

ENGINEERING CHEMISTRY (20A51201T)

LECTURE NOTES

I-B.TECH & I-SEM

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VEMU INSTITUTE OF TECHNOLOGY

(Approved By AICTE, New Delhi and Affiliated to JNTUA, Anantapur)

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R20 Regulations

JAWAHARLAL NEHRU TECHNOLOGICAL UNIVERSITY ANATAPUR
(Established by Govt. of A.P., ACT NO.30 OF 2008)
ANANTHAPURAMU – 515 002 (A.P) INDIA

HUMANITIES AND SCIENCES

Course Code	ENGINEERING CHEMISTRY	L	T	P	C
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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 electrochemistry, polymers, surface chemistry, and cement

Course Outcomes (CO): After completion of the course, the student can able to

CO-1: List the differences between temporary and permanent hardness of water & explain the principles of reverse osmosis and electro dialysis. Compare quality of drinking water with BIS and WHO standards. illustrate problems associated with hard water.

CO-2: Apply Nernst equation for calculating electrode and cell potentials & Apply Pilling Bed worth rule for corrosion. Demonstrate the corrosion prevention methods and factors affecting corrosion & compare different batteries and their applications

CO-3: Explain different types of polymers and their applications & solve the numerical problems based on Calorific value, octane number, refining of petroleum and cracking of oils.

CO-4: Explain the constituents of Composites and its classification & identify the factors affecting the refractory material. Illustrate the functions and properties of lubricants, Demonstrate the phases and reactivity of concrete formation. Identify the constituents of Portland cement & enumerate the reactions at setting and hardening of the cement

CO-5: Summarize the concepts of colloids, micelle and nanomaterials, Explain the synthesis of colloids with examples & identify the application of colloids and nanomaterials in medicine, sensors and catalysis

Unit – I: Water Technology

Water Technology Introduction –Soft Water and hardness of water, Estimation of hardness of water by EDTA Method - 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 electro dialysis.

Unit-II: Electrochemistry and Applications

Electrochemistry and Applications: Electrodes – concepts, electrochemical cell, Nernst equation, cell potential calculations. Primary cells – Zinc-air battery, Secondary cells – Nickel-Cadmium (NiCad), and lithium-ion batteries working of the batteries including cell reactions; Fuel cells, hydrogen-oxygen, methanol fuel cells – working of the cells. Corrosion: Introduction to corrosion, electrochemical theory of corrosion, differential aeration cell corrosion, galvanic corrosion, metal oxide formation by dry electrochemical corrosion, Pilling Bed worth ratios and uses, Factors affecting the corrosion, cathodic and anodic protection, electroplating and electro less plating (Nickel and Copper).

Unit-III: Polymers and Fuel Chemistry

Polymers and Fuel Chemistry: Introduction to polymers, functionality of monomers, Mechanism of chain growth, step growth and coordination polymerization

Thermoplastics and Thermo-setting plastics:- Preparation, properties and applications of poly styrene. PVC and Bakelite,

Elastomers – Preparation, properties and applications of Buna S, Buna N, Thiokol

Fuels – Types of fuels, calorific value, numerical problems based on calorific value; Analysis of coal,

Liquid Fuels refining of petroleum, fuels for IC engines, knocking and anti-knock agents, Octane and Cetane values, cracking of oils; alternative fuels- propane, methanol and ethanol, bio-fuels.

Unit – IV: Advanced Engineering Materials

Advanced Engineering Materials Composites: Definition, Constituents, Classification- Particle, Fiber 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, saponification and Applications. Building materials- Portland Cement, constituents, phases and reactivity of clinker, Setting and Hardening of cement

Unit-V: Surface Chemistry & Applications

Surface Chemistry and Applications: Introduction to surface chemistry, colloids, micelle formation, synthesis of colloids (any two methods with examples), chemical and electrochemical methods (not more than two methods) of preparation of nanometals and metal oxides, stabilization of colloids and nanomaterials by stabilizing agents, solidgas interface, solid-liquid interface, adsorption isotherm, BET equation (no derivation) applications of colloids and nanomaterials – catalysis, medicine, sensors

Textbooks:

1. Jain and Jain, Engineering Chemistry, 16/e, Dhan Patrai, 2013. 2. Peter Atkins, Julio de Paula and James Keeler, Atkins' Physical Chemistry, 10/e, Oxford University Press, 2010

Reference Books:

1. G.V.Subba Reddy, K.N.Jayaveera and C. Ramachandra, Engineering Chemistry, Mc Graw Hill, 2020. 2. Skoog and West, Principles of Instrumental Analysis, 6/e, Thomson, 2007. 3. H.F.W. Taylor, Cement Chemistry, 2/e, Thomas Telford Publications, 1997. 4. D.J. Shaw, Introduction to Colloids and Surface Chemistry, Butterworth-Heineman, 1992.

UNIT-I: Water Technology

Lecture notes

WATER TECHNOLOGY**Introduction:**

Water is one of most abundant and widely distributed substance but is also most misused one. It covers 3/4th of earth's surface and essential for all organisms like animals, plants, human beings. It is not only essential for organisms but also used in engineering side for steam generation. In addition to it, it is used in domestic purposes like drinking, washing, bathing, cooking used in industries like production of paper, rayon, textiles, tires, irrigation, atomic energy, steel etc....

Sources of water: Based on their availability, sources of water are broadly divided into 2 types

- 1) Surface water
- 2) Underground water

I. Surface water:**1. Rain Water:**

- It is the purest form of water. It is obtained from evaporation of surface water.
- During the downward movement through the atmosphere, it dissolves considerable amount of industrial gases (CO₂, SO₂) and suspended particles (organic & inorganic).

2. River water:

- Rivers are fed by rain water and spring water. Water from these sources flow over the surface of earth and dissolves soluble minerals present in the soil.
- River water also contains organic matter derived from decomposition of plants and small particles of sand and rock in suspension i.e., it contains both dissolved and suspended impurities.

3. Lake water:

- It belongs to still water type. It contains constant chemical composition.
- It consists of much lesser amounts of dissolved impurities than well water.
- It has high concentration of organic matter.

4. Sea water:

- It is the most impure form of natural water. All rivers join sea along with their impurities.
- It contains 3.5% dissolved salts of which 2.6% is NaCl and other salts are sulphates of Na⁺, bicarbonates of K⁺, Mg⁺², Ca⁺² and bromides of K⁺ and number of other compounds.

II. Underground water:

- The rain water passed down to the lower layers of earth continuously until it comes in contact with rocks. It comes out of the earth in the form of spring water.
- Well and spring water has high organic purity and consists of more amount of dissolved salts. It has more hardness.

Impurities of Water:

Water has following impurities. They are

1. Inorganic Impurities
2. Organic Impurities
3. Biological impurities

Hardness of water: -

- Hardness is the characteristic property of water, which prevents formation of lather with soap.
- This is due to the presence of certain salts of Ca, Mg, Fe & heavy metals dissolved in water.
- When a sample of hard water is treated with soap it forms a white precipitate called **Scum** instead of lather.
- Soaps are Na/K salts of higher fatty acid like palmitic acid, stearic acid, oleic acids.
- Reactions of soap with hard water [CaCl₂, MgSO₄] are as follows: -
$$2C_{17}H_{35}CooNa + CaCl_2 \longrightarrow (C_{17}H_{35}Coo)_2Ca + 2NaCl$$
$$2C_{17}H_{35}CooNa + MgSO_4 \longrightarrow (C_{17}H_{35}Coo)_2Mg + Na_2SO_4$$
- Based on hardness present or not, water is classified in to two types. They are

Soft water: - A sample of water which produce lather easily with soap is called as soft water. This doesn't have salts of Ca, Mg, Fe& heavy metals.

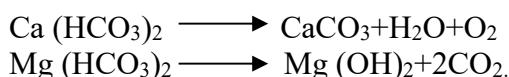
Hard water: The water which doesn't give lather easily with soap is called hard water. This water contains dissolved salts present in it.

Types of Hardness: - Hardness of water is of two types

- 1) Temporary hardness
- 2) Permanent hardness

1. Temporary or carbonate hardness:

- It is caused by the presence of bicarbonates of Calcium, Magnesium, heavy metals and carbonates of Fe.
- It can be removed by boiling. On boiling the soluble bicarbonates are converted to insoluble carbonates and hydroxides which get precipitated and can be removed by filtration.



2. Permanent or non-carbonate hardness:

- It is caused due to the presence of chlorides, sulphates of Ca, Mg and heavy metals. Unlike temporary hardness it cannot be removed by boiling.

Disadvantage of hard water: - There are several disadvantages with hard water when used in domestic & industrial purposes and also in boilers.

1. Domestic use
2. Industrial use
3. Boilers

I. Domestic Use:

Drinking: - If hard is used for drinking, it destroys the digestive system and it also forms Calcium Oxalates (Stones) in urinary track and Kidneys.

Washing: - When hard water is used for washing, it does not produce lather freely with soap and produces sticky precipitates of it. A lot of soap gets wasted and a sticky precipitate get

adhered on to the fabrics of cloth giving spots and presence of Fe salts may cause staining of cloth.

Bathing: - Wastage of soap takes place and forms sticky scum on the bath tub and body.

Cooking: - Due to the presence of calcium and magnesium salts, water boiling point gets elevated, hence more time and fuel are required for cooking. Certain foods such as pulses, peas are not cooked soft with hard water if it is used to making of tea and coffee it exhibits unpleasant odor and muddy looking extract.

II. In industrial use:

Textile industry: - The precipitates of Ca and Mg soaps adheres on the fabric and do not produce correct shapes to fabric and iron stain the cloth and produces spots on fabric. Hard water destroys the beauty of fabrics.

Sugar industry: - SO_4^{-2} , NO_3^{-2} , Alkali, carbonates of hard water arise the problem in cyclisation of sugar. The resulting sugar may be deliquescent.

Dying industry: - Hard water gives improper shades to the cloth in dying industry due to the presence of precipitates of Ca and Mg.

Paper industry: - Chlorides and sulfates of Ca and Mg affect the quality of paper.

Laundry: - A lot of soap was wasted in laundry due to the formation of precipitates of Ca and Mg.

Concrete making: - Chlorides and sulfates of hard water affect the hydration of cement and final strength of the hardened concrete.

Pharmaceuticals: - Hard water may form some undesirable products while preparation of the pharmaceuticals (drugs, ointments, injections)

III. For Steam making in boilers: -

Boilers are used for steam generation. If hard water is used in boilers it may lead to the following boiler troubles

- | | | |
|---|---|-----------------|
| 1. Formation of scales & sludges.
2. Boiler corrosion
3. Caustic embrittlement.
4. Priming & foaming | } | Boiler troubles |
|---|---|-----------------|

Degree of Hardness:

Hardness of water is expressed in terms of CaCO_3 equivalents. The molecular weight of CaCO_3 is 100 and its equivalent weight is 50 which is easy for calculation and CaCO_3 is the most insoluble salt present in hard water. All the dissolved salts present in hard water are converted in to CaCO_3 equivalents.

$$\begin{aligned} \text{CaCO}_3 \text{ equivalent} &= \frac{\text{Weight of the salt} \times \text{Equivalent of CaCO}_3 (50)}{\text{Eq wt of that salt}} \\ &\text{OR} \\ &= \frac{\text{Weight of the salt} \times \text{Molecular weight of CaCO}_3 (100)}{\text{Mol wt of that salt}} \end{aligned}$$

Units of hardness: - The following units are used to measure hardness. They are

1. Parts per million (PPM)
2. Milligrams per liter (mg/L)
3. Degree Clark ($^{\circ}\text{Cl}$)
4. Degree French ($^{\circ}\text{Fr}$)

1. PPM: - PPM is the parts of CaCO_3 equivalent hardness present per one million parts of water i.e. 10^6 parts of water.

$1\text{PPM} = 1$ part of CaCO_3 equivalent hardness in 10^6 parts of water.

2. Milligrams per liter: - It is defined as number of milligrams of CaCO_3 equivalent hardness present per liter of water.

$1\text{mg/L} = 1\text{mg}$ of CaCO_3 equivalent hardness present in one liter of water.

1 liter water weighs $1\text{kg} = 1000\text{g} = 1000 \times 1000 = 10^6\text{mg}$

Therefore $1\text{mg/L} = 1\text{mg}$ of CaCO_3 Equivalent hardness per 10^6mg of water.

$$1\text{ppm} = 1\text{mg/L}$$

3. Degree Clark ($^{\circ}\text{Cl}$):- It is defined as number of parts of CaCO_3 equivalent hardness present in 70,000 parts of water or one gallon of water.

$1^{\circ}\text{Cl} = 1$ parts of CaCO_3 eq: hardness per 70,000 parts of water.

$$1\text{PPM} = 0.07^{\circ}\text{Cl}$$

4. Degree French ($^{\circ}\text{Fr}$):- It is defined as number of parts of CaCO_3 equivalent hardness present in 10^5 parts of water.

$1^{\circ}\text{Fr} = 1$ parts of CaCO_3 equivalent hardness in 10^5 parts of water

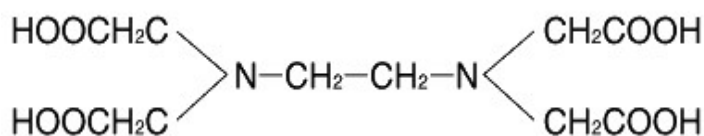
$$1\text{PPM} = 0.1^{\circ}\text{Fr}$$

$$1\text{ppm} = 1\text{mg/L} = 0.07^{\circ}\text{Cl} = 0.10\text{Fr}$$

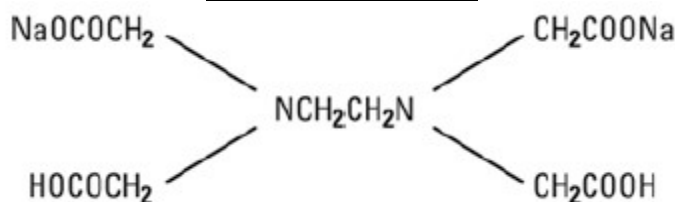
Estimation of hardness by EDTA method:

Principle:

The hardness of water is quantitatively measured by EDTA method. Ethylene diamine tetra acetic acid (EDTA) is used to estimate hardness. Disodium salt of EDTA can form stable complex (M-EDTA) with Ca & Mg ions present in hard water. The amount of EDTA consumed in the reaction gives the amount of Ca and Mg salts present in hard water.

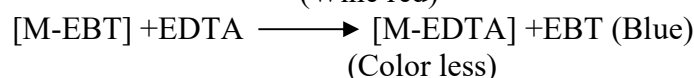
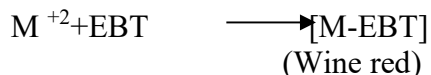


Structure of EDTA



Disodium salt of EDTA

An indicator Eriochrome black-T is used, which forms an unstable wine-red complex with Ca^{+2} & Mg^{+2} ions (in hard water) at pH-10. When this solution is titrated against EDTA solution, the color of complex changes from wine red to blue which indicates end point i.e., M-EDTA Complex release blue colored indicator EBT into water.



Preparation of solutions: -

Standard hard water: - Dissolve 1 gm of pure, dry CaCO_3 in small quantity of dil. HCl & then evaporate the solution to dryness. Dissolve the residue in distilled water and make up to 1 liter with distilled water.

Therefore 1 ml of solution contains 1mg of CaCO_3 equivalent hardness.

EDTA solution: - Dissolve 3.72 gm of pure Di-sodium salt of EDTA crystals along in 1 liter of distilled water.

Indicator: - Dissolve 0.5 gm of EBT in 100ml of alcohol.

Buffer: - Add 67.5 gm of NH_4Cl to 570 ml of conc. NH_3 solution and make up with distilled H_2O to 1 liter.

Procedure: -

A. Standardization of EDTA: -

- Rinse and fill the burette with EDTA solution.
- Pipette out 50ml of standard hard water in to a clean conical flask.
- Add 5 ml of Ammoniac buffer and few drops of EBT indicator to the sample.
- Titrate with EDTA solution till wine red color changes to clear blue.

Let the volume of EDTA used be V_1 ml

B. Estimation of total hardness: -

- Take 50ml of given hard water.
- To this add 5 ml of buffer and few drops of EBT indicator and then titrate with EDTA solution until end point.

Let the volume of EDTA used be V_2 ml

C. Estimation of permanent hardness: -

- Take 250ml of hard water sample in to a beaker and evaporate it until final volume becomes nearly 50 ml (all bicarbonates are converted to carbonates and hydroxides).
- Filter, wash and make up the filtrate to 250ml with distilled water.
- From this pipette out 50ml boiled water.
- To this add buffer and few drops of indicator.
- Titrate with EDTA until wine red color changes to deep blue.

Let the volume of EDTA used be V_3 ml

CALCULATIONS:

Standardization of EDTA: -

1ml of standard hard water = 1mg of CaCO_3 equivalent

50 ml of standard hard water = V_1 ml of EDTA

50 mg of CaCO_3 = V_1 ml of EDTA

1 ml of EDTA = $50/V_1$ mg of CaCO_3 eq.

Estimation of total hardness: -

50 ml of given hard water = V_2 ml of EDTA

50 ml of given hard water = $V_2 \times 50 / V_1$ mg of CaCO_3 eq

1 ml of given hard water = $V_2 / 50 \times 50 / V_1$ mg of CaCO_3

1 liter of given hard water = $V_2 / V_1 \times 1000$ mg/L

Total hardness = $V_2 / V_1 \times 1000$ mg/L

Estimation of permanent hardness: -

50 ml of given boiled H_2O = V_3 ml of EDTA

= $V_3 \times 50 / V_1$ mg of CaCO_3 eq

1 ml of given boiled H_2O = $V_3 / 50 \times 50 / V_1$ mg of CaCO_3 eq

1 liter of given boiled H_2O = $V_3 / V_1 \times 1000$ mg/L

Permanent hardness = $V_3 / V_1 \times 1000$ mg/L

Estimation of temporary hardness: -

$$\begin{aligned} \text{Temporary hardness} &= \text{Total hardness} - \text{Permanent hardness} \\ &= (V_2/V_1 \times 1000 - V_3/V_1 \times 1000) \\ &= (V_2 - V_3/V_1) \times 1000 \text{PPM} \\ \text{Temporary hardness} &= (V_2 - V_3/V_1) \times 1000 \text{ mg/l.} \end{aligned}$$

WATER FOR INDUSTRIAL USES

Water for steam generation: -

Water is used for making steam. Such water should be free from dissolved salts, gases, suspended impurities, oils & silica etc... Usually boilers are used for of steam generation. The boilers are heated with fuels such as coal. The steam generated rotates the blades of turbines fast to produce electricity. This electricity produced by making use of water in boiler. The turbine is a magnet wounded by coil wire.

Boiler Troubles: -

If hard water is used in boilers the following problems arise

1. Priming and foaming
2. Boiler corrosion
3. Formation of scales and sludge's
4. Caustic embrittlement.

(I) Priming & foaming (or) Carry over: - The process of formation of wet steam is called as priming or carry over. The steam carrying water droplets is called as wet steam.

(A) Priming: The phenomenon of steam production along with water droplets by rapid boiling of water is nothing but priming.

Reasons: -

1. Very high steam velocity.
2. Sudden boiling.
3. Improper boiler design.
4. High water levels.
5. Presence of large amounts of dissolved salts.

Prevention: -

1. Maintaining low water levels
2. Using softened water
3. Fitting mechanical steam purifiers.
4. Using well designed boiler

(B) Foaming: - The production of persistent bubbles or foam in boiler water surface is called foaming.

Reasons: -

1. The presence of oily or soapy substances.
2. Certain dissolved salts.

Prevention: -

1. It can be avoided by adding anti-foaming agents like cotton seed oil & castor oil
2. By adding NaAlO_2 which coagulates oily or soapy substances.

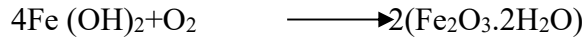
(II) Boiler corrosion: - The decay of boiler material by chemical or electro chemical attack by its environment is called boiler corrosion.

Reasons: -

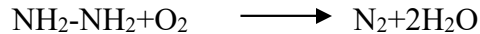
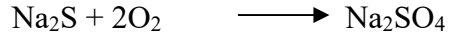
1. Due to presence of dissolved O_2
2. Dissolved CO_2
3. Acids from f dissolved salts.

1. Dissolved O_2 : - At room temperature one liter water consists eight mg of dissolved O_2 . It attacks boiler material causing rust formation.





Removal: - Dissolved oxygen is eliminated by adding calculated quantity of sodium sulphate and sodium sulphide or hydrazine.

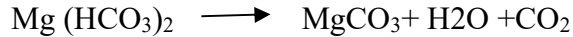


Among these the hydrazine method is ideal method for removal of dissolved oxygen. The liberated in not harmful to boilers.

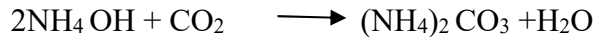
2. Dissolved CO₂: -It gives carbonic acid with water. This carbonic acid has corrosive effect on boiler material.



Carbon dioxide is also produced from decomposition of bi carbonate salts usually present in water.



Removal: - It is removed from water by adding calculated quantity of NH₃ in the form of NH₄ OH to produce ammonium carbonate.

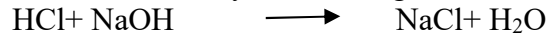


3. Acids from dissolved Salts: Acids that are produced from dissolved salts are also mainly responsible for corrosion. Certain salts like magnesium chloride, calcium chloride etc....produce acids by their hydrolysis.



The liberated HCl reacts with Fe produces HCL again and finally leads to formation of rust.

Removal: - It can be removed by neutralizing acids with alkali.



(iii) Scales & Sludge's: - In boilers, water evaporates continuously and the concentration of dissolved salts increase progressively. When their concentration reaches saturation point, they are thrown out of water in the form of precipitates on the surface or inner walls of boilers. The precipitation takes place in two ways.

1. Scales
2. Sludge's

1. Sludge's: - 1. Sludges are soft, loose, slimy non – stick precipitates produced due to higher conc. of dissolved salts.

2. It can eerily be scrapped off by wire brush.

Reason: - Sludge's are formed by substances which have greater solubility in hot water than in cold water.

Eg; MgCl₂, Mg (CO₃)₂, Mg SO₄, CaCl₂ etc.

Disadvantages: - 1. Sludges are bad conductors of heat; hence it wastes portion of heat generated.

2. Excessive sludge formation reduces the efficiency of boiler.

3. It settles in the region of poor circulation areas such as pipe connection,

Plug opening, gauze glass connection leading to checking of the pipes.

Prevention: - 1. By using well softened water.

2. Frequently carried out blow down operations (removal of conc. water from the Bottom of boiler).

2. Scales: - 1. Scales are hard, sticky deposits formed on inner walls of boiler.

2. The main source of boiler troubles are scales and are very difficult to remove once they are deposited on the inner walls of boiler.

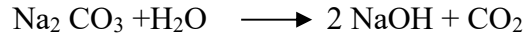
Disadvantages: -

1. Wastage of fuel.
2. Decrease in efficiency.
3. Low boiler safety & danger of explosion (at high temp. cracks may be formed on boilers scale leading to explosion).
4. Scales are bad conductor of heat.

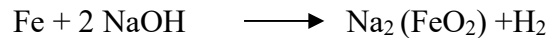
Removal of scales: -

1. Scales are not easily removed by wire brush, scrappers or wiped piece.
2. Scale can be removed by thermal shocks (sudden heating and cooling).
3. Using certain chemicals to removal of scales
 - a. 5-10% of HCl - used to removal of CaCO₃ scales.
 - b. EDTA- removal of CaSO₄ scales.
 - c. MgO - removal of silica
4. By adding of anti –coagulants (removal of silica scales)

IV. Caustic Embrittlement: - It is at type of corrosion produced by caustic alkalinity (NaOH). Usually, water consists of Na₂CO₃ which is hydrolyzed to alkali at high temp.



The NaHCO₃ present in water produce Na₂CO₃ which in turn give NaOH. This NaOH passes in to the small cracks or stress areas on the boiler by capillary action and attacks the surrounding area and dissolves the Fe of boilers as sodium ferro ate.



This causes embrittlement of boiler parts particularly at joints, bends, pipes etc.

Disadvantages: - Failure of boiler.

Prevention: -

1. Neutralizing the alkali with very small quantity of acid.
2. By adding sodium phosphate as softening agent to water.
3. By adding sodium sulphate, lignin to boiler water which blocks hair cracks.

WATER TREATMENT FOR BOILERS:

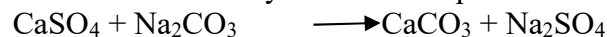
Water treatment is used for prevention of scales & softening of water. They are two types.

