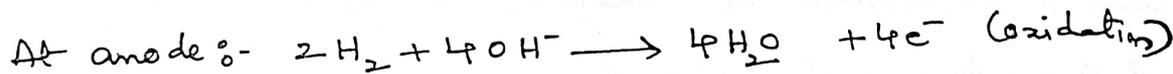
① Hydrogen-oxygen fuel cell (H₂-O₂ fuel cell):-



The cell consists of two porous electrodes anode and cathode.

These electrodes are made of graphite (compressed carbon) with small amount of Pt (or) Ag catalyst. In between the two electrodes an electrolytic solution such as KOH (or) NaOH is filled. The two electrodes are connected through the voltmeter.

Working:- The fuel hydrogen is passed through the anode compartment, where it is oxidised, the oxidant (oxygen) is passed through the cathode compartment where it is reduced.

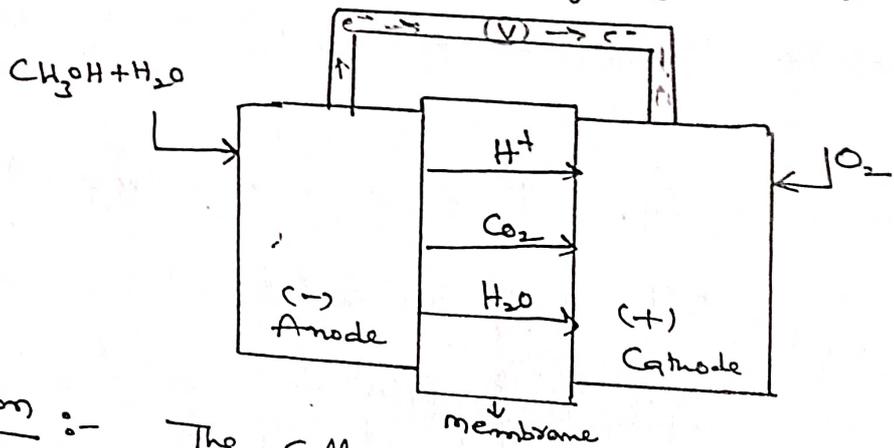


Applications:- (i) These are used as auxiliary energy source in space vehicles, military vehicles, submarines etc.

(ii) In H₂-O₂ fuel cells, the product of water is proved to be a valuable source of fresh water for astronauts.

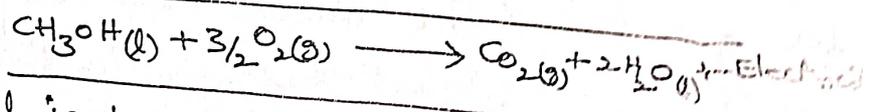
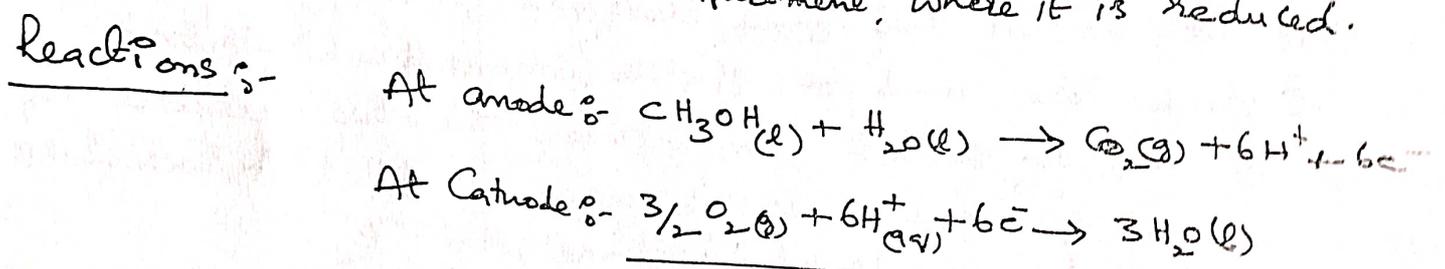
Direct Fuel Cell :-

Methanol-oxygen fuel cell is another important fuel cell. It is also called proton-exchange fuel cell.



Description :- The cell consists of two porous electrodes anode and Cathode. These electrodes are made of Nickel with small amount of Pt (or) Ag Catalyst. These two electrodes are linked by one membrane (Nafion). These two electrodes are connected through the Voltmeter.

Working :- The fuel methanol mixed with water and passed through the anode compartment where it is oxidised. The oxygen is passed through the cathode compartment, where it is reduced.



The emf of this cell is 1.21 Volts

Applications :-

- (i) Storage of methanol is much easier than H_2 gas.
- (ii) The energy density of methanol (the amount of energy contained in a given volume) is greater than H_2 gas.

SCIENCE OF CORROSION

Corrosion: The Process of decay of metal by environmental attack is called Corrosion.

Types of Corrosion:

On the basis of environment to which it is exposed, corrosion is divided into two types.

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

Dry Corrosion (or) Chemical Corrosion:

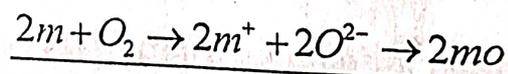
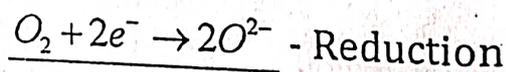
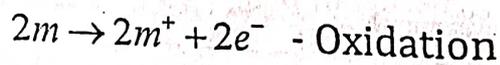
By direct chemical action of the environment on the surface of metal in absence of moisture is called Dry Corrosion (or) Chemical Corrosion.

These are 3 types:

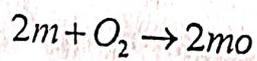
- a) Oxidation Corrosion
- b) Corrosion by other gases
- c) Liquid metal Corrosion

a) Oxidation Corrosion:

Direct attack of oxygen on the metal in the absence of moisture is called Corrosion. Alkali and alkaline earth metals are rapidly oxidized at low temperatures. At high temperatures except silver, gold all metals get oxidized.



(or)



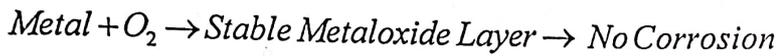
MO = Metal Oxide

Mechanism:

The nature of the metal oxide formed plays an important role in Oxidation Corrosion.

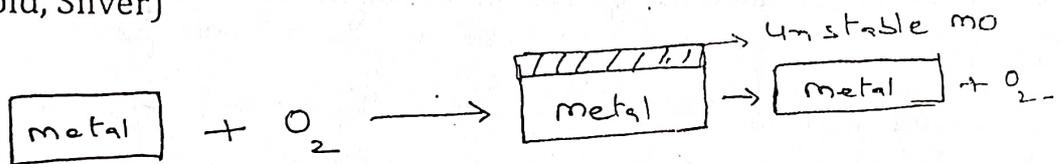
Case - I: If stable layer: If a stable metal oxide layer is formed it tightly adhere to the metal surface. It is a protective film and shields the metal from further corrosion.

Ex: Oxide film on Al, Sn, Pb, Cu, W, etc.,



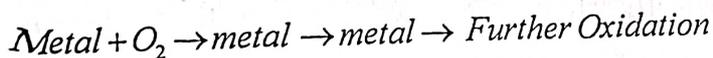
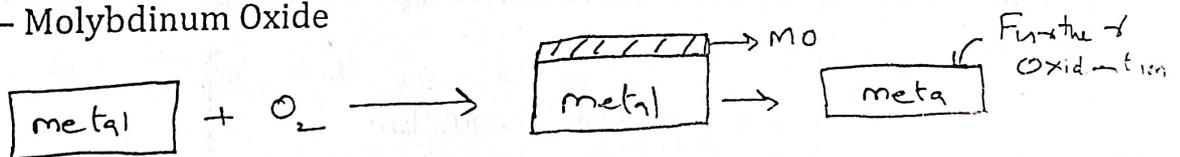
Case - II: If unstable layer: If unstable oxide film formed on the metal surface it decomposes back into metal and oxygen. Hence metal is retained and corrosion is not possible.

Ex: Au, Ag (Gold, Silver)



Case-III: If Volatile: If a volatile oxide layer is formed evaporates soon leaving the metal surface for further attack. This causes rapid and continuous corrosion.

Ex: MoO_3 - Molybdenum Oxide



Case-IV: If Porous: If porous metal oxide layer formed, it contains pores, cracks, provide access to oxygen to reach the underlying metal. Hence corrosion continuous till the entire metal converts into metal oxide.



Pilling - Bed worth rule:

This rule states that an metal oxide layer is protective, the volume of oxide layer is at least as greater as the volume of the metal. Then no corrosion occurs.

$$\text{Specific Ratio} = \frac{\text{Volume of Metal Oxide}}{\text{Volume of Metal}}$$

b) Corrosion by other gases:

The gases like SO_2 , CO_2 , Cl_2 , H_2 , F_2 , etc., cause Chemical Corrosion. The extent of corrosion depends mainly on reactivity of the gas and metal. The degree of corrosion depends on the formation of Protective (or) Non-Protective film on the metal surface.

Ex: Protective film: AgCl formed on the surface of Silver protects it from further corrosion.

Ex: Non-Protective film: Formation of volatile SnCl_4 by the attack of chlorine gas on the tin.

c) Liquid - Metal Corrosion:

When a solid metal (or) its alloy dissolution in liquid metal (or) the liquid metal penetrates into the solid metal, latter undergoes corrosion, in which metal becomes weak.

Wet Corrosion (or) Electro Chemical Corrosion

According to electro chemical theory wet corrosion takes place.

- i) When conducting liquid is in contact with metal.
- ii) When two dissimilar metals (or) dissimilar parts of same metal are in contact with an electro chemical solution.
- iii) When two metals (or) two parts of the same metals are immersed (or) partially dipped in a solution.

This type of corrosion takes place due to existence of separate Cathodic & Anodic areas.

Wet (or) Electro Chemical Corrosion is two types.

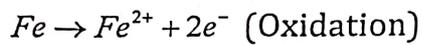
- a) Evolution of hydrogen type corrosion
- b) Absorption of oxygen type corrosion

a) Evolution of Hydrogen type Corrosion:

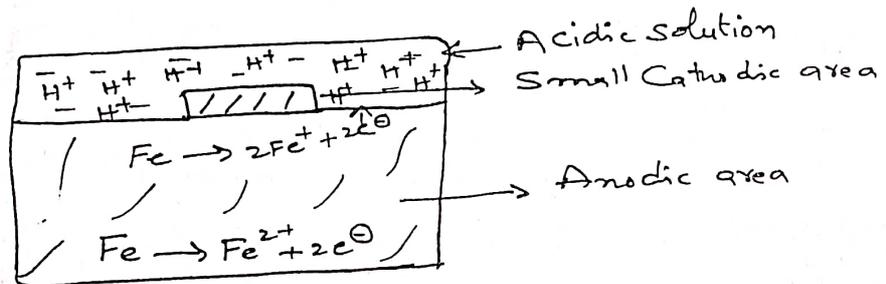
This type of corrosion takes place when electrolyte solution is acidic in nature.

When Iron (Fe) metal is immersed (or) contact with acidic medium.

At Anode: Iron metal converted into the metal ion by loss of electrons.



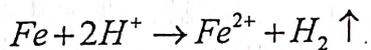
The released electrons from anode, flow through the metal from anode to cathode.



At Cathode: The H+ ions absorb the electrons and are converted into hydrogen gas.



The total reaction:



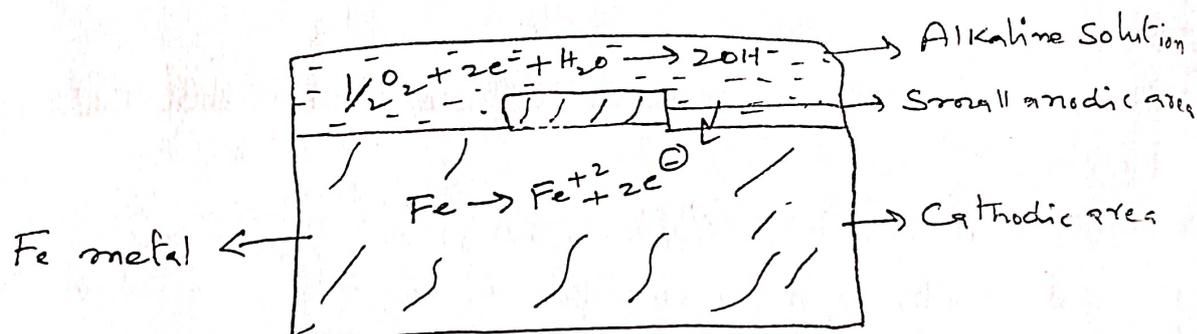
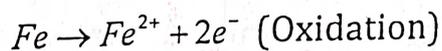
So, the metal dissolved in the solution releasing hydrogen gas. Hence metal gets corroded. This corrosion is called evolution of Hydrogen type corrosion.

b) Absorption of Oxygen type Corrosion:

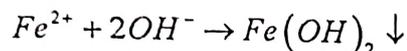
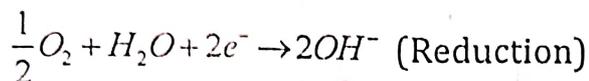
When metals are in contact with slightly alkaline (or) neutral solution with some amount of dissolved oxygen. This type of corrosion takes place.

Ex: Rusting of Iron is the absorption of oxygen type corrosion.

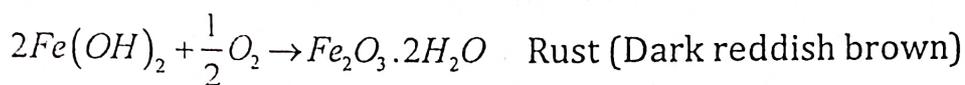
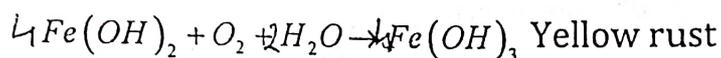
At Anode: Iron dissolves as Fe²⁺ with release of electrons



At Cathode: The liberated electrons flow from the anodic to cathodic area through iron metal where electrons are taken up by dissolved oxygen to form OH^- ions.



In case of sufficient oxygen



In case of limited oxygen: The corrosion product is Fe_3O_4

Comparison of Chemical & Electro Chemical Corrosion	
Chemical Corrosion	Electro Chemical Corrosion
1) This corrosion is due to direct chemical attack by environment.	1) It is due to the formation of large number of Anodic & Cathodic areas.
2) It is explained by absorption mechanism.	2) It is explained by Electro Chemical reactions.
3) Corrosion products are produced at the place where corrosion takes place.	3) Corrosion occurs at the anode and corrosion product at cathode.
4) It occurs both on homogenous & heterogeneous solutions.	4) It takes place only on heterogeneous processes.
5) It is slow process.	5) It is fast process.

GALVANIC CORROSION

When two dissimilar metals are connected electrically and exposed to an electrolyte, the metal possessing higher oxidation potential (or) higher in electrochemical series becomes anodic and undergoes Corrosion. This type of Corrosion is known as Galvanic Corrosion.

For example: Zn and Cu, Zn and Ag, Fe and Cu

Zn and Cu: When Zinc and Copper connected and exposed to corroding environment zinc becomes anodic because of its higher oxidation potential. Hence Zn gets corroded whereas copper undergoes reduction and is protected.

Mechanism:

At Anode: $zn \rightarrow zn^{2+} + 2e^-$ (Oxidation)

At Cathode: $cu^{2+} + 2e^- \rightarrow cu$ (Reduction)

This corrosion occurs at the anodic metal.

While cathodic part (Cu) is protected from corrosion.

Galvanic Corrosion can be prevented by

- i) Avoiding Galvanic Couple
- ii) Keeping an insulating material between two metals

Examples:

- i) A steel pipe (anode) connected to bronze plumbing.
- ii) Lead antimony solder (anode) around copper wire.
- iii) Steel screws in a brass marine hardware.

Galvanic Series:

Oxidation potentials of various metals and alloys are measured by using standard calomel electrode. When those oxidation potentials are arranged in decreasing order, a series is formed known as Galvanic Series.

The Galvanic Series

		Anodic		
1.	Mg	Anodic	13.	Brass
2.	Mg Alloy		14.	Monel
3.	Zn		15.	Silver Solder
4.	Al		16.	Cu
5.	Al Alloy		17.	Ni
6.	Mild Steel		18.	Ca Stain less steel
7.	Cast Iron		19.	18-08 Stain less steel
8.	High Ni Cast Iron		20.	18-08 Mo Steel

Pb	21. Ag
0. Sn	22. Ti
1. Icenel	23. Graphite
2. Ni-Mo-Fe alloy	24. Au
	25. Pt

Cathodic

Cathodic

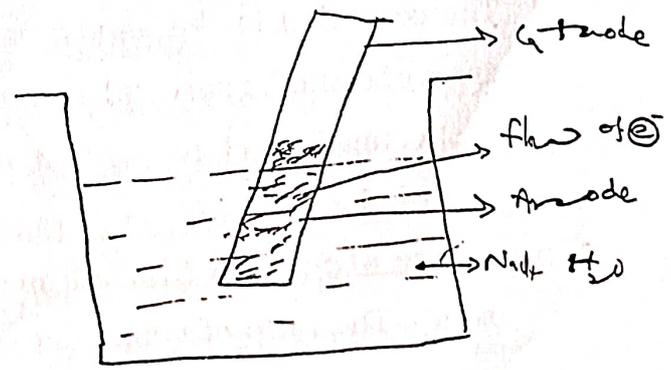
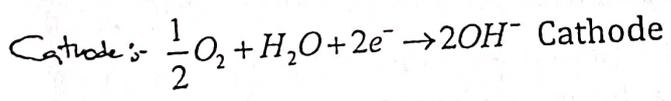
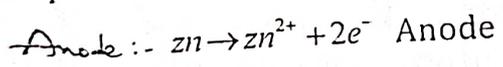
CONCENTRATION CELL CORROSION (OR) DIFFERENTIAL AERATION OF CORROSION

This kind of electro chemical corrosion is due to the formation of concentration cell formed by the variations of concentration mainly oxygen (or) any electrolyte on the surface of the base metal.

The most common type of concentration cell corrosion is differential aeration corrosion. Which occurs when one part of metal is exposed to different air concentration from other part. This causes a difference in potentials between the different areas. Poor oxygenated metallic part becomes anodic and undergo oxidation well oxygenated part act as cathodic in nature.

Example: Zinc metal partially dipped in brakish water (Nacl + H₂O)

The zinc rod above the solution is more oxygenated and hence is cathode. Whereas parts immersed have less access to oxygen and it acts as anode. Hence a difference of potential is developed on the same metal and the flow of electrons takes place from anode producing metal ion or corrosion.



Factors influencing Corrosion

The rate of corrosion mainly depends on

- a) The nature of the metal
- b) The nature of the environment

A) Nature of the metal

i) Position in Galvanic Series: The rate and extent of corrosion depends on the difference in their positions in the galvanic series when a pair of metals / Alloy are considered. [When two metals (or) alloys are in contact with conducting medium, then the metal at a higher galvanic series is more active towards corrosion].

ii) Over Voltage: The decrease in hydrogen over voltage of a metal increase the rate of corrosion. For example: If Zn metal is dipped in 1N H_2SO_4 Corrosion takes place with evolution of hydrogen gas. But, when few drops of $CuSO_4$ solution are added Zn gets corroded rapidly. The initial rate of corrosion slow because of high hydrogen over voltage of Zn which is 0.70V. After adding $CuSO_4$ some copper gets deposited on Zn metal forming cathodes and the hydrogen over voltage becomes 0.33 V. Thus the decrease in over voltage enhance the corrosion of metal.

iii) Relative areas of Anode and Cathode: The rate of corrosion depends on the small anodic area and large cathodic area. The large cathodic area, the demand for electrons will be more and hence the greater the rate of corrosion of the anodic area.

(or)

The corrosion in the anodic part is directly proportional to the ratio of areas of cathodic part and anodic part.

Ex: A small steel pipe fitted to a large copper tank undergoes rapid corrosion.

iv) Nature of Surface film: All metals produce a thin surface film of their oxides. The ratio of volume of metal oxide to the volume of the metal is

called Specific Volume Ratio. [S.V.R]. If the Specific Volume Ratio is more the corrosion is less.

Forex: Ni, Cr and W are having 1.6, 2.0 and 3.6 specific volume ratios. Hence the rate of corrosion for (W) tungsten is least even at high temperature.

v) **Purity of the Metal:** The rate and tendency of corrosion increase with increase in exposure and extent of the impurities. The corrosion of metal is low when its purity is at high.

Ex: Zn metal containing impurities such as Pb (or) Fe undergoes corrosion due to formation of local electrochemical cells.

vi) **Physical state of metal:** Metals in the form of granules, crystals etc, undergo greater corrosion. The smaller the size greater will be corrosion, because they undergo greater stress.

vii) **Passive Character of Metal:** Some metals like Ti, Al, Cr, Ni and Co show passive due to formation of non-porous thin and protective film of self-healing nature. Passivity of metal decrease corrosion rate.

For ex: Corrosion resistance of stainless steel due to passive character of Chromium present in steel.

viii) **Volatility of corrosion products:** If the corrosion products is volatile, the underlying metal is exposed further and cause severe corrosion.

Ex: Corrosion product of MoO_3 is volatile.

ix) **Solubility of Corrosion Product:** If the oxide film formed as corrosion product is soluble in contact medium then the corrosion is rapid.

B) **Nature of the Environment (Corroding Medium):**

i) **Temperature:** An increased temperature enhance the rate of corrosion.

ii) **Humidity of air:** The humidity of air is the deciding factor in atmospheric corrosion "Critical Humidity". It is defined as "the relative humidity above which atmospheric corrosion rate of metal increases sharply". The value of critical humidity depends on nature of metal and corrosion product.

In humidity environment (a) The rate of corrosion is higher due to gases and vapours present in atmosphere furnish water to the electrolyte, essential to establish an electro chemical corrosion cell. (b) The oxide film formed, has tendency to absorb moisture which creates another electrochemical cell corrosion.

iii) **Presence of impurities in atmosphere:** Presence of corrosion gases such as SO_2 , CO_2 , H_2S , O_2 etc., in atmosphere increases acidity and high electrical conductivity which causes severe corrosion.

iv) **Presence of suspended particles in atmosphere:** Presence of suspended particles like NaCl , $(\text{NH}_4)_2\text{SO}_4$ absorb moisture and acts as strong electrolyte there by enhancing electro chemical corrosion. If charcoal present absorbs sulphur gases and moisture and slowly increase the rate of corrosion.

v) **Influence of pH:** The corrosion is higher in acidic media than basic and neutral media.

Ex: It undergoes corrosion more rapidly in acidic media but undergoes minimum corrosion in alkaline medium ($\text{pH} = 11$)

vi) **Nature of ions present in the environment:** If the ions present chlorides, silicates etc., enhance the rate of corrosion.

For ex: Chlorides present in the medium destroys the protective film on the surface of metal.

If silicates present, they inhibit further corrosion forming insoluble silicates on the metal surface.

Control of Corrosion: (Protection Against Corrosion)

Following are some methods for control of corrosion.

i) **Cathodic Protection:** In this method, the metal to be protected is forced to act as cathode, thus avoiding corrosion. It is two types.

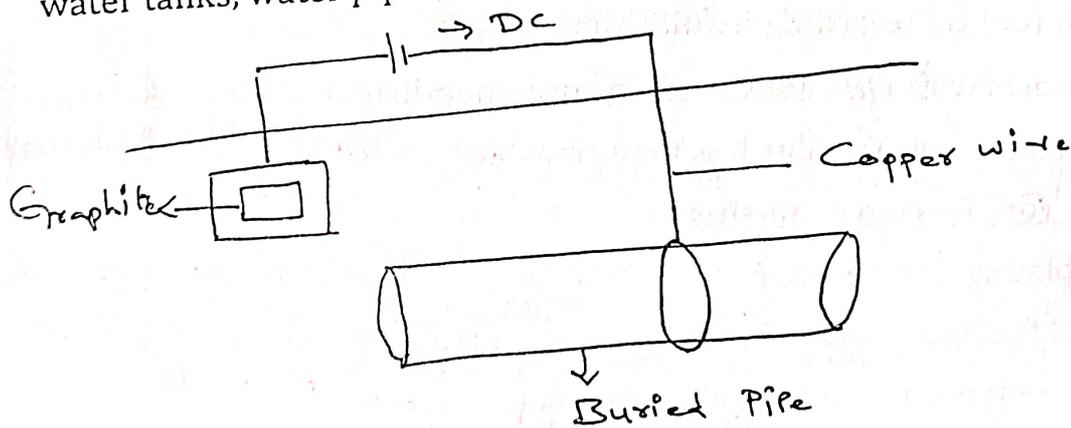
i) **Sacrificial anodic protection:** In this method the metal (or) metallic structure is protected by a more anodic metal which gets corroded. The more active metal (acting as anode) is called sacrificial anode. The

corroded sacrificial metal is replaced by a fresh one when consumed completely.

Ex: Mg, Al, Zn and their alloys are used as a Sacrificial anodes.

Protection of buried pipe lines, underground cables, marine structures etc., is made by this method.

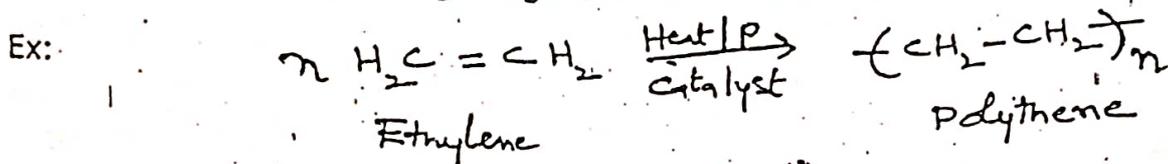
ii) Impressed current Cathodic protection: In this method, an impressed current is applied in opposite to the corrosion current to nullify and convert the corroding metal from anode to cathode. Now the metal become cathodic, it is protected from corrosion. The commonly used anodic materials are graphite, carbon steel, scrap, iron and platinum.
Ex: This type of cathodic protection is applied to open water box coolers, water tanks, water pipes, marine pipes, etc.,



UNIT-III

POLYMERS

Definition: Polymers are macro molecules (giant molecule (or) High molecular weight compound) made by linking a large number of small molecules.



Poly = Many Mer = Parts

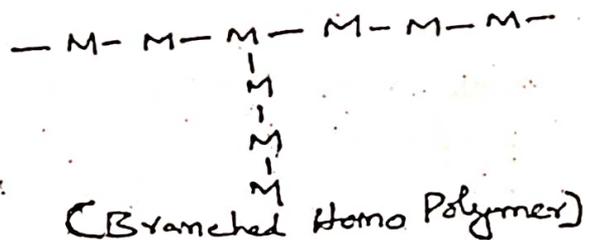
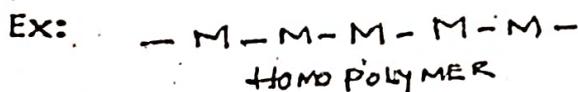
The repeating units in a polymer are called monomers

Polymerisation: The reaction by which monomer units combine to form polymers is termed as polymerization.

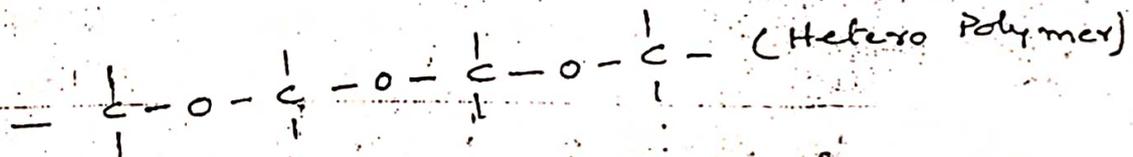
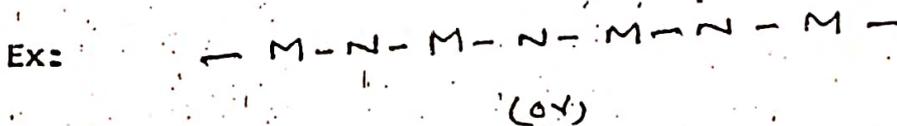
Degree of polymerization: The number of repeating units in a chain is known as "Degree of Polymerisation".

Nomenclature of Polymer

a) **Homo polymer:** Polymer made out of same (or) identical monomer units are known as homo polymer.



b) **Hetero polymer:** Polymers are made from different types of monomers are hetero polymer (or) Co-Polymer.

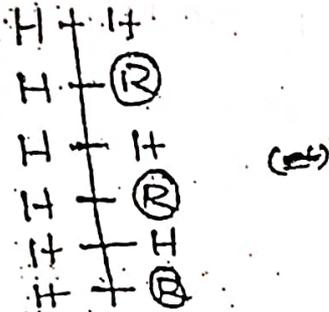


Tacticity: It is the Orientation (or) arrangement of functional groups in polymer in an orderly (or) disorderly manner with respect to main chain is called tacticity.

There are mainly three kinds of tacticity.

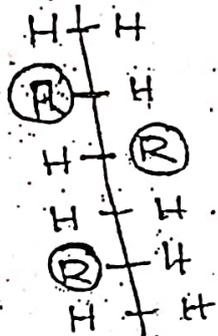
a) **Isotactic polymer:** If the functional groups are arranged on the same side of the chain. It is called isotactic polymer.

Ex:

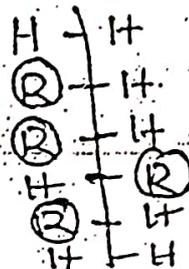


b) **Syndiotactic polymer:** If the functional groups are arranged in alternative fashion in the main chain. It is called syndiotactic polymer.

Ex:

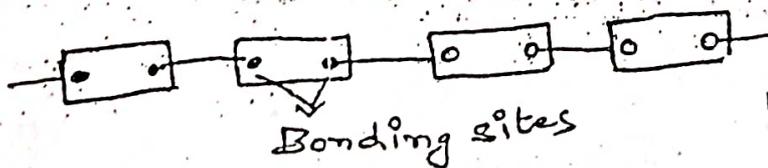


c) **Atactic polymer:** If the functional groups are arranged at random around the chain. It is called atactic polymer.



Functionality: The number of bonding sites present in a monomer is called as its functionality.

Every monomer must have minimum two bonding sites for polymerization process.



Polymerisation:

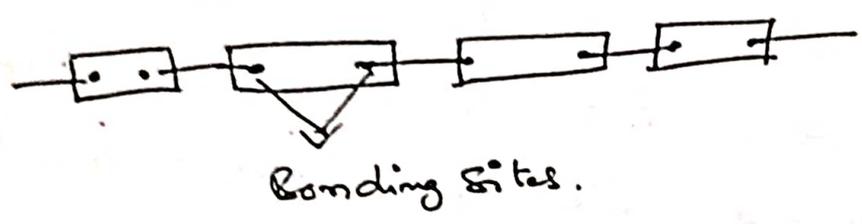
The process (or) chemical reaction by which the no. of small molecules to form a big polymer is called polymerization.

Monomer :-

Monomer is a micro molecule (small molecule) which combines with each other to form a polymer.

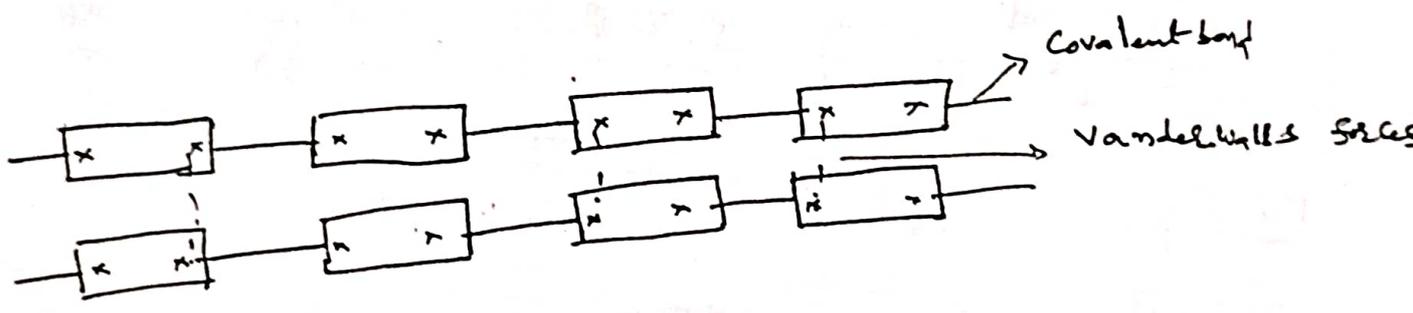
Functionality :-

The number of bonding sites (or) reactive sites (or) functional groups, present in a monomer is known as its functionality.



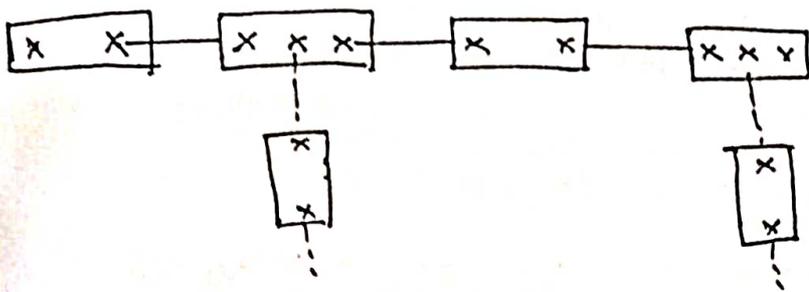
Bi-functional monomers :-

Bi-functional monomers mainly form linear (or) straight chain polymer



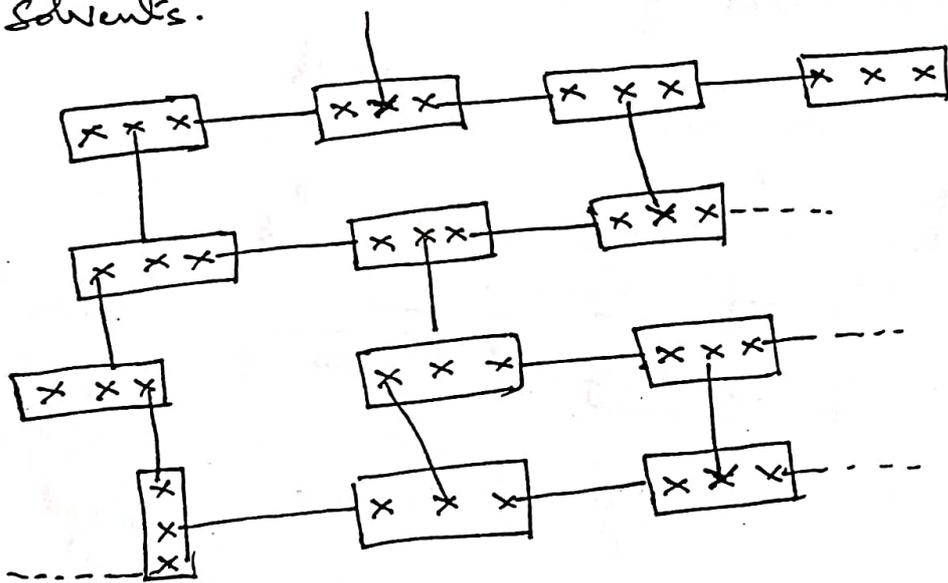
Mixed functional monomers :-

When a trifunctional monomer is mixed with a bifunctional monomer, they form branched chain polymer.



3. Poly functional monomers :

Poly functional monomers form cross-linked polymer.
 (Three-dimensional network polymer). All the monomers in the polymer are connected to each other by strong covalent bonds. This type of polymers are hard and brittle and possess very high strength and heat resistance and also insoluble in almost all organic solvents.



Polymerisation :-

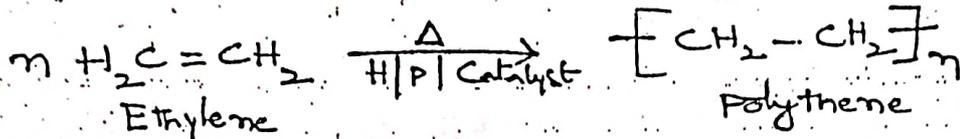
The process (or) chemical reaction by which the no. of small molecules to form a big polymer is called Polymerisation.

Types of polymerization: (i) Addition polymerization (ii) Condensation polymerization (iii) Co-polymerisation.

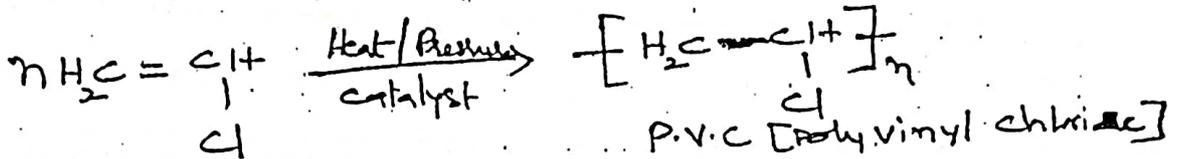
Addition polymerization (or) chain polymerization:

This type of polymerization several bi functional monomers combine to form polymer by addition reaction with out elimination of any byproduct.

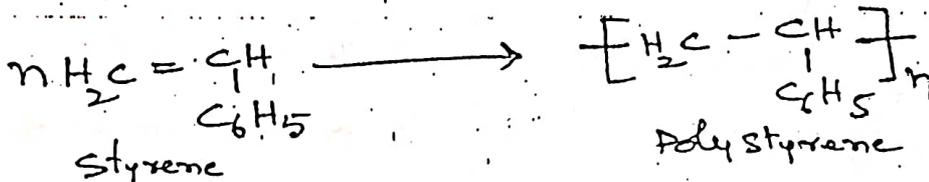
Ex: (i) Polymerisation of ethylene:



Ex: (ii) Polymerisation of vinyl chloride:



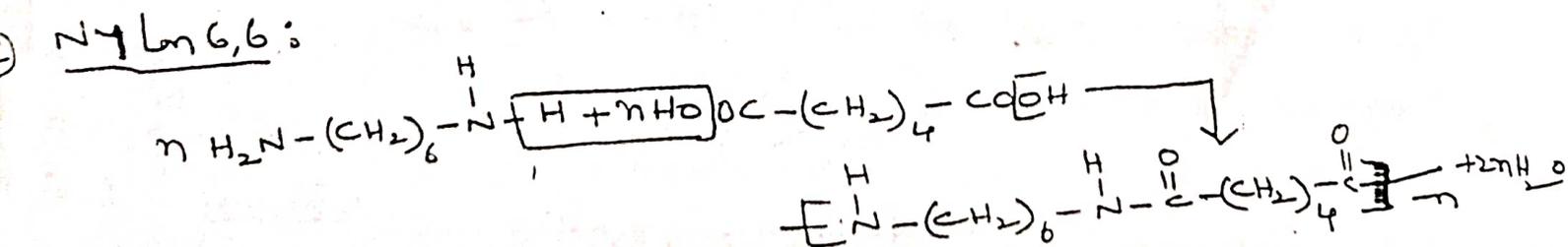
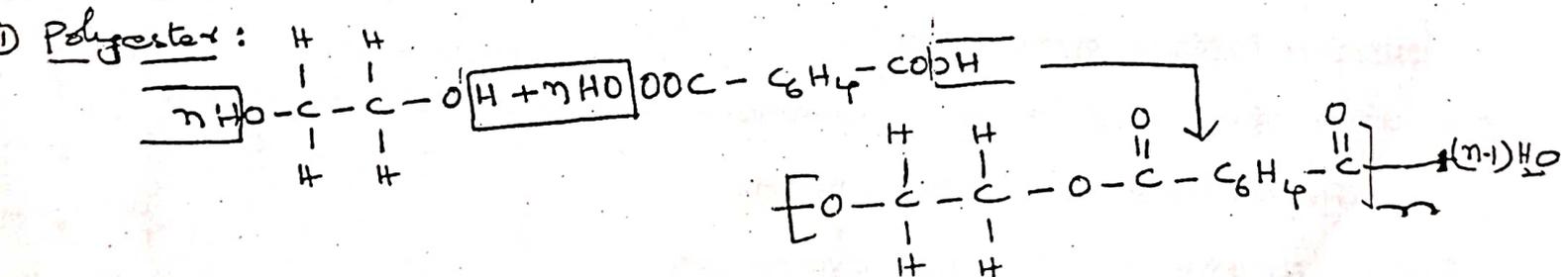
Ex: (iii) Polymerisation of styrene:



Condensation polymerization (or) Step wise polymerization:

In condensation polymerization, the polymer will form by step-wise reaction between the same (or) different polar group containing monomers with elimination of small molecules like H₂O and HCl and NH₃.