1. Internal treatment used to remove scales
2. External treatment for softening water.

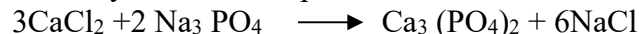
Internal treatment: - The following internal conditioning methods are used prevention of scales.

1. Colloidal conditioning: - **When** certain chemicals like tannin, agar - agar, kerosene are added to water, these substances coat the outer surfaces of crystalline ppts, and thus forms colloidal non – sticky, sludge like ppt which can be easily removed by mechanical methods like blow – down operation.

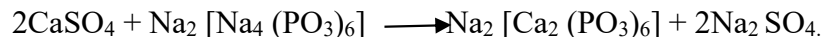
2. Carbonate conditioning: - In low pressure boilers scale formation can be avoided by treating boiler water with Na₂CO₃. The scale forming salts like CaSO₄ are partially converted to CaCO₃ (loose sludge) , which can be removed by blow down operation .



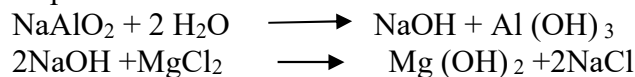
3. Phosphate conditioning: - In high pressure boilers Na₂PO₄ reacts with water forms loose ppt. when can be easily removed by blow down operation.



4. Calgon conditioning: - Na [Na₄ (PO₃)₆] [Calgon] is added to boiler scales forms soluble complex with CaSO₄.



5. NaAlO₂ conditioning: - In water sodium aluminate gives aluminum hydroxide & NaOH. This NaOH reacts with magnesium salts to form Mg (OH)₂ ppt. This hydroxide interacts with finely divided particles and neutralizes the charge on colloidal particles and forms loose, soft ppt. removed by blow down operation.



2. External treatment: - This is used for softening of water. The removal of hardness causing salts from water is nothing but softening of water. The most important method for softening is ion exchange process and Zeolite process.

Ion – exchange process / Demineralization / Deionization: -

Ion exchange resins are used for softening of water. Resins are insoluble, cross linked, long chain, organic polymers with a micro- porous structure, and their functional groups are attached to the chains responsible for the ion –exchanging properties. These Resins are two types.

1. Cation exchanger
2. Anion exchanger

Cation exchanger (RH⁺): These resins contain acidic functional groups (COOH/SO₃H). These are capable of exchanging their H⁺ ions with cations of the dissolved salts which comes in their contact. They are represented by the general formula RH⁺.

R—Structure of the resin,

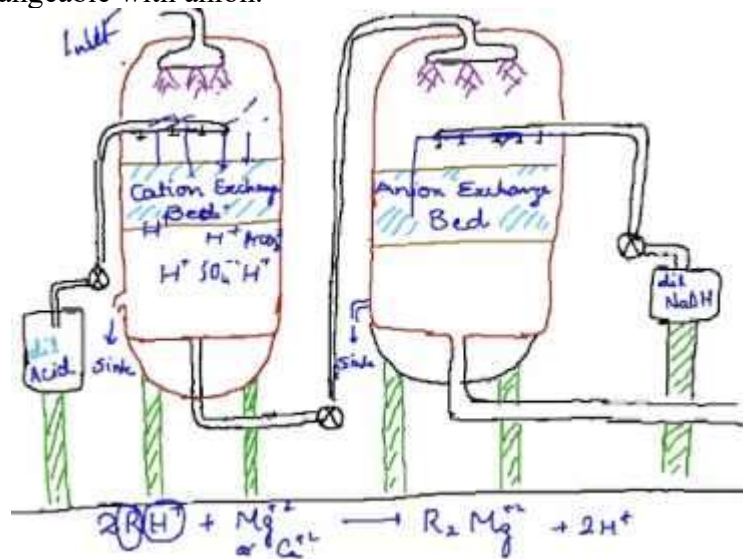
H⁺-- exchangeable with cation.

Usually, they are styrene di vinyl benzene copolymers.

Anion exchanger (ROH⁻): R— general structure of resin Styrene divinyl benzene (or) amino formaldehyde (or) phenol formaldehyde copolymers which contain amino or quaternary ammonium or quaternary their OH⁻ ions with any anion present in the dissolved salts. These are represented by the formula ROH⁻. phosphate or ternary sulphonium groups as an internal part of the resin matrix. These resins exchange

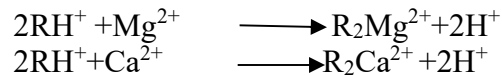
R—Structure of the resin,

OH⁻-- exchangeable with anion.



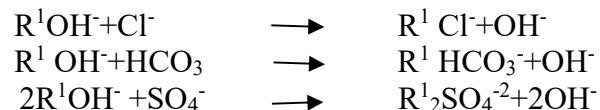
Process: - In demineralization plant the first chamber is filled with cation exchange resin and second one is with anion exchange resin.

Step 1: - When hard water is passed through bed of cation exchange resin, it exchanges H⁺ ions with Ca²⁺, Mg²⁺, Na⁺ of hard water



Thus, hardness producing cations are removed.

Step 2: - Then the water is passed through anion exchange resin, it exchanges anions like Cl⁻, HCO₃⁻, SO₄²⁻ which enter from 1st chamber to 2nd.



Thus hardness causing anions are removed.

Step 3: - The H⁺ ions that are produced from 1st chamber combine with OH⁻ ions produced from 2nd chamber to form water.



Hence the water produced from ion exchange process is completely free from all cations & anions of hard water.

Regeneration of resins: - After deionization of certain amounts of water, the cationic and anionic exchangers will be exhausted. Hence, they are employed to regeneration for further uses.

- The exhausted cationic exchange resin can be regenerated by passing dil. HCl.

$$\begin{aligned} R_2Mg^{2+} + 2HCl &\rightarrow 2RH^+ + MgCl_2 \\ R_2Ca^{2+} + 2HCl &\rightarrow 2RH^+ + Ca_2Cl \end{aligned}$$
- The exhausted anionic exchange resin can be regenerated by passing dil. NaOH.

$$\begin{aligned} R^1Cl + NaOH &\rightarrow R^1OH + NaCl \\ R^1HCO_3 + NaOH &\rightarrow R^1OH + NaHCO_3 \\ R^1SO_4^{2-} + 2NaOH &\rightarrow 2R^1OH + Na_2SO_4 \end{aligned}$$

Advantages	Disadvantages
<ol style="list-style-type: none"> Highly acidic or alkaline water can be treated by this method. It produces very low hardness nearly 2ppm. the softened water is completely free from salts and fit for use in boilers. 	<ol style="list-style-type: none"> This equipment is costly. More expensive chemicals are required for regeneration. Turbid water cannot be treated by this method.

Demineralization /Desalination Of Brackish Water: -

Reverse Osmosis:

Reverse osmosis is used for desalination of sea water. The process of removal of salts from sea water is nothing but desalination. Sea water contains an average of about 3.5% of salts. This water is totally unfit for drinking and other domestic uses.

A semi permeable membrane is used for desalination which is made of cellulose acetate, polymethacrylate, polyamide polymers which don't allow dissolved solute particles, molecules, salts, ions etc.... By osmosis solvent flow from low conc. to high conc. at constant pressure. However, an excess of osmotic pressure is applied to sea water, so that the solvent flow in reverse direction i.e. solvent is forced to move from high conc. to low conc. across the membrane. This means semi permeable membrane doesn't allow dissolved salts of sea water through it. This process is called reverse osmosis & this membrane filtration is called super/hyper filtration.

Advantages:

- It is used for removal of ionic, non-ionic, colloidal, high molecular weight organic matter.
- Removes colloidal silica which is not removed by ion exchange process.
- The life span of semi permeable membrane is about 2 years.
- The membrane can be replaced within few minutes.
- This method is a simple, economical, & highly reliable.

Electro dialysis:

- This is one of the efficient methods used for the Desalination of water.
- The Process of decreasing the concentration of salts in saline water using ion selective membranes under the influence of a direct current is called "**Electro-Dialysis**".
- It is based on ion migration towards oppositely charged electrodes by passing direct current using ion selective permeable membrane.
- The cation membranes are permeable to only cations and anion membranes are permeable to only anions.
- This process gives pure water by decreasing salt concentration.

Working:

- Electro dialysis cell consists of a series of alternative cation permeable membrane (C) and anion permeable membrane (A).
- Cation and anion permeable membranes are formed as compartments i.e., CA and AC.

- Two electrodes are immersed in saline water to apply electric field.
- Saline water is passed under pressure of about $5-6\text{Kg m}^{-2}$ between membrane pairs and electric field is applied across the two electrodes.
- The Positive ions moves through 'C' while anions moves through 'A' from each compartment of 'CA'.
- The salt content in Compartment 'CA' is decreases and increase salt concentration in 'AC' compartments.
- The fresh water is collected from Compartment 'CA' and concentrated brine from 'AC' is discharged.

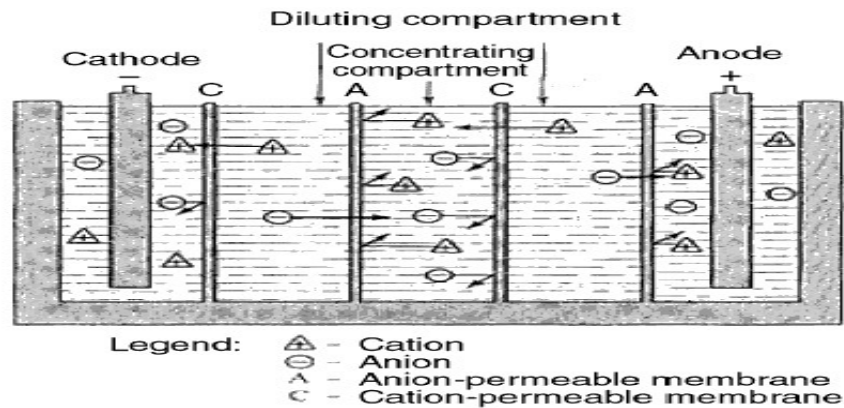


Fig: Electro-dialysis Cell

UNIT-II: Electrochemistry and Applications

Lecture notes

Electro chemistry: This is a branch of physical chemistry that deals with conversion of chemical energy into electrical energy and vice versa.

Electrolyte: -A Substance, which decomposes as a result of passage of electric current, is called "Electrolyte".

Electrolysis: -The phenomenon of decomposition/ breakdown/ lysis of electrolyte by passing electricity is called electrolysis.

Electric current: -The flow of electrons that are generated by a battery when the circuit is complete is called electric current.

Electric conductor: -Any substance which allows or passes electric current through it is called as 'electric conductor'.

Anode: It is an electrode at which Oxidation occurs.

Cathode: It is an electrode at which Reduction occurs.

Types of Electrolytes: Electrolytes may be classified into

1. Strong electrolytes
2. Weak electrolytes

1. Strong electrolytes: It is a substance that gives a solution in which almost all the molecules are ionized and having increasing value of equivalent conductance at low dilution.

Eg: Strong acids : HCl, H₂SO₄, HNO₃, HBr etc.
 Strong bases : NaOH, KOH, Ca (OH)₂, Mg (OH)₂ etc.
 Salts : NaCl, KCl, AgCl₂

2. Weak electrolytes: The electrolytes which ionize to a small extent on dilution are called weak electrolytes. They are poor conductors in solution.

Eg: Weak acids : All organic acids like Acetic acid, Propionic acid etc.
 Weak bases : Alkyl amines, NH₄OH
 Weak salts : HgCl₂ and Lead acetate.

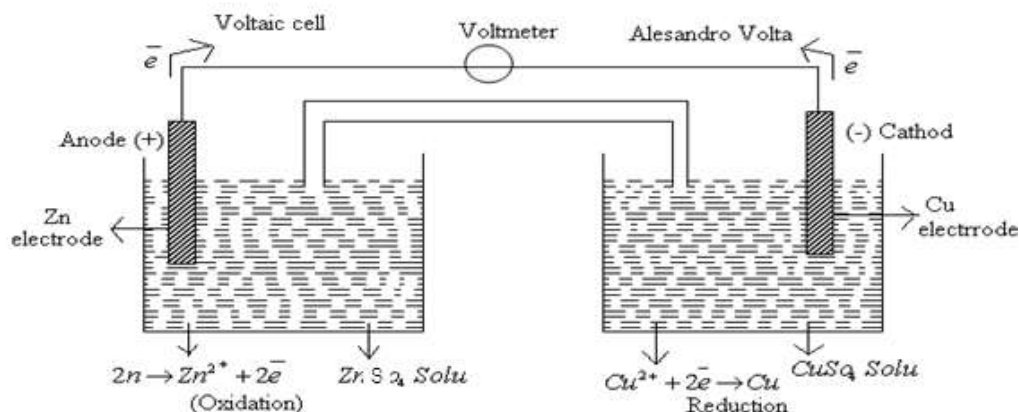
Galvanic Cells or Voltaic Cells: -

- A Voltaic cell is a device which is used for converting chemical energy into electrical energy. A redox reaction is utilized to get electrical energy.
- In galvanic cells electric current results from a redox reaction in which oxidation occurs at one electrode and reduction at the other.
- The substance which loses electrons is called **oxidized** and the process is called **Oxidation** and the substance which gains electrons is called **Reduced** and the process is **Reduction**.

- The apparatus that provides electricity through redox reaction is called galvanic cell, invented by Luigi Galvani (1737-1798) and also called as voltaic cell (Alessandro Volta (1745-1827).

- Ex: Daniel Cell

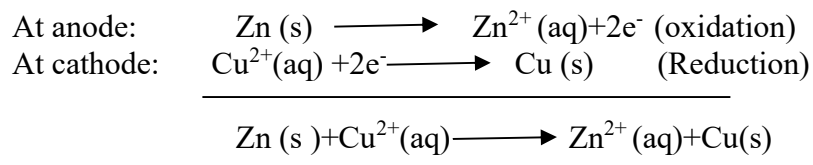
- **Daniel Cell:** A Daniel cell is made up of two half cells (an individual oxidation and reduction takes place at two electrodes).
- On the left Zinc electrode dips into a solution of ZnSO₄ (oxidation) and on the right a Copper electrode dips into a solution of CuSO₄ (Reduction).
- The two electrodes are connected by an external electrical circuit and two solutions are connected by a salt bridge.



Reactions occurring in the cell: The electrode reactions are:

At anode: Oxidation takes place in the Zn electrode by the liberation of electrons. This electrode is negative electrode or anode.

At Cathode: Reduction takes place in the Cu electrode by the acceptance of electrons. This electrode is positive electrode or Cathode.

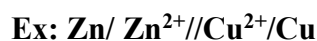


- When these reactions take place, electrons left behind by oxidation of the Zinc travel through external circuit to the other electrode where they are transferred to the Cu ions and are reduced to Cu metal.
- The overall reaction that takes place in a galvanic cell is called **cell reaction**.
- Electric current flows from positive electrode to negative electrode.
- The flow of electrons from one electrode to other electrode in a galvanic cell indicates that the electrodes have different potentials.
- The difference of potentials which causes electrons to flow or current from one electrode which is at higher potential to another electrode which is at lower potential is called **Electro motive force (EMF)** of the cell.

Representation of a galvanic cell:

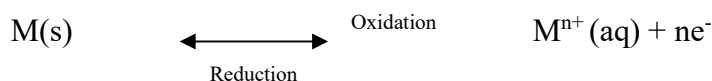
- A galvanic cell consists of two electrodes- Anode and Cathode
- The anode is written on the left side while the cathode is written on the right-hand side.
- Anode must be written writing electrode metal first and then electrolyte. These two are separated by a vertical line.

- The cathode may be written by writing electrolyte first and then the 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.



Electrode potential:

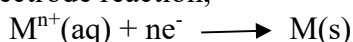
- Metal ions have a tendency to go into solution as metal ions. This tendency is called ‘**electrode potential**’ of that metal.
- Electrode potential can be defined as the tendency of metal atoms to go in to solution in the form of metal ions.
- The electrode equilibrium is represented as



- Electric current flows between two electrodes if the contact is established between two metals.
- The flow of current from one electrode to another electrode in a galvanic cell indicates that the two electrodes have different potentials.
- The difference of potential which causes the flow of current from one electrode which is at higher potential to another electrode which is at lower potential is called “EMF of the cell”

Nernst Equation for EMF of a cell:

Electrode potential for the electrode reaction,



Relative to hydrogen electrode is given by a simple form of the Nernst equation as

$$E_{M^{n+}/M} = E^{\circ}_{M^{n+}/M} + \frac{RT}{nF} \ln (M^{n+})$$

Here

$E^{\circ}_{M^{n+}/M}$ = Standard electrode potential for a molar solution of a metal ion at 298°K
(This is determined by using the standard hydrogen electrode)

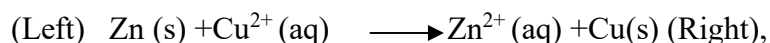
R= Universal gas constant (8.31 J/K/mol)

T= Temperature in Kelvin

n= Number of moles of electrons

F= Faraday (96500 C/mol)

In the Daniel cell,



The electrode potential of the right-hand electrode is written as:

$$E_{Cu^{+2}/Cu} = E^{\circ}_{Cu^{+2}/Cu} + \frac{RT}{nF} \ln [Cu^{+2}(aq)]$$

The electrode potential of the left-hand electrode is written as:

$$E_{Zn^{+2}/Zn} = E^{\circ}_{Zn^{+2}/Zn} + \frac{RT}{nF} \ln [Zn^{+2}(aq)]$$

∴ The cell potential E_{cell} = Electrode potential of right-hand electrode –

Electrode potential of left-hand electrode

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

$$\begin{aligned} \therefore E_{cell} &= \left\{ E^{\circ}_{Cu^{+2}/Cu} + \frac{RT}{nF} \ln [Cu^{+2}(aq)] \right\} - \left\{ E^{\circ}_{Zn^{+2}/Zn} + \frac{RT}{nF} \ln [Zn^{+2}(aq)] \right\} \\ &= (E^{\circ}_{Cu^{+2}/Cu} - E^{\circ}_{Zn^{+2}/Zn}) + \frac{RT}{nF} \ln \frac{[Cu^{+2}(aq)]}{[Zn^{+2}(aq)]} \end{aligned}$$

$$E_{\text{Cell}} = E^{\circ} \text{ cell} + \frac{RT}{nF} \ln \frac{[\text{Cu}^{+2}(\text{aq})]}{[\text{Zn}^{+2}(\text{aq})]} \quad (\cdot E^{\circ} \text{ cell} = E^{\circ} \text{ Cu}^{+2}/\text{Cu} - E^{\circ} \text{ Zn}^{+2}/\text{Zn})$$

$E^{\circ} \text{ cell}$ is cell potential in standard state. By converting natural logarithm to the base 10, and substituting the values R, T (298K) and F, we get

$$E_{\text{Cell}} = E^{\circ} \text{ cell} + \frac{0.0591}{2} \log \frac{[\text{Cu}^{+2}(\text{aq})]}{[\text{Zn}^{+2}(\text{aq})]}$$

In general Nernst Equation is

$$E_{\text{Cell}} = E^{\circ} \text{ cell} + \frac{0.0591}{n} \log \frac{\text{Right hand side electrode}}{\text{Left hand side electrode}}$$

Standard electrode potential :-($E^{\circ} \text{ cell}$)

- The tendency of an electrode to lose or gain electrons when it is in contact with a solution of its own salt is called "Electrode potential".
- The potential difference between the metal and its salt solution in which it is dipped is called single electrode potential.
- When this electrode potential is measured under standard conditions like 25°C, 1.0 M solute concentration and a pressure of 1 atm, then the electrode potential is called '**Standard Electrode Potential**'.
- The SEP is represented by $E^{\circ} \text{ cell}$.
- When 2 half cells are connected to make galvanic cell, one half cell having larger standard electrode potential (the one with the greater tendency to undergo reduction) accepts electrons from the half cell with lower standard electrode potential (greater tendency to undergo oxidation).

$$E^{\circ} \text{ cell} = (\text{SEP of the reduced substance}) - (\text{SEP of the oxidized substance})$$

- The values of standard electrode potentials arranged in the decreasing order is called "**Electro chemical series**".

These values are on Hydrogen Cycle because standard hydrogen electrode is used as the reference electrode and its value is taken as zero.

- The table shows that Fluorine has maximum positive value of SEP and hence it has maximum tendency to accept electrons and get reduced to Fluoride ion.
- The negative sign indicates that the half-cell reaction occurs in the opposite direction, the reduced form has a greater tendency to get oxidized and leave electrons.
- Li has maximum negative value of the electrode potential and hence it has the maximum tendency to lose electrons and get oxidized to Li^{+} ions.

Batteries: -

- A battery is an electrochemical cell or often several electrochemical cells connected in series that can be used as a source of direct electric current at a constant voltage.
- A cell contains only one anode and cathode where as a battery contains many anodes and cathodes.
- They are of 3 types.
 1. Primary cells
 2. Secondary Cells
 3. Fuel cells

1. Primary cells: -

- In these cells the cell reaction is not reversible.
- When the reactants are converted in to products, further no more electricity is produced and the battery becomes dead. Hence, they cannot be recharged.

Eg: - **i) Voltaic cell** (Cu and Zn electrodes dipped in H_2SO_4)

ii) Daniel cell (Zn in $ZnSO_4$ and Cu in $CuSO_4$ separated with porous diaphragm).

iii) Dry (Laclanche) cell: - This is a cell without fluid component. It is the most familiar of all batteries. In these Anode is 'Zn can' with NH_4Cl or $ZnCl_2$ and MnO_2 as electrolytes and to which starch is added to make it thick paste to prevent leakages and a 'carbon/graphite rod' serve as cathode which is immersed in the Centre of electrolyte. Dry cell is cheap and gives a voltage of 1.5V. It is used in flash lights, transistor, radios, calculators etc.,

2. Secondary cells: -

- In these cells, the cell reaction can be reversed by passing direct electric current in opposite direction. They can be used again and again by recharging the cell.

Eg: - Ni-Cd storage cell,

Mercury battery,

Ni—metal hydride lithium batteries.

1. Lead Storage cell or Acid storage cell:

- It is secondary battery which can be used as a voltaic cell and as an electrolytic cell.
- It acts as a voltaic cell and supplies electrical energy and becomes run down. During recharge the cell acts as an electrolytic cell.
- It consists of a number of voltaic cell 3-6.
- It provides a voltage of 6-12V.
- Anode is made up of Pb and PbO_2 acts as a cathode.
- Many anodes and cathodes are connected in parallel and are separated by insulators like rubber or glass fiber.
- Then the entire combination is immersed in dil. H_2SO_4 having a density of 1.30g/ml.
- The cell may be represented as



2. Ni—Cd storage cell / Ni-Cad battery: - This is recently developed, portable, rechargeable cell and its voltage is fairly constant (about 1.4V). It consists of 'Cd' anode, a cathode composed of a paste of ' $Ni(OH)_2$ '(s).

Anode: $Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^-$

Cathode: $2NiO(OH)_2(s) + H_2O(l) + 2e^- \longrightarrow 2Ni(OH)_2(s) + 2OH^-(aq)$

Net reaction : $2NiO(OH)_2(s) + Cd(s) + H_2O(l) \longrightarrow Cd(OH)_2(s) + 2Ni(OH)_2(s)$

- This reaction can be readily reversed, because the reaction products, $Cd(OH)_2$ and $Ni(OH)_2$ adhere to electrode surfaces.
- They are mainly used in electronic calculators, CD players, electronic cars, cordless electronic shavers and transistors.
- They have long durability without any maintenance.

Lithium Batteries: - The cells having lithium anodes are called lithium cells, irrespective of the cathode used. It is very light metal. It belongs to two categories.

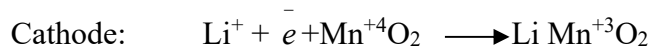
(a) Lithium primary batteries

(b) Rechargeable cells / Li^+ Ion cells.

a) Li primary cells: -

- The most common Li primary cell is the lithium manganese dioxide battery ($LiMnO_2$).
- Anode is Li and Cathode is MnO_2 which is heated above $300^{\circ}C$ to remove H_2O before incorporating it in the cathode. This increases the efficiency of cell.
- A mixture of propylene carbonate and dimethoxy ethane containing dissolved salt such as $LiClO_4$ is taken as electrolyte.

The cell reaction is, Anode: $Li \longrightarrow Li^+ + e^-$



- This cell produces a voltage of about 3.4v, which is more than twice that of dry cell due to light weight of Li.
- They are widely used in applications that require higher current drain like fully automatic cameras, electronic devices such as calculators and watches.