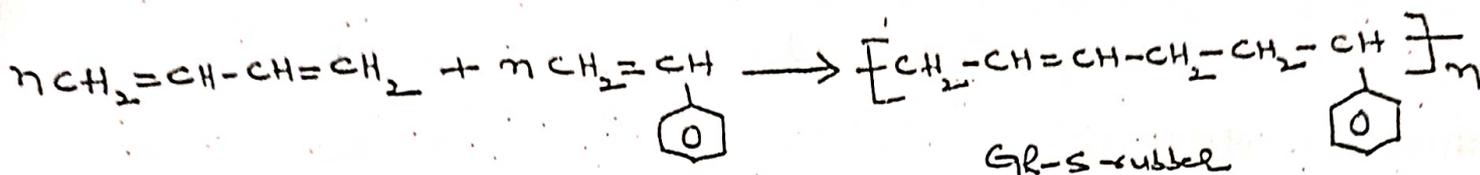
Ex: Nylon6,6, Novolac, Bakelite, polyester.



CO-Polymerisation:

When two (or) more different types of monomers undergo simultaneous polymerization. It is called co-polymerisation.

Ex: GR-S rubber (or) styrene rubber (or) IBUNA-S Rubber



Addition polymerisation	Condensation polymerisation
<ol style="list-style-type: none">1. Addition polymerisation takes place between same monomer units2. This reaction proceeds a fast manner3. No byproduct is formed.4. High molecular weight polymer is formed5. Thermoplastics are produced6. Homo-chain polymer is obtained	<ol style="list-style-type: none">1. Condensation polymerisation takes place between two (or) more monomer.2. Reaction proceeds comparatively3. By products are formed.4. Molecular weight of the polymer steadily throughout the reaction.5. Thermosetting plastics are produced.6. Hetero-chain polymer is obtained

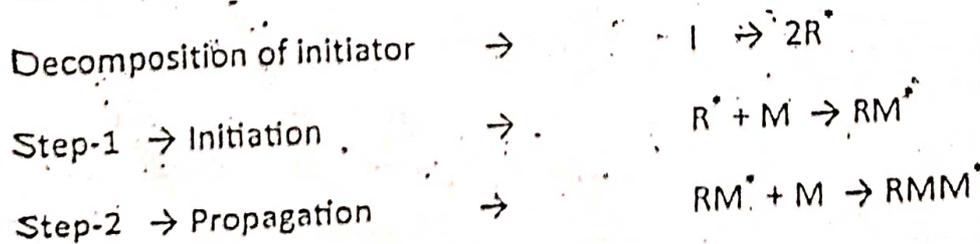
Mechanism of addition polymerization:

Mechanism of addition polymerization can be explained by any one of the following types

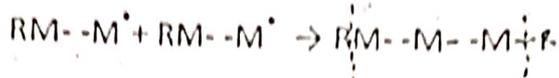
1. Free radical mechanism
2. Ionic mechanism.

Free radical mechanism (or) Free radical polymerization:

The reaction proceeds as follow:



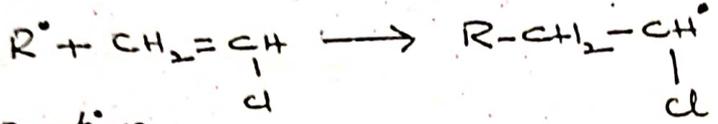
→ Termination →



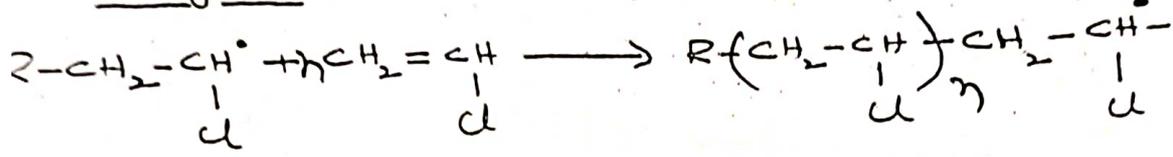
molecular weight compounds like azo compounds, peroxide, Hydro peroxides are as initiators.

can be explained by the polymerization of vinyl chloride.

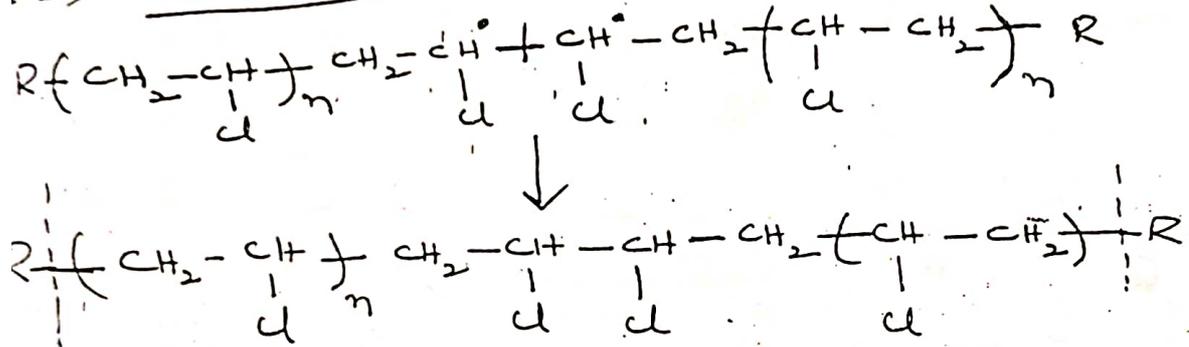
→ Initiation → $I \rightarrow 2R^\bullet$ (Free radical)
Initiator



→ Propagation →



→ Termination →



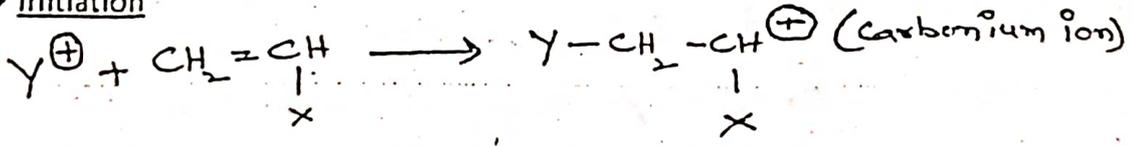
Termination by coupling.

Mechanism (or) Ionic polymerization

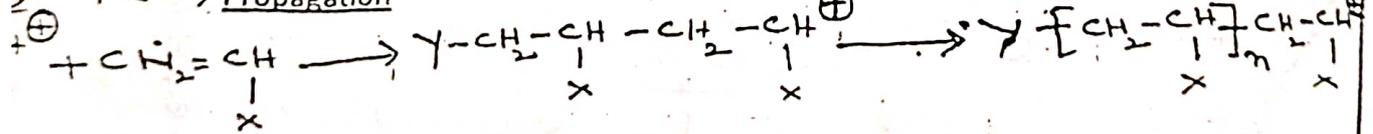
Depending on the nature of ions ionic polymerization takes place in two ways.

Cationic addition polymerization

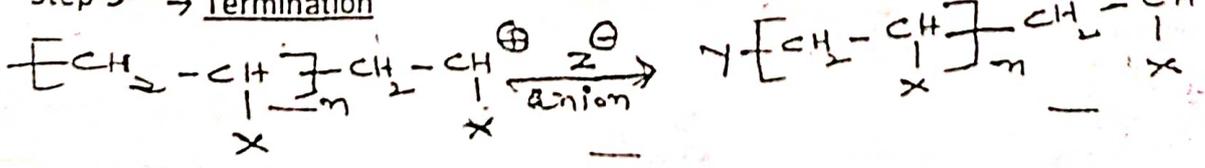
Step-1 → Initiation



Step-2 → Propagation



Step-3 → Termination

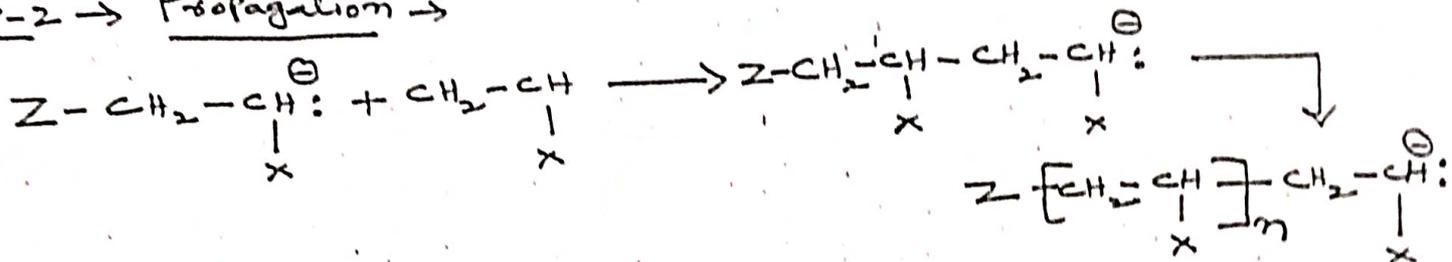


(ii) Anionic addition polymerization

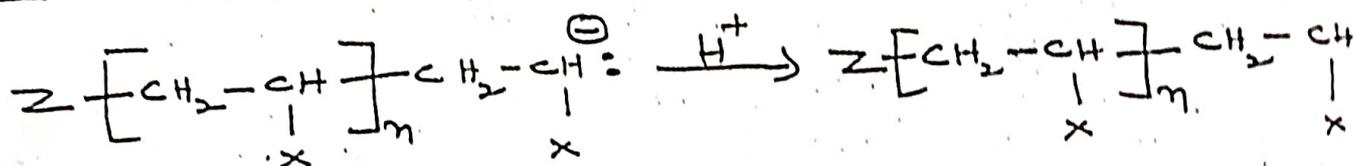
Step-1 → Initiation →



Step-2 → Propagation →

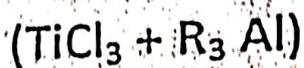


Step-3 → Termination →

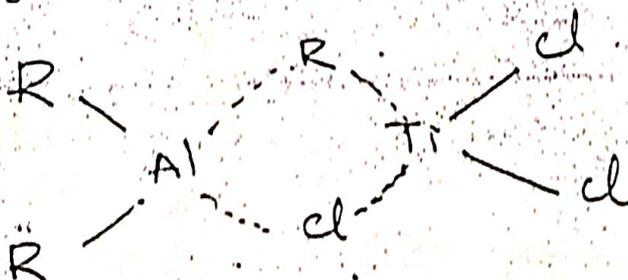


Ziegler-Natta polymerization (or) Co-ordination polymerization

The mixture of titanium halides and tri alkyl aluminum is known as Ziegler-Natta catalyst



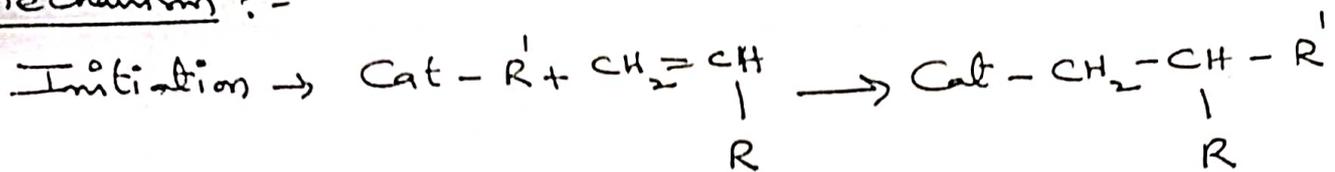
In this process tri alkyl aluminum adsorbs on the surface of titanium chloride and forms electron deficiency bridge structure



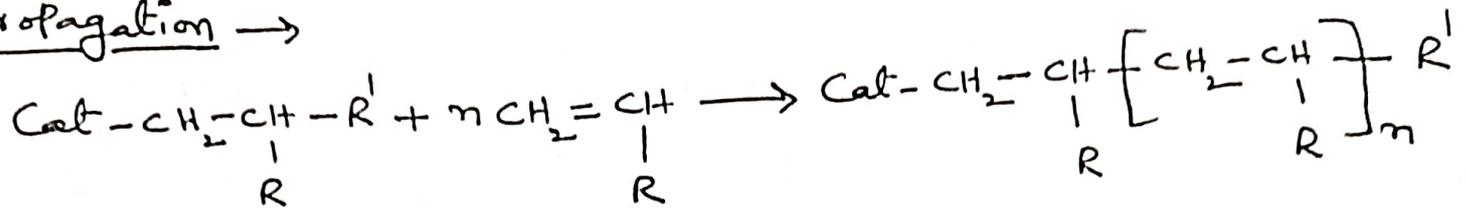
In this structure, titanium chloride acts as catalyst and alkyl aluminum acts as co-catalyst.

In the presence of Ziegler-Natta catalyst co-ordination polymerization occurs and gives isotactic polymer.

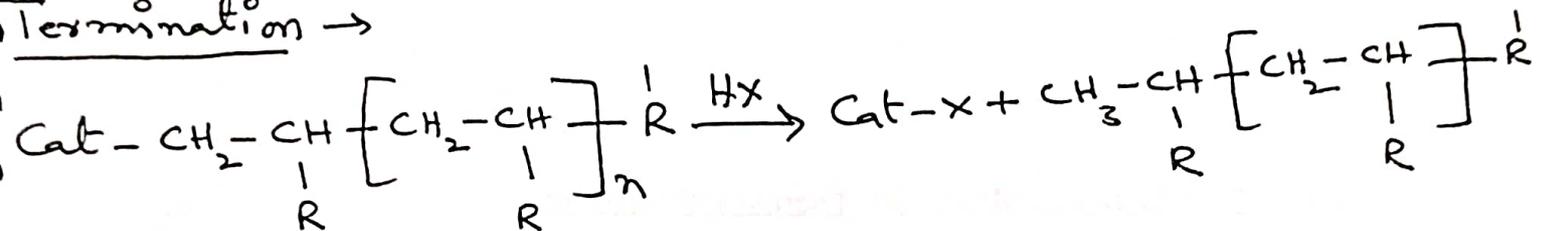
Mechanism :-



Propagation \rightarrow



Termination \rightarrow



Condensation Polymerisation mechanism

Generally two types of Condensation Polymerisation occurs

- (i) AA-BB type polymerisation
 $n \text{A-A} + n \text{B-B} \rightarrow \text{A} - (\text{AB})_n - \text{B} + 2n - 1 \text{ By products}$
- (ii) A-B type polymerisation
 $n \text{A-B} \rightarrow \text{B} - (\text{AB})_n - \text{A} + n - 1 \text{ Products}$

Plastic (or) Resins :-

plastics are high polymers which can be moulded in to any shape by application of heat and pressure in presence of catalyst

- Properties :-
- (i) Light weight & high strength to weight ratio
 - (ii) Good thermal and electrical insulation
 - (iii) High chemical resistance
 - (iv) Easy workability ~~and~~ Casting, molding, drilling etc.
 - (v) High chemical inertness
 - (vi) Low maintenance cost.

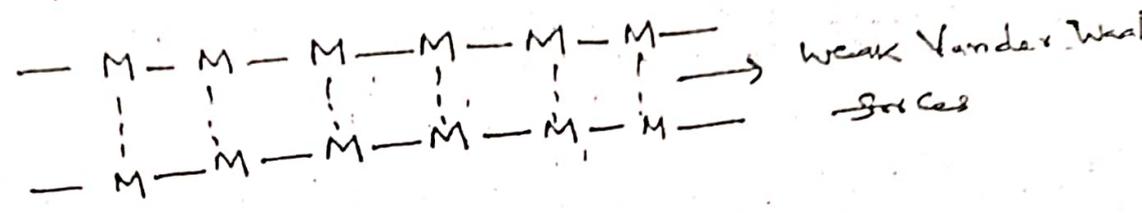
Classification of Plastics:

Plastics are classified in to two types

- (i) Thermoplastics
- (ii) Thermosetting plastics

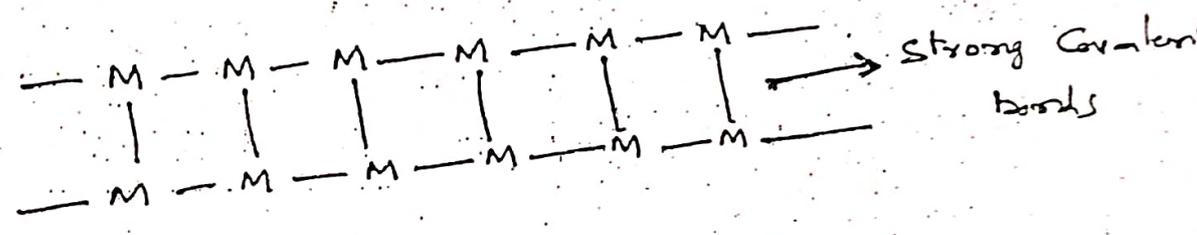
Thermoplastics (or) Thermo plastic resins:

These are the polymers which become soft on heating and hard on cooling. On reheating, they become soft again and can be remolded to desired shape. During the action of heating weak secondary vanderwaal's forces are broken while on cooling, these secondary bonds are re-established. Ex: PVC, Polythene, Teflon, Polystyrene.



ii) Thermo setting plastics (or) Thermo setting resins

These are the polymers which are fusible on initial heating and later cannot be softened by heating. Once they are set on heating they cannot be reformed. Because of strong covalent bonds. Ex: Bakelite, polyester, Urea formaldehyde resin etc.

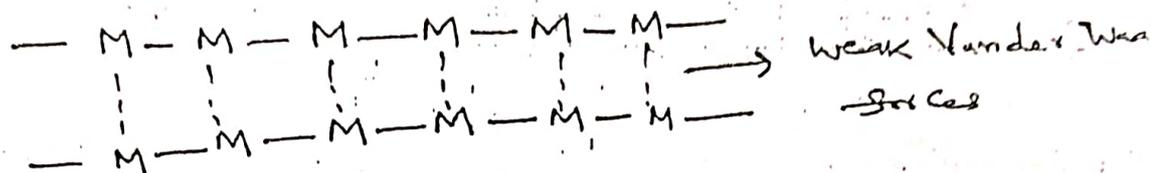


Differences between Thermo & Thermosetting plastics:

Thermoplastics	Thermosetting plastics
1. The resins are produced by addition polymerisation	1. Resins are produced by condensation polymerisation
2. They are made up of long chain	2. These resins have three dimensional network structure connected bonds.
3. They are soften on heating and harden on cooling.	3. They are fusible on initial heating only
4. High molecular weight polymer is formed	4. Molecular weight of the polymer is steadily throughout the reaction.
5. Thermoplastics are produced	5. Thermosetting plastics are produced.
6. Homo- chain polymer is obtained	6. Hetero- chain polymer is obtained

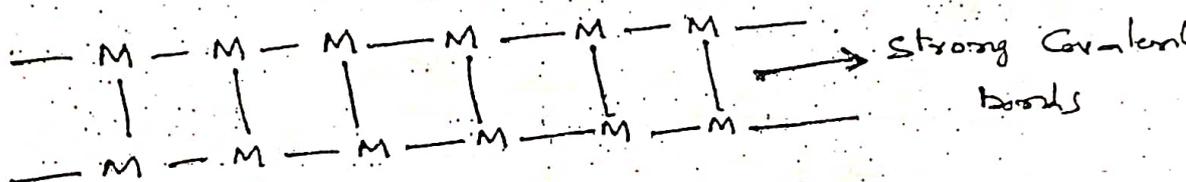
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These are the polymers which become soft on heating and hard on cooling. On reheating, they become soft again and can be remolded to desired shape. During the action of heating weak secondary vanderwaal's forces are broken while on cooling, these secondary bonds are re-established. Ex: PVC, Polythene, Teflon, Polystyrene.



ii) Thermo setting plastics (or) Thermo setting resins

These are the polymers which are fusible on initial heating and later cannot be softened by heating. Once they are set on heating they cannot be reformed. Because of strong covalent bonds. Ex: Bakelite, polyester, Urea formaldehyde resin etc.



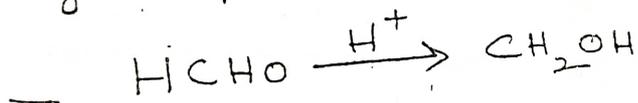
Differences between Thermo & Thermosetting plastics:

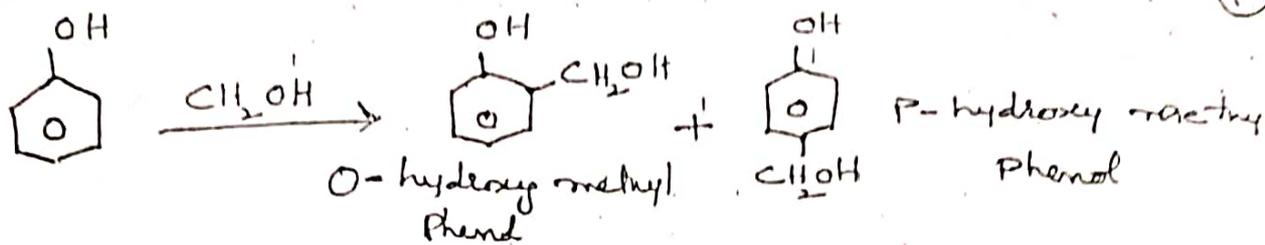
Thermoplastics	Thermosetting plastics
1. The resins are produced by addition polymerisation	1. Resins are produced by condensation polymerisation
2. They are made up of long chain	2. These resins have three dimensional network structure connected bonds.
3. They are soften on heating and harden on cooling.	3. They are fusible on initial heating only.
4. High molecular weight polymer is formed	4. Molecular weight of the polymer rises steadily throughout the reaction.
5. Thermoplastics are produced	5. Thermosetting plastics are produced.
6. Homo- chain polymer is obtained	6. Hetero- chain polymer is obtained

Bakelite (or) Phenol-formaldehyde resin (or) Phenoplasts:

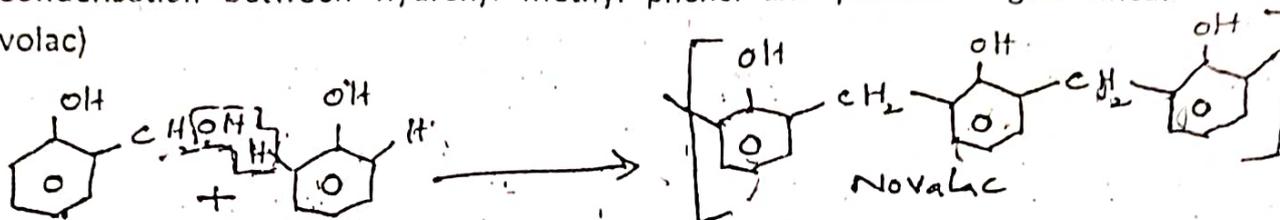
Preparation:- ~~Bakelite~~ Bakelite is obtained by the condensation polymerization of phenol and formaldehyde in the presence of an acid (or) alkali catalyst.

1st step: Phenol reacts with formaldehyde to form O-hydroxy-methyl phenol and p-hydroxy-methyl phenol.

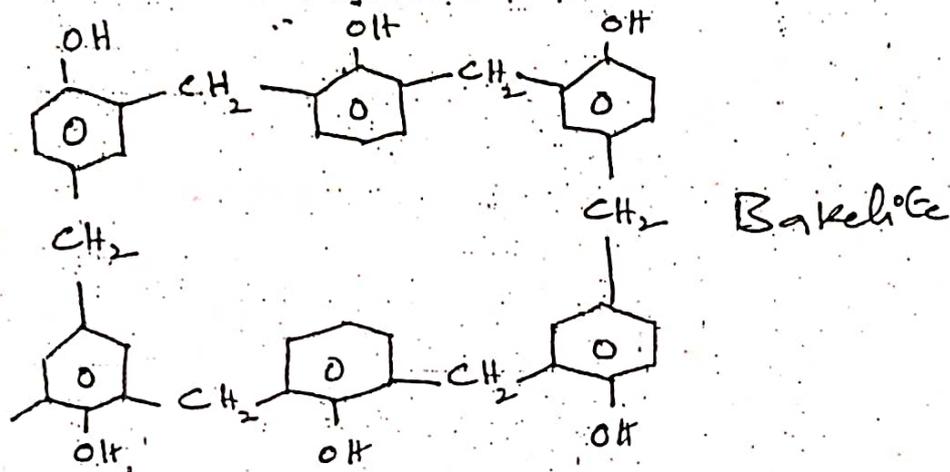




2^d Step: Condensation between hydroxyl methyl phenol and phenol to give linear polymer (Novolac)



3^d Step: Small amount of hexamethylene-tetramine is added. It produces formaldehyde and ammonia. Formaldehyde converts the soluble and fusible novolac into hard. This infusible solid cross-linked three dimensional polymer called bakelite.



Properties: i) Bakelite is very hard, infusible and rigid.

ii) It has high resistance towards heat, moisture and chemicals.

iii) It has very good electrical insulating properties.

USES: i) Bakelite is used for making electric insulator parts like switches, plugs, switch boards etc.

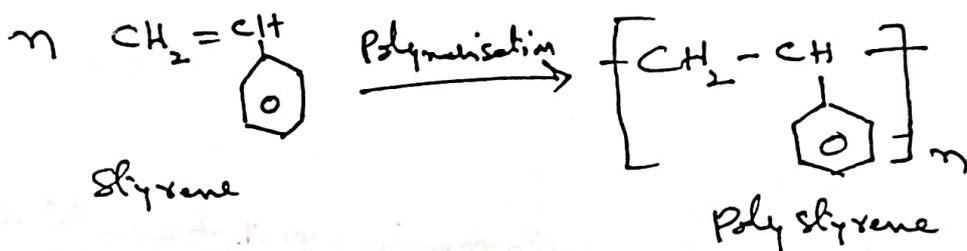
ii) It is used for making articles like telephone parts, radio, and T.V. Cabinets.

iii) Bakelite used in paints and varnishes iv) It is used For making bearings and in grinding wheels.

Poly styrene

Preparation

Poly styrene is prepared by the polymerisation of styrene in presence of benzoyl Peroxide Catalyst.



Properties :-

- (i) Poly styrene is a light, transparent material
- (ii) It is excellent moisture resistant
- (iii) It possess electrical insulating property

Uses :- It is used in the manufacture of jars, bottles, toys, Combs, buttons, etc.

PVC (Poly vinyl chloride)

Preparation :-



- Properties :-
- (i) PVC is colourless, odourless and chemically inert powder.
 - (ii) It is insoluble in inorganic acids and alkalis, but soluble in hot chlorinated hydrocarbons such as ethylchloride.
 - (iii) It undergoes degradation in presence of light.

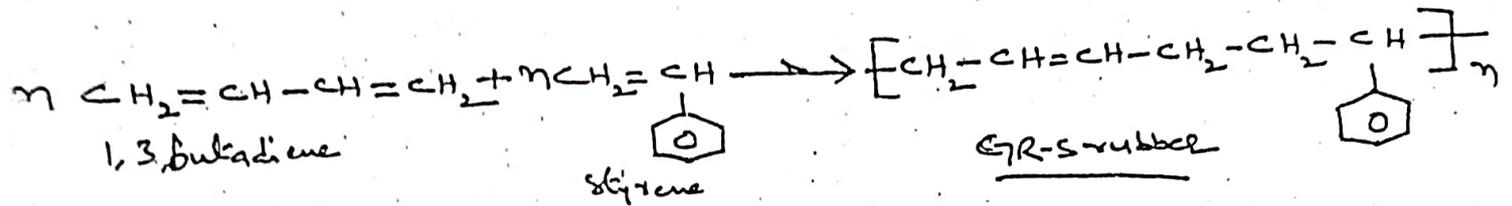
Uses :-

- (i) It is used in the production of pipes, cable insulations, table covers and rain coats etc.
- (ii) It is also used for making sheets, Refrigerator components, Automotive interiors etc.

Synthetic Rubbers (or) Elastomers

Buna-S (or) Styrene (or) GR-S rubber :-

- is styrene-butadiene polymer. It contains 75% butadiene and 25% of styrene.

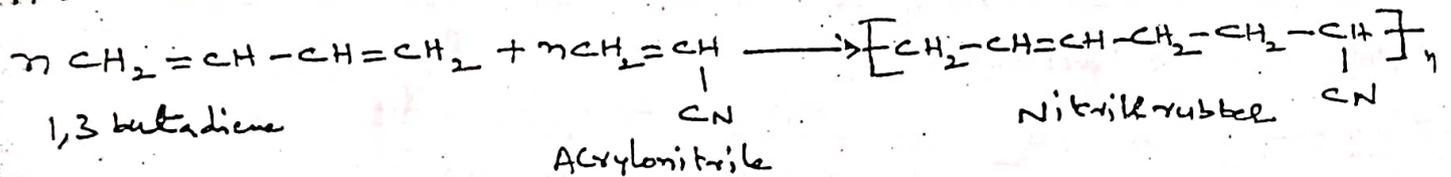


Properties :- (i) Buna-S shows excellent abrasion resistance
(ii) It gets easily oxidized and swells in oils

Uses :- It is used in making automobile tyres, floor tiles, footwear components, adhesive and tank lining.

Buna-N (or) Nitrile rubber (or) GR-A rubber

It is prepared by co-polymerization of 1,3 butadiene and acrylonitrile.

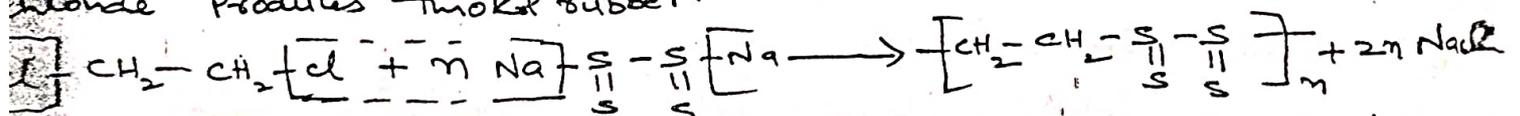


Properties :- (i) It is excellent resistance towards heat, sunlight, oils and acids but less resistance to alkalis.

Uses :- (i) making aircraft components, automobile parts, conveyor belts, tank linings, gaskets, hoses, printing roll etc.

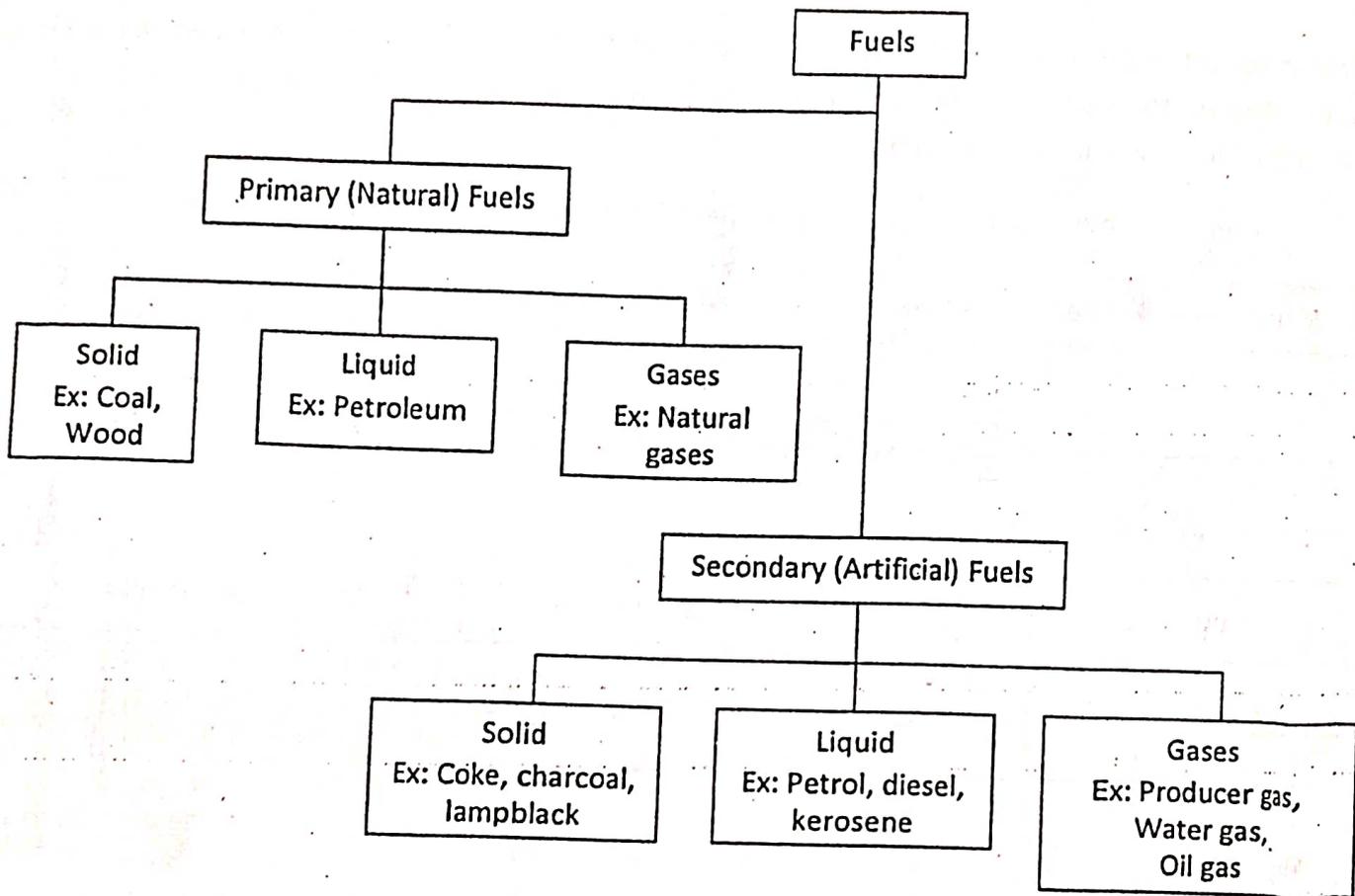
Thiokol Rubber (or) Poly sulphide rubber (or) GPR-rubber :-

The condensation polymerisation of polysulphide (Na_2S_4) and ethylene chloride produces thiokol rubber.



Properties -> (i) They have excellent oil-resistance (ii) It cannot be vulcanized
(iii) They have poor abrasion-resistance

Uses -> (i) Thiokol are used as gaskets, balloons, fabric coating
(ii) Thiokol are used for life rafts and jackets which are insulated by



Characteristics of a good fuel:

A good fuel should have the following properties

- (i) It should have high carbon content
- (ii) It should have high calorific value
- (iii) The velocity of the combustion should be moderate
- (iv) It should be cheap and readily available
- (v) It must be easy to handle, store and transport minimum cost.
- (vi) It should have less moisture and ash
- (vii) It should not produce undesirable (or) toxic gases.

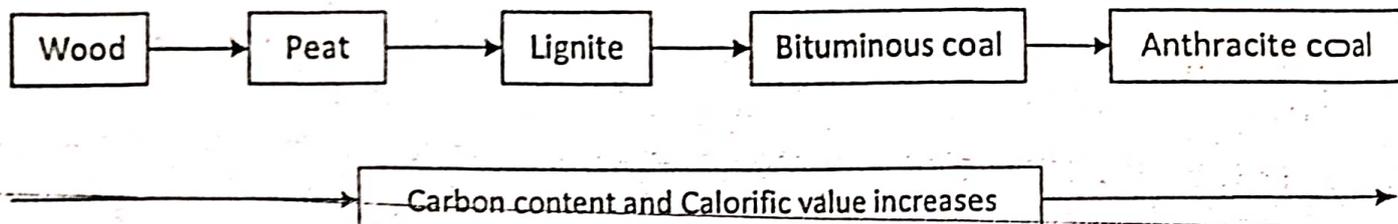
Solid fuels: Solid fuels are the fuels in the solid state. Ex: Coal, Coke

Coal: Coal is a primary solid fuel. It is formed by the particle decay of plant material under the influence of heat, pressure and bacterial action underneath the earth.

Classification of coal:

Coal is an important kind of solid fuel that is derived from vegetable matter. The vegetations under the earth with the effects of pressure, temperature and bacterial action have been converted into various kinds of coal.

There are four kinds of coal based on their "carbon content" and "calorific value".



Fuel	Percentage of Carbon	Calorific value	Main Applications
1. Peat	50	4125 – 5400 K. cal/kg	It is a brown fibrous jelly like mass. It is first stage of coal. H – 6%, Ash – 2.5 – 6%
2. Lignite	67	6500 – 7100 K. cal/kg	Dark brown coloured coal. It can be easily ignite and burns with long brown flame. H – 5%, Ash – 0 – 20%
3. Bituminous (a) Sub-bituminous (b) Bituminous (c) Semi-bituminous	83	8000 – 8500 K. cal/kg	Used in making coal gas of metallurgical coke
4. Anthracite	93	8650 – 8700 K. cal/kg	It is the highest rank of coal. It has low volatile matter and moisture.

Analysis of coal:

To assess the quality of coal, the following two types of analysis carried out.

(i) Proximate analysis

(ii) Ultimate analysis

(i) Proximate analysis: it is a quantitative analysis of the following parameters.

(a) Moisture content

(b) Volatile matter

(c) Ash content

(d) Fixed carbon

(a) **Moisture content:** the coal sample (1g) is finely powdered dried is weighed in a silica crucible and the crucible heated in oven at 105 - 110° C for one hour, cooled in desiccators and weighed.

From that,
$$\% \text{ moisture} = \frac{\text{loss in weight}}{\text{weight of coal taken}} \times 100$$

(b) **Volatile matter:** The moisture free coal is taken in silica crucible taken out and heated 7 minutes at temperature of 925° C ± 20° C and then crucible taken out and cooled.

On the basis,

$$\% \text{ of Volatile matter} = \frac{\text{loss in weight due to removal of volatile matter}}{\text{weight of coal taken}} \times 100$$

(c) **Ash:** the residual coal in the crucible is heated without lid in a muffle furnace at 700° C ± 50° C for 30 minutes, then taken out and cooled.

$$\% \text{ Ash} = \frac{\text{weight of residue}}{\text{weight of coal taken}} \times 100$$

(d) **Fixed carbon:** The sum total of the percentage of moisture, volatile matter, ash are subtracted from 100,

$$\text{fixed carbon} = 100 - \%(\text{moisture} + \text{volatile matter} + \text{ash})$$

(b) Volatile matter

(c) Ash content

(d) Fixed carbon

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Ultimate analysis: It is the elemental analysis of coal used for the determination of carbon, hydrogen, sulphur, nitrogen ash and oxygen.