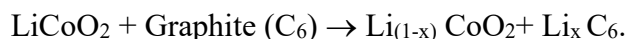
b) Lithium Ion cells or Rechargeable cells:

- These cells do not contain metallic 'Li' instead it contains lithium ions (Li^+).

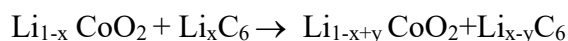
Anode: Carbon compound, graphite

Cathode: Lithium Cobalt oxide

- In these cells the true oxidation/ reduction does not takes place, instead of that transport of Li^+ ions through the electrolyte from one electrode to the other takes place.
- When the cell is constructed, it is in its uncharged state with no Li^+ ions between the layers of 'C' atoms in the graphite.
- When the cell is charging, Li^+ ions leave LiCoO_2 and travel through the electrolyte to the graphite C_6 .



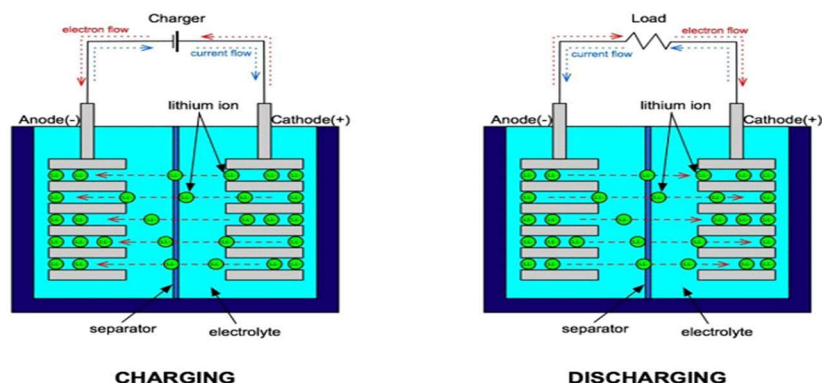
- When the cell spontaneously discharges to provide electrical power, Li^+ ions move back through the electrolyte to the cobalt oxide while electrons move through the external circuit from the graphite electrode to the cobalt oxide electrode.



Y=amount of Li^+ transferring from $\text{Li}_x \text{C}_6$. LiCoO_2 $_{1-x}$

X= transferring amount of Li^+ from LiCoO_2 to graphite.

- Thus the charging and discharging cycle simply sweep Li^+ ions back and forth between two electrodes with electrons flowing through external circuit to keep the charge balance.



Fuel cell/Flow battery: -

- The reactants are continuously supplied from an external source to the cell and the reaction products continuously removed, such cells are called as fuel cells.
- In a fuel cell electrical energy is obtained without combustion from O_2 and gas can be oxidized. Hence fuel cell converts chemical energy of the fuel directly to electricity.

The important steps in the fuel cell

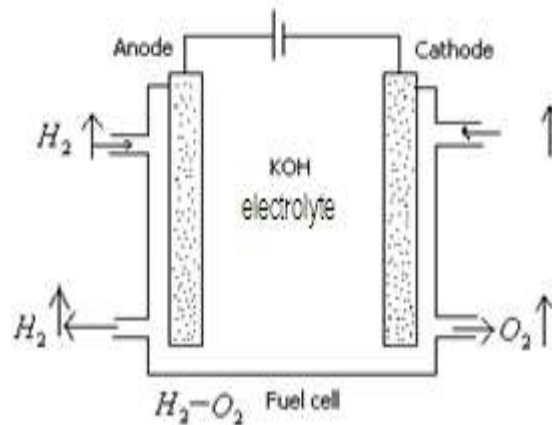
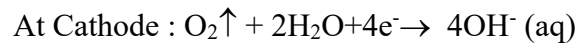


- In these cells, fuel is gas/liquid and oxygen is the oxidizing agent.
- In fuel cell the chemical energy of fuel is easily converted in to electrical energy.
- Fuel cells are characterized by,
 - (1) High efficiency
 - (2) Low noise levels
 - (3) Free from vibration, heat transfer.

- The most important fuel cells are
 - (1) H₂-O₂ fuel cell
 - (2) Methanol fuel cell

(1) H₂-O₂ Fuel cell/ Alkaline Fuel cell: - It is successful and simplest cell.

- **Electrodes:** - Porous Platinum electrode, electrolyte -- 35-40% KOH.
- It consists of hot concentrated KOH electrolyte solution in the center in which two porous Pt electrodes are dipped.
- At anode H₂ gas and at cathode O₂ gas are supplied.
- When they come in contact with electrodes the following reactions takes place.



Applications: -

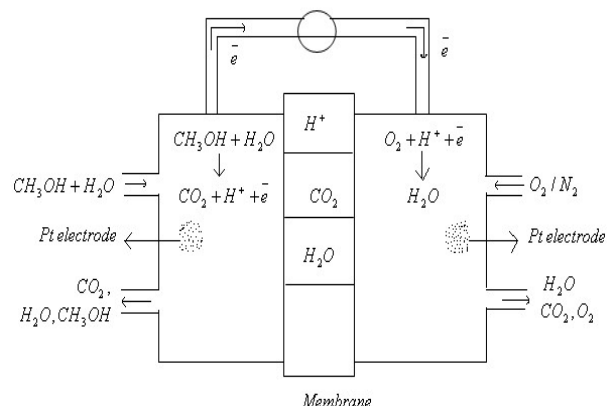
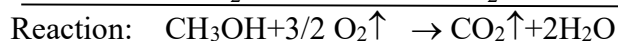
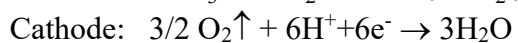
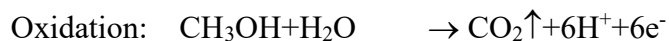
- (1) They are used as energy source in space vehicles, submarines or military vehicles.
- (2) The reaction product is water, which is harmless and used as source of fresh water to the astronauts.
- (3) The weight of fuel battery for 15 days is about 250 Kg.

Disadvantages: -

- (1) Energy cost of generating H₂ fuel.
- (2) Difficult in storage and distribution of highly flammable.
- (3) Availability of alternative fuels.

(2) Methanol- O₂ Fuel Cell/Proton Exchange Fuel Cells: -

- **Electrodes:** - Porous Pt electrodes, separated by proton transport membrane.
- **Anode:** Oxidation of CH₃OH and H₂O takes place and forms CO₂ with loss of H⁺ (Protons) and electrons.
- **Cathode:** - H₂O is liberated by reduction of O₂ accepts electrons and protons and liberates H₂O. Protons are transported from anode to cathode through proton transport membrane, while electrons transport through electric circuit.
- The liberated H₂O at cathode is consumed at anode.



Advantages: -

- (1) Storage of methanol is much easier than H₂ (does not need high pressure or low temperature) since methanol is in liquid form at -97.0⁰ C to 64.7⁰ C (-142.6⁰F to 148.5⁰F)
- (2) The energy density of methanol is greater than H₂.

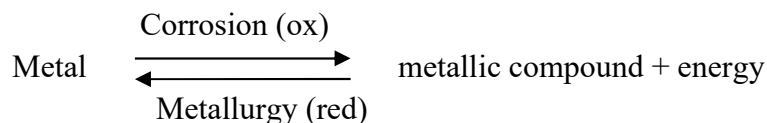
Disadvantages: -

- (1) During methanol oxidation, CO formed which strongly adheres on to Pt catalyst, reducing, the surface area and lowering the performance.
- (2) CH₃OH is highly toxic and flammable and so utmost care is necessary.

SCIENCE OF CORROSION

Introduction: Most of the metals (except noble metals like Au, Pt, and Ag) occur in nature in combined form of their oxides, hydroxides, sulphides, chlorides, carbonates and silicates. All these metals have natural tendency to revert back to combined state for stability.

The natural combined form of metal is more stable than the other metals. So metals after extraction from its ore tends to revert back to the stable natural combined form when it comes in contact with other elements in the environment. That is why metal after extraction from its ore tends to revert back to the stable natural combined form. So corrosion is reverse process of metallurgy.



The surface of all metals begins to decay when exposed to atmospheric gases, water & other reactive liquid medium as a result they are converted to oxides, hydroxides, carbonates, nitrates, sulphates etc. This natural process is called corrosion.

Definition: - The process of gradual decay or deterioration / eating of metal from its surface by unwanted chemical / electro-chemical attack by its surrounding environment is called corrosion.

Example for corrosion: -

- A reddish-brown layer formed on to the surface of Fe
- Green film on surface of copper, etc....

Reason for corrosion: -

- All metals except (Pt, Au, Ag) occurs in a combined state in nature. During extraction of metal from its ore, they are reduced to metallic compound using energy. Hence an isolated metal will be present in its excited unstable state. However, all the metals have natural tendency to go back to their combined state for its stability. As a result, metal exposed to environmental factors or chemicals get converted in to its original combined state which is called corrosion.
- The corrosion process is a reversible process and is measured in units such as milli inches / year or millimeter/year.

Dis-advantages of corrosion:

1. Poor in appearance
2. The plant may be shut down due to failure.
3. Decrease in production rate and replacement of equipment is time consuming.
4. Contamination of product.
5. Decreased safety from a fire hazard or explosion or release of toxic product.
6. Health hazards from pollution due to corrosion product or due to escaping of chemical from a corroded environment.

Types corrosion: - Based on the process how corrosion occurs, it is classified in to two types.

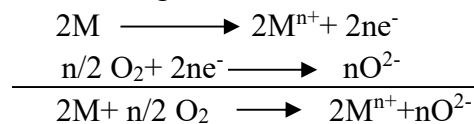
1. Chemical/Dry corrosion
2. Electrochemical/Wet corrosion

1. Chemical/Dry corrosion: - This occurs mainly due to the direct action of environment or atmospheric gases like O₂ , SO₂, H₂S, Halogens , Anhydrous in-organic liquids with metal surface that are present in its immediate proximity . It is classified into 3 types based on how corrosion is taking place.

- A. Oxidation corrosion
- B. Corrosion by other gases
- C. Liquid metal corrosion.

A. Oxidation corrosion: -It is brought about by O₂ at low & high temperature on metals, usually in absence of moisture. At ordinary temperature metals are slowly attacked, at low temperature alkali and alkaline earth metals (II group) are rapidly oxidized and at high temperature all metals except Pt, Au, Ag are oxidized.

- The reactions that occur during oxidation corrosion are



∨
Metal oxide (M₂O_n)

Mechanism: -

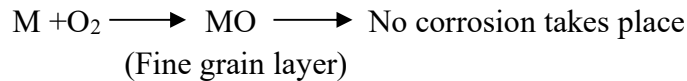
- When oxidation takes place at surface of metal, it forms a metal oxide layer on its surface which prevents further oxidation. This layer is called as ‘scale’.
- If oxidation continues, either metal diffuse out wards through scale or oxygen diffuses in wards through scale.

- Both cases can take place but the outward diffusion of metal is predominant than inward diffusion of O₂, since the size of metal is smaller than O₂ ion and is having much higher mobility.

Types of scales: The following types of metal oxide layers (scales) are formed by corrosion

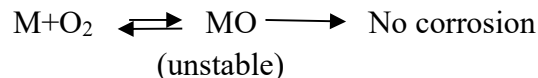
1. Stable
2. Unstable
3. Volatile
4. Porous

1. **Stable:** - It is a fine-grained layer in texture and it tightly adheres to metal surface, hence this layer doesn't permit further corrosion.



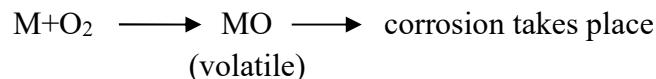
Examples of metals that form stable scales are-- Al, Cu, Pt etc.

2. **Unstable:** - The metal oxide film immediately decomposes to metal & O₂ as soon as it is formed, hence further oxidation doesn't take place.

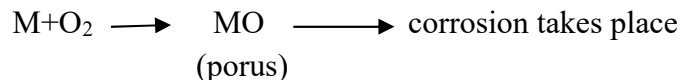


Examples of metals that form stable scales are -- Pt, Au, Ag

3. **Volatile:** - This type of metal oxide layer gets continuously evaporated and hence fresh metal surface again get exposed for further corrosion leading to rapid corrosion of the metal. This type is seen in Mb (molybdenum)



4. **Porous:** - The metal oxide layer that is formed contains pores or cracks on its surface and through these pores atmospheric O₂ passes up to the metal surface, hence corrosion continues till the entire metal is converted to metal oxide.



S. No	Type of metal oxide	Example	Corrosion
1.	Stable	Cu, Al	Doesn't take place
2.	unstable	Pt, Au, Ag	Doesn't take place
3.	Volatile	Mb	Takes place
4.	porous	alkali & alkaline earth metals	Takes place

Pilling – Bed worth Rule:

- The rule states that 'an oxide is protective or non-porous if the volume of the oxide is at least as great as the volume of the metal from which it is formed'.
- This is expressed in terms of **specific volume ratio**.

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

- The smaller the specific volume ratio, greater the oxide corrosion since the formed oxide film will be porous. So, oxygen can diffuse and further corrosion takes place.

Ex: 1. Oxides formed by Alkali and Alkaline earth metals have less volume than the volume of metal, so they form porous scales and have high corrosion.

2. Metals like 'Al' form oxides whose volume is greater than the volume of metals, so they form non-porous scales and have low corrosion.

B. Corrosion By Other Gases (SO₂, H₂S, CO₂, F₂, Cl₂) :-

- This type of corrosion mainly depends on chemical affinity between metal & the gas involved.
- The intensity of attack depends on formation of protective or non-protective films on metal surface.
- If the film is protective or non-porous, the volume of metal oxide layer is greater than that of metal. So further corrosion of metal doesn't take place.

Eg: Formation of AgCl film by the attack of chlorine on Ag. The intensity of corrosion decreases due to formation AgCl non porous film on its surface which is tightly adherent on Ag.

- If the film is non- protective or porous, the volume of metal oxide layer is lesser than that of metal so further corrosion takes place.

Eg: SnCl₄ formed by attack of Cl₂ on Sn (tin) which volatiles immediately there by leaving fresh metal surface for further corrosion.

C. Liquid metal corrosion: -

- This is due to chemical action of flowing liquid metal at high temperature on solid metal or alloy.
- This type of corrosion is seen in devices used for nuclear plant.
- The corrosion reaction is carried out either by dissolution of solid metal by liquid metal or internal penetration of liquid metal into solid metal. Both reactions lead to weakening of solid metal.

Eg: Na metal causes corrosion of Cd in nuclear reactor.

2. Electrochemical / wet corrosion: - This type of corrosion takes place when a conducting liquid is in contact with a metal or two dissimilar metals are either dipped or immersed partially in a solution.

- Usually, it takes place in liquid medium.
- The electro chemical corrosion involves the following-
 1. Existence of separate anodic or cathodic parts between which current flows through conducting medium.
 2. **At anode:** Oxidation takes place at anodic part and releases electrons, forms metallic ions. Hence corrosion always occurs at anode.
$$M \longrightarrow M^{n+} + ne^{-}$$
 3. **At cathode:** Reduction reaction takes place at cathode, so the released electrons from anode are accepted by non-metals and forms non-metallic ions such as OH⁻ & O²⁻
 4. The metallic & non-metallic ions diffuse towards each other through conducting medium & form corrosion product in the medium.

Mechanism: -

- Electro chemical corrosion involves flow of electrons between anode & cathode.
- The anodic reaction involves dissolution of metal as metal ion with liberation of electrons.

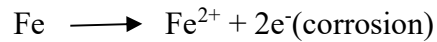


- On the other hand, cathodic reactions consume electrons in two ways depending on nature of corroding environment. They are

- a) Evolution of hydrogen
- b) Absorption of O₂

a) Evolution of H₂: - This type of corrosion takes place generally in acidic medium.

- For example, if Fe metal is in contact with acidic medium, anodic reaction is dissolution of Fe as ferrous with liberation of electrons.



The reduced electrons from anode flow through metal to cathode where H^{+} ions are reduced to H_2 .



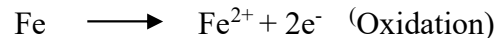
- The overall reaction is $\text{Fe}^{2+} + 2\text{H}^{+} \longrightarrow \text{Fe}^{2+} + \text{H}_2$
- This type of corrosion causes displacement of H^{+} ions by metal ion.
- All the metals above hydrogen in electro chemical series have a tendency to get dissolved in acidic solution with simultaneously liberation of H_2 gas.

b) Absorption of O_2 :-

- When metals are in contact with slightly alkaline or neutral solution (water) with some amount of dissolved O_2 , this type of corrosion takes place.

Ex: Rusting of iron in neutral aqueous electrolyte solution in presence of atmospheric O_2 .

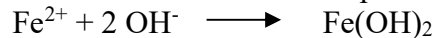
- The surface of Fe is usually coated with thin film of FeO. However, the oxide film develops cracks, which behave as anodic area & remaining metal part acts a cathode. It shows that anodes are of small area while rest of metallic part forms large area of cathode.
- **At anode:** - Fe dissolves in aqueous solution forms Fe^{2+} with release of electrons.



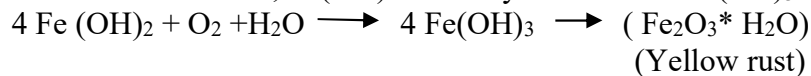
- **At cathode:** - The liberated e^{-} flows from anode to cathode through Fe metal, these electrons are accepted by dissolved O_2 to form OH^{-} ions.



- The Fe^{2+} at anode & 2OH^{-} at cathode react to produce $\text{Fe}(\text{OH})_2$ precipitate



- If O_2 is available in excess, $\text{Fe}(\text{OH})_2$ is easily oxidized to $\text{Fe}(\text{OH})_3$.



- If supply of O_2 is limited the corrosion product may be black anhydrous magnetite Fe_3O_4 .

THEORIES OF CORROSION:-

The following theories explain about tendency & process of corrosion.

1. Direct chemical attack
2. Acid theory
3. Electro chemical theory

1. Direct chemical attack:-

- This theory explains about dry or chemical corrosion.
- The corrosion takes place by direct chemical attack.
- The film of a corrosive product normally formed on surface of metal, protects the metal, so further corrosion doesn't take place.

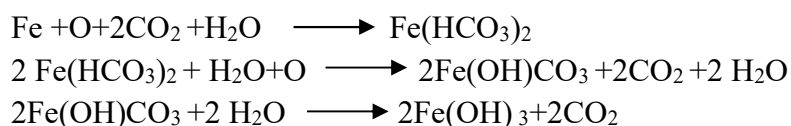


- If corrosion product is soluble, then metal is exposed to further corrosion, then metals are attacked by atmospheric O_2 to produce metal oxide at their respective temperatures.
- The intensity of corrosion depends on the nature of oxide deposit.
- If the formed metal oxide is non-porous, then the metal surface becomes protective and if it is porous, then O_2 diffuses inside the metal & thus further corrosion takes place.

Ex:Al and Cr forms extremely protective oxide layers and hence these metals are normally used for alloy formation with metals that undergo easy corrosion.

2. Acid theory: --

- This theory states that presence of acid is essential for corrosion.
- Rusting of Fe is well explained by this theory.
- Fe reacts with O₂, CO₂ and moisture present in atmosphere and results in formation of a soluble Ferrous carbonate, which is further oxidized to basic ferric carbonate and finally ferric hydroxide is formed.



3. Electro chemical theory: -

- This theory explains about electro chemical corrosion.
- The modern electro chemical theory is based on Nernst theory. This states that all metals have tendency to pass into solution when immersed in its own salt solution (Zn – metal – immersed in ZnSO₄ salt). This tendency is called as electrode potential.
- If a metal having higher electrode potential comes in contact with a metal having lower electrode potential, a galvanic cell set up occurs and metal at higher electrode potential becomes anode and goes in to solution.
- If the solution is acidic then, H₂ gas evolves at cathode while anodic metal dissolves in it.
- The greater the difference in potential b/n anode & cathode, the greater will be corrosion and also if the anode area is smaller than cathodic area, then more severe corrosion takes place.

Galvanic series: -

- Electrochemical series gives useful information regarding chemical reactivity of metals; however this series doesn't give sufficient information about corrosion behavior of metal in a particular set environmental conditions.
- Passivation makes effective electrode potential of some metals more passive and makes them act like cathode and exhibits noble behavior. This behavior is exactly opposite to electro chemical series.
- So a more practical series have been prepared by studying the corrosion of metals and alloys in common electrolyte called sea water using calomel electrode as reference electrode.
- Then the metals electrode potentials are arranged in increasing order towards down. This series is called **galvanic series**.
- A metal present high in series is more anodic & undergoes corrosion faster than metal below.
- This series gives real and useful information about corrosion behavior of metals and alloys in a given environment.
- Galvanic series predicts the tendency of both metals and non- metals in actual environment where as electrochemical series predicts the displacement of metals and non-metals in electrolyte.

<ol style="list-style-type: none"> 1. Mg 2. Mg alloy 3. Zn 4. Al 5. Al alloy 6. Mild steel 7. Fe 8. High Ni cast iron 9. Pb- Sn solder 10. Pb 11. Sn 12. Inconel. 13. Ni – Mo – Fe alloy 	<p style="margin: 0;">anodic (active) ↑</p> <p style="margin: 0;">↓</p> <p style="margin: 0;">cathodic (stable/ noble)</p>	<ol style="list-style-type: none"> 14. Brass 15. Monel 16. Silver. 17. Cu 18. Ni 19. Stainless steel 20. 18-08 Stainless steel 21. 18-08 MO steel 22. Ag 23. Ti 24. Graphite 25. Au 26. Pt
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- Eg: Zn corrodes faster than Fe & Cu corrodes faster than Ag, Fe corrodes faster than Sn.
- However, some exceptions to this generalization are known.

Eg: Ti is less reactive than Ag.

In Zn – Al couple, Zn is less corroded, while Al acts as cathode and is protected.

- These experiments clearly prove that metals like Ti & Al develop strongly adhering oxide layers on their surfaces, thereby making their effective electrode potential more +ve.

Galvanic corrosion or Bimetallic corrosion: -

- When two dissimilar metals are electrically connected & exposed to electrolyte, metal higher in electrochemical series undergoes corrosion. This is called galvanic corrosion.

Eg: Zn –Cu galvanic cell:- Here Zn acts as anode where oxidation takes place, corrosion occurs & Cu act as cathode & is protected.

Mechanism: -

- In acidic solution, corrosion occurs by evolution of H₂, while in neutral & slightly alkaline solution absorption of O₂ occur.
- The e⁻ flow from anodic metal to cathodic metal.



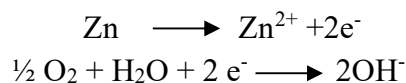
- This means corrosion occurs at anodic metal, while cathodic part is protected from attack eg: Steel pipe connected to copper plumbing.

Concentration Cell Corrosion / Differential Aeration Corrosion :-

- This type of corrosion is due to electrochemical attack on metal surface exposed to an electrolyte of varying concentrations or of varying aeration.
- The most common type of concentration cell corrosion is differential aeration corrosion.
- This occurs when one part of metal is exposed to different air concentration from other part.
- This causes a difference in potentials between differently aerated areas.
- Poorly oxygenated metallic part becomes anodic & undergoes oxidation where as well oxygenated part acts as cathode.
- Eg: When Zn metal is partially immersed in dilute neutral NaCl solution, the part above & closely adjacent to water line are well aerated. Hence become cathodic. On the other hand, part that is immersed to greater depth show a smaller oxygen concentration, thus become

anodic. So a difference of potential is created which causes flow of current between two differentially aerated areas of same metal.

Zn can dissolve at anode & releases electrons which are accepted by O₂ at cathodic area to form hydroxyl ions.



Factors influencing corrosion:- The intensity and rate of corrosion depends on two types of factors

1. Nature of metal
2. Nature of environment

I. Nature of metal :- Many factors influence corrosion of metal that depend on its nature. They are--

- i. Position of in galvanic series
- ii. Over voltage
- iii. Relative areas of cathode & anode
- iv. Purity of metal
- v. Physical state of metal
- vi. Nature of surface film.
- vii. Passivity of metal.
- viii. Solubility of corrosion product
- ix. Volatility of corrosion product

1. **Position in galvanic series :-** When two metals or alloys are in contact with conducting medium the more active metal suffers corrosion. The intensity of corrosion depends on difference in their position, the faster will be corrosion of anodic metal /alloy.

2. **Over voltage :-** It is defined as difference of potential between practical & theoretical decomposition potentials for same solution.

Eg: Electrolysis of H₂SO₄ with Pt electrode, its practical potential is about 1.70 v where as its theoretical potential is 1.229v. The diff is 0.471v which is over voltage of H₂SO₄.

Reduction in over voltage of corroding metal or alloy increases corrosion rate.

3. **Relative areas of anode & cathode:-** Small anodic & large cathodic area causes severe corrosion when two dissimilar metals or alloys are in contact the corrosion of anode part is directly proportional to ratio of areas of cathodic & anodic part.

Eg: A small steel pipe fitted in a large copper tank.

4. **Purity of metal:-** Impurities in metal cause heterogeneity and form tiny electrochemical cells (at exposed parts) & anodic part gets corroded.

Eg: Zn metal containing impurities Pb / Fe undergoes corrosion due to formation of local electrochemical cells.

- The rate & extent of corrosion increases with increase in exposure and extent of impurities.
- The intensity of corrosion is less when its purity is high.

5. **Physical state of metal:-** The rate of corrosion is influenced by physical state of metal such as grain size, orientation of crystals, stress etc.

- If grain size is smaller, its solubility is more and hence greater will be its corrosion.
- Moreover, areas under stress, even in pure metal tend to be anodic and corrosion takes place at these areas.

6. **Nature of surface film:-** In aerated atmosphere practically all metals get covered with a thin surface film of metal oxide.

- The ratio of volume of metal oxide to metal is called specific volume ratio.
- Greater the specific volume ratio (SVR), lesser is oxidation corrosion rate.

For eg: The S.V.R of Ni, Cr, Ware 1.6, 2.0 &3.6 respectively.

The rate of corrosion of tungsten is least even at elevated temperature.

7. **Passivity of metal:** - Passivity is a phenomenon in which metal/ alloy exhibits a much greater corrosion resistance the resulting film is highly protective but very thin & thin & quiet invisible film on surface of metal / alloy, which makes it more noble.

- Metal like Ti, Al, Cr, Mg, Ni &CO are passive and they exhibit much higher corrosion resistance than expected from their positions in galvanic series. Passivity of metal decrease corrosion rate.

Eg : Corrosion resistance of stainless steel is due to passive character of Cr present in steel.

8. **Solubility of corrosion product:** - In electrochemical corrosion if corrosion product is soluble in corroding medium, then corrosion proceeds at faster rate. If corrosion product is insoluble in medium or it forms another insoluble product which create physical barrier there by corrosion is suppressed.

Eg: corrosion of Pb in H₂SO₄ decreases due to formation of insoluble PbSO₄.

9. **Volatility of corrosion product:** - If corrosion product is volatile nature, underlined metal is exposed further and causes severe corrosion.

Eg: MoO₃ is volatile.

II. Nature of the corroding environment: The following environmental factors influence intensity of corrosion.

1. Temperature.
2. Humidity of air.
3. Presence of impurities.
4. Presence of suspended particles in atmosphere.
5. Influence of p^H.
6. Nature of ions.
7. Conductance of conducting medium.
8. Formation of O₂ conc cell.

1. **Temperature:** - With rise in temp. of environment, the reaction rate and also diffusion rate increases there by generally corrosion rate also increases.

2. **Humidity of air:** - It is the deciding factor in atmospheric corrosion.

- Critical Humidity is defined as relative humidity above which the atmospheric corrosion rate of metal increases sharply.
- The value of critical humidity depends on physical characters of metal & corrosion product.
- In Humid environment the rate of corrosion is higher due to gases & vapors present in atmosphere furnish (give) water to form electrolyte, essential for setting up an electrochemical corrosion cell.
- More over the oxide film on metal surface has a property to absorb the moisture, then corrosion rate enhanced.
- The nature of moisture sources also plays important role.

Eg: Rain water apart from supplying moisture for electrochemical attack, may also wash away a good part of oxide film from metal surface (unless the oxide film is exceptionally adherent).

3. Presence of impurities in atmosphere: -

- Presence of corrosive gases like SO_2 , CO_2 , H_2S , O_2 etc. in atmosphere increases acidity and increase electrical conductivity which causes severe corrosion.
- In marine atmosphere presence of Na & other chlorides leads to increase in conductivity there by corrosion increases.

4. Presence of suspended particles in atmosphere: -

- The suspended particles in atmosphere may be are of two types.
- **i) Chemically active:** - If suspended particles are active (NaCl , $(\text{NH}_4)_2\text{SO}_4$) they absorb moisture & act as strong electrolytes, thereby causing enhance corrosion.
- **ii) Chemically in-active:** - If suspended particles are chemically inactive, in nature (charcoal) they absorb both Sulphur gas & moisture & slowly enhances corrosion rate.

5. Influence of pH: -

- Generally acidic media ($\text{pH} < 7$) are more corrosive than alkaline & neutral media.
- The metals are readily attacked by acid, so corrosion of metal can be reduced by increase of pH of attacking environment.

Eg: Zn rapidly corrodes in weak acidic solution and suffers minimum corrosion at pH-11.

6. Nature of ions present: -

- Some ions increase corrosion while others decrease it.
- The presence of anions like silicate in medium leads to formation of insoluble reaction products (silica gel), which inhibit further corrosion.
- On other hand Cl^- ions destroy protective & passive surface film, hence metal surface is exposed for fresh corrosion.
- Presence of NH_4 salts increase corrosion of Fe.
- The presence of even traces of Cu in mine water accelerates corrosion of Fe pipes, used for carrying such water.

7. Conductance of conducting medium: -

- Conductance of conducting media is important in case of underground & submerged structures.
- Conductance of dry sandy soil is lower than those of mineralized/ clayey soils.
- Stray currents (from power breakages) will cause more damage to metallic structures buried under clay & mineralized soil than those under dry sandy soils.

8. Formation of O_2 concentration cell:-

- As percentage of O_2 increases, the rate of corrosion also increases due to formation of O_2 conc. Cell.
- The decay of metal occurs at anodic part & cathodic part is protected.
Anodic reaction for Fe :- $\text{Fe} \longrightarrow \text{Fe}^{2+} + 2\text{e}^-$
Cathodic reaction for Fe:- $2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \longrightarrow 4\text{OH}^-$
- Thus formation of concentration cell promotes corrosion, but it occurs where O_2 conc. is lower.

Control of corrosion (protection against corrosion):-

- There are several disadvantages by corrosion. Hence controlling of corrosion is essential.
- The following methods are used for corrosion control.
 1. Use of inhibitors
 2. Cathodic protection
 3. Application of protective coatings

1. Use of inhibitors: -

- A corrosion inhibitor is a substance which when added in small quantities to aqueous corrosive environment, effectively decreases corrosion of metal.
- Inhibitors are of 2 types.
 1. Anodic inhibitor
 2. Cathodic inhibitor

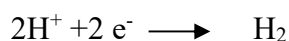
1. Anodic inhibitor: -

- Chromates, phosphates, tungstate's or other ions of transition elements with higher oxygen are used as anodic inhibitors.
- They are adsorbed on the metal surface forming protective coating, thereby reducing rate of corrosion forming sparingly soluble compound.
- This type of control is effective, yet may be dangerous if certain areas are left unprotected by depletion of inhibitor.

2. Cathodic inhibitors: -

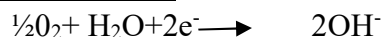
- Eg: Organic inhibitors (like amines, mercaptans, heterocyclic nitrogenous compounds, substituted urea and thiourea, heavy metal soaps).

In acidic environment the corrosion reaction takes place with evolution of H₂.



- Corrosion may be reduced by
 - i. Slowing down diffusion of hydrated H⁺ ions to cathode.
 - ii. By increasing over voltage of hydrogen evolution.
- The diffusion of H⁺ is decreased by addition of organic inhibitors.
- Sn and Arsenic oxides act as inhibitors because they deposit adherent film of metallic arsenic or antimony at cathodic areas, thereby increasing H₂ over voltage.

In neutral & aqueous medium the cathodic reaction is



- The corrosion can be controlled by eliminating O₂ from conducting medium or retarding its diffusion to cathodic area.
- The former is attained by addition of Na₂SO₃ or by de-aeration.
- Later is carried out by Mg, Zn or Ni salts which react with OH⁻ ions (at cathode) forming corresponding insoluble hydroxides which are deposited on cathode forming more or less impermeable self-barriers The table shows that Fluorine has maximum positive value of SEP and hence it has maximum tendency to accept electrons and get reduced to Fluoride ion.
- The negative sign indicates that the half-cell reaction occurs in the opposite direction, the reduced form has a greater tendency to get oxidized and leave electrons.
- Li has maximum negative value of the electrode potential and hence it has the maximum tendency to lose electrons and get oxidized to Li⁺ ions.

Batteries: -

- A battery is an electrochemical cell or often several electrochemical cells connected in series that can be used as a source of direct electric current at a constant voltage.
- A cell contains only one anode and cathode where as a battery contains many anodes and cathodes.
- They are of 3 types.
 4. Primary cells
 5. Secondary Cells
 6. Fuel cells

3. Primary cells: -

- In these cells the cell reaction is not reversible.
- When the reactants are converted in to products, further no more electricity is produced and the battery becomes dead. Hence, they cannot be recharged.

Eg: - **i) Voltaic cell** (Cu and Zn electrodes dipped in H_2SO_4)

ii) Daniel cell (Zn in $ZnSO_4$ and Cu in $CuSO_4$ separated with porous diaphragm).

iii) Dry (LaChance) cell: - This is a cell without fluid component. It is the most familiar of all batteries. In these Anode is 'Zn can' with NH_4Cl or $ZnCl_2$ and MnO_2 as electrolytes and to which starch is added to make it thick paste to prevent leakages and a 'carbon/graphite rod' serve as cathode which is immersed in the center of electrolyte. Dry cell is cheap and gives a voltage of 1.5V. It is used in flash lights, transistor, radios, calculators etc.,

4. Secondary cells: -

- In these cells, the cell reaction can be reversed by passing direct electric current in opposite direction. They can be used again and again by recharging the cell.

Eg: - Ni-Cd storage cell,

Mercury battery,

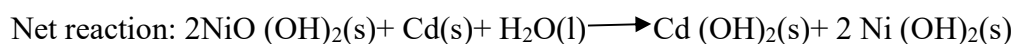
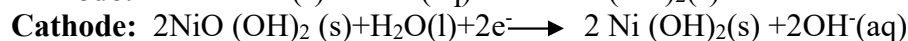
Ni—metal hydride lithium batteries.

3. Lead Storage cell or Acid storage cell:

- It is secondary battery which can be used as a voltaic cell and as an electrolytic cell.
- It acts as a voltaic cell and supplies electrical energy and becomes run down. During recharge the cell acts as an electrolytic cell.
- It consists of a number of voltaic cell 3-6.
- It provides a voltage of 6-12V.
- Anode is made up of Pb and PbO_2 acts as a cathode.
- Many anodes and cathodes are connected in parallel and are separated by insulators like rubber or glass fiber.
- Then the entire combination is immersed in dil. H_2SO_4 having a density of 1.30g.ml.
- The cell may be represented as



4. **Ni—Cd storage cell / Ni-Cad battery:** - This is recently developed, portable, rechargeable cell and its voltage is fairly constant (about 1.4V). It consists of 'Cd' anode, a cathode composed of a paste of 'NiO (OH) $_2$ '(s).



- This reaction can be readily reversed, because the reaction products, Cd (OH)₂ and Ni (OH)₂ adhere to electrode surfaces.
- They are mainly used in electronic calculators, CD players, electronic cars, cordless electronic shavers and transistors.
- They have long durability without any maintenance.

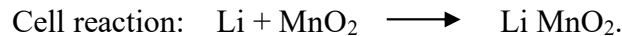
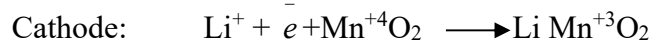
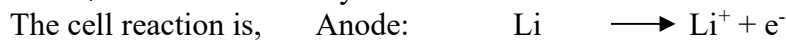
Lithium Batteries: - The cells having lithium anodes are called lithium cells, irrespective of the cathode used. It is very light metal. It belongs to two categories.

(a) Lithium primary batteries

(b) Rechargeable cells / Li⁺ Ion cells.

a) Li primary cells: -

- The most common Li primary cell is the lithium manganese dioxide battery (LiMnO₂).
- Anode is Li and Cathode is MnO₂ which is heated above 300⁰C to remove H₂O before incorporating it in the cathode. This increases the efficiency of cell.
- A mixture of propylene carbonate and dimethoxy ethane containing dissolved salt such as LiClO₄ is taken as electrolyte.



- This cell produces a voltage of about 3.4v, which is more than twice that of dry cell due to light weight of Li.
- They are widely used in applications that require higher current drain like fully automatic cameras, electronic devices such as calculators and watches.

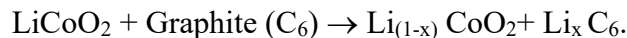
b) Lithium-Ion cells or Rechargeable cells:

- These cells do not contain metallic 'Li' instead it contains lithium ions (Li⁺).

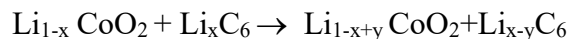
Anode: Carbon compound, graphite

Cathode: Lithium Cobalt oxide

- In these cells the true oxidation/ reduction does not takes place, instead of that transport of Li⁺ ions through the electrolyte from one electrode to the other takes place.
- When the cell is constructed, it is in its uncharged state with no Li⁺ ions between the layers of 'C' atoms in the graphite.
- When the cell is charging, Li⁺ ions leave LiCoO₂ and travel through the electrolyte to the graphite C₆.



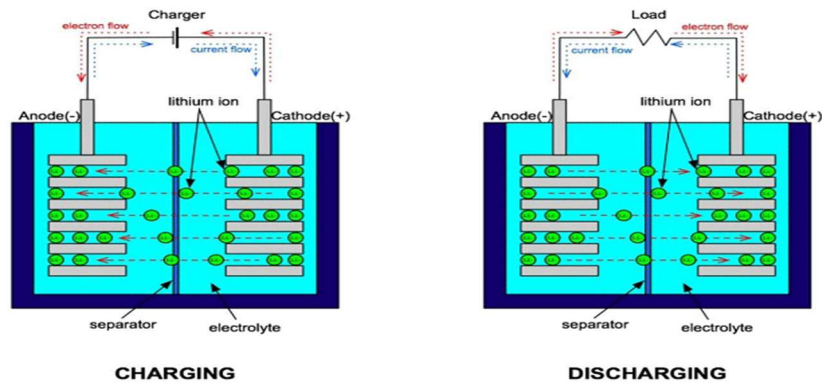
- When the cell spontaneously discharges to provide electrical power, Li⁺ ions move back through the electrolyte to the cobalt oxide while electrons move through the external circuit from the graphite electrode to the cobalt oxide electrode.



Y=amount of Li⁺ transferring from Li_xC₆ . LiCoO_{2 1-x}

X= transferring amount of Li⁺ from LiCoO₂ to graphite.

- Thus, the charging and discharging cycle simply sweep Li⁺ ions back and forth between two electrodes with electrons flowing through external circuit to keep the charge balance.



Fuel cell/Flow battery: -

- The reactants are continuously supplied from an external source to the cell and the reaction products continuously removed, such cells are called as fuel cells.
- In a fuel cell electrical energy is obtained without combustion from O_2 and gas can be oxidized. Hence fuel cell converts chemical energy of the fuel directly to electricity.

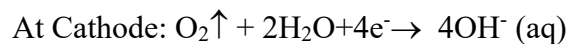
The important steps in the fuel cell

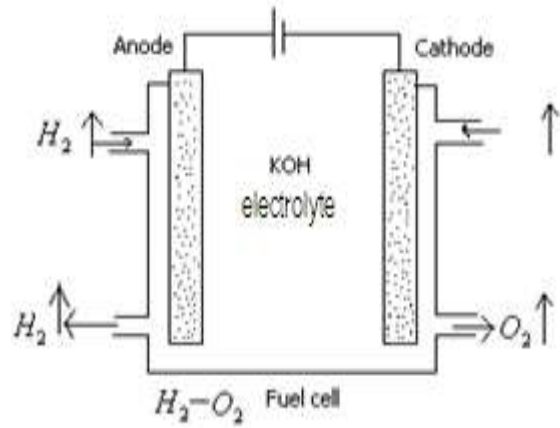
Fuel + $O_2 \rightarrow$ oxidation product + electricity

- In these cells, fuel is gas/liquid and oxygen is the oxidizing agent.
- In fuel cell the chemical energy of fuel is easily converted in to electrical energy.
- Fuel cells are characterized by,
 - (1) High efficiency
 - (2) Low noise levels
 - (3) Free from vibration, heat transfer.
- The most important fuel cells are
 - (1) H_2-O_2 fuel cell
 - (2) Methanol fuel cell

(3) **H_2-O_2 Fuel cell/ Alkaline Fuel cell:** - It is successful and simplest cell.

- **Electrodes:** - Porous Platinum electrode, electrolyte -- 35-40% KOH.
- It consists of hot concentrated KOH electrolyte solution in the center in which two porous Pt electrodes are dipped.
- At anode H_2 gas and at cathode O_2 gas are supplied.
- When they come in contact with electrodes the following reactions takes place.





Applications: -

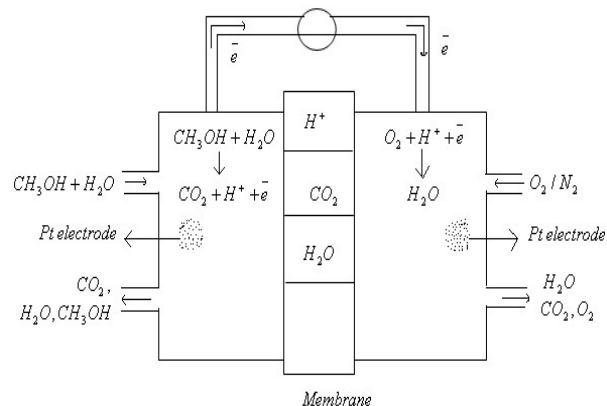
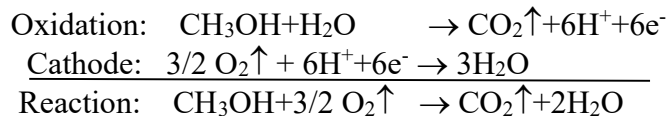
- (1) They are used as energy source in space vehicles, submarines or military vehicles.
- (2) The reaction product is water, which is harmless and used as source of fresh water to the astronauts.
- (3) The weight of fuel battery for 15 days is about 250 Kg.

Disadvantages: -

- (1) Energy cost of generating H₂ fuel.
- (2) Difficult in storage and distribution of highly flammable.
- (3) Availability of alternative fuels.

(4) Methanol- O₂ Fuel Cell/Proton Exchange Fuel Cells: -

- **Electrodes:** - Porous Pt electrodes, separated by proton transport membrane.
- **Anode:** Oxidation of CH₃OH and H₂O takes place and forms CO₂ with loss of H⁺ (Protons) and electrons.
- **Cathode:** - H₂O is liberated by reduction of O₂ accepts electrons and protons and liberates H₂O. Protons are transported from anode to cathode through proton transport membrane, while electrons transport through electric circuit.
- The liberated H₂O at cathode is consumed at anode.



Advantages: -

- (1) Storage of methanol is much easier than H₂ (does not need high pressure or low temperature) since methanol is in liquid form at -97.0⁰ C to 64.7⁰ C (-142.6⁰F to 148.5⁰F)
- (2) The energy density of methanol is greater than H₂.

Disadvantages: -

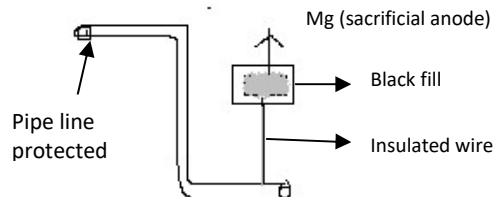
- (1) During methanol oxidation, CO formed which strongly adheres on to Pt catalyst, reducing, the surface area and lowering the performance.
- (2) CH₃OH is highly toxic and flammable and so utmost care is necessary.

Cathodic protection: -

- In this method of protection, a metal that acts as anode is forced to behave like cathode there by its corrosion doesn't occur.
- This is done by two methods
 1. Sacrificial anodic protection
 2. Impressed current cathodic protection

1. Sacrificial anodic protection: -

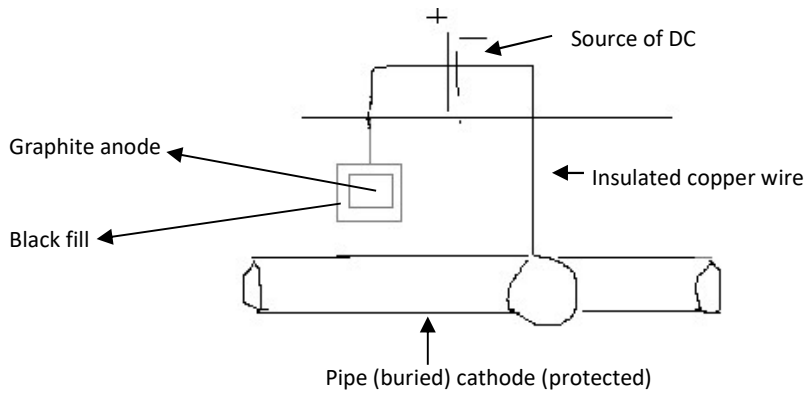
- In this method of protection, metallic structure to be protected is called base metal.
- Using more active metal called sacrificial anode, base metal is protected by connecting it to sacrificial anode through a wire.
- Hence all corrosion is concentrated at sacrificial anode while base metal is protected.
- Corroded sacrificial anode block is replaced by fresh one.
- The commonly used anodic metals are Mg, Zn, Al and their alloys. Zn is used as sacrificial anode in good electrolytes as sea water. Mg is used in high resistive electrolytes due to its more -ve potential & it can provide highest current output.

**2. Impressed current cathode protection: -**

- In this method all impressed current is applied in opposite direction to corrosion current to nullify & convert corroding metal from anode to cathode.
- Once the metal becomes cathode it is protected from corrosion.
- The impressed current is taken from battery or rectified AC line.
- The anode may be either an inert material or insoluble material such as graphite, Pt, stainless steel, high silica iron, scrap Fe etc.
- Usually sufficient DC current is passed on to insoluble anode kept in back fill composed of coke /gypsum. So as to increase electrical contact with surrounding soil.
-
- This protection technique is mainly used to buried structures like water tanks, water pipelines, transmission line towers, marine pipes , laid up ships etc.

Anode

Cathode

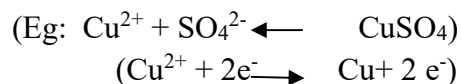


3. Application of protective coatings: -

- Coating of coat metal on base metal to protect from corrosion is said to be protective coating method.
- It is oldest, traditional & best method to prevent corrosion.
- The most important coating methods are electroplating & electro-less plating.

Electroplating: -

- It is a technique by which deposition of coat metal is done on base metal by passing direct current through electrolyte solution which contains soluble salt of coat metal.
- If base metal is having impurities like oils or greases, it should be cleaned with organic solvents like tetrachloride ethylene and if it contains surface scales, oxides are removed by applying HCl (Ni or Cu plating) or H₂SO₄.
- The cleaned metal is used as cathode and anode is either an inert material of good electrical conductivity or coating metal itself.
- Electrolyte is soluble salt of coat metal.
- The anode and cathode are dipped in electrolytic solution kept in an electroplating cell or bath.
- When direct current passed through coating metal ion migrate towards cathode and deposit as thin adherent film on base metal.



Electroplating of Ni: - Ni plating gives hard, adherent and good wear resistant surface to base metal. After Ni plating article is finely coated with Cr.

Requirements: -

Electrolyte bath: NiSO₄(20 gm/L) , NiCl (450 gm/L) & boric acid (30 gm/L)

pH: 4.0 by Boric acid buffer

Operating temp: 40-70⁰C

Current density: 20-30 m A/cm²

Additive agent: Saccharin / Coumarin derivatives

Cathode: Metal

Electro-less plating / immersed plating / displacement plating: -

- This is also widely used technique to protect base metal from corrosion.

- It is a technique in which deposition of coat metal on base metal is done by employing reducing substances (HCHO / Sodium Hypophosphate) in place of electric current.
- In this method, the base metal to be coated is immersed in noble metal salt solution used for plating.
- The noble metal ion is displaced from its salt solution by base metal ion and forms thin uniform deposit on base metal.

Eg: Electro-less plating of Ni :-

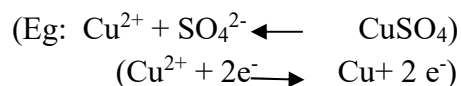
- The base metal is immersed in bath containing Sodium hypophosphate & NiSO₄ at pH 4.5 - 5.0 and temperature is maintained at about 100⁰ C.
- The Sodium hypophosphate reduces Ni⁺² ions to Ni metal and finally converts into Ni phosphate.
- The alloy of Ni & Ni phosphate deposited on base metal surface forms a strong adherent, non-porous coating with higher corrosion resistance.