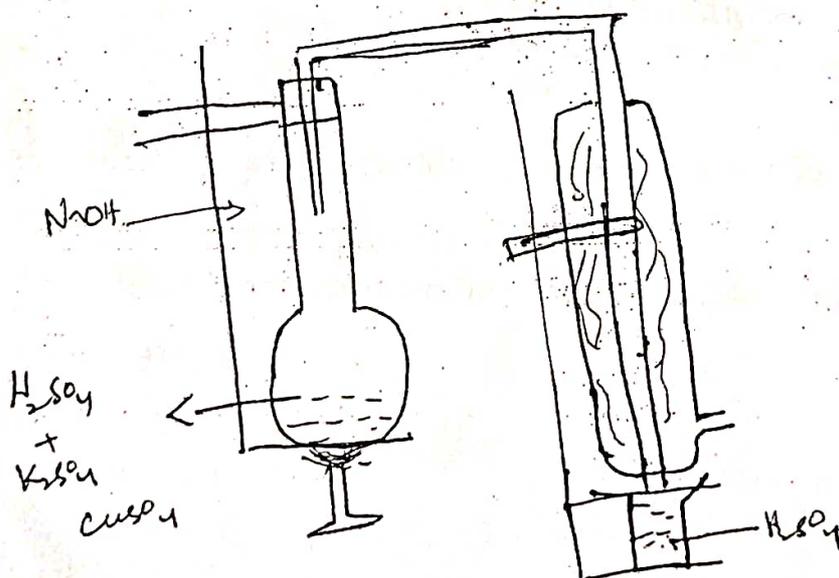
(a) **Carbon and Hydrogen:** about 1g of weighed coal is completely burnt in a stream of oxygen in a combustion tube. Carbon and Hydrogen present in the coal sample are converted into CO_2 , H_2O . The CO_2 and H_2O are absorbed separately in anhydrous CaCl_2 and KOH bulbs respectively. From the increased weights of the tubes the percentage of carbon and hydrogen can be calculated

$$\% \text{H} = \frac{\text{Increase in weight of CaCl}_2}{\text{weight of coal sample taken}} \times \frac{2}{18} \times 100$$

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

(b) **Nitrogen (Kjeldal's method):** the determination of nitrogen content is carried out by kjeldal's method. The known amount of powdered coal sample is heated with Conc. H_2SO_4 along with K_2SO_4 in long necked flask (kjeldal's flask). Nitrogen in the coal is converted into Ammonium Sulphate and clear solution is obtained. The clear solution is then reacted with excess of NaOH and the liberated Ammonia is distilled over and is absorbed in a known volume of acid solution. The unused acid is determined by titration with standard NaOH . From the volume of acid used, the percentage of Nitrogen in coal can be calculated.

$$\% \text{ of N}_2 \text{ in Coal} = \frac{\text{Volume of acid used} \times \text{Normality of acid}}{\text{weight of coal sample taken}} \times \frac{14}{1000} \times 100$$



(c) Sulphur Content: a known amount of coal sample is burnt completely in a bomb calorimeter. During this process sulphur is converted into sulphate, which is extracted with water. The extract is then treated with BaCl_2 solution so that sulphates are precipitated as BaSO_4 . The precipitate is filtered, dried and weighed. From the weight of BaSO_4 percentage of Sulphur can be calculated.

$$\% \text{ of Sulphur} = \frac{\text{weight of BaSO}_4}{\text{weight of coal sample taken}} \times \frac{32}{233} \times 100$$

Ash: it is carried out in the same way as in proximate analysis.

Oxygen: percentage of oxygen is obtained by subtracting the sum of percentage C, H, N, S and ash from 100.

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

Significance of Ultimate Analysis:

- (a) Carbon and Hydrogen: the quality of coal is based on the percentage of Carbon in it. Higher the percentage of carbon and hydrogen, better is the quality of coal and higher is its calorific value.
 - (b) Nitrogen: it has no calorific value and hence its presence in coal is undesirable.
 - (c) Sulphur: through, Sulphur increases the calorific value, its presence is undesirable because the combustion products SO_2 and SO_3 can corrode the equipment and also causes air pollution.
 - (d) Oxygen: High oxygen content can reduce the calorific value.
- Carbonization: when coal is heated strongly in the absence of air. It is converted into lustrous, dense, porous and coherent mass known as coke. This process of converting coal into coke is known as "Carbonization".

Liquid Fuels:

The fuels present in the liquid state are called Liquid Fuels. The liquid fuels have some advantages and disadvantages follows

Advantages:

1. Liquid fuels are clean and require less amount of air for complete combustion.
2. They possess higher calorific value than solid fuels.
3. They burn without forming dust, ash etc.
4. They can be easily ignited and emission can easily controlled.
5. They are used as internal combustion fuels.

Disadvantages:

1. Care must be taken during ~~strong~~ storage.
2. Cost is relatively higher than solid fuels.
3. They give bad odour.
4. There is risk of fire accidents.

Petroleum (or) Crude oil:

The word petroleum is derived from Latin.

Petra - rock, oleum - oil, It is also known as crude oil. It is dark greenish brown coloured oil obtained from a greater depth under earth's crust. The average composition of petroleum is

C: 79.5 - 87.1%

H: 11.5 - 14.8%

S: 0.1 - 3.5%

O + N : 0.1 - 0.5%

Classification of petroleum:

According to chemical nature of petroleum (3) types

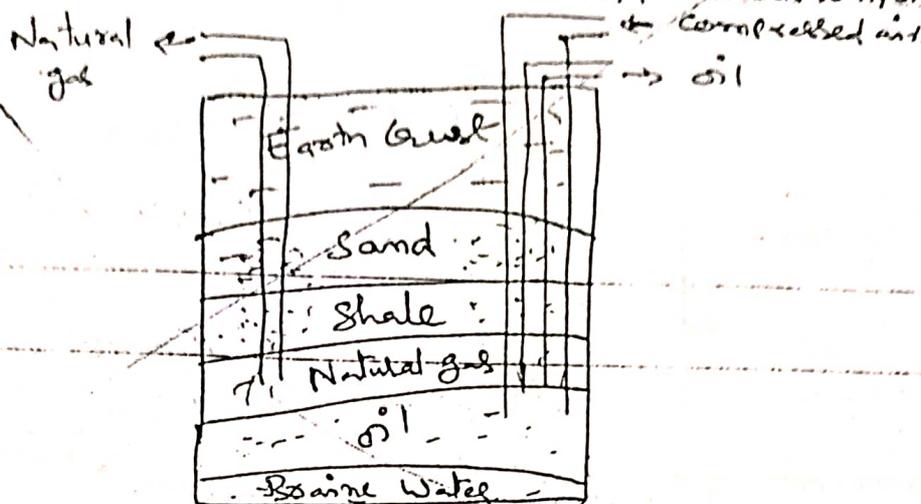
Paraffin - Base type
Hydrocarbons containing
 $C_{25}H_{52}$ to $C_{35}H_{72}$

Asphaltic - Base type
Paraffin + Aromatic hydrocarbons

Mixed - Base type
Paraffin + Asphaltic + Aromatic hydrocarbons

Mining of petroleum:

Mining of petroleum is generally done by drilling holes in the earth crust using drilling machines with rigs. Pipes are introduced up to oil level. Oil usually pushed out to hydraulic pressure of natural gas.



When the pressure of natural gas is not sufficient, then compressed air is sent through a parallel pipe to the first pipe that is two co-axial pipes to the first pipe. Air under pressure is passed through the outer pipe and the oil comes out through the inner pipe.

Refining of petroleum (or) Crude oil:

Petroleum obtained from the earth crust is a mixture of oil and water, dist, sulphur compounds etc. the process of removal of impurities from crude oil and separation of various fractions at different temperatures is called refining of petroleum.

Step I: Separation of water (Cottrell's process)

The crude oil will always mix with brine water (salt water) forming emulsions. The crude oil is allowed to flow through two highly charged electrodes. The colloidal emulsion of oil and water coalesce (separate form) to form large water droplets which is separated from the oil.

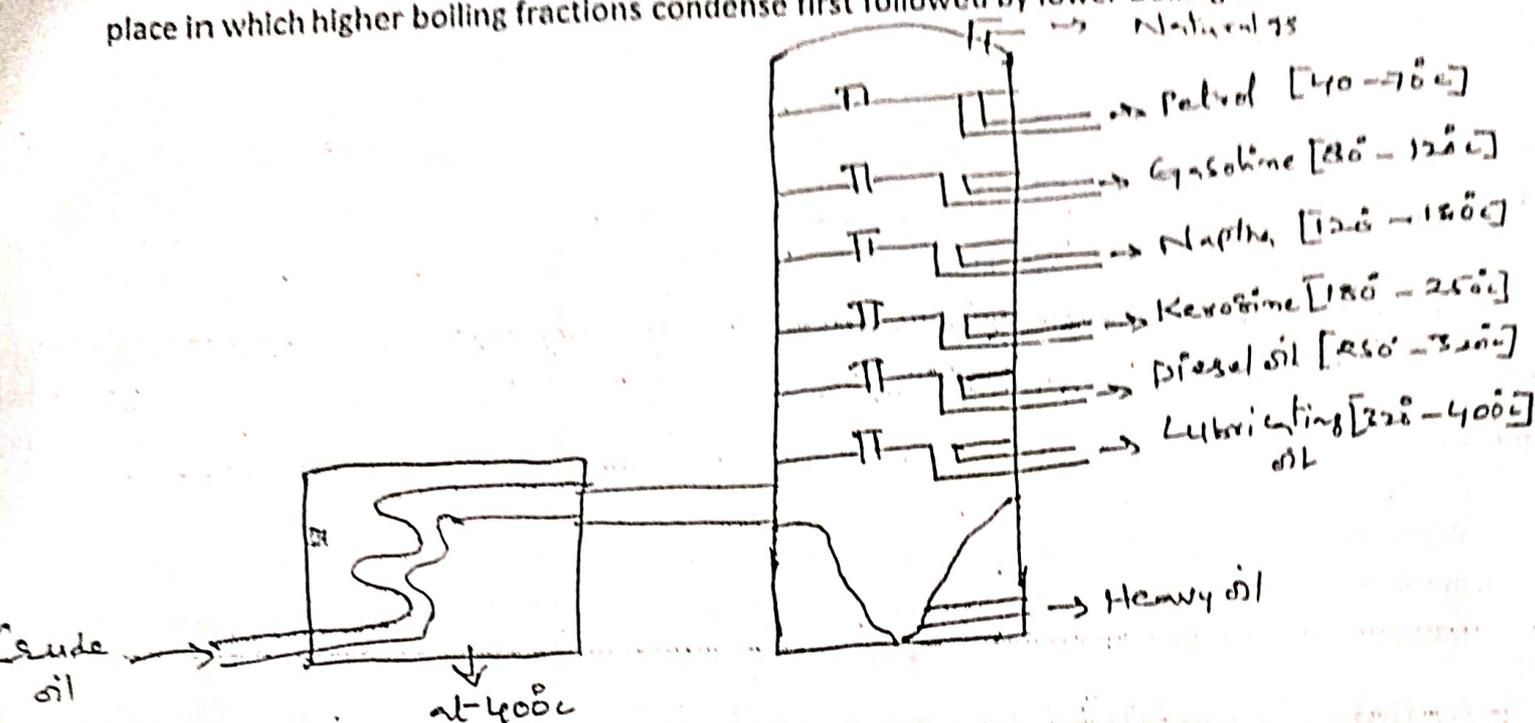
Step II: Removal of sulphur compounds

In this step harmful sulphur compounds are separated by treating the oil with copper oxide forming solid copper sulphide which is separated by filtration.

Step III: Fractional distillation

This step involves the fractional distillation in which the crude oil is heated to about 350°C in an iron retort to remove the volatile components by evaporation. The hot vapours are then passed through a tall cylindrical tower consisting of a number of horizontal stainless steel trays

at short distance called the fractional column. In this column fractional condensation takes place in which higher boiling fractions condense first followed by lower boiling fractions.



Important petroleum products:

1. **Gasoline oil (or) petrol:** It is obtained between 40°C - 120°C . It is a mixture of hydrocarbons from C_5H_{12} to C_9H_{20} . It has composition of C - 84%, H - 15%, N + S + O = 1%. Its calorific value is 11,250 K.cal/kg.

2. **Kerosene oil:** It is obtained between 180°C - 250°C and is a mixture of hydrocarbons such as $\text{C}_{10}\text{H}_{22}$ to $\text{C}_{16}\text{H}_{34}$. Approximate composition is C - 84%, H - 16%, S < 0.1%. Its calorific value is 11,100 K.cal/kg.

3. **Diesel oil:** It is a fraction obtained between 250°C - 320°C and is mixing of $\text{C}_{15}\text{H}_{32}$ to $\text{C}_{18}\text{H}_{38}$ hydrocarbons. Its calorific value is 11,000 K.cal/kg.

Knocking (Gasoline): Knocking is a kind of explosive due to rapid pressure rise occurring in an engine.

Octane number (or) Octane rating:

Octane number is introduced to express the knocking characteristics of petrol. It has been found that n - heptane knocks very badly, its anti knocking value has been given zero on the other hand iso - octane gives very little knocking. So, its anti - knocking value has been given 100.

Fuels for Internal Combustion (IC) Engines :-

In an Internal Combustion Engine (ICE), the chemical energy available in the fuel is changed to mechanical energy by burning (oxidising) the fuel inside the combustion chamber of the engine.

Function of fuel in IC engine :-

In an internal combustion petrol engine, a mixture of vapour of gasoline and air is used as a fuel. After the initiation of combustion by spark in the cylinder the flame spreads rapidly and the expansion of gas drives the piston down the cylinder.

Types of IC engine fuels

(a) Gasoline (or) Petrol (a mixture of hydrocarbons including pentane, hexane, heptane & octane) (b) Diesel (c) Ethanol (d) Methanol (e) Vegetable oil (f) Natural gas (g) Hydrogen.

1) Gasoline oil (or) Petrol: It is obtained between 40° - 120°C and is a mixture of hydrocarbons such as from C_5H_{12} to C_9H_{20} . It has composition of C - 84%, H - 15%. N + S + O = 1%. Its calorific value is 11,250 K.cal/kg.

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Knocking

Def: knocking is a kind of explosion due to rapid pressure rise occurring in an IC engine.

Improvement of anti knocking characteristics :-

1. Blending petrol of high octane number with petrol of low octane number
2. The addition of anti-knock agents like Tetra-Ethyl Lead (TEL)
3. Now a days aromatic phosphates are used as antiknock agent because it avoids lead pollution.

Factors affecting knocking :- (i) Design of engine

(ii) operation conditions

(iii) Chemical structure of the hydrocarbon in fuel.

Anti - Knock Agent (Leaded Petrol)

The anti-knock properties of petrol can be improved by the addition of suitable additives. Tetra Ethyl Lead (TEL) $(C_2H_5)_4Pb$ is an important additive added to petrol. Thus the petrol containing tetra ethyl lead is called leaded petrol.

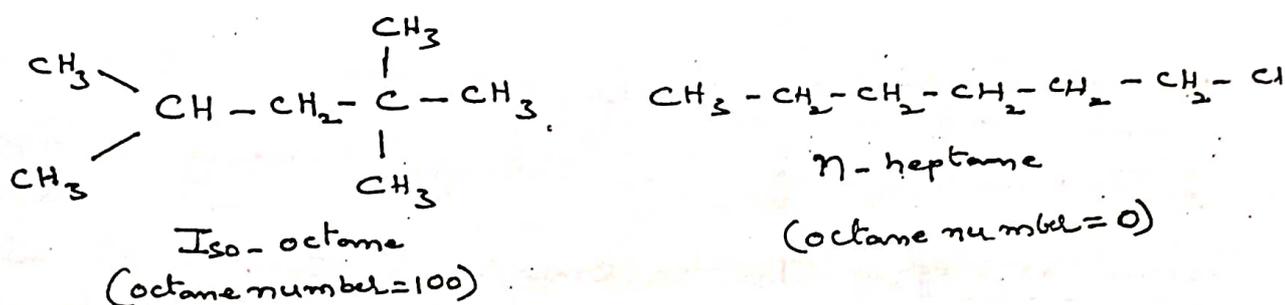
Disadvantages of using TEL:

When the leaded petrol is used as a fuel, the TEL converted to lead oxide (PbO) and metallic lead (Pb). This lead deposits on the spark plug and on cylinder walls which harmful to engine life and lead oxide goes out along with exhaust gases ~~which~~ and creates atmospheric pollution. So now a days aromatic phosphates are used instead of TEL.

Octane Number (or) Octane Rating:

Octane number is introduced to express the knocking character of petrol. It has been found that n -heptane knocks very badly, its anti-knocking value has been given zero on the other hand iso-o gives very little knocking. So, its anti-knocking value has been given 100.

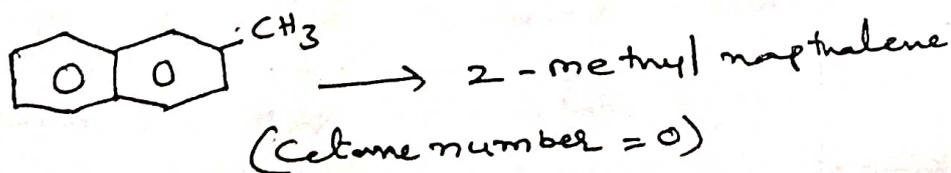
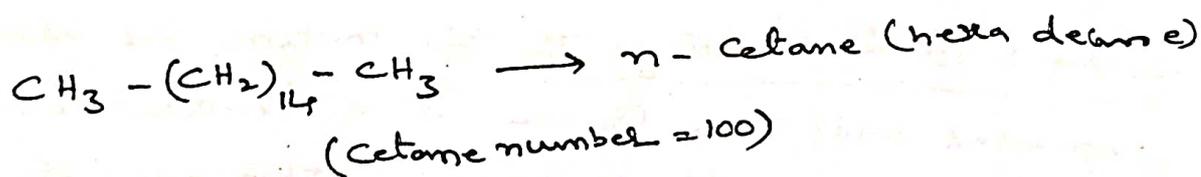
Definition: Thus, octane number is defined as "the percentage of iso-octane present in a mixture of iso-octane and n -heptane".



Cetane number (or) Cetane Rating:-

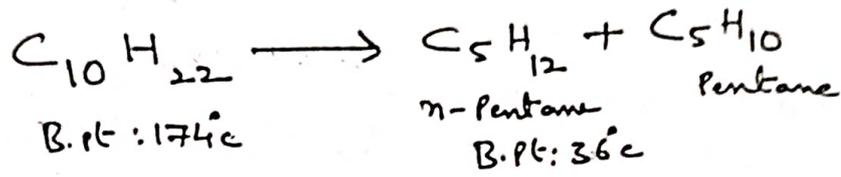
Cetane number is introduced to express the knocking character of diesel.

Cetane number is defined as "the percentage of hexa decane present in a mixture of hexa decane and 2-methyl naphthalene which the same ignition lag as the fuel under test".



Cracking of Oils:

Def: Cracking is defined as "the decomposition of high boiling hydrocarbons of high molecular weight into simpler, low boiling hydrocarbons of low molecular weight."



Types of Cracking: → There are two kinds of Cracking

1. Thermal Cracking
2. Catalytic Cracking

1. Thermal Cracking: - If the cracking is carried out at higher temperature and pressure without any catalyst, it is called thermal cracking. There are two types of thermal cracking.

(i) Liquid phase Thermal Cracking (ii) Vapour phase Thermal Cracking

Liquid phase Thermal Cracking: In this method, the heavy oil is cracked at a temperature of $475-530^\circ\text{C}$ under pressure 100kg/cm^2 to keep reaction product in liquid state. The resulted oil is found with an octane number of 65-70.

Vapour phase Thermal Cracking: In this method, the heavy oil is first vapourised and then cracked at a temperature of $600-650^\circ\text{C}$ under a lower pressure of $10-20\text{kg/cm}^2$. The yield of gasoline is about 70%.

2. Catalytic Cracking:

If the cracking is carried out at lower temperature and pressure in the presence of suitable catalyst, it is called catalytic cracking. The catalyst used are aluminium silicate (α) alumina.