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UNIT-III: Polymers and Fuel Chemistry

Lecture notes

INTRODUCTION:

- Matter is composed of many small units called molecules, which are in different sizes and shapes and associated with atoms. Polymers are giants or macro molecules which play a vital role in our daily life and provide the basic needs of our life (food, clothing and shelter).
- The word polymer was derived from Greek word 'poly'= 'many' and 'mers' = 'parts /units'.

Polymer: It is defined as a high molecular weight compound (macro molecule) made by linking together a large number of small molecules called **monomers**.

Ex: PVC, Polyethylene, Starch, Poly styrene, Proteins, DNA etc.

Monomer: The basic repeating units present in a polymer are called monomer.

Ex: Vinyl chloride is a monomer of PVC.

Ethylene is a monomer of poly ethylene.

Glucose is a monomer of starch.

Styrene is a monomer of polystyrene.

Amino acids are the monomers of proteins.

Nucleotides are the monomers of Nucleic acids.

Degree of polymerization: The number of repeating units (or) monomers present in the polymer is called as degree of polymerization. They may be hundreds (or) thousands (or) ten thousand.

$$\text{Degree of polymerization (D.P)} = \frac{\text{Mol.wt of polymer}}{\text{Mol.wt of monomer}}$$

$$\text{Molecular wt of polymer} = \text{D.P} \times \text{Mol.wt of monomer.}$$

Classification of Polymers:

1. Based on degree of polymerization:

- Polymers having high DP (having of more number of monomers) are called **High polymers**. Their molecular weight range is about 10,000 to 10,00,000 Daltons.
- Polymers with low DP are called **Oligopolymers**. Their molecular weight ranges from 5,000 to 2,00,000 Daltons.

2. Based on occurrence:

- Polymers may be either **Natural** (natural rubber, proteins, cellulose, starch etc) (or) **Synthetic** (PVC, PE, PS, Teflon, Nylon, Bakelite etc.....).

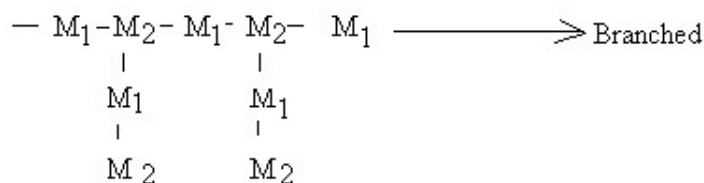
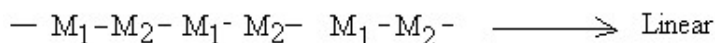
Basic Concepts:

1) Functionality:

- The number of bonding sites (or) reactive sites present in a monomer is called as functionality.
- Each monomer should have minimum two bonding sides for polymerization.
 - a) If the functionality of monomer is 2, the resulting polymer is linear (or) straight chained.

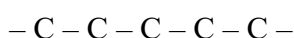
Ex: Ethylene, styrene, vinyl chloride.

b) Hetero or Co-polymers: If a polymer is composed of different types of monomers, then it is called Hetero / co – polymers. They may be generally **linear (or) Branched**.

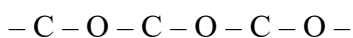


(ii) Type of atoms present in back bone chain:

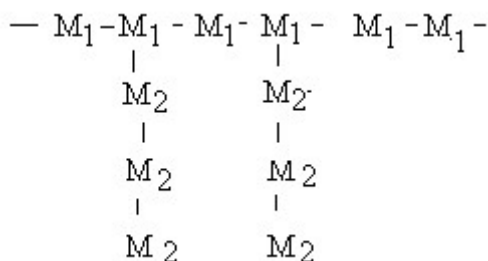
a) Homo chain polymer: If the main chain is made up of same species of atoms is called homo chain polymer.



b) Hetero chain polymer: If main chain is composed of different atoms is said to be Hetero chain polymer

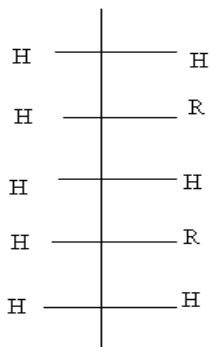


e) Graft co-polymers: These polymers are branched structures in which the monomer units on the branches and back bone differ.



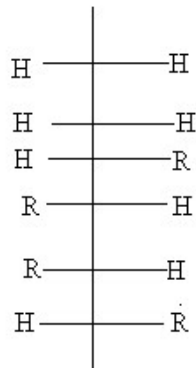
3) Tacticity: The orientation of functional groups in polymer is called as configuration. The difference in configuration of polymers because of the difference in arrangement of functional groups around main chain is called as Tacticity. Based on tacticity, polymers are of three types.

a) Isotactic: If all the functional groups are arranged on the same side of the chain, the polymer is called Isotactic polymer.

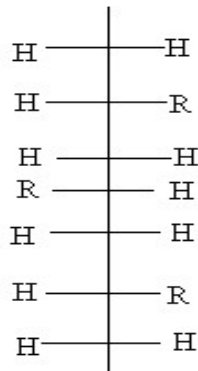


b) Atactic: If all the functional are arranged randomly around the main chain, the polymer is called

Atactic polymer.



c) Syndiotactic: If all the functional groups are arranged alternately with respect to the main chain, the polymer is called syndiotactic polymer.



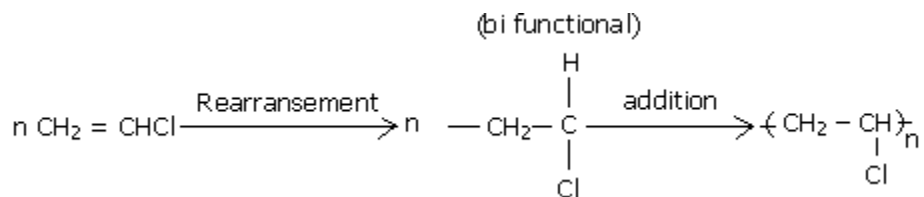
Polymerization:

1) Addition Polymerization:

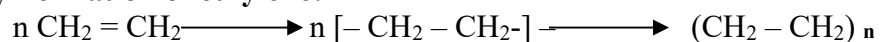
- This polymerization takes place between monomers that are bifunctional and contains double bonds in its structure.
- This can be defined as binding of several bifunctional monomers to form polymers without elimination of by products by addition reactions.
- This polymerization results in the formation of linear polymers.
- The produced polymer has same chemical composition as that of monomers.
- The molecular weight of polymer is an integral multiple of the monomer.

Examples:

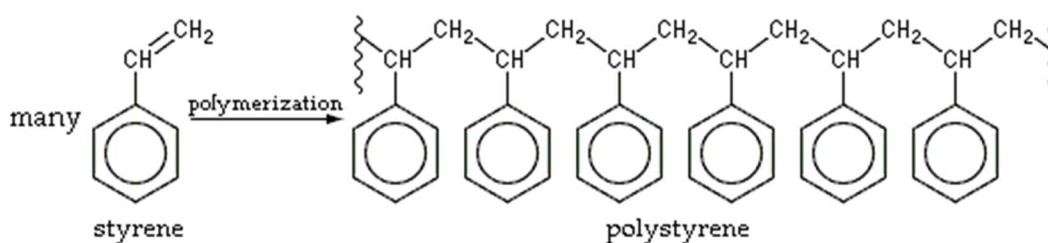
1. Formation of PVC:



2. Polymerization of ethylene:



3. Polymerization of Styrene:

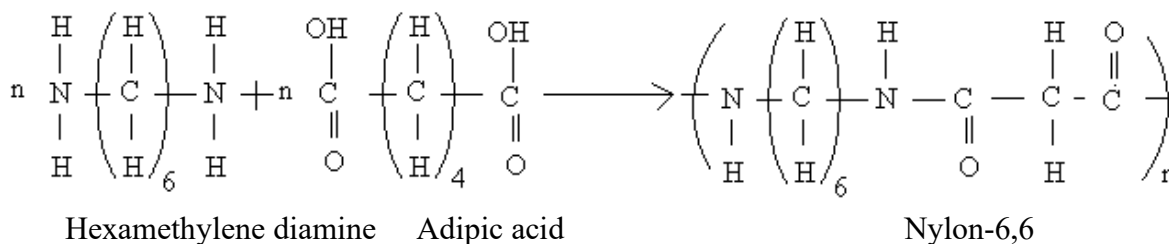


2) Condensation Polymerization:

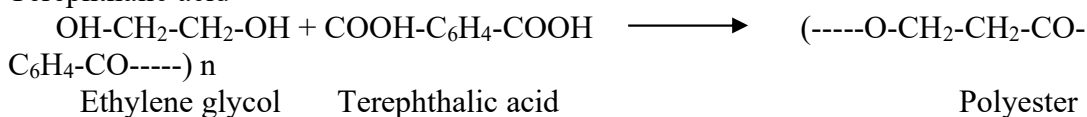
- This is also called Step-wise polymerization.
- This occurs between monomers that contain polar side groups.
- A reaction occurring between the same (or) different polar groups containing monomers with elimination of small molecules like ammonia, water, HCl etc..... and forms linear (or) Cross – linked polymers is called condensation polymerization.
- The molecular weight of polymer is not an integral multiple of the mol-wt. of monomer.
- The chemical composition of monomer and polymer are different.
- It results in the formation of linear or cross-linked polymers.

Example:

1. **Formation of Nylon-6,6:** Formed by the condensation of Hexamethylenediamine with adipic acid (Tetra methylene dicarboxylic acid)



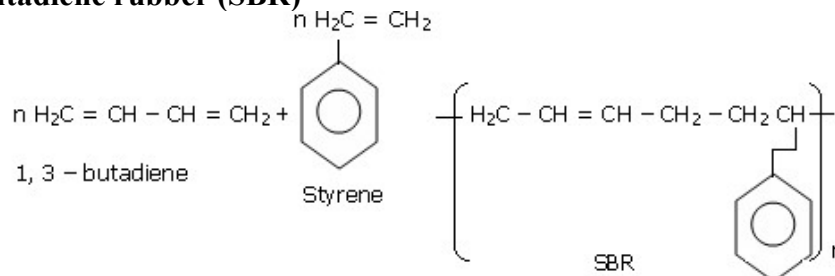
2. **Formation of Polyester:** Formed by the condensation between ethylene glycol and Terephthalic acid



3) Co-polymerization:

- When two (or) more different types of monomers undergo simultaneous polymerization then it is called Co-Polymerization.
- The properties of co-polymer are different from those of individual monomers.
- The copolymers may be alternating, random, block and graft polymers.

Ex: Styrene butadiene rubber (SBR)



Plastics:

- An organic substance with high molecular weight, which can be moulded in to any desired form when subjected to heat (or) pressure in the presence of catalyst is called as plastic.
- The term plastic must be differentiated from resins.
- Resins are basic binding materials, which form a major part of the plastic and which actually undergo polymerization and condensation reactions during their preparations
- However, the term resin and plastic are considered as synonyms.

Advantages:

Now a days, plastics play a important role in daily life because of their certain unique properties.

- Light in weight
- Transparent
- Low maintenance cost
- Chemically inert
- Corrosion resistance
- Insect resistance
- Easy transportability
- Easy workability
- Impermeable to water
- High resistance to abrasion

Disadvantages:

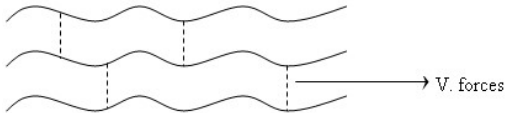
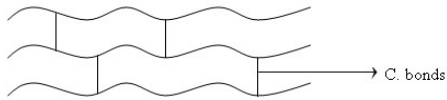
- Low heat resistance, so combustible
- High softness
- Poor ductility
- Major pollutant not degraded by soil

Uses:

- For Making many house hold articles
- For making furniture
- For making electric goods

Types of Plastics: Plastics are classified in to two types

- Thermo plastics
- Thermo setting plastics.

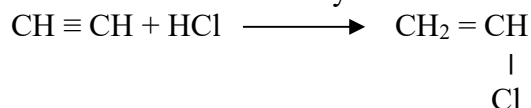
THERMOPLASTICS	THERMO SETING PLASTICS
<ul style="list-style-type: none"> • They are formed by addition reactions. (sometimes formed by condensation r/n) • They become softened on heating & hardened on cooling • They are soft, weak and less – brittle. • Adjacent polymer chains are held together by weak Vander Waal's forces  <ul style="list-style-type: none"> • They have either linear (or) branched structures • The chemical nature is not altered during heating & cooling. • They can be remoulded, reshaped & reused so they can be reclaimed from waste. • Low molecular weight thermoplastics are soluble in suitable organic solvents <p>Ex: PE, PVS, PS, Nylon Teflón etc....</p>	<ul style="list-style-type: none"> • Formed by condensation reactions. • They become soft on initial heating and hard on cooling. On reheating they become more hard. • They are hard, strong and more – brittle. • Adjacent polymer chins are held together by strong covalent bonds.  <ul style="list-style-type: none"> • Due to strong bonds, they exhibit cross-linked 3D-structure. • Chemical changes take place during moulding process. • They cannot be remoulded and reused so they cannot be reclaimed from the waste. • Due to strong bonds and cross links, they are not soluble in almost all organic solvents. <p>Ex: Bakelite, amino resins, poly ester resins, poly urethanes epoxy resins etc.....</p>

Important plastics:

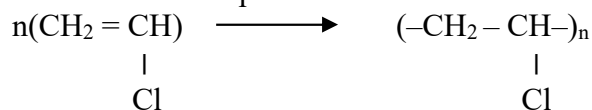
Polythene, PVC, Polystyrene, Teflon, Nylon, Bakelite

1. Poly Vinyl Chloride (PVC):

Preparation: Vinyl chloride is used as monomer for the manufacture of polyvinyl chloride. Vinyl chloride is prepared by reacting acetylene with hydrogen chloride at 100-150°C in the presence of metal salt catalyst.



PVC is prepared by heating a water- emulsion of vinyl chloride in presence of Benzoyl Peroxide in a autoclave under pressure.



Properties:

- PVC is colorless and odorless Powder.
- It is non-inflammable and chemically inert.
- It is soluble in chlorinated hydrocarbons like ethyl chloride, etc. and ketones.
- It has high resistance to light, inorganic acids, alkalis, and atmospheric oxygen.

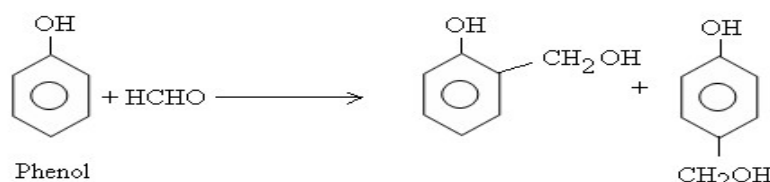
Uses:

- Plasticized PVC is used for making table cloths, rain coats, coatings for electric wire and cables, toilet articles, radio, T.V components, pipes, coupling valves, etc.
- Un-plasticized PVC or rigid PVC is used for making refrigerator components, cycle and motor cycle mudguards, tubes, pipes, etc.

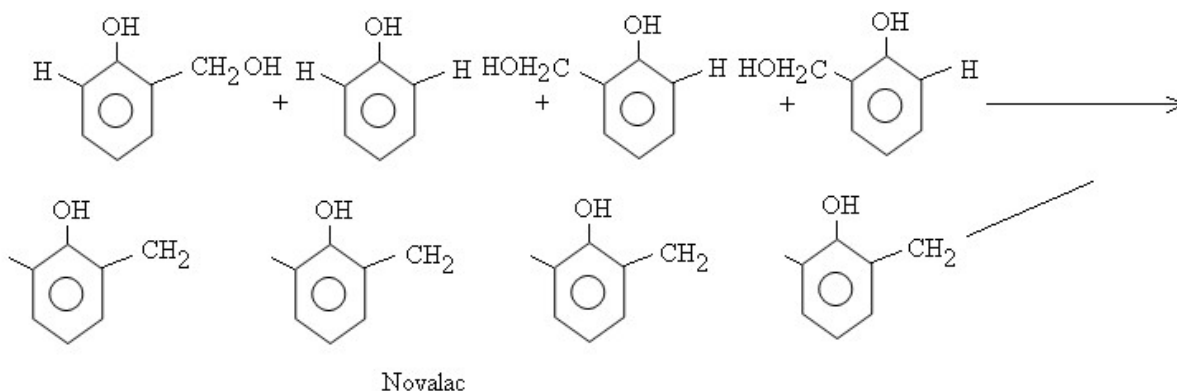
BAKELITE: (Phenol formaldehyde resin / phenolic resin / phenoplasts)

- Bakelite is a important thermosetting resin named after the scientist Baekeland, who synthesized this resin in they year 1909.
- It is prepared by the step polymerization of phenol with formaldehyde in presence of an acid (or) Alkali as a catalyst.
- This polymerization takes place in three steps:

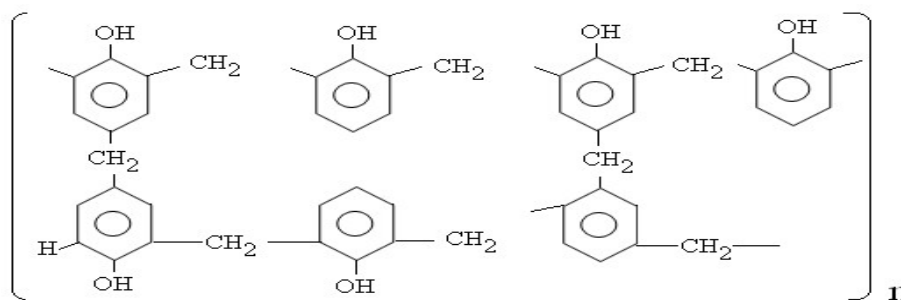
Step I: Phenol can condense with formaldehyde to produce O – hydroxy methyl phenol and P – hydroxy methyl phenol



Step II: condensation takes place between O – hydroxy methyl phenol and phenol to give linear polymer called Novalac



Step III: During molding, Hexa methylene tetraamine ((CH₂)₆ N₄) is added, it produces formaldehyde and ammonia. Formaldehyde converts the soluble and fusible Novalac in to a hard infusible and insoluble solid of cross – linked structure called Bakelite, whereas NH₃ neutralizes the acid.



Properties:

- * Bakelite are rigid, hard, scratch resistant, infusible, water resistant, solid substance.
- * Resistant to acids, salts and most organic solvents but attacked by alkali due to the presence of hydroxyl groups.
- * Good electrical insulator

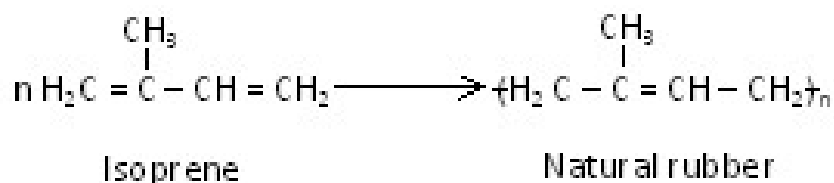
Applications:

- * For making electric insulator parts like switches, plugs, holders, switch boards, heater etc.....
- * For making moulded article like telephone parts, cabinets for radio and T.V.
- * Used in paints and varnishes
- * as adhesives for grinding and wheels.
- * In the product of ion exchange resin
- * For making bearings used in propeller shops, for paper industry and Rolling mills.

RUBBER (ELASTOMERS):

- The polymers which possess the property of elasticity are called as rubber.
- Rubbers are high polymers, which have elastic properties in excess of 300%.
- The molecular weight of raw rubber is about 1,00,000 to 1,50,000 Daltons.
- Most of the Indian production comes from Kerala state.

Natural rubber: It is a high polymer of polyisoprene, which are arranged in Cis – Configuration (functional groups are arranged on the same side).



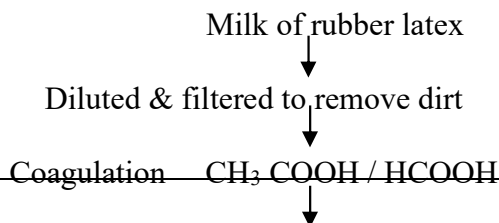
Natural rubber is mainly produced from the milk of the rubber tree “*Havea brasiliensis*”. Small quantities of natural rubber is also produced from the milk of a shrub known as “guayule”.

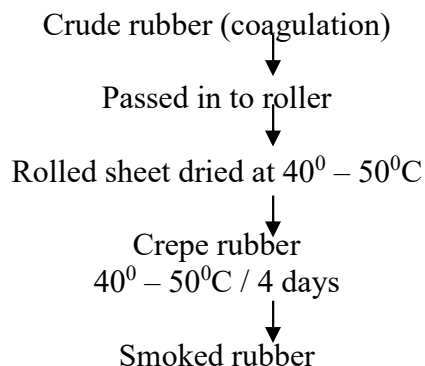
Processing of natural rubber:

- The milk of rubber tree is called latex.
- It is a colloidal emulsion consists a 25 – 45% of rubber and the remainder are protein and resinous materials
- The Latex was collected by cutting the bark of rubber trees.
- There after the Latex is diluted with water and filtered to eliminate dirt present in it. The Latex then coagulates by the addition of acetic acid (or) formic acid.
- The coagulated rubber is called as crude rubber. It is then made (or) rolled out in to sheets.
- The rubber sheets are dried under sunlight or mild heat and then subjected to further processing of rubber.

a) Crepe rubber: To the crude rubber, a small amount of sodium bi-sulphite is added to bleach the color and passed into rollers which produce one mm or more thickness sheets which are dried in air about 40 to 50°C. The dried thin sheet of rubber are known as crepe rubber.

b) Smoked rubber: The crepe rubber sheets are placed inside smoke rooms maintaining a temperature 40 to 50°C for 4 days. The dried rubber sheets are called smoked rubber, which are sent to rubber factories for further processing.





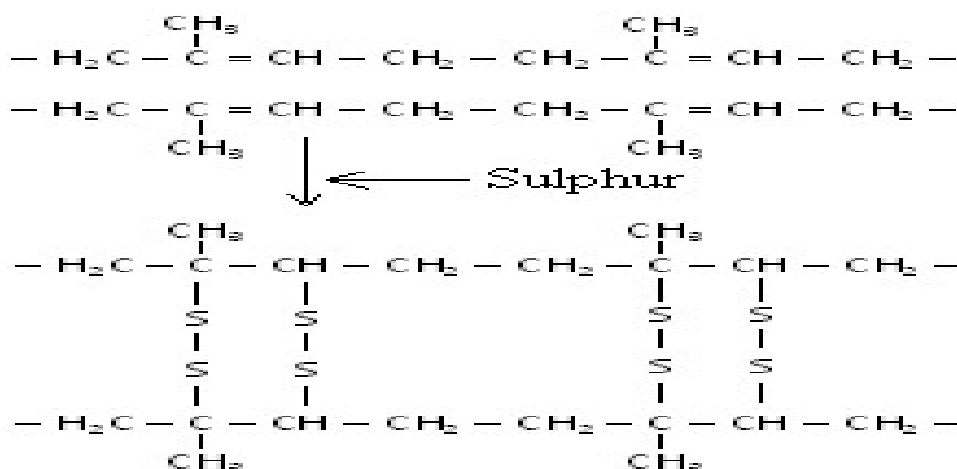
Draw backs of crude rubber (or) raw rubber: Crude rubber has following drawbacks.

1. Soft at high temperature and brittle at low temp.
2. It shows large water capacity
3. Shows little durability
4. Shows high elasticity
5. Attacks easily by oxidizing agents
6. Swells in organic solvents
7. Possess tackiness
8. Show low tensile strength.

The draw backs can be crude are rectified by the process of vulcanization.

Vulcanization:

- This was discovered by “Charles Good year” in 1839.
- The process of addition of Sulphur at 110-140⁰C to natural rubber to improve its properties is called as “Vulcanization”.
- The added Sulphur combines at the double bonds of rubber chains and cross – links of the linear polymer chains, resulting in a three-dimensional network structure.
- Thus, the rubber loses plastic state and acquires elastic state.
- The stiffness of vulcanized rubber depends on the amount of the Sulphur added.
- A flexible tyre rubber contains about 3 – 5% if Sulphur whereas hard rubber contains 32% of Sulphur.



Advantages of Vulcanization:

Vulcanization process brings excellent changes in the properties of rubber.

A Vulcanized rubber has

- (i) Low water absorption tendency
- (ii) Higher resistance to oxidation
- (iii) High stiffness
- (iv) Slight tackiness
- (v) Good durability
- (vi) Good resistant to changing temperature
- (vii) Resistance to swelling in organic solvents etc.....

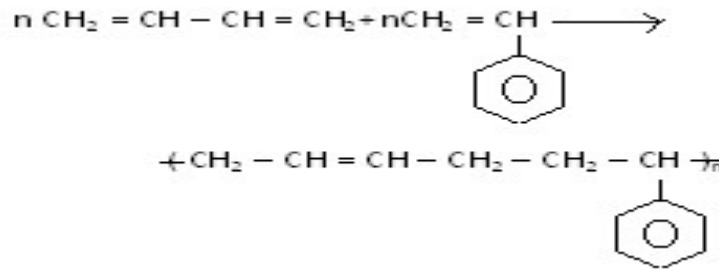
SYNTHETIC RUBBER: (ELASTOMERS):

The following rubbers are considered as synthetic rubbers.

- 1. Buna – S - Rubber
- 2. Buna – N – Rubber
- 3. Polyurethane rubber
- 4. Silicone rubber

1. Buna – S / Styrene / GR – S rubber:

Preparation: It is prepared by copolymerization of 1, 3 – butadiene and styrene.



Properties:

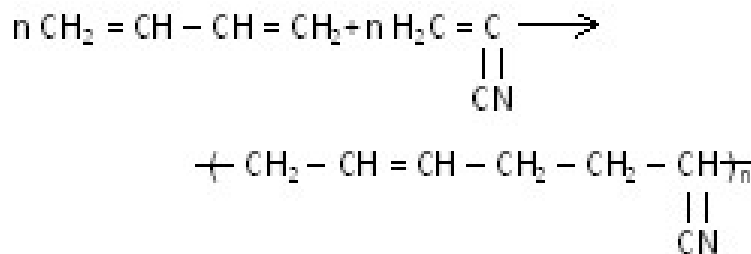
- a) It has high abrasion resistance and high load bearing capacity
- b) Easily oxidized in presence of ozone
- c) It swells in oils and organic solvents
- d) Its Vulcanization process is similar to natural rubber.

Applications / Uses:

- 1. It is mainly used for manufacture of tyres.
- 2. It is also used for floor tiles, shoe soles, gaskets, wire and cable insulations, Tank linings etc.....

2. Buna – N / Nitrile rubber: / GR – A rubber:

It is formed by copolymerization of 1, 3 but a – diene an Acrylo Nitrile.



Properties:

- It can be vulcanized in same way as natural rubber.
- It has good oil resistance, heat resistance and abrasion resistance

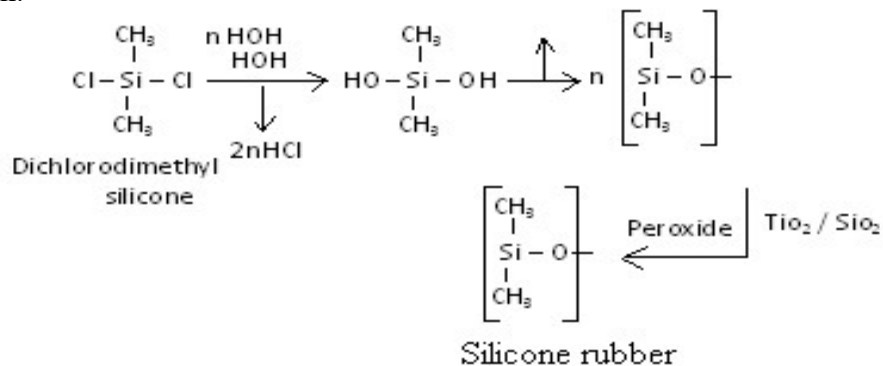
- It is attacked by alkalis, due to presence of cynogroups.

Uses: making air craft components, conveyor belts, tank linings, gaskets, hoses, printing rollers, automobile parts etc.

3. Silicone rubber:

Preparation: It is formed by the polymerization of dihydroxy dimethyl silicon, which is formed by dichloride methyl silicon. This step requires water molecules and HCL elimination takes place.

Dihydroxy dimethyl silicon forms an unstable silicon rubber by dehydration which yields silicon rubber in the presence of peroxide and in organic fillers like TiO₂, SiO₂ etc. by the polymerization.



Properties:

- It has good resistant to Oils, dilute acids, alkalis and sunlight.
- It retains rubber properties at elevated temperatures.
- It is also resistant to air and ozone at high temperature.

Uses:

- It is mainly used in making lubricants, paints etc.
- For making artificial heart valves, transfusion tubing's, for special boots to be used at low temperature.

Fuel Technology

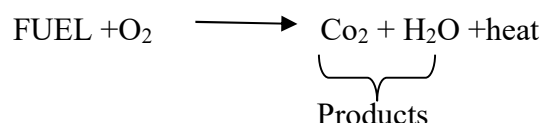
Introduction:

With rapid growth I world population, the energy requirements have also increased. Heat energy is one of the main sources of power that is produced by burning of fuels.

Definition: A fuel is a combustible substance, which on proper burning gives large amount of heat that can be used economically for domestic & industrial purposes. The main elements of any fuel are C&H.

Eg: wood, petroleum, petrol, charcoal, coal, kerosene, producer gas, oil gas, natural gas, water gas.

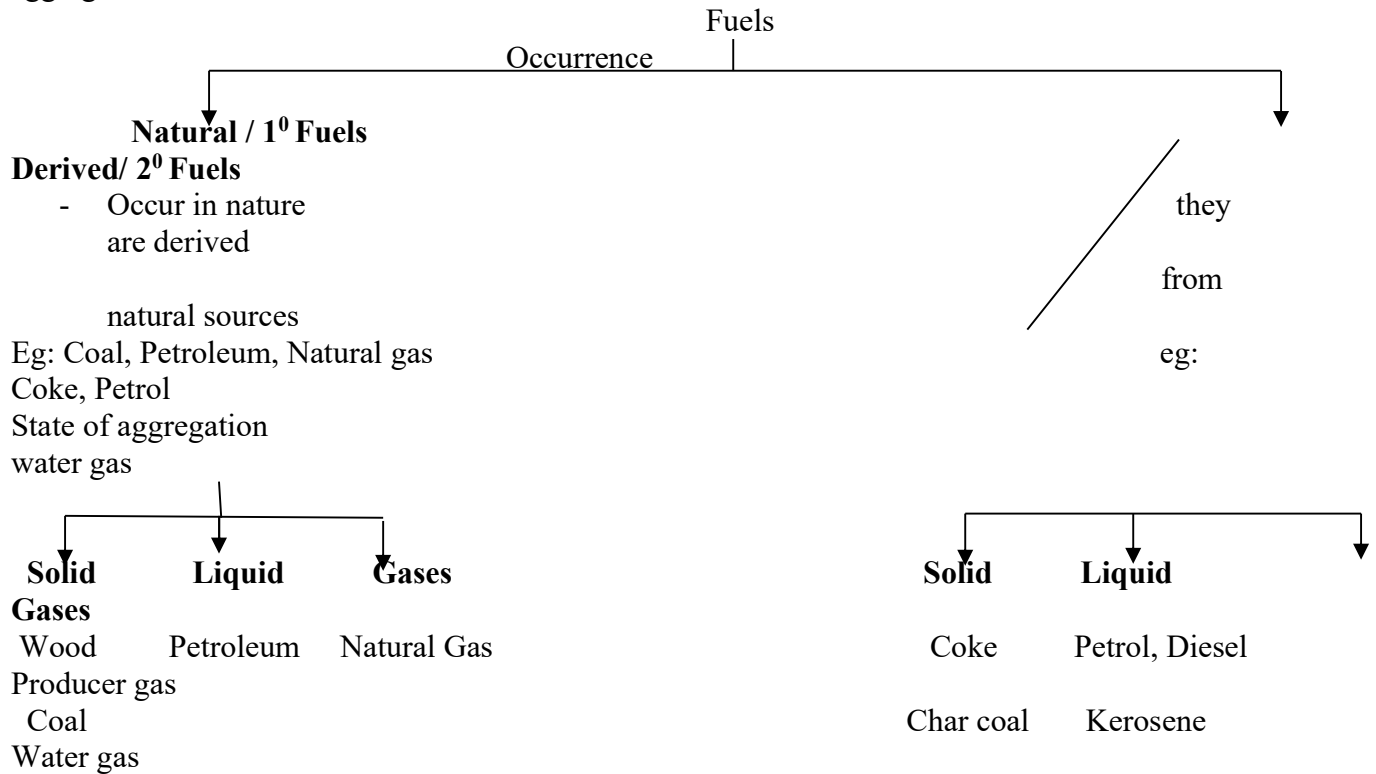
- During the process of combustion of a fuel, these elements combine with O₂ to produce CO₂ & H₂O with the liberation of heat.



- The stored fuels available in earth's crust are called fossil fuels.

Classification of FUEL: -

Fuels are classified in to following types based on their occurrence, & state of aggregation.



Characteristics of good fuel: - A good fuel should possess the following properties for its selection for a particular purpose. .

1. **High calorific value:** - The total amount of heat liberated when unit quantity fuel is completely burnt is called as calorific value. A good fuel should possess high calorific value.
2. **Low moisture content:** A good fuel should contain low moisture content. Moisture present in the fuel reduces the heating value.
3. **Moderate velocity of combustion** - If the rate of combustion is low, regaining of high temp is not possible and if the rate of combustion is too high control of combustion becomes difficult.
4. **Combustion products should not be harmful:** - The combustion products should not pollute the atmosphere so it should not produce undesirable products or objectionable gases.
5. **Low cost:** - It should be cheap & readily available.
6. **Easy to transport:** - it must be easy to handle, store & transport at a low cost. Solid & liquid fuels can easily be transported from one place to another whereas transportation of gaseous fuels is costly & can even cause fire hazards.
7. **Combustion should be easily controllable:** - Combustion of the fuel should be easy to start of stop when required.
8. **Moderate ignition temp:** -Ignition temp is the lowest temp to which the fuel must be preheated so that it starts burning smoothly. Lowest ignition temp is dangerous to store & transport of fuel since it can cause fire hazards and highest ignition Temp cause difficulty in igniting the fuel.

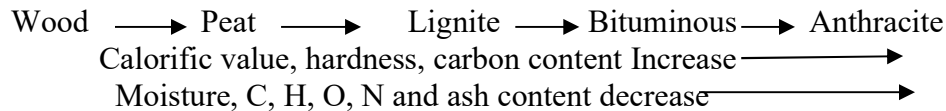
SOLID FUELS: -

- Advantages: -**
1. Easy to transport.
 2. They are convenient to store without any risk.
 3. They possess moderate ignition temp.
 4. Their cost of production is less.

- Disadvantages: -**
1. They contain high ash content.
 2. Excess of air is required for complete combustion.
 3. Calorific value is less compared to liquid or gaseous fuels.
 4. Cannot be used as fuel internal combustion engine fuels.
 5. Combustion operation cannot be controlled easily.

Coal: - Coal is a solid fuel & lightly carbonaceous matter, which is formed from the remains of deceased regrettably matter under the influence of heat, presence & bacterial action under health of the earth. It is composed of C, H, O, N, & S atoms besides some non-combustible in organic matter.

Classification of coal: - Various forms of coal are replenished on the basis of rank or degree of alteration or coalification from parent material wood.



Liquid fuels:

Advantages: -

1. Liquid fuels are clean & require less amount of air for complete combustion.
2. They possess higher calorific value than solid fuels.
3. They are easy to transport through pipes.
4. They are used as internal engine fuels.
5. They burn without forming dust, ash etc.
6. Easily ignited and emission can be easily controlled.
7. Requires less amount of air for complete combustion.

Disadvantages: -

1. Care must be taking during storage.
2. Cost is relatively higher than solid fuels.
3. They give bad dour.
4. Greater risk of fire hazards.

Petroleum: -

- It is also called as crude oil or mineral oil.
- The name '**petroleum**' has been derived from Latin. In Latin **Petra** means Rock and **Oleum** means Oil.
- It is available from earth's crust and it is dark greenish brown, viscous oil.
- It is the basic for all types of liquid fuels.
- It is mainly composed of various hydro carbons such as paraffin's, olefins (alkenes), naphthalene's & small amounts of inorganic compounds such as O, N, S.
- The average composition of petroleum: -

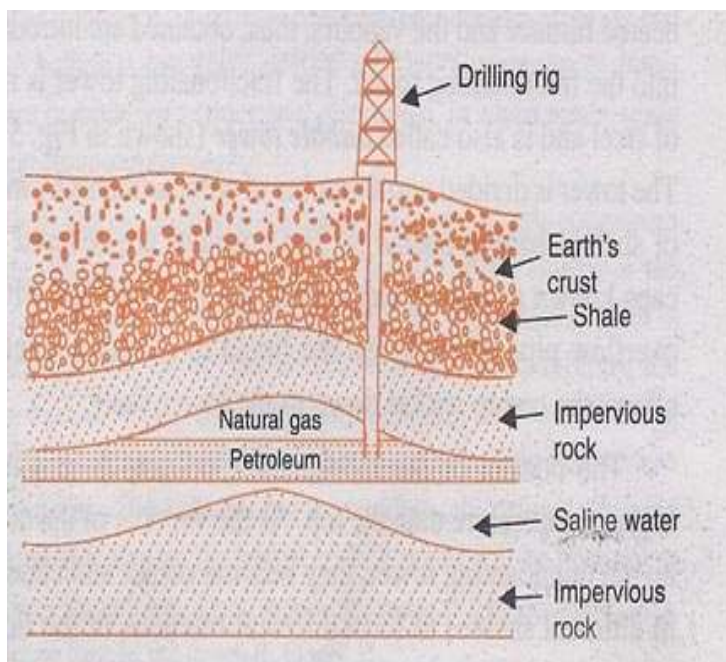
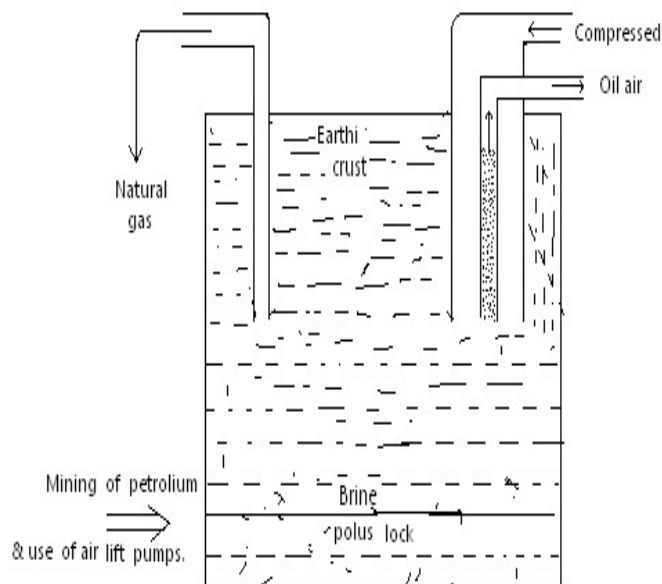
C	→	79.5 to 87.1%	H	→	11.5 to 14.8%
S	→	0.1 to 3.5%	N+O	→	0.1 to 0.5%

Classification of petroleum: - According to chemical nature, there are three types of petroleum

1. **Paraffin base type crude:** - Contains saturated hydro carbons up to $C_{35}H_{72}$
The hydro carbons from $C_{18}H_{38}$ to $C_{35}H_{72}$ are semi solids called waxes.
2. **Asphaltic base type crude:** - Composed mainly of naphthalene and cyclo-paraffin's with small amount of paraffin's & aromatic hydro carbons.
3. **Mixed base type crude:** - Contains both paraffin and naphthalene hydro carbons and is generally rich in semi solid waxes.

Mining of petroleum: -

- It is done by drilling holes in the earth's crust and sinking pipes up to oil bearing porous rocks.
- Oil is pushed out itself due to hydrostatic pressure of natural gas.
- When the pressure of natural gas is not sufficient, then air pressure is applied through lift pumps to force the oil out of the well.
- The co-axial pipes are lowered to the oil reservoir and compressed air is forced through the outer pipe, where oil comes out through the inner pipe which is sent to the refineries for further processing.



Refining of petroleum: -

- The resulting petroleum contains unwanted impurities like H_2O , Cl_2 , S compounds.
- The process of removal of impurities from crude oil and separation into various useful fractions with different boiling ranges is called “**Refining of petroleum**”.
- The plants used for this purpose are called **oil refineries**.
- The following steps are involved in the refining.

Step-1: - Separation of H_2O (Cottrell’s process): -

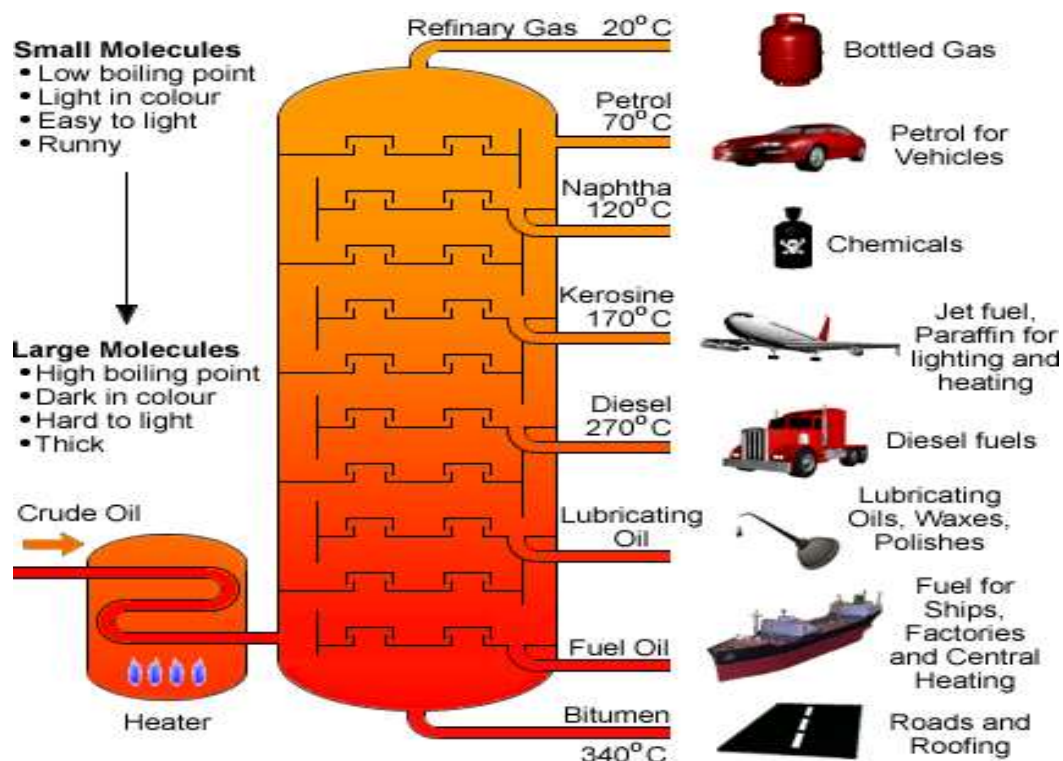
- The crude oil is an emulsion of oil and salt water.
- It is allowed to flow through two highly charged electrodes.
- The colloidal water droplets coalesce to form large drops which separate out from the oil.

Step-2: - Removal of ‘S’ compounds: -

- Sulphur compounds cause pollution.
- When crude oil is treated with copper oxide, it reacts with Sulphur compounds and forms copper sulphite precipitate, which is then removed by filtration.

Step-3: - Fractional distillation: -

- The crude oil is then subjected to about $400^{\circ}C$ temperature in an iron retort. All volatile constituents are evaporated except the residue (tar or asphalt).
- The hot vapors are then passed through a fractionating column.
- It is a tall cylindrical tower containing a number of horizontal stainless-steel trays at a short distance.
- Each tray is provided with a small chimney, covered with a loose cap.
- As the vapors go up, they begin to cool and fractional condensation takes place at different heights of column.
- Higher boiling fractions condense first while lower boiling fractions condense next. Thus crude oil is fractionated into different fractions depending upon their boiling ranges.



Fraction	Boiling range	Composition	Use
1. Uncondensed gas	Below $30^{\circ}C$	$C_1 - C_4$	As domestic/ industrial

			fuel
2. Petroleum ether	30 ⁰ to 70 ⁰ C	C3 – C7	As a solvent
3. Gasoline / petrol	40 ⁰ C- 120 ⁰ C	C5- C9	As a solvent, motor fuel and in dry cleaning
4. Naphtha	120 ⁰ C-180 ⁰ C	C9-C10	As a solvent and dry cleaning.
5. Kerosene	180 ⁰ C- 250 ⁰ C	C10- C16	Fuel for stores and aluminum
6. Diesel oil	250 ⁰ C-320 ⁰ C	C15 – C18	Fuel for diesel engines
7. Heavy oil Lubricating oil Petroleum jelly Grease Paraffin wax	320 ⁰ C- 400 ⁰ C	C17- C30	For setting gasoline by cracking process As lubricant Used in cosmetics & medicines As lubricant In candles, shoe polishes, wax paper.

Gasoline:

Knocking:

- In an internal combustion engine, a mixture of fuel and air is highly compressed before it is ignited in order to have maximum efficiency.
- During this process, there will be a sharp metallic sound known as '**Knocking**'. This causes more loss of energy and more engine wear.
- Knocking tendency of various hydrocarbons is

Straight chain paraffins > Branched chain Paraffins > Olefins > Cyclo Paraffins > Aromatics.

- Knocking can be decreased by addition of certain compounds to the fuel.
- These compounds are called **Antiknock agents**.
Ex: Tetra Ethyl Lead (TEL) – It is a alkylated product and used as principle antiknock agent for gasoline.

OCTANE NUMBER:

- The gasoline varies in their resistance to knocking.
- The quality of gasoline can be evaluated by measuring their knocking characteristics on **Octane Scale**.
- Octane number can be defined with reference to **n-heptane** and **iso-octane** and measured in a scale range of **0-100**.
- N-heptane produces maximum knocking, so its octane number is taken as Zero whereas Iso-octane produces minimum knocking so its octane number is taken as 100.

n-Heptane	-	0
Iso-octane	-	100
- The octane number of Gasoline can be defined as the **“the % of iso-octane present in a mixture of Iso-octane and n-heptane mixture that has the same knocking characteristics as that of the gasoline under test.”**
- Higher the octane number of Gasoline, least is the tendency for knocking, but higher is its combustion characteristics.
- Ex: if the Octane number of fuel is 80 means it has the same combustion characteristics as of a mixture of 80% Iso-octane and 20% n-heptane.

POWER ALCOHOL:

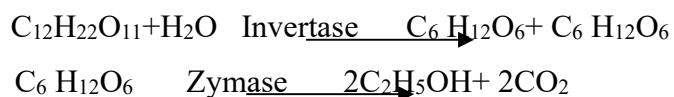
If Ethyl alcohol is added as an additive to act as a fuel for internal combustion engines, it is called **power alcohol**. Mixtures containing up to 20% alcohol with Petrol are used.

Manufacture of Power Alcohol:

The important raw materials required for manufacture of ethyl alcohol are saccharine materials such as molasses, Sugar Beets etc. or Starch materials such as Starch, Potatoes, Cereal Grains etc.

Ethyl alcohol from Molasses:

- Fermentation process is used for manufacture of ethyl alcohol from molasses.
- Molasses is a dark-colored viscous liquid left after crystallization of cane sugar from cane juice.
- It contains 20-30% of Sugar or Sucrose.
- It is converted to ethyl alcohol with the help of Yeast which gives enzymes **invertase** and **Zymase**.
- These two enzymes cause fermentation of molasses.
- Before adding Yeast, the molasses is diluted with water and pH is maintained between 4-5 by adding Sulphuric acid at 30°C.
- The process is completed within 2-3 days.
- By using distillation process many times, the concentration of ethyl alcohol can be increased up to 97.6%.



Advantages:

1. Addition of alcohol to petrol increases the Octane number, so power alcohol contains better anti knock properties.
2. Starting difficulties will not be there with power alcohol.
3. Air required for complete combustion is less.
4. It can be used in engines with higher compression ratio.

Disadvantages:

1. Alcohol is easily oxidized to acids. Hence it may cause corrosion.
2. Calorific value of petrol is decreased by adding alcohol.
3. Because of high surface tension, it is difficult to atomize alcohol at low temperature. So special arrangements must be provided to start alcohol-petrol mixing in carburetor.

CALORIFIC VALUE: -

- The efficiency of fuel is expressed in terms of calorific value.
- It is defined as the total quantity of heat liberated by burning a unit mass or volume of fuel completely.
- Units of heat: -
 1. Calorie / gram.
 2. Kilo calorie /kilogram calorie.