There are two types of catalytic cracking

- (i) Fixed bed catalytic cracking
- (ii) moving bed (α) Fluid bed

Fixed Bed Catalytic Cracking:

The heavy oil vapour is heated to $420-450^{\circ}\text{C}$ in a pre heater. The hot vapours are then passed through a catalytic chamber, maintained at $425-450^{\circ}\text{C}$ and 1.5 kg/cm^2 pressure, where catalysts (artificial clay mixed with zirconium oxide), are kept in fixed beds. During passage through the catalytic chamber, about 40% of the heavy oil is converted into gasoline and about 2-4% carbon is formed.

Moving bed (or) Fluid bed Catalytic Cracking:-

The catalyst used in this process is in the form of a fine powder which is circulated through the cracking reactor with the help of oil vapours or air. The heavy oil vapour is heated to $420-450^{\circ}\text{C}$ in a pre heater and it is mixed with catalyst powder. Then this mixture is forced into the reactor, which is maintained at a temperature of 500°C and pressure of 5 kg/cm^2 . The cracked gases and gasoline are separated from the top of the fractionating column and sent to cooling where gasoline is liquefied.

Advantages of Catalytic Cracking over - Thermal Cracking:-

1. The yield of petrol is higher
2. The quality of petrol produced is better
3. The production cost is very less, since high temperature & high pressure are not required
4. The products contain less sulphur compounds.
5. The cracking process can be easily controlled.

Alternative Fuels (or) Advanced Fuels:

Alternative Fuels are any materials (or) substances that can be used as fuels other than conventional fuels like fossil fuel (Petroleum oil, Coal and Natural gas), nuclear materials (Uranium, thorium).

Ex:- Methanol, Ethanol, Propane, Bio-fuels etc.

1) Methanol :-

It is an alternate fuel for IC engine, either in combination with gasoline (or) directly.

Preparation :- (a) It is made from hydrocarbon (or) renewable resource in particular natural gas and biomass respectively.

(b) It can also be synthesized from CO_2 and hydrogen.

(c) Methanol is 1st produced by the destructive distillation of wood.

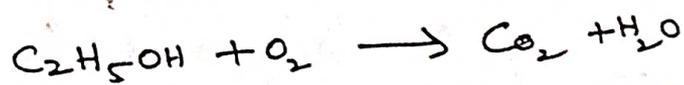
Advantages :- (a) It is free from sulphur (b) methanol burns at lower temperatures

Dis-Advantages :- (a) It will absorb water easily, causing separation in methanol-gasoline blends (b) It contains soluble and insoluble contaminants like chloride ions, which increase the corrosivity of alcohol.

2) Ethanol :-

Ethanol is derived from sugar cane, corn, etc., It is also the main type of alcohol in most alcoholic beverages.

Preparation :- It is obtained by the fermentation of sugar. Ethanol is commonly blended with gasoline to oxygenate the fuel and also increases the octane rating of the fuel.



Fixed Bed Catalytic Cracking:

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5. The cracking process can be easily controlled.

Advantages :-

- 1) It is cost effective compare to other bio fuels.
- 2) It does not cause pollution to the environment and ecologically effective.
- 3) It is easily accessible
- 4) It minimizes dependences on fossil fuel.
- 5) Ethanol is a source of hydrogen

Dis-Advantages :-

- 1) Distillation process is not good for environment
- 2) Vapourization of ethanol is difficult.

Propane :-

Propane is a hydrocarbon fuel and is a member of the natural gas family. It is also known by names LPG (Liquid propane gas) LPA (Liquid Propane Autogas).

- ### Advantages :
- ① Higher octane rating so, better engine efficiencies
 - ② It is non toxic causing no harm to soil or water.
 - ③ It is cheaper than gasoline (or) diesel fuel.

Dis-Advantages

- ① It contains some methane

1) Bio-fuels

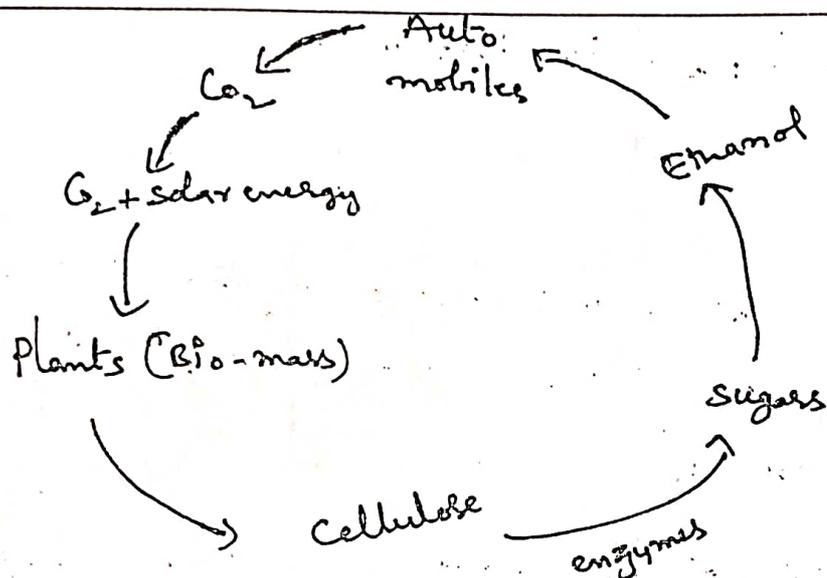
Bio-fuels are the fuels derived from the living organisms (plants animals) and their waste products. These are available in solid liquid (or) gaseous states.

Production :- The Biomass can be converted to convenient energy containing substances in three different ways.

- (a) Mechanical Conversion
- (b) Chemical Conversion
- (c) Biochemical Conversion

Bio-fuels are Carbon-neutral because the CO_2 that is absorbed by the plants is equal to the CO_2 that is released when the fuel is burnt.

Carbon-Neutral Process:- From the organic waste, Cellulose is produced. This Cellulose is degraded by enzymes and converted into sugar. The microbes ferment the sugar molecules and convert them into Ethanol. When ethanol is burnt and CO_2 is emitted. The emitted CO_2 is again consumed by plants.



Important Bio-fuels (i) Bio-diesel (ii) Bio-ethanol

Bio-diesel:- It is the most common bio-fuel obtained by the transesterification of oils and fats.

Bio-ethanol:- It is also the important bio-fuel obtained by the fermentation of cane sugar.

UNIT-IV

Advanced Engineering MaterialsComposites

Definition:- Composite materials can be defined as materials that consist of two or more chemically and physically dissimilar phases separated by distinct interface.

Advantages (or) Characteristics of Composites

- 1) They possess higher specific strength and lower specific gravity.
- 2) They possess lower electrical conductivity and thermal expansion.
- 3) They possess better creep, fatigue strength, corrosion and oxidation resistance.
- 4) They maintain very good strength, even up to high temperatures.

Constituents of Composites

Composites consist of two important constituents

- 1) Matrix phase (or) Matrix resin
- 2) Dispersed phase (or) Reinforcement

1. Matrix phase (or) Matrix resin

Matrix phase which is also called as continuous phase, which encloses the composite. Matrix phase binds the fibers together and acts as medium by which an externally applied stress is transmitted and distributed to the fibers. Only a very small portion of the applied load is sustained by the matrix phase.

Matrix phase may be metals, ceramics, or polymers, Composites using

These matrix are known as (i) metal matrix Composites (MMC).

(ii) Ceramic Matrix Composite (iii) Polymer Matrix Composite (PMC) etc.

② Dispersed phase (or) Reinforcement

Dispersed phase is the structural constituent which determines the internal structure of composite. Ex - Fibres, Particulates, Flake whiskers

Reinforcement

Reinforcements for the composites can be fibres, fabrics, particle or whiskers. Reinforcing constituents in composites, as the word indicates provide the strength that makes the composite what it is. But they also serve certain additional purposes of heat resistance (or) Conduction, resistance to corrosion and provide rigidity. Reinforcement can be made to perform all or one of these functions as per the requirements.

TYPES OF COMPOSITES

Composites are classified into three types

- (i) Polymer Composites (or) Fibre Reinforced Polymer Composites
 - (ii) Particle Reinforced Composites (iii) Structural Composites
- ~~Large particle~~

(i) Polymer Composites (or) Fibre Reinforced Polymer Composites :-
The fibre reinforced polymer composites constitute more than 90% (by weight) of the total composites used in various industries

Preparation:

Fibre-reinforced plastics are produced by suitably bonding a fibre material with a resin matrix and curing them under pressure and heat. The main reinforcing agents used in FRP Composites are glass, graphite, alumina, Carbon, boron, etc. The reinforcement material can be in different forms such as short fibres, continuous filaments (or) woven fabrics.

Some of the important fibre reinforced Composites are
(i) Glass fibre reinforced Composites (ii) Carbon fibre-reinforced polymer composite (iii) Aramid fibre reinforced polymer Composite.

Characteristic (or) Properties of FRP

- It possesses superior properties like higher yield strength, fracture strength & fatigue life.
- Since fibre prevents slip and crack propagation, the mechanical properties of FRP gets increased.
- It possesses high corrosion resistance and heat resistance.

Particle - Reinforced Composite:

In Particle - Reinforced Composite, the dispersed phase is a particle. The behaviour of this composite depends on the size of the particles. Large particle - Reinforced Composites are subdivided into large particle composites and (ii) Dispersion-strengthened Composites.

Large - Particle Composites :- In large - Particle Composite, the interaction between particle and matrix phases are not

On the atomic (or) molecular level.

Example → Vulcanized rubber → Vulcanized rubber reinforced by adding 15-30% by volume of Carbon-black Particle.

It has very good tensile strength, toughness and abrasion resistance. It is used in making automobile tyres.

(v) Dispersion - Strengthened Composites :-

In dispersion - strengthened composites, the reinforcement is done by the dispersion of particle in inert material. As the reinforcement is a inert particle, they do not react with the matrix phase hence strengthening is retained at elevated temperatures.

Ex → (i) Thoria - dispersed nickel → 3% ThO_2 is dispersed in nickel to improve high-temperature strength of nickel alloys.

(ii) Sintered aluminium powder → Aluminium oxide is dispersed in aluminium metal matrix to improve high temperature strength.

Structural Composites :-

Structural composites are the composites that are formed by combining materials together to form an overall structure with properties that differ from that of the individual components.

Types of structural Composites → Two types of structural composites

(i) Laminar Composites (ii) Sandwich Composites.

Laminar Composites

These are one type laminated Composites formed by joining sheets (or) layers that are stacked (or) cemented together. The resulting laminar Composites have high strength in number of directions.

Sandwich Composites

A Sandwich panel is any structure made of three layers. A low density core and a thin skin-layer bonded to each side.

These materials are light in weight, able to transmit load from one facing to the other and have high corrosion resistance.

- Applications →
- (i) It is used in air craft
 - (ii) It finds application in automotive and transportation.
 - (iii) It is used to design hull of ships and boats.
 - (iv) It is also used in fabrication of roofs, floors etc.

UNIT-IV(Engineering materials)

Cement: cement is a material having the property of setting and hardening when made into a paste with water and has adhesive and cohesive properties capable of binding materials like bricks, stones etc.

(or)

A finely powdered mixture of calcium silicate and calcium aluminates is called "cement".

Classification of cement: cement is classified into 4 types. They are

(1) **Natural Cement:** This is obtained by calcining and pulverizing natural rocks consists of clay and lime stones. Calcium silicates and calcium aluminates are formed because of the combination of silica and alumina with calcium oxide.

Properties: Natural cement is quick setting and possesses low strength.

(2) **Puzzolana cement:** This cement has been prepared and used by Romans. In Italy there was a place called Puzzolana where the volcanic ash contains calcium silicates, aluminates iron etc.

(3) **Slag cement:** It is obtained from the blast furnace slag and hydrated lime mixed together in powdered form. Slag cement sets very slowly and also has relatively low strengths.

(4) **Portland cement:** Portland cement was discovered by Joseph Aspidin in the year 1824. Portland cement is a mixture of calcium silicate and calcium aluminate and 2 to 3% of Gypsum.

Properties: (1) It is a hydraulic.

(2) It has high strength.

(3) Setting and hardening takes 3 to 7 hrs.

(5) **Special cement:** Present days a number of special kinds of cement like water proof cement, white cement, rapid hardening cement etc are available in the market which are with some special properties. These cement have some specialized applications (additives) only.

Chemical Composition of Portland Cement

Chemical Composition of Portland cement: According to IS 269-1975. Composition of Portland cement should satisfy.

(a) Ratio of the percentage of lime (CaO) silica (SiO₂) alumina (Al₂O₃) and iron oxide when calculated.

Therefore

$$\frac{\text{CaO}}{2.8\text{SiO}_2 + 1.2\text{Al}_2\text{O}_3 + 0.65\text{Fe}_2\text{O}_3} = 0.66 \text{ to } 1.02$$

Should be greater than 1.02 and not less than 0.66.

(b) The ratio Al₂O₃/Fe₂O₃ not less than 0.66.

(c) Magnesium oxide (MgO) not more than 6%.

(d) Sulphur trioxide (SO₃) not more than 2.75%

(e) Insoluble residue not more than 2%.

Chemical composition: 1. CaO (lime) ----- 60.66%

2. SiO₂ (silica) ----- 17.25%

3. Fe₂O₃ (Iron oxide) - 0.5 - 6%

4. Al₂O₃ (alumina) - 3 - 8%

5. MgO (magnesia) - 0.1 - 5.5%

6. SO₃ (sulphur trioxide) - 1 - 3%

7. Na₂O + K₂O (alkali) - 0.3 - 1.5%

Average compound composition:

1. C₃S (Tricalcium silicate) - 48%

2. C₂S (Dicalcium silicate) - 27%

3. C₃A (Tricalcium aluminate) - 10%

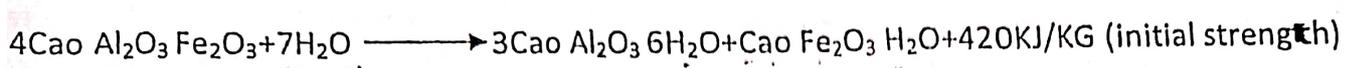
4. C₄AF (Tetra calcium alumino Ferrite) - 8%

5. CaO (Free calcium oxide) - 0.9%

6. MgO (Free magnesium oxide) - 2.5%

7. CaSO₄ (calcium sulphate) - 2.8%

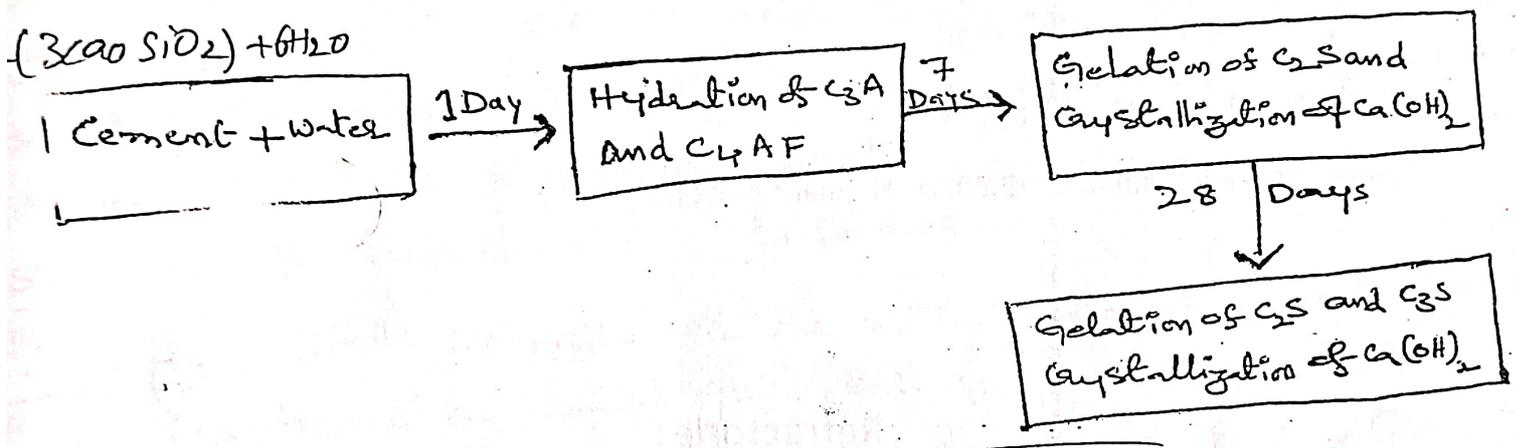
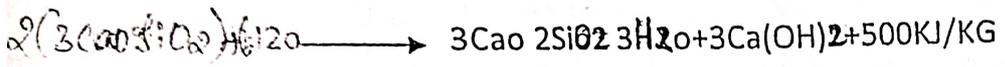
Day-2 to 7:



Day 7-28:



The final setting and hardening of element



Analysis of cement or testing of cement

As per Indian standard: 269-1969

I. Lime saturation factor =
$$\frac{\text{CaO}}{2.8\text{SiO}_2 + 1.2\text{Al}_2\text{O}_3 + 0.65\text{Fe}_2\text{O}_3} = 0.66 \text{ to } 1.02$$

Bogue's equation percent

$C_3S = 54.1\%$

$C_3A = 10.8\%$

$C_4AF = 5.1\%$

II The ratio of $\text{Al}_2\text{O}_3 / \text{Fe}_2\text{O}_3$ shall not be less than 0.66

III In soluble residue not more than 2%

than 6% & SO_3 not more than 2.75%

V. Setting times=30 min(initial) Final=10hrs

VI. Heat of hydration = after 7 days \leq 65 cal/gm

After 25 days \leq 75 cal/gm

Compressive strength: after 3 days \geq 1600 lb/sq inch

After 7 days \geq 2500 lb/sq inch

(or)

3days: not less than 1.6 kgf/mm^2

17days: not less than 2.2 kgf/mm^2

Here kgf is kilogram force= 9.807 N N means newton.

Refractories

Refractories may be defined as any material that can withstand high temperature without softening melting or undergoing deformation in shape and size.

Classification refractories

- (1) Acidic refractories: These consists of acidic materials like aluminum(Al_2O_3) and silica (SiO_2) Zirconia
- (2) Basic refractories: These are consists of basic substance like Cao, Mgo
- (3) Natural refractories: These are made from weak acidic and basic substance like carbon, chromite, graphite, zirconia, layborum dum.

Criteria of a good refractory material:

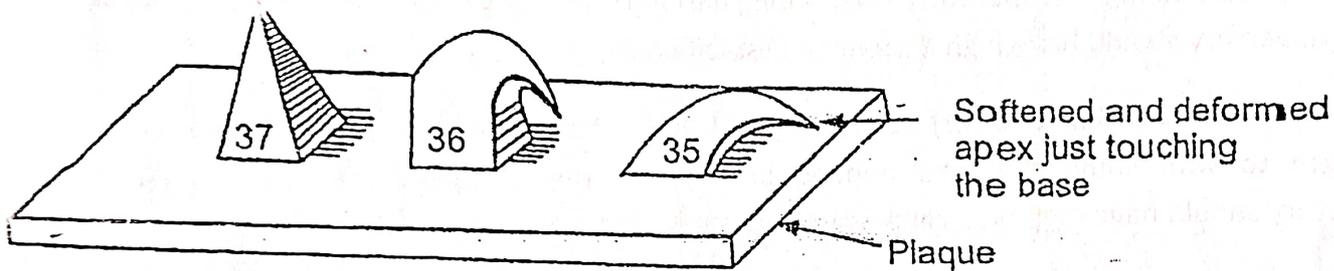
- I. It should not be affected by a sudden change of temperature and should withstand high temperature
- II. It should not melt at the operating temperature
- III. It should be chemically inert to the corrosive gases molten Metals, Slags, etc
- IV. Not crack and suffer loss in size at operating temperature
- V. Its expansion and contraction should be uniform with change of temperature

Properties of refractories (or) criteria of refractories:

1. Refractoriness: It is the ability of the refractory to withstand high temperature without any deformation.

Measurements of Refractoriness: This ability can be tested using Pyrometric cone test (or) Seger cone test. So refractoriness is expressed in terms of PCE (Pyrometric Cone Equivalent) which is a number representing the softening temperature of a refractory material of standard cone.

Measurements of these cones are small pyramid shaped, 38mm high and 19mm long sides with triangular base. The test cone and standard cone are heated under standard conditions. The cone number is the PCE value of test cone if the test cone softens earlier than standard cone. The PCE of test cone is taken as average value of two standard cones. If the test cone softens along with standard cone, the PCE value of test cone will be same of standard one. Thus a good refractory should have high refractoriness.



3. **Chemical inertness:** This is the property of showing inactiveness to the chemical reaction with, fuel ashes, Slags, furnace gases etc.

4. **Thermal expansion:** The expansion of a refractory under heat is called thermal expansion. A refractory should have least possible thermal expansion.

5. **Porosity:** Refractories generally contains pores either due to manufacturing defects or incorporation of saw dust etc. during manufacture. Porosity is defined as the ratio of its porous volume to the bulk volume.

$$\text{Porosity} = \frac{W - D}{W - A} * 100$$

W = Weight of saturated specimen (with water) in air.

D = weight of dry specimen

A = Weight of saturated specimen (with water) in water

W = weight of saturated specimen, D = weight of dry specimen, A = weight of saturated specimen in water.

Advantages:

- Highly porous refractory reduce thermal spalling
- Highly porous refractory can be used in furnaces oven retorts etc.

Disadvantages: Highly porous refractory reduces,

- (a) Strength
- (b) Resistance to corrosion
- (c) Resistance to abrasion

6 Thermal spalling: This is the property of breaking, cracking (or) peeling off a refractory under high temperature so, a good refractory must have thermal spalling.

7 Thermal conductivity: It depends up on the chemical composition and porosity of refractory. Most of the furnaces are lined inside with refractory materials of low thermal conductivity in order to heat losses to outside by radiation.

8. Dimensional stability: This is the resistance of refractory material to any volume changes on its exposure to high temperature over a long period time is called dimensional stability. A good refractory should have high dimensional stability.

9. Refractoriness under load (or) Strength (RUL): Refractory should have high mechanical strength to with stand the load applied under operating temperature. Thus a good refractory should have high load capacity which can be measured by RUL test.

10. Abrasion Resistance: A good refractory should resist the abrasion action of fuel gases, flames, Slags etc.

11. Electrical conductivity: Generally, refractories are poor conductors of electricity. (Except graphite) so refractories have low electricity conductivity.

Causes for the failure or refractory materials:

- 1) The most common cause for failure of refractory is chemical reaction with the environment. The acidic refractory is affected by basic atmosphere and basic refractory is affected by acidic environment.
- 2) If the refractories are highly porous then the atmospheric particles like smoke, dust, carbon, co etc many get trapped in the pores so that the ability of the refractory gets decreased.
- 3) Overheating (or) high temperature the rate of chemical reaction gradually increases. Sometimes, rise in temperature beyond the safe limit it may leads to distraction of refractory.
- 4) The thermal spalling and mechanical spalling also causes the failure of refractory material.

Lubricants

Lubricant :- A substance which applied in between two moving parts (or) sliding surfaces in order to reduce the frictional resistance between them is called Lubricant.

Functions of Lubricant :- (1) The important function of a lubricant is to reduce frictional resistance.

- (ii) It reduces frictional heat acting as a coolant between the rubbing surfaces.
- (iii) It enhances the efficiency of the machine and reduces the maintenance cost.
- (iv) Lubricants also absorb shocks produced in machine parts.
- (v) In the case of leakage of gases at high pressure, lubricants act as seal.
- (vi) Lubricants prevent corrosion, rusting and also reduce the noise of the machine.

Classification of Lubricants

Lubricants are classified into following types.

- (i) Liquid Lubricants (or) Lubricating oils
- (ii) Semi solid Lubricants (or) Greases
- (iii) Solid Lubricants

(i) Lubricating oils (or) Liquid Lubricants :- A lubricant in liquid state is called lubricating oil. It reduces the friction and wear & tear of the machinery.

- A good liquid lubricant has
- (i) Ideal viscosity, High boiling point, low freezing point.
 - (ii) Non-corrosive property.

Lubricating oils are classified into 4 types

- (i) Animal + Vegetable oils
- (ii) Mineral (or) Petroleum oils
- (iii) Blended oils
- (iv) Synthetic oils

(1) Animal + vegetable oils :- Animal + Vegetable oil are used before introduction of Petroleum oils.

Ex: Veg oils :- Castor oil, olive oil, Palm oil,
Animal oils :- whale oil, Cod liver oil, Lard oil (from pig)

(2) Mineral (or) Petroleum oils :- These oils are obtained by distillation of petroleum at a temperature of 300c. The length of the hydrocarbon chain varies from 12 to 50 Carbon atoms. The oils having shorter Carbon chain have lower viscosity than the oils having longer Carbon chain.

(3) Blended oils :- In these oils some additives can be added to improve oiliness, reduce rusting and other good characters.

The additives can be vegetable oils, Fatty acids, Sulphonates etc.

(4) Synthetic lubricating oils :- Synthetic lubricating oils are used under very severe conditions where other lubricating oils are not to work. Ex: Silicones, Dibasic acid esters.

(i) Graphite :- It contains hexagonal structures arranged layer by layer. The parallel layers slide over one another

Properties :- (i) The distance between two layers may be around 3.4 \AA

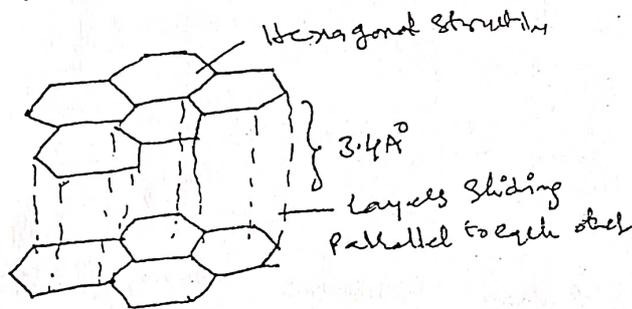
(ii) The little Vanderwaals forces allow the layers to slide over on each other

(iii) Graphite is soapy to touch, non-flammable and not easily oxidised below 375°C

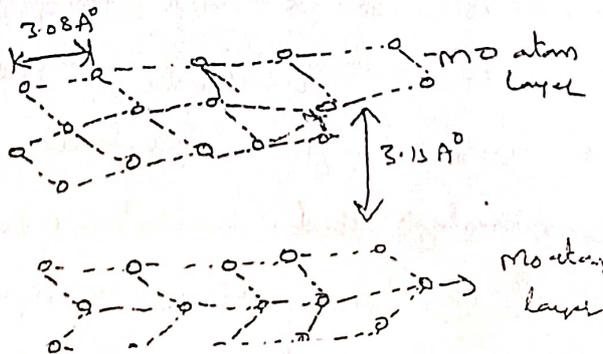
(iv) It can be used either in dry powdered form (or) as a suspension in oil (or) water

(v) Carbon has sp^2 hybridization. (\checkmark) sp^2 hybridization

USE :- It is used as lubricant in air-compressors, railway track joints, open gears, chains, cast iron bearings etc.



Molybdenum Disulphide :- It has a sandwich-like structure in which a layer of molybdenum atoms lies between two layers of sulphur atoms. The layers are held together by sp^2 inter laminar attraction. It has low frictional coefficient and can be used up to 400°C . It can be used in powder form (or) in solvents (or) greases.



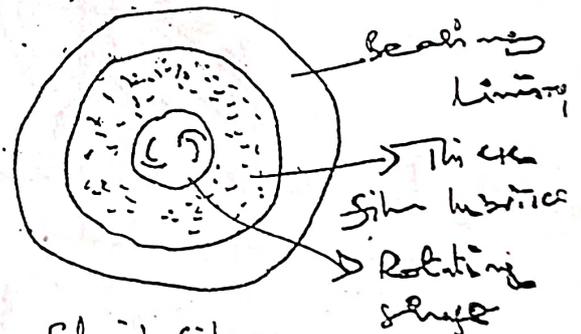
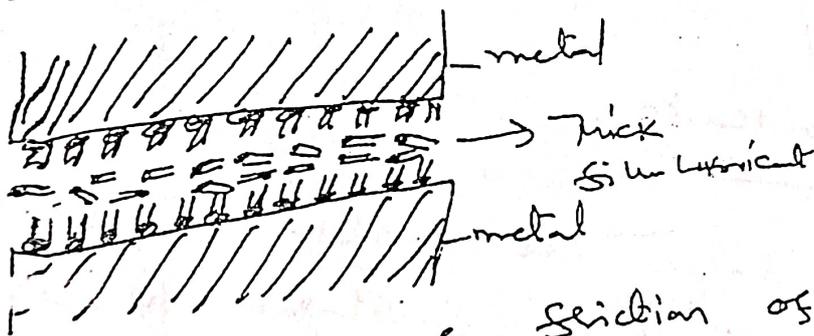
Theory of Lubrication (or) Mechanism of Lubricants

There are mainly three kinds of lubrication processes

- (i) Fluid film (or) Thick film (or) Hydrodynamic lubrication
- (ii) Thin film (or) Boundary lubrication
- (iii) High Pressure lubrication

Fluid film (or) Thick (or) Hydrodynamic lubrication :-

In thick film lubrication process, a thick film of lubricant is applied between the moving surface. So that the contact between moving surfaces is mostly prevented. The lubricant selected for this kind of lubrication should have moderate viscosity and sufficient oiliness to adhere to the machine parts.



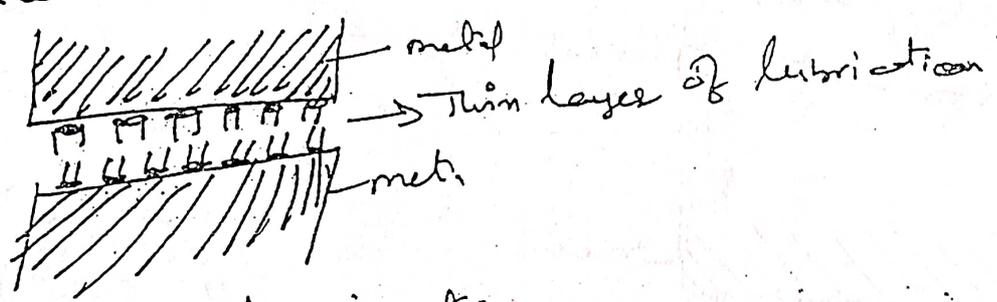
The coefficient of friction of fluid film (or) hydrodynamic lubrication process is very less (0.001 to 0.003).

A good example of this kind of lubrication is the case of shaft running at a good speed which is placed inside a well lubricated bearing.

② Thin film Lubrication (or) Boundary Lubrication:

In this kind of lubrication process, lubricant is absorbed on the metallic surface in the form of thin layer which avoid the metal-to-metal direct contact. The load is carried by the thin layer adsorbed on the both the metal surfaces.

The useful materials for boundary lubrication should have (i) Long hydrocarbon chain (ii) with polar groups (iii) active function groups (iv) high viscosity Index (v) Resistance to heat & oxidation



High pressure lubricants: -

When moving surfaces are under high pressure and speed frictional heat is developed resulting in high temperature at the surface which causes the lubricant film to melt and break down. In these conditions, the metal surfaces come in direct contact and undergoes wear, deformation and seizure.

UNIT-V

Unit-V

Surface Chemistry and Applications

Introduction :-

Surface chemistry is the branch of chemistry that deals with the study of the phenomena occurring at the surface (or) interfaces of substances like adsorption, heterogeneous catalysis, formation of colloids, corrosion, crystallization, dissolution, chromatography, etc., surface chemistry finds its applications in industry as well as in daily life.

Colloids :

It is a heterogeneous solution of two immiscible phases (dispersed phase + dispersion medium) containing particles of size 10-1000 nm.

Ex → paint, milk, ink

(i) Dispersed phase :- The particles of the dispersed substance, in colloids is called dispersed phase

(ii) Dispersion medium :- The insoluble medium, in which the colloidal particles are dispersed is called dispersion medium.

Types of Colloids

Based on the affinity between dispersed phase and dispersion medium, colloids are classified into two types.

1. Hydrophilic Colloids (or) Solvent loving Colloids

They have more affinity between dispersed phase and dispersion medium.

Ex → starch solution, gum solution.

2. Lyophobic Colloids (or) Solvent hating Colloids

They have less affinity between dispersed phase and dispersion medium. Ex → Colloidal silver, Colloidal gold.

Differences between Lyophilic colloids and Lyophobic Colloid

Lyophilic Colloid

- ① Solvent loving
- ② Preparation is easy
- ③ viscosity higher than that of medium
- ④ visibility cannot be seen
- ⑤ Tyndall effect exhibits

Lyophobic colloid

- ① Solvent hating
- ② Preparation is difficult
- ③ Viscosity same as that of medium
- ④ visibility can be seen
- ⑤ Tyndall effect not exhibit.

Characteristics of Colloids

- (i) It is the heterogeneous system
- (ii) The colloidal particles may not settle down under gravity, even long time keeping.
- (iii) Colloidal particles are either positively (or) negatively charged.

Synthesis of Colloids

As we know, the colloid is a intermediate between true solution and suspension, Colloids may be prepared by the following methods

- ① Condensation methods
- ② Dispersion (or) Disintegration method

I. Condensation methods :- In this method, a large number of particles of molecular size are allowed to condense to form big particles of colloidal dimension.

Colloidal arsenious sulphide

i) It is obtained by passing slowly H_2S gas through a cold dilute solution of As_2O_3 in water.



Colloidal Silver chloride

It is obtained by mixing dilute solution of silver nitrate and sodium chloride in equivalent amounts.



Disintegration method:-

Mechanical dispersion method

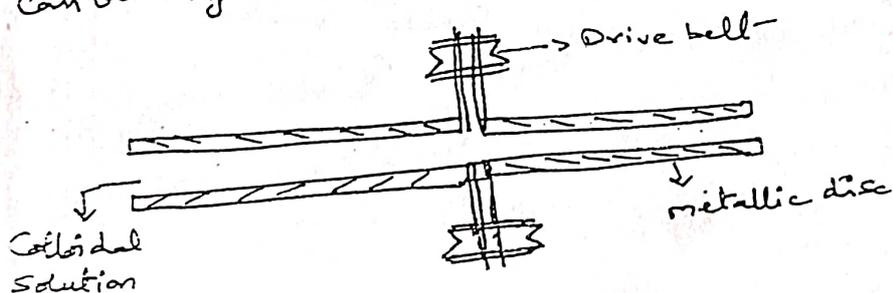
Colloids like black ink, paints, varnishes are prepared by this method. This method is carried out in three steps.

Step-1 → First, the substance to be dispersed, is ground as finely as possible, by the usual methods.

Step-2 → The ground substance is suspended in dispersion medium to get coarse suspension.

Step-3 → The coarse suspension, thus obtained, is introduced into the colloidal mill for obtaining the colloid.

Colloidal mill It consists of two metal discs, which touch each other and rotate in opposite direction at a high speed. The space between the disc can be adjusted to get the colloid of the required size.



Stabilization of Colloids

The colloid is stable when particles remain suspended in solution without settling down. In order to stabilize the colloidal system, we need to reduce the interfacial tension between colloidal particles by adding suitable stabilizing agent.

Types of Stabilization

- ① Electrostatic stabilization ② polymeric stabilization ③ Adsorption of solvent layer around colloids ④ Peptisation

① Electrostatic stabilization :- It is based on the mutual repulsion of like electrical charges. Colloidal particles possess a like electric charge on their surface. Thus the electrolytes, which increase the repulsive forces between the colloid particles, are added as a stabilizing agent.

② Polymeric stabilization :- The polymeric molecules create a repulsive ~~force~~ force counterbalancing the attractive van der Waals forces acting on a particle approaching another particle.

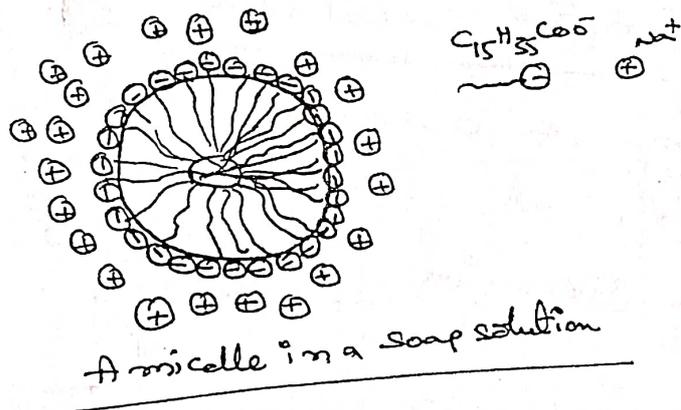
③ Adsorption of solvent layer around colloids (or) solution :- The colloids are charged particles, a layer of solvent is bound to the surface. Ex → Gelatin is stabilized by water.

④ Peptisation :- The conversion of a freshly formed precipitate into a colloid by the addition of a small amount of a suitable electrolyte is called peptisation. Precipitates like silver chloride, ferric hydroxide, aluminium hydroxide can be converted into colloids stabilized by the addition of a small amount of a suitable electrolyte.

MICELLE Formation (or) Associated Colloids - 2m (or) 5M

Micelles are the colloidal solutions, in which the colloidal particles behave as normal strong electrolytes at low concentrations. At higher concentrations, they form aggregated particles called micelles (or) associated colloids.

Example → Soap (or) detergents
When soap is dissolved in water, the negative ions aggregate to form an ionic micelle. Micelles are approximately spherical in shape. The long chain hydrocarbon portion of the anion of soap is inside the micelle and the positive ions are free to move.



Adsorption Isotherms - 5M

Definition :- Adsorption isotherm is a relationship (or a graph) between magnitude of adsorption with pressure at constant temperature.

$$\text{i.e. } x/m = KP^{1/n}$$

The extent of adsorption (x/m) (where x = mass of adsorbate, m = mass of adsorbent) depends on pressure (P) and temperature (T). It can be understood by plotting a graph between (x/m) against P .

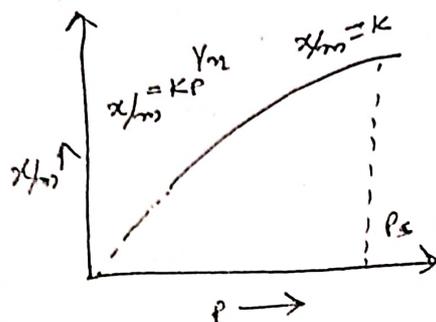
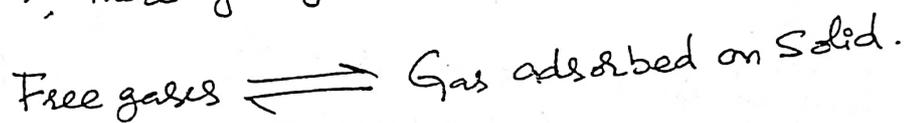


Fig: Adsorption isotherm

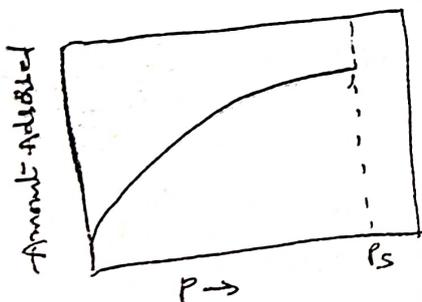
From the graph, it is clear that the extent of adsorption increases with increasing of pressure (P) and becomes maximum at (saturation pressure). At P_s the rate of adsorption becomes to rate of desorption, thereby dynamic equilibrium is reached.



Types of Adsorption Isotherms

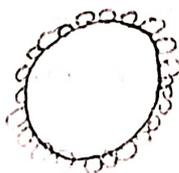
A large number of adsorption isotherms of gases on variety of adsorbents at different temperatures have been. Their results are given into five different types of adsorption isotherms.