1. Calorie or gram calorie: - The amount of heat required to raise the temperature of 1 gm of H₂O through 1°C is called calorie.

$$1 \text{ cal} = 4.185 \text{ joules} = 4.18 \times 10^7 \text{ ergs.}$$

2. Kilocalorie or Kilogram calorie (K.cal):- The amount of heat required to raise the temperature of 1 kg of H₂O through 1°C is called kilocalorie.

$$1 \text{ K.cal} = 1000 \text{ Cal}$$

3. British thermal unit (B.Th.):- The amount of heat required to raise the temperature of 1 pound (lb.) of H₂O through 1°F is called British thermal unit.

$$\text{B.Th.} = 252 \text{ Cal} = 1054.6 \text{ Joules} = 1054.6 \times 10^7 \text{ ergs.}$$

4. Centigrade heat unit (C.H.U.):- The amount of heat required to raise the temperature of 1 pound of H₂O through 1°C is called Centigrade heat unit.

$$1 \text{ K.cal} = 1000 \text{ Cal} = 3.968 \text{ B.Th.} = 2.2 \text{ C.H. U}$$

Units of calorific value: -

The calorific value for liquids and solids \longrightarrow Cal/gm/ k.cal/kg/ BTH. /Lb.
 For gaseous fuels \longrightarrow K.cal/m³ / B.Th.ft³

1. Gross calorific value (GCV)/ Higher calorific value (HCV):-

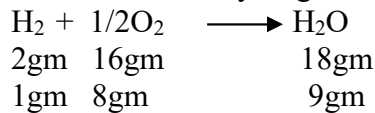
- The total amount of heat produced when a unit quantity of fuel is completely burnt and products of combustion are cooled down to room temperature (150C) is called **Gross calorific value**.
- H₂ that is present in almost all fuels undergo combustion to produce steam and steam is then cooled to room temperature and condensed to water.
- Latent (internal) heat that is evolved is also included in the gross calorific value.

2. Net calorific value (NCV)/Lower calorific value (LCV):-

- The amount of heat liberated when a unit quantity of fuel is completely burnt and combustion products are allowed to escape is called as Net calorific value.
- Generally during combustion of a fuel. The water vapours escape along with combustion products and are not condensed.

$$\text{NCV} = \text{GCV} - \text{latent heat of H}_2\text{O vapour formed.}$$

$$= \text{GCV} - \text{Mass of hydrogen} \times 9 \times \text{latent heat of steam.}$$



One part by weight of hydrogen gives 9 parts by weight of H₂O.

The latent heat of steam is 587 Cal/gm of 1060 B.Th./lb.

$$\text{NCV} = \text{GCV} - 9 \times \text{H}/100 \times 587 \quad \text{where H} = \% \text{ of H}_2 \text{ in the fuel.}$$

$$\text{NCV} = \text{GCV} - 0.09 \times \text{H} \times 587$$

UNIT- IV

Building Materials

Cement: -

- Cement is a dirty greenish heavy powder, used as a building material. It is a material which posse's adhesive & cohesive properties to bind rigid masses like stones, bricks, Building blocks etc.
- It has the property of setting & hardening in the presence of water i.e., hydraulic in nature.
- Chemically it is composed of mixture of calcium silicate & Calcium aluminate in which Calcium materials are called as **calcareous** & Alumina and silica are called as **argillaceous**.

Classification of cement: - Cements are classified into following types.

- (1) Natural cement
- (2) Pozzolana cement
- (3) Slag cement.
- (4) Port land cement

(1) Natural cement: - This is obtained by calcining & pulverizing natural rocks consisting of clay & limestone. During heating, silica & alumina present in the clay react with lime

to produce calcium silicate & Calcium aluminates. Natural cement is usually used for construction of big structure such as dams.

Properties: -

- (1) It is hydraulic in nature with low strength
- (2) Its setting time is very less.

(2) Pozzolana cement: - It is obtained by volcanic ash. (The place Pozzuoli in Italy), which consist of silicates of Ca, Fe, Al mixed with lime on heating forms pozzolana cement.

Properties: -

- (1) Hydraulic in nature.
- (2) Mixed with port land cement for different applications.

(3) Slag cement: - It is prepared by mixing hydrated lime + mixture of Ca, Al silicates (Blast furnace slag) in a stream of cold H₂O. It is dried & then pulverized to fine powder. Sometimes accelerators like clay or caustic soda are added for hardening process.

Mainly used in making concrete in bulk construction

Properties: -

- (1) Decreased strength.
- (2) The time required for setting & hardening is more i.e., a week.

(4) Portland cement: -

It is obtained by heating a mixture of lime stone & clay & crushing the resulting product to a fine powder.

It is also known as magic powder.

It is a mixture of Ca silicates & aluminate with small amount of gypsum.

⇒ William Aspidin (1824) was father of modern Portland cement Industry.

⇒ It is a type of cement & not a brand name.

Chemical Composition of Portland Cement:

It is a finely powdered mixture of calcium silicate and aluminates of varying compositions. Ratio of % of lime (CaO) to that of silica (SiO₂), Alumina (Al₂O₃) and iron oxide is calculated by the formula

$$\frac{\text{Cao}}{2.8 \text{ SiO}_2 + 1.2 \text{ Al}_2\text{O}_3 + 0.65 \text{ Fe}_2\text{O}_3}$$

A good sample of Portland cement has the composition of.

Ingredient	Percentages (%)
1. CaO	60-70
2. Silica	20-29
3. Alumina	5-7.5
4. Magnesia	2-3
5. Ferric oxide	1-2.5
6. SO ₃	1-1.5
7. Na ₂ O	1
8. K ₂ O	1

Manufacture of Portland cement: -

Raw materials for manufacturing of Portland cement

(1) Calcareous: - They are rich in lime such as limestone, chalk, and cement rock.

⇒ The limestone should not contain more than 5% of MgO, it leads to cracking.

(2) **Argillaceous:** - Those contain silica, alumina & iron oxide

Eg: -Clay, blast furnace slag (ashes).

(3) **Gypsum:** - It is added during the final grinding & it control the ratio of setting & hardening.

Methods of manufacturing process: - These are two methods for manufacturing

(1) Dry method

(2) Wet method.

- The two methods differ only in the treatment of raw material. In dry process water is not added to the material during grinding.

- The following steps are involved in manufacture of Portland cement.

(1) Mixing of Raw material

(2) Burning

(3) Grinding

(4) Packing

(1) Mixing of Raw material; -

Dry process:

- This process is employed if the lime stone and clay are hard.

- Initially lime stone is crushed in to pieces and then it is mixed with clay in the proportion of 3:1.

- This mixture is pulverized to a fine powder and is stored in storage bins and later on it is introduced in to the upper end of the rotary kiln.

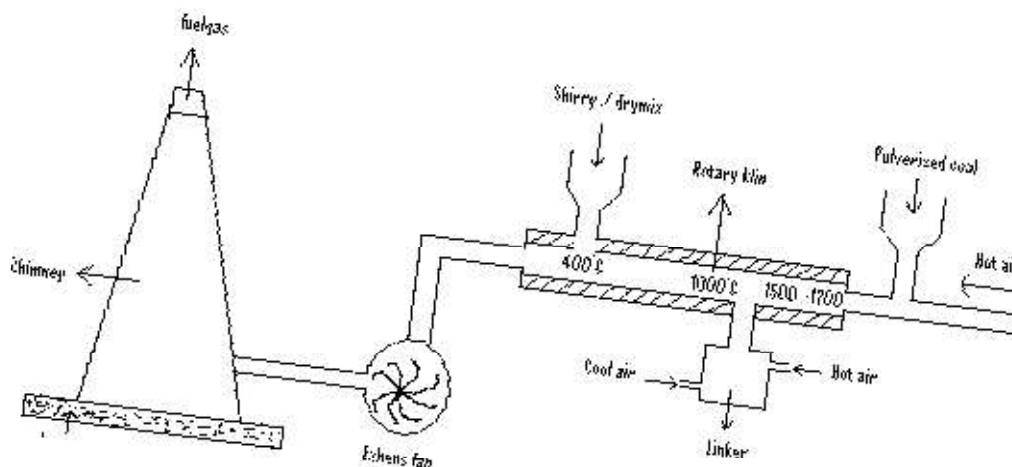
Wet process:

- This process is performed when the raw materials are soft.

- The clay is washed with water in wash mills to remove any foreign material or organic material.

- Powdered lime stone is then mixed with the clay paste in a proper proportion 3:1.

- The mixture is then finally ground and homogenized to form slurry containing about 40% water and stored in storage bins.



Difference between dry & wet process:

Dry process	Wet process
1. This process is adopted when the raw	1. This method is performed when the raw

materials are quite hard.
 2. It is a slow and costly process
 3. The final consumption is low, hence smaller kiln is used.
 4. The process is not suitable if the raw material has moisture content of 15% or more.

materials are soft.
 2. Comparatively cheaper and fast process.
 3. Fuel consumption is high so longer kiln is used.
 4. This process can be adopted even in wet conditions.

(2) Burning: -

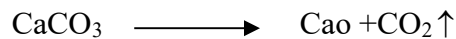
- Rotary kilns are used for burning of cement.
- A Rotary kiln is an inclined steel cylinder, length is about 150—200m & 2-10m diameter and it is lined with fire bricks.
- The kiln can be rotated at desired speed, (usually 0.5 to 2 rotations/minute) as it is mounted on rollers.
- As the kiln rotates the raw materials passes slowly from the upper end of rotary kiln to lower end, while the burning fuel (pulverized coal, oil / natural gas) moves from lower to upper end and escape after the removal of dust.
- As the mixture or slurry gradually descends with increasing temperature the following reactions take place in rotary kiln.

(a) Drying zone: -

- Present in the upper part of the kiln, where the temp around 400⁰ C
- The slurry gets dried because of hot gases.
- The clay is broken as Al₂O₃, SiO₂ & Fe₂O₃.

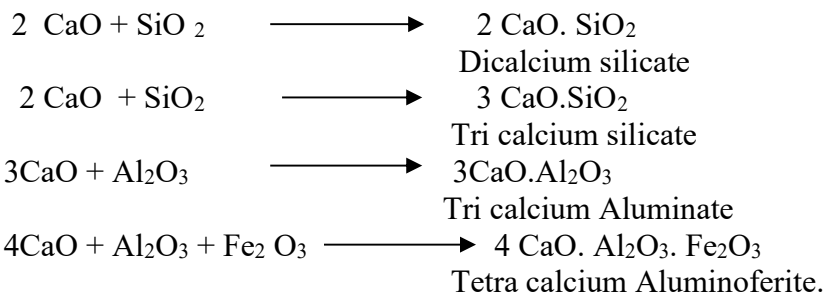
(b) Calcination zone / decarbonating zone: -

- It is present in the central part of the kiln, where the temp is around 1000⁰C.
- In this zone, lime stone of dry mix /slurry completely decomposed into quick lime (CaO) & CO₂.



(c) Clinkering zone / Burning Zone: -

- It is present in the lower part of the rotary kiln.
- The temperature is between 1500⁰C to 1700⁰C.
- In this zone lime & clay reacts to each other forming aluminates & silicates.



- These aluminates & Silicates of calcium fuse together to form hard greenish stones called clinkers.
- This reaction is exothermic.
- The cooled clinkers are collected in trolleys.

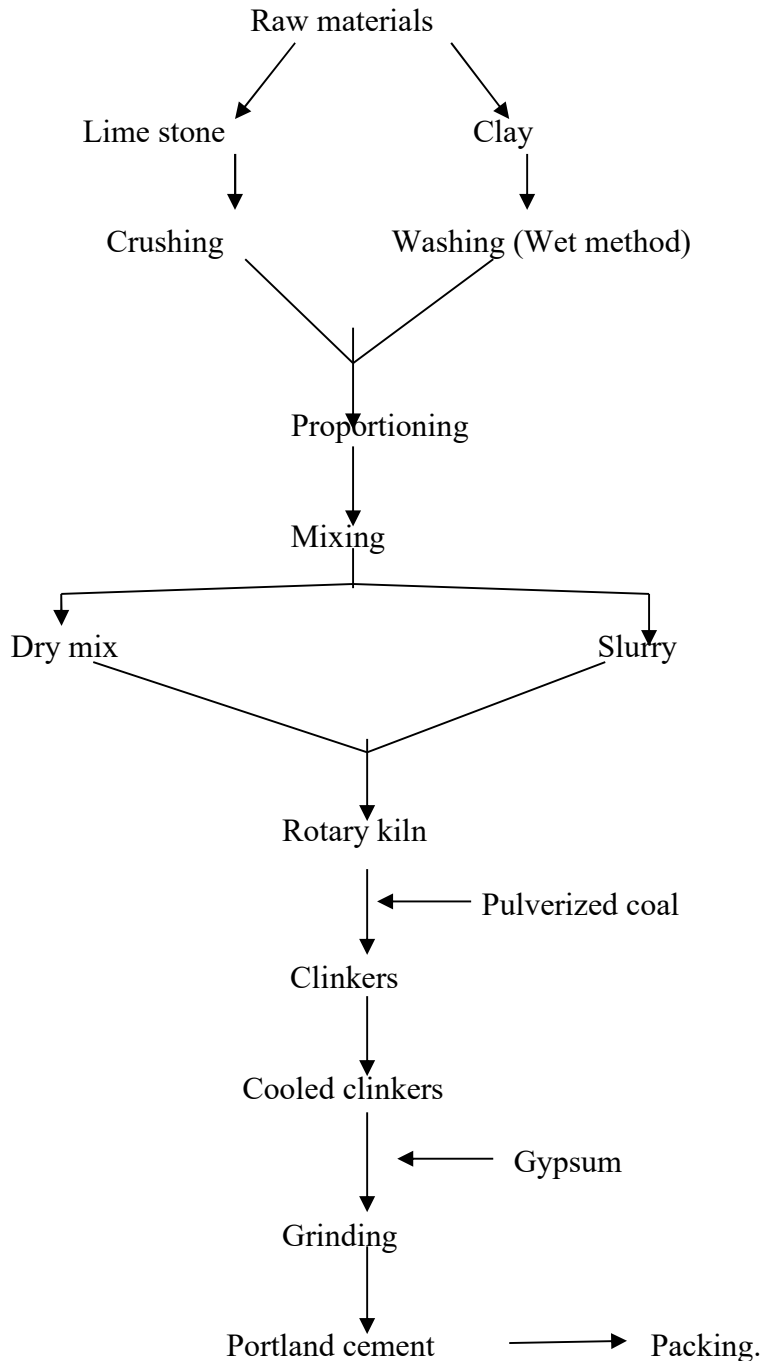
(3) Grinding: -

- The cooled clinkers are passed to ball mills and are pulverized to form powdered mixture.
- This finely powdered clinkers set quick rapidly. So, the cement mortar will unworkable.
- Therefore, its setting decreases used retarders. Commonly gypsum (CaSO₄·2H₂O) is used as retarder.

- Usually about 2-6% gypsum is mixed with clinkers in long tube mills.
Mixture of clinkers + 2-6% gypsum → Portland cement.

(4) Packing: - The resulting Portland cement is stored in silos (air tight bins) from which it is bagged or loaded for shipment.

Flow chart of manufacture of cement: -



Setting & hardening of cement: -

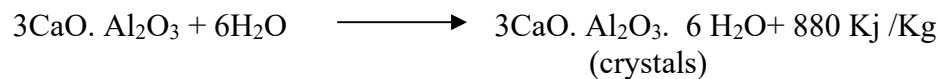
- When Portland is mixed with H₂O, it is converted in to a plastic mass called Cement paste (initial set) which slowly loses its plasticity & becomes stiff & ultimately a rocky mass is obtained (final set). This process is called as **setting**.
- The time for the initial set should not be less than 45min and for the final set should not be more than 10 hours.
- After hydration, anhydrous compounds become hydrated, which have less solubility. Hence, they are precipitated as insoluble gels or crystals.

- These have ability to surround sand, crushed stones, other inert materials & bind them strongly.
- The process of stiffening of original plastic mass is called as **setting of cement**.
- Development of strength due to crystallization is called as **Hardening**, which continues to increase for years.
- The process of setting & hardening is collectively called as solidification.

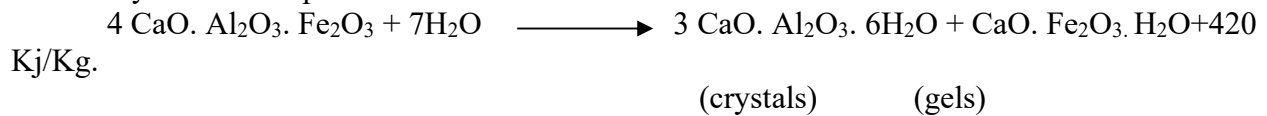
Name	Formula	Abbreviation	%	Setting time
Tri calcium silicate	3CaO. SiO ₂	C ₃ S	45	7days
Di calcium silicate	2 CaO.SiO ₂	C ₂ S	25	28days
Tricalcium Aluminate	3 CaO. Al ₂ O ₃	C ₃ A	10	1day
Tetra calcium alumino ferrite	4 CaO.Al ₂ O ₃ . Fe ₂ O ₃	C ₄ AF	10	1day

Reactions involved in setting & Hardening: -

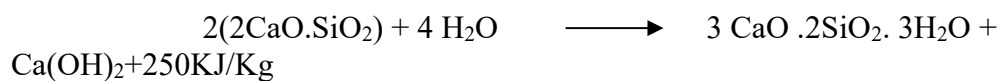
- When cement is mixed with water, the paste becomes quite rigid within a short time known as Initial set / flash set. This is due to rapid hydration of C₃A.



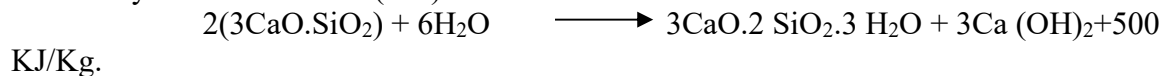
- The tetra calcium alumino ferrite (C₄AF) then reacts with water forming both gels & crystalline compounds.



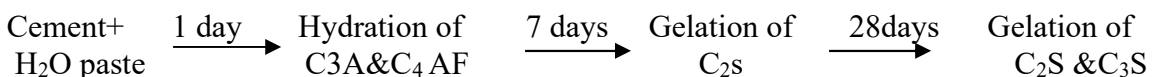
- Now C₃S & C₂S undergo further hydration & hydrolysis reactions increase the development of greater strength.
- The initial hardening of cement paste is due to the formation of tobermonite gel.



- The final hardening of cement paste is due to formation of tobermonite gel and crystallization of Ca (OH)₂.



Sequence changes during setting & hardening of cement: -



Refractories:

An inorganic material which can withstand very high temp without softening or deformation in shape, is called as “Refractories”.

Or

Any substance that is difficult to fuse / melt is a Refractory & used as constructing material.

Characteristics: -

- They should be chemically inert to the action of Corrosive gases, molten metal's, slag's etc.
- They should have high abrasion resistance.
- Does not change their size at operating temperature.
- Expand & contract uniformly at increasing & decreasing temperature.
- They should have high load bearing capacity.

Classification: - Refractories are classified into following categories based

I) On their chemical properties:

1. Acidic refractories: - These refractories consist of acidic materials such as Al_2O_3 , Silica (SiO_2). They can with stand acidic materials but easily attacked by basic materials like Cao, MgO etc....

Eg: - Alumina, Silica & Fire clay refractories.

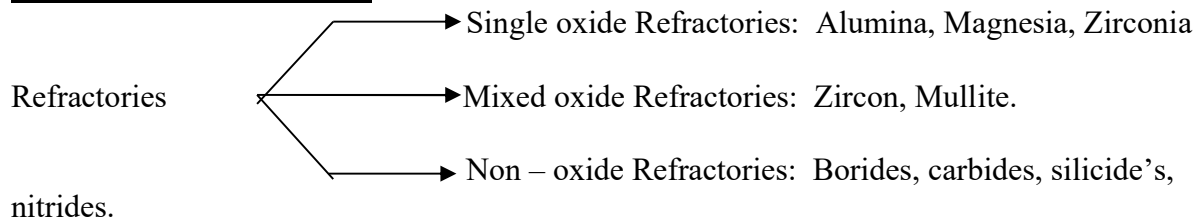
2. Basic refractories: - These refractories consist of basic materials like Cao, MgO etc. & are easily attacked by acid materials.

Eg :- Magnesite, dolomite bricks, chromo magnesite.

3. Neutral Refractories: - They made of weakly acidic /basic materials like carbon, zirconia (ZrO_2) & chromite ($FeO.CrO_2$). They show resistance to the action of acidic & basic materials & also show good chemical stability.

Eg: - Graphite, Zirconia & Carborundum (Sic).

II) On their oxide content:



III) On the basis of fusion temperature ranges:

	<u>Fusion temp</u>	<u>Example</u>
Ref	Normal Refractory → 1580-1780°C	Eg: Fireclay
	High Refractory → 1780-2000°C	Eg: Chromite
	Super Refractory → > 2000°C	Eg: Zircon

Properties of Refractories:

1. Refractoriness: -

- It is the ability of a material to with stand high temp without appreciable deformation or softening under working conditions.
- It is usually measured by the softening temperature of the material.
- The material to be used as refractory, should have a softening temp much higher than the operating temperature of the furnace in which it is to be used as refractory.
- The softening temperature of the material is usually determined by the 'Pyrometric cone test' or 'Seger cone test'.

Measurement of Refractoriness / Pyrometric Cone Test (Seger cone) :-

- Refractoriness is usually determined by comparing the softening behavior of test cone with that of standard cone (Seger cone).
- The refractoriness is expressed in terms of pyrometric cone equivalent (PCE).

- These cones are small, pyramid shaped -38 mm high, 19 mm long sides with a triangular base.
 - Test cone along with standard cones are heated under standard conditions of 10°C / minute.
 - Each standard cone is made of particular refractory with a definite softening temperature and are arranged with increasing softening temperature.
 - Standard cone fuses (melts) along with the test cone, the temperature at which the fusion of the test cone occurs is indicated by its apex (tip) touching the base.
 - If test cone softens earlier than one standard cone but later than the next cone, the PCE value of test cone is taken as the average value of the 2 standard cones.
- Eg : - Silica bricks – PCE no –32 & softening temperature 1710°C
Magnesite bricks -- PCE no--- 38 & softening temperature 1850°C

2. Refractoriness Under Load / Strength: -

- This property gives an idea of strength of refractory.
- Refractory should have high load bearing capacity under operating temperature, which can be measured by RUL test.
- This test is done in a rectangular container by applying a load of 1.75 Kg /cm² on to the refractory & heating at a constant rate of 10°C / minute.
- During this process the material will soften & its height will decrease under the load.
- This decrease in height is measured and when there is 10 % decrease to that of original height the temperature is noted.
- The RUL is then expressed as the temperature at which this 10% deformation occurs.

3. Chemical inertness: - The refractory selected for a specific purpose should be chemically inert and should not react with the slags, furnace gases etc. An acidic refractory should not be used in a basic furnace vice versa.

4. Dimensional stability: - It is defined as the resistance of material to any volume changes which may occur because of its exposure to high temperature over a prolonged period of time. These changes may be reversible/ irreversible. Further the irreversible change may result in contraction/ expansion. A good refractory should have high dimensional stability.

5. Thermal expansion& contraction: - The refractory tends to expand when temperature increases& contract when temperature decreases which affect the properties of the refractory. So, a good refractory should have low thermal expansion& contraction.

6. Thermal conductivity: - The conductivity of refractory primarily depends on its chemical composition & porosity. As porosity increases thermal conductivity decreases because the entrapped air in the pores function as insulator. Depending on the type of furnaces low thermal conductivity and high thermal conductivity refractories are used.

7. Abrasion resistance: - A good refractory should resist the abrasion action of fuel gases, flames, slags etc...

8. Porosity: - Refractories usually contain pores due to manufacturing defects etc. It is the important property of a refractory, which affect many physical & chemical properties. It is the ratio of pore volume to the bulk volume.

$$P = \frac{W - D}{W - A} \times 100$$

P = Porosity

W = Saturated weight of specimen (with H₂O)

D = Dry weight of the specimen

A = saturated weight+ moisture content of specimen.

⇒ Good refractory should have low porosity.

9. Electrical conductivity: - In general refractories are poor conductors of electricity except graphite. However electrical conductivity of refractories increases with increasing temperature.

10. Thermal spalling: - It is the property of breaking, cracking / fracturing of the refractory due to rapid fluctuations in temperature causing uneven stresses & strains in the body of the refractory. A good refractory must show good resistance to thermal spalling. It is avoided by

- i. Avoiding sudden fluctuations in temp
- ii. By modification of furnace design
- iii. Low porosity & low co-efficient of expansion.