Type - I

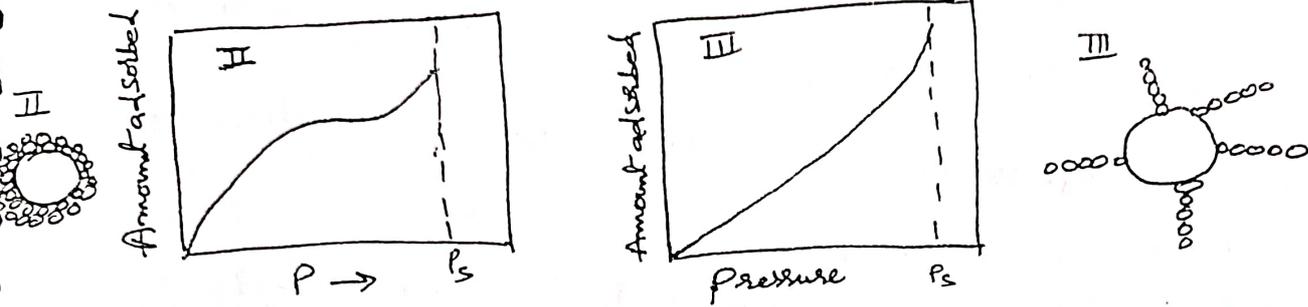


It corresponds to monomolecular adsorption. The volume of the gas adsorbed approaches a constant value P_s , which is just enough to complete monomolecular layer, even when the gas pressure is further increase in pressure will not increase the amount of adsorption.

Example → Adsorption of N_2 or H_2 on charcoal at $-180^\circ C$



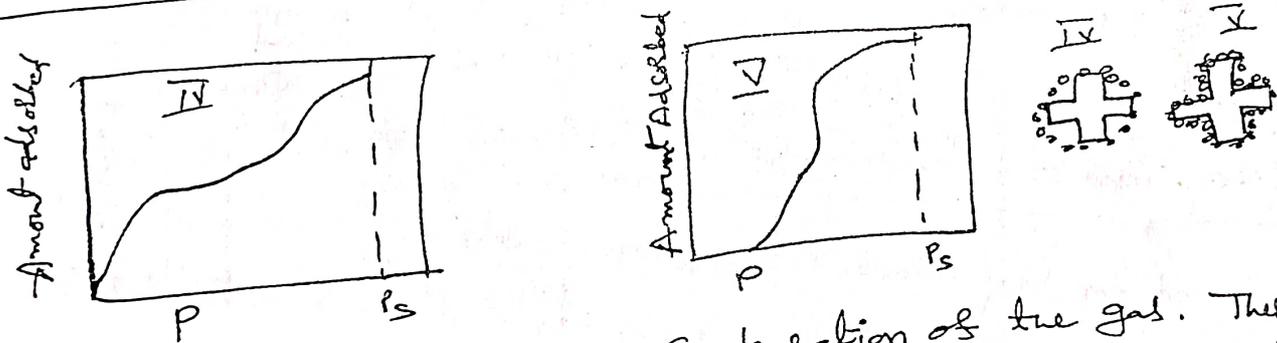
Type II and III



The amount of adsorption, in each type, is going on increasing with ~~more~~ increase in pressure. This is due to the "formation of additional layer" over the monolayer by Vanderwaals forces of attraction.

Ex :- Type II \rightarrow Adsorption of N_2 on Fe (or) Pt Catalyst at $-195^\circ C$
Ex :- Type III \rightarrow Adsorption of Br_2 on silica (or) Alumina gel at $80^\circ C$.

Type IV and V



This is known as Capillary Condensation of the gas. These isotherms indicate a possibility of Condensation of gases in the minute capillary pores of the adsorbent at the pressures even below the saturation pressure P_s .

Ex :- \rightarrow Type IV: Adsorption of benzene on silica gel at $50^\circ C$
Ex :- \rightarrow Type V: Adsorption of H_2O vapour on activated Carbon at $100^\circ C$

BET Theory (or) BET Equation

BET theory is an extension of Langmuir theory for monolayer molecular adsorption to multilayer adsorption with the following hypotheses.

- (i) Gas molecules physically adsorb on a solid in layers infinitely
- (ii) Gas molecules only interact with adjacent layers
- (iii) The Langmuir theory can be applied to each layer.

Based on the above consideration, they derived the following equation called BET equation.

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_{mc}} = \frac{V-1}{V_{mc}} \cdot \frac{P}{P_0}$$

V = Volume of the gas adsorbed at pressure P

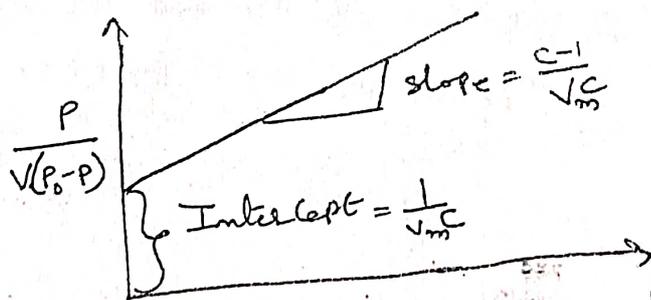
V_{m0} = Volume of the gas adsorbed when the surface of solid is covered completely with a mono layer of molecules

C = Constant

Verification of BET Equation

If C and V_{m0} are constants for a given gas-solid system, the plot of $\frac{P}{V(P_0 - P)}$ against $\frac{P}{P_0}$ will give a straight line with slope = $\frac{C-1}{V_{m0}C}$ and intercept $\frac{1}{V_{m0}C}$. Thus from the slope and the intercept both V_{m0} and C can be evaluated.

Knowing V_{m0} , the surface area of the adsorbent can be easily calculated.



Verification of BET Equation.

NanoMetals and NanoMetal Oxides

Metal nanoparticles are the particles, the size of which ranges from 1-50nm. Generally they are obtained as colloids. Colloid particles have a tendency to remain single crystal and are called as metal nanocrystals.

Properties of metal nanocrystal nanoparticles

Metal nanocrystals possess electronic, magnetic and optical properties. Since the metal nanoparticles exhibit an electronic behavior governed by quantum physics. They are also called as quantum dots.

Hardness of nanometals is 5 times more than the parent metal.
Strength of nanoparticle is 3-10 times more than the metal.

Nanometal possesses very good corrosion resistance property.
Nanometal, due to its size, possesses unexpected optical properties.

Nanometals possess lower melting point.
Electrical properties of nanometals are increased by 3 times than the corresponding metals.

Suspension of nanometal is possible because nanometals possess high surface area.

The wear resistance of nanometals are 170 times higher than the metals.

Nano metal oxides

Nano metal oxides play an important role in many areas of Chemistry, Physics and material science. They find applications in the fabrication of microelectric circuits, sensors fuel cells, coating for the passivation of surfaces against corrosion and as a catalyst.

Properties of nano metal oxides

Nano structures (or) Nano array made with nano-metal oxides possess

Special properties with respect to those bulk.

- (ii) oxides nanoparticles exhibit unique physical and chemical properties due to their limited size and a high density of corner (or) edge surface sites
- (iii) Nanometaloxides possess good transport property than the bulk metaloxides.
- (iv) The orbital conductivity of nanometal oxides are found to be very good
- (v) As the redox and acid, base properties of nanometal oxides are very good, they find many applications in various industries.

PREPARATION OF NANOMETAL AND NANOMETAL OXIDES

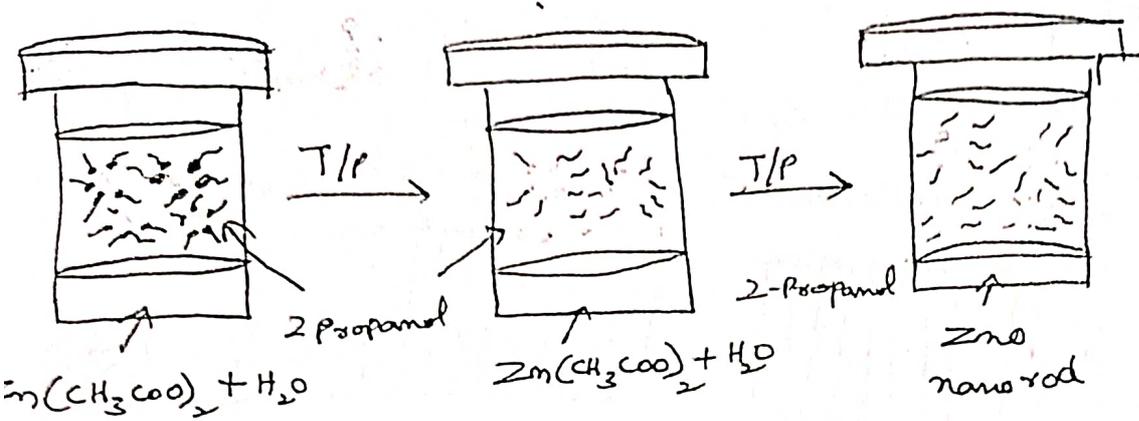
(1) Chemical method for preparation of Nanometal oxides

(i) Solvothermal Synthesis

Solvothermal synthesis involves the use of solvent under high temperature (between 100°C to 1000°C) and moderate to high pressure (1 atm to 10,000 atm) interaction of precursors during synthesis.

Solvothermal Synthesis of Zinc oxide

Zinc acetate dihydrate is dissolved in 2-propanol at 5°C . Subsequently, the solution is cooled to 0°C and NaOH is added to precipitate ZnO. The solution is then heated to 65°C to allow ZnO growth for some period of time before a capping agent (1-dodecanol) is injected into suspension to arrest the growth. The red slurry ZnO nano-crystal is obtained.



3-1. Many geometries including thin film, bulk powder, single crystals are prepared.

Thermodynamically stable novel materials can also be prepared by.

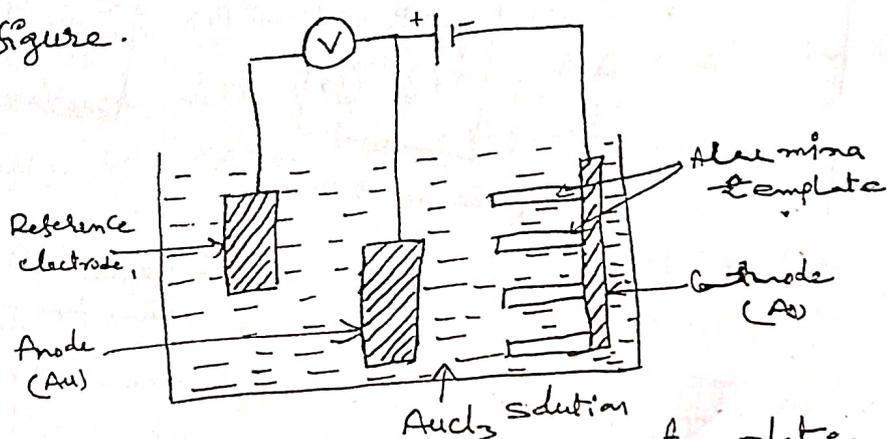
Electrochemical method of preparation of nanometals

Electro-deposition method :-

Electro-deposition method is an electrochemical method in which metal ions from the solution are deposited at the surface of the cathode.

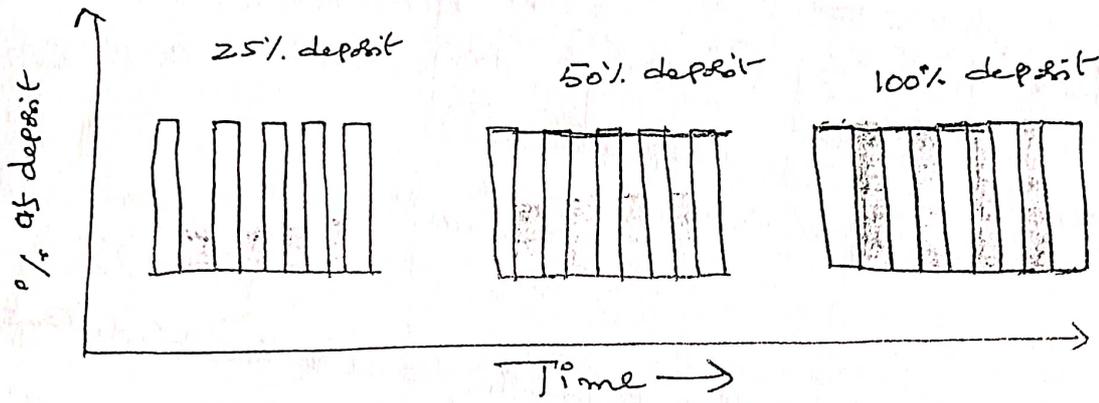
Process of electro-deposition :-

The cell consists of a reference electrode, specially designed anode and cathode. (All these electrodes are connected with the battery through a voltmeter and dipped in an electrolytic solution of a metal as shown in figure.



When the current is passed through the electrodes of template, metal ions from the solution enter into the pores and get reduced at the cathode, resulting in the growth of nanowire inside.

the pores of the template

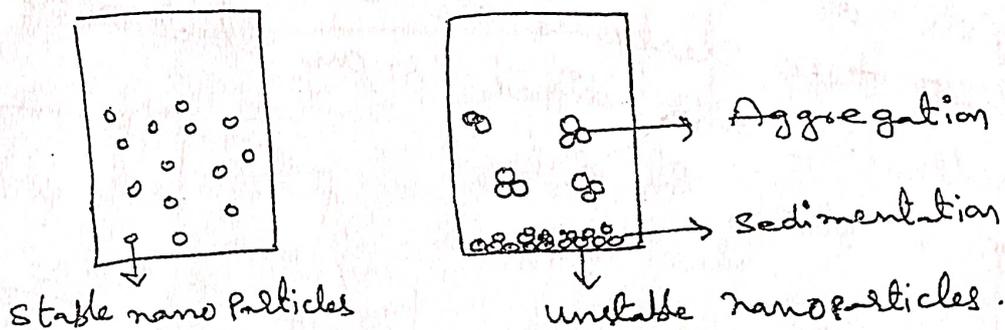


Advantages of Electro-deposition

1. This method is relatively cheap and fast
2. Complex shaped objects can be coated
3. The film (or) wire obtained is uniform
4. Metal nanowires including Ni, Co, Cu and Au can be fabricated by this method.

Stabilization of Nanomaterials by Stabilizing Agents

Most of the metal nanoparticles are unstable in environment and undergoes coalescing agglomerations oxidation. In order to avoid agglomeration and coagulation required stabilizing agent.



Methods of Stabilization

In order to avoid agglomeration and coagulation, the following methods can be adopted to stabilise the metal nanoparticles.

Electrostatic Stabilization

The metal nanoparticles are stabilized over an extended period of time only by the charges induced by the presence of small ions.

Steric Stabilization

Steric repulsion between molecules (or) ions adsorbed on neighboring particles also increases the stability of the nanoparticles.

When the length of the stabilizer is significantly longer than the nanoparticles, a sphere can be formed encapsulating the nanoparticle. Thus high molecular weight polymers are often employed as stabilizers for nanoparticles.

Stabilization by Ionic liquid

The best stabilizers for nanoparticles are ionic compounds.

Ex → The bromide anions of tetraoctylammonium bromide adsorb very strongly on many metal surfaces. It provides the bulky geometry, necessary for steric repulsion.

Stability against oxidation

Metal nanoparticles are protected from oxidation by preventing the adsorption of oxygen. So the metal surface can be modified with protective agents before exposing them to air.

Ex → Ni nanoparticle stabilized with $[Ni^{+}][BF_4^{-}]$ are stable in air and keep the dark-brown colour for more than 2 years.

Stabilization by Size

The stability of metal nanoparticles can be improved by decreasing the size of the metal nanoparticles.

Capping agent

These capping agents form bonding themselves and act as a cage.

It prevents the capping interaction of nanoparticles with one another. Thus the capping agent prevents the agglomeration of nanoparticles.

- Ex → 1. PVP (Polyvinylpyrrolidone) can be used as capping agent.
2. Sulfacet (or) Polymel (or) Cysteine may also be used as a coating material over the nanoparticles to stabilize them.
 3. Gold nano-particles can be stabilised by thiols.
 4. Silver nano-particles can be stabilised by using polyethylene glycol (PEG), EDTA, PVP and PVA.

CHARACTERISATION OF SURFACE BY PHYSICO-CHEMICAL METHODS

The followings are some important techniques used to characterise the surface of the material.

1) X-Ray diffraction (XRD)

X-Ray diffraction (XRD) has been widely used for the determination of crystalline character, crystalline size, crystalline structure and lattice constants of nanoparticles, nanowires and thin films.

The fact that the wave energy of X-rays and inter-atomic distance in a crystal are of same order led to suggest that crystals diffract X-rays. Thus, XRD is extensively used to study crystal structure of solids, defects and stresses.

The relationship is given by Bragg's equation

$$n\lambda = 2d \sin\theta$$

n = order of the
 λ = wave length
 d = inter planar d
 θ = diffraction

The diffraction pattern can be used to identify the crystalline phases and their structural characteristics.

Applications of Nanomaterials and Colloids

(1) Applications of Nanomaterials
Nano-technology finds significant impact on almost all the industries and all areas of society.

(a) Catalysis \rightarrow Catalytic property of nanomaterials depend on the surface area of the materials. Nano-catalysts are mostly heterogeneous catalysts. (i) Nano-catalyst can be used effectively where many of the traditional catalyst will not fit.

(ii) As the surface area of nano-catalyst are very high, the porosity of the catalyst is very good.

(iii) Bond breaking and bond making can be done at a more efficient scale using nano-catalysts.

Ex \rightarrow Bulk gold is chemically inert, whereas gold nanoparticles have excellent catalytic property.

(b) Medicine (i) Nano drugs \rightarrow Nano materials are used as nano drugs for the cancer and TB therapy.

(ii) Laboratories on a chip \rightarrow Nanotechnology is used in the production of laboratories on a chip.

(iii) Nano-medibots \rightarrow Nano particles function as nano-medibots that release anticancer drug & treat cancer.

(iv) Protein analysis \rightarrow Protein analysis can also be done using nano materials.

(v) Gold nanoshells for blood immuno assay \rightarrow Gold nanoshells are used for blood immuno assay.

(c) Sensors \rightarrow Nanomaterials and nano-structures play an important role in the development of more sensitive and more specific sensors.

The nano materials used in sensor development, are:

Different forms (i) It can be nanowires (ii) can be semi conductive particles (iii) can be various allotropes of Carbon (iv) can be unpaired polymeric spheres.

Ex: \rightarrow Graphene oxide \rightarrow It is used as a very good sensor. Selectively adsorb single-stranded DNA from a mixture of ss and double-stranded material.

Applications of Colloids

1) In medicine \rightarrow Colloidal medicines are found to be much more effective because of their easy assimilation and absorption. Medicines in colloidal form easily adsorbed by the body tissues and hence are more effective.

Ex: \rightarrow Argysol & Protargol are the colloidal solutions of Ag. These are used as eye-lotions.

(i) Colloidal solutions of gold, sodium and iron are used as oral medicines as well as insecticide for raising the vitality of human systems.

(ii) Alum (or) Ferric chloride is used for the coagulation of blood on minor wounds (or) cuts.

Catalyst \rightarrow Colloidal metal nanoparticles of controlled sizes and shapes play a major role in various fields.

Ex: \rightarrow Leather industry \rightarrow During the tanning the charged particles of skin are coagulated using the negatively charged colloidal materials like tannin and some compounds of aluminium and chromium.

Artificial Rain :- The water molecules, in clouds, have electric charge on them, if the charges are neutralized, they will start raining. It is done by spraying colloidal electrolytes over the clouds.

Metallurgy :- In both floatation process, sulphide ores are separated using the colloidal pine oil water mixture.

Sensors :- Colloidal crystals also can be effectively used as a very good sensors for sensing pH, temperature, pressure, mechanical deformation.

Synthetic polymers and colloids are used to measure gene expression, sequence genomes, monitor metabolic disorders and detect the presence of disease.