LUBRICANTS:

- All materials how smooth they are, they show many irregularities in the form of peaks or asperities. In all machines, when one solid surface is moving over another solid surface resistance will be formed due to mutual rubbing. This resistance is called as friction.
- This friction causes lot of **wares (loss of surface) and tear** (roughness or brittle) of surface of moving or sliding or rolling parts which consequently requires **repeated replacement**.
- Friction also generates heat which dissipated thereby causing the **loss of efficiency** of the machine. Moreover, the moving parts gets heated up, damaged and even sometimes result in **seizure** (welding of two surfaces due to heat)
- These problems can be overcome or minimized by using a substance called **lubricant**.
- **Lubricant** is defined as a substance used between two moving surfaces as a thin layer to reduce the frictional resistance.
- The process of reduction of frictional resistance between two moving surfaces using lubricants is called **lubrication**.
- The study of wear – tear or mechanism of friction between two surfaces and lubrication is called **tribology**.

Functions of lubricants:

- The first and foremost imp. function is to **reduce the frictional** resistance.
- It **reduces wear and tear** and **surface deformation** due to avoiding contact between two surfaces.
- **Act as coolant** by reducing the energy in the form of heat.
- It **prevents rust and corrosion**, thereby **reduces the maintenance and running cost** of the machines.
- It reduces **expansion of metals and seizure of metals** and seizure of moving surfaces by local frictional heat.
- They may also **absorb shocks** between bearings and other engine parts.
- They cover the surface of moving parts. Hence, they **act as seal**.

Ex 1: Lubricant used b/n pistol & Cylinder of internal combustion engine

Ex 2: Lubricant act as seal, so it avoids the leakage of gases under high pressure than the cylinder.

CLASSIFICATION OF LUBRICANTS: On the basis of their physical state, lubricants are classified into following types.

1. Liquid lubricants/ Lubricating oils
2. Semisolid lubricants / greases
3. Solid lubricants

1. Lubricating oils:

- These lubricating oils provide a continuous fluid film over the moving or sliding surfaces. They act as
 1. Cooling & sealing agent
 2. Corrosion inhibitors.
- A good lubricating oils should possess
 - (i) Ideal viscosity
 - (ii) Thermal stability
 - (iii) High Boiling point
 - (iv) Non corrosive properties
 - (v) Low freezing point
 - (vi) High oxidation resistance
 - (vii) Stability to decomposition
- The lubricating oils are further classified into 4 types.
 - i. Animal & vegetable oils
 - ii. Mineral / petroleum oils
 - iii. Blended oils
 - iv. Synthetic oils

1. Animal & Vegetable oils:

- Before invention of petroleum products animal & vegetable oils are most commonly used as lubricants.
- They possess good oiliness, have the property of sticking with metal surface even under increased pressure and heavy load.
- However, they have the following disadvantages—
 - (1) Costly
 - (2) Undergo oxidation easily
 - (3) Forming gummy and acidic products
 - (4) Have some tendency to hydrolyze.

	<u>Source</u>	<u>Use</u>
Ex : a) Vegetable Oil	Castor oil	- Castorseed → for process of ↑ seed & ↓ pressure
	Palmoil	- Kernels of palm tree
	Olive oil	- Olive tree → for process of ↑ seed & ↓ pressure

Ex: In Watches and scientific measurements.

Animal oil	Source	Use
Whale oil	Whale fish	light machines lubricants
lard oil	pig	Ordinary machines

2. Minerals / petroleum oil:

- They are derived from fractional distillation of petroleum at a temperature of 300°C.
- The length of the hydrocarbon chain in petroleum oils varies between about 12 to 15 carbon atoms.
- The shorter chain oils have lower viscosity than the longer chain hydro carbons.
- They are widely used lubricants, because they are
 - (1) Cheap
 - (2) Available in abundance
 - (3) Quite stable under service conditions.

- However, they possess poor oiliness as compared to that of animal & Vegetable Oils.

Example

- | | | |
|---------------|---|--|
| 1. Light Oil | → | Spindles, transformers & refrigerators |
| 2. Medium Oil | → | Compressor, light machinery. |
| 3. Heavy Oil | → | Internal combustion engines, gear oil, heavy machinery |
| 4. Residue | → | Gear Oil, Steam Cylinder Oil |

Used as lubricants in

3. Blended Oils:

- No single oils serve as the most satisfactory lubricant for many of the modern machineries.
- The best properties of lubricating oils can be achieved by addition of certain chemicals called ‘additives’.
- These oils with additives are called as Blended oils.
- The following types of additives are employed.

Additive	Function	Examples
Oiliness carriers	To improve oiliness	Vegetable, fatty acids
Viscosity index Improvers	Thinning at high temp and freezing at low temp. is prevented	Hexanol, polyisobutylene, polystyrene
Thickness	Provides high viscosity	poly styrene, polyester
Detergents	They carry away dirt particles from metal surface	Sulphonates
Corrosion inhibitors	Reduce corrosion of bearings and other metal surfaces	Organic compound of P & Sb
Antioxidants	Resists the oxidation of lubricant	Aromatic phenolic amino compounds.
Abrasion inhibitors	Decrease abrasion	Tricresol PO ₄
Emulsifiers	They promote formation of emulsion acid between oil and water	Sodium salt of sulphonic acid
Boundary lubrication Improvers	They create long wearing lubricant film	Compound containing O, S or P, castor oil

4. Synthetic Oils:

- Synthetic lubricating oils are used under very severe conditions when petroleum lubricants fail to work effectively.
- They are used in military jet engines, submarines, rocket motors and atomic energy plants.
- They have high thermal stability, high flash points, high viscosity index etc....

Lubricant	imp-property	used in
Di base acid ester	With stand high temp	Jet engine, sub marine Engines & lubricants
Silicones	high Viscosity index, H ₂ O repellent & corrosive resistance	Furnace doors, electro plating equipment under highly corrosive environment

II. Semi – solid lubricants / Greases: (Soap + liquid lubricating oil)

- Grease is a semi – solid consisting of a soap dispersed in a liquid lubricating oil.
- The liquid lubricant may be petroleum oil or even a synthetic oil and may contain any of the additives for specific requirements.
- Greases are prepared by **saponification** of fat with **alkali**, followed by addition of hot lubricating oil.

- At high temp, the soap dissolves in the oil, where upon an interconnected structures ceases to exist and the grease is liquified.
- Greases have **high frictional resistance than oils** and can support much heavier loads at lower speeds.
- Greases are used
 - (1) In bearing & gears that work at high temp.
 - (2) In situations where oil cannot remain in place, due to high load, low speed, sudden jerk etc.....
- The main function of soap is it acts as a **thickening agent** so that grease sticks firmly to the metal surface.
- Greases are classified in to following types on the basis of soaps used in their manufacture of
 - (1) Ca based greases
 - (2) Soda based greases
 - (3) Lithium based greases
 - (4) Axle grease.

a) Ca based greases (CUP greases):

- They are emulsions of petroleum oils with calcium soap. They are prepared by adding requisite amount of Ca (HO)₂ to the hot oil while under agitation.

$$\text{Ca (OH)}_2 + \text{hot oil} \rightarrow \text{Ca based grease}$$
- They are cheapest, most commonly used, water resistant.
- They are used at low temp because above 80⁰C, oil & soap begin to separate out.

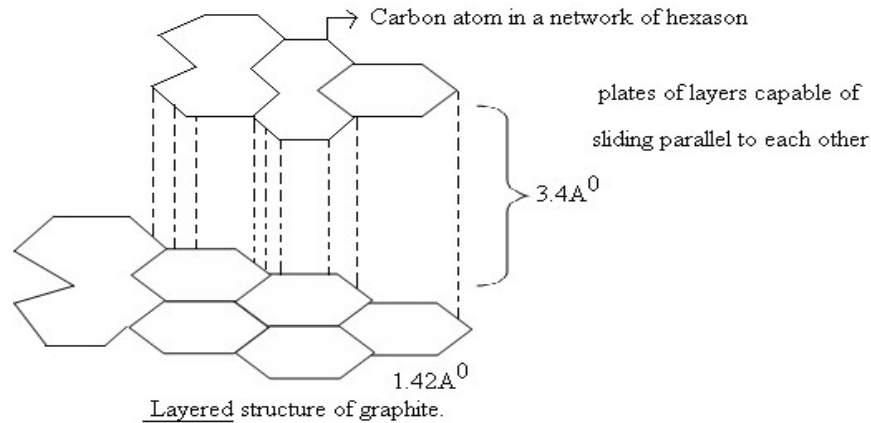
b) Soda based: These are petroleum oils thickened by mixing Na soap. They are not H₂O resistant, used at high temp (175⁰C) and suitable for use in ball bearings.

c) Li based: These are petroleum oils, thickened by mixing ‘Li’ soaps. They are H₂O resistant & suitable at low temp (150⁰C).

d) Axle: These are very cheap resin greases, prepared by adding lime to resin and fatty oils. They are H₂O resistant and suitable for less delicate equipment’s working under high loads and at low speeds.

III Solid lubricants:

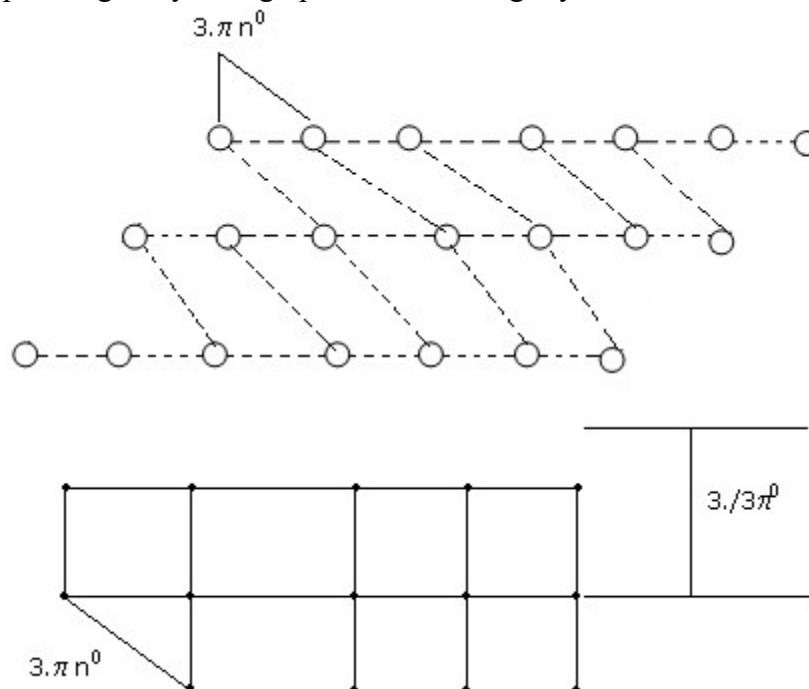
- Some of the solid substances possess strong adherence property, little shearing strength and good plastic properties.
- They are very important under high temp and heavy load.
- The most common solid lubricants are the minerals such as graphite, talc, soapstone, mica, Molybdenum disulphide and ZnO.
- The most commonly used solid lubricants are
 - (1) Graphite
 - (2) Molybdenum disulphide.



- It consists of many flat plates made up of a network hexagon in which each 'C' is in SP^2 hybridization.
- The separation between the plate's length is about 3.4\AA & little Van der Waal's forces slides the layers parallel to each other. Hence it has low coefficient of friction.
- It is very soapy to touch, nonflammable & not oxidized in air below 375°C .
- It is used as lubricant in the form of powder or suspension in oil or water.
- The suspension of graphite in oil is termed as "Oil – Dag" and used in internal combustion engines.
- Graphite is dispersed in H_2O is termed as "aqua - Dag" used in food industries.
- Graphite is used as lubricant in air compressors, food stuff industries, railway track joints, open gases, machine work etc.

MoS₂:

It has a sandwich like structure in which 'Mo' atoms lie between two layers of 'S' atoms. MoS₂ has high specific gravity than graphite but is slightly softer.



- Commercially available as "molykotes".
- The inter laminar attraction is very weak ($3.3/\pi^\circ$)
- It has low frictional strength
- It is stable up to 400°C
- It is used in space vehicles (70% MoS₂ + 7% graphite + 28% silicate)
- It can with stand extreme temp & low pressure and nuclear radiations.

PROPERTIES

- The selection of a lubricant for a specific application is based on properties of the lubricant.
- Lubricants show following properties.

1. Viscosity:

- It is one of the important properties of lubricating oil.
- It is the property of the fluid that determines its 'resistance to flow'
- Viscosity is measured in terms of viscosity coefficient.
- Viscosity coefficient is defined as **force per unit area required to maintain a unit velocity gradient between two parallel layers.**

Measurement: It is measured with viscometers.

Red wood Viscometer-I	Red wood Viscometer-II
Used to determine viscosities of lubricating oils. It has a jet of base diameter 1.62 mm & length of 10 mm	Used to measure viscosities of high viscous oils like fuel oils. It has 3.8 mm & length 15mm

Red wood viscometer: Parts are (1) Oil cup (2) Heating bath (3) stirrer (4) Kohlrausch flask (5) spirit level & leveling screws.

(1) Oil cup:

- Is a silver-plated brass cylinder (90 mm height 96.5 mm dia).
- The bottom of cylinder is opened or closed by a valve rod, which is a small silver-plated brass ball fixed to a stout wire.
- Oil is filled in the cylinder up to level of pointer.
- The lid of the cup is fitted with a thermometer, which indicates oil temp.

(2) Heating bath: Oil cup is surrounded by a cylindrical copper bath, containing H₂O.

(3) Stirrer: A stirrer is fitted outside the oil cylinder; it has 4 blades for stirring the H₂O to maintain uniform temp. This stirrer provides a circular shield at the top, to prevent any H₂O splashing into the oil cylinder.

(4) Kohlrausch flask: A specially shaped flask, it receiver the oil from outlet. Its capacity is 50 ml.

(5) Leveling Screws: The lid of the cup is provided with a spirit level and the entire apparatus rest on Tripod stand with leveling screws.

Working Procedure:

The oil to be tested is filled in the oil cup up to the pointer level after the ball of valve rod is placed on the agate jet to close.



The Kohlrausch flask is kept below jet to collect the oil.



Water is filled in heating bath & heating is initiated



When the oil reaches desired temp, heating is stopped & valve is removed from jet hole.



Time taken to collect 50 ml of oil in to the flask is noted.



The result is expressed in Red wood No.1 seconds at the definite temp.

It is observed that higher the flow of time, higher is the viscosity of the oil.

Viscosity index:

- A good lubricating oil viscosity should not change with temperature.
- Generally, the viscosity of liquids decreases with increase in temperature. As a result, the lubricant becomes thinner.
- Hence viscosity of good lubricating oil should not change with temperature.
- **The rate at which viscosity of an oil changes with temperature is indicated by viscosity index.**
- If viscosity index is high, it indicates that the change in viscosity with temperature is low and vice versa.

Measurement of Viscosity Index:

- The viscosity index of test oil is measured with the help of two types of standard oils namely Pennsylvanian oil and Gulf oil having VI's 100 and 0 respectively.
- The Pennsylvanian oil consisting mainly of paraffin's, its a viscosity index (VI) value is considered as 100 i.e., it shows little variation in viscosity with increase in temperature.
- The other oil i.e Gulf oil Viscosity index is considered as 0 because it shows high variation in its viscosity with increase in temperature. This oil is rich in naphthalene.
- VI can be calculated using the formula

$$VI = \frac{L-U \times 100}{L-H}$$

- VI=Viscosity index of the oil under test.
- L= Viscosity of gulf oil at 100⁰ F and also having same viscosity as the oil under test at 210⁰ F
- U= Viscosity of oil under test at 100⁰ F
- H= Viscosity of Pennsylvanian oil at 100⁰ F and also having the same viscosity as the oil under test 210⁰ F.

(2) Flash & Fire points:

- A good lubricating oil should not be volatile in working temp.
- Under working conditions of lubrication, if some volatilization takes place, the formed vapors should not form inflammable mixture with air. So, flash & fire points are preferred to avoid explosion.

Flash Point:

1. The lowest temp, at which the lubricant gives off enough vapors to ignite for a moment, when a tiny flame brought near it.
2. A good lubricant should have flash point above the operating temp.

Fire Point:

1. The lowest temp, at which the vapors of oil burn continuously for at least 5sec when a tiny flame brought near to it.
2. In majority cases, the fire point of oil is about 5⁰ to 40⁰F higher than its flash points.

Determination of Flash and Fire point: Flash fire points are determined by **Pensky Martens apparatus.**

Oil under examination is filled in the oil cup up to mark and heated by heating air bath.



The stirrer maintains the uniform heating in the oil cup.



Heat is applied to raise the temp at about 5⁰ c per minute



At every 1°C rise of temp, test flame is introduced for a moment through opening.



The temp at which distinct flash (combination of weak sound and light) appears inside the cup – is recorded as flash point.



The heating is continued at the rate of $4 - 5^{\circ}\text{C}$ per/min.



The temp at whom oil ignites & continues to burn for at least 5° seconds, the temp recorded as fire point of oil.

Cloud and Pour point:

- Petroleum oils are complex mixtures of chemical compounds & do not show a fixed C – P.
- Cloud & pour points indicate the suitability of lubricants in cold conditions.

Cloud Point: Cloud point is temp at which oil becomes cloudy / hazy appearance when oil is cooled slowly.

Pour Point: The pour point is “Temp at which oil ceases to flow or pour”

- Cloud & pour points indicate the suitability of lubricants in cold conditions.

Determination of cloud & pour point: With Pour Point apparatus.

It has a flat bottom tube of 3cm diameter & 2cm high.



This is kept in an air jacket which is closed certainly with freezing mixture (ice + CaCl_2)



The tube is half filled with oil & thermometer is introduced in the oil.



As temp proceeds slowly via air – jacket, the temp falls continuously



With every 1°C fall of temp of oil, the tube is withdrawn from jacket for a moment (about 2 – 3 sec) and examined and replaced immediately.



The temp at which cloudiness is noticed is recorded as cloud point.



The cooling is continued and the above procedure repeated.



The temp at which oil does not flow in the test tube, even when kept horizontal for 5sec, is recorded as “pour point”.

IV. Aniline point:

- It is defined as “The lowest equilibrium solution temperature at which equal volume of lubricating oil dissolves in equal volume of aniline.

It is determined by mixing equal volumes of aniline & Lubricating Oil in to a test tube & heating the mixture until homogeneous solution is obtained.



Then the tube is allowed to cool at a controlled rate.



The temperature at which oil and aniline separates is noted

- Aniline point gives indication of possible **deterioration of an oil in contact with rubber sealing's, packings** etc.
- Aromatic hydrocarbons have a tendency to dissolve natural rubber & certain types of synthetic rubber. So, **low aromatic content in the lubricant is desirable**
- If aromatic content is high, aniline point is low and vice versa.
- So, lubricants with higher aniline point are preferred.

V. Neutralization Number:

- It is also called "**acid number or value**".
- It is defined a "The number of milli grams of KOH required to neutralize free acids in 1 gram of oil.
- A lubricating should possess an acid values less than 0.1.
- The acid values higher than 0.1 shows that, the oil has been oxidized, which lead to corrosion in addition to gum and sludge formation.

VI. Mechanical Strength:

- To judge the suitability of a lubricant under the condition of very high pressure, different mechanical tests are carried out.
- One of the tests is "4 balls extreme pressure lubricant test".
- In this the lubricant under test is placed in machine containing 4 balls.
- Among that lower 3 balls are stationary and upper ball is rotate.
- The load is gradually increased and the ball with drawn & examined at specific intervals for scale formation etc.
- If the lubricant is satisfactory under given load, the ball bearings after the test comes out clear / clean.
- However, when load is progressively increased, the liberated heat causes the weld the balls, from the lubricant is failed.
- This test carried out to examine the maximum load that can be conducted safely with a lubricant.

UNIT-V: Surface Chemistry and Applications

Lecture notes

INTRODUCTION

- According to the diffusing nature of substances through semi-permeable membranes, substances are divided in to two kinds- **Crystalloids and Colloids**.
- The substances having tendency to diffuse rapidly in solution and can pass through the semi-permeable membrane are called **crystalloids**.

Ex: Sugar, NaCl, Urea etc.

- The substances which diffuse very slowly in solution and which cannot pass through semi-permeable membrane are called **colloids**.

Ex: Glue, Gelatin, Gum etc.

- The word colloid is derived from Greek in which **Kolla= Glue** and **eidōs= like** which means glue like substances.

Irrespective of nature of substance, any substance can be converted in to a colloid by reduction of particle in to colloid size

Types of Solutions

Based on the **visibility and settling nature** of substances dissolved, solutions are divided into three types.

1. True Solutions:

- The solutions in which the particles are **invisible** and **don't settle** on long standing are called **true solutions**.
- In these solutions, the solute particles are dispersed **homogenously** in to the solvent as a single molecule or ions.
- The diameter of the dispersed particle ranges from 1Å to 10Å .

Ex: Molecules of sugar in water.

2. Suspensions:

- The solutions in which the particles are **visible** and **settle down** on long standing and can be **separated** easily from the solvent are called as **Suspensions**
- The solute and solvent form **heterogeneous** mixtures i.e., they can be seen separately through microscope or visible to the naked eye.
- The diameter of the dispersed particle ranges from 2000Å to more.

Ex: Sand in water

3. Colloidal Solutions:

- The solutions in which the particle size is between 10\AA to 2000\AA , that type of solutions are called **Colloidal solutions**.
- These are **intermediary** between True solutions and suspensions.

They are also called as **Colloidal system or colloidal dispersions or Colloids**.

- A Colloidal system consists of two phases namely **Dispersed Phase and Dispersion Medium**.
- The substance **distributed** as the colloidal particles is called as **Dispersed phase**.
- The substance in which the colloidal particles are **distributed** is called as **Dispersion Medium**.
- The dispersed phase or dispersion medium can be gas or liquid or solid.
- There are **eight types of colloidal systems** based on the dispersed phase or medium.

Colloidal Systems:

Dispersed phase	Dispersed medium	Name	Examples
Solid	Solid	Solid -sol sol	Rubby glass, paint, ink
Solid	liquid	Aerosol	Alloys
Solid	gas	Gel	Smoke hage
Liquid	solid	Emulsion	Curd, cheese
Liquid	liquid	Liquid aerosol	Milk, cream
Liquid	gas	Solid form	Cloud, mist
gas	solid	foam	Cork, pumicstone
	liquid		Forth of air

Classification of Colloidal Systems:

- Colloidal systems in which **a solid is dispersed in liquid** are called as '**Sols**'.
- If water is the **dispersion medium**, they are called as **Hydrosols or aqua sols**, if alcohol is the dispersion medium, they are called as **Alco sols** and if benzene is the dispersion medium, they are called as **Benzo sols**.
- The **colloids or Sols** are divided in to two types based on the **affinity of phase towards dispersion medium**.

1. Lyophilic sols (Solvent-loving)

2. Lyophobic sols (Solvent-hating/ repellent)

Lyophilic Solutions:

- These are the solutions in which the dispersed phase has **strong affinity for the medium or solvent**.

- The affinity is mainly due to the **formation of hydrogen bonding** between the particles and the medium.
- They are **reversible** in nature i.e on evaporation of medium, the residue will be formed. The formed residue can be reconverted in to colloidal state on addition of medium.

Ex: Starch in water

Protein in water

Gum in water etc.

Lyophobic Solutions:

- These are the solutions in which the dispersed phase has **no affinity for the medium or solvent**.
- There is no affinity between particles and medium because **there is no formation of hydrogen bonding** between the particles and the medium.
- They are not stable and can be readily precipitated.

Ex: Iron in water

Gold in water

Sulphur in water etc.

Preparation of Colloidal Solutions:

- There are two main methods for the preparation of colloidal solutions.
 1. Condensation method
 2. Dispersion or Disintegration method

1. Condensation Method:

- In this method, a **large number of small particles are condensed** to form bigger particles of colloidal dimension.
- This can be done by following ways.

i. By exchange of Solvent: If the dispersed phase is insoluble in the medium, then it is first dissolved in another soluble medium and then the two mediums are mixed. Then the dispersed phase will dissolve in the insoluble medium and form colloidal solution.

Ex: Sulphur Colloid solution in water is prepared by dissolving it first in alcohol and when mixed with water, then Sulphur dissolves in water.

ii. By changing physical state: In this method, the dispersed phase is mixed with insoluble medium by changing its state.

Ex: Mercury or Sulphur solution is prepared by passing their vapours through the cold water as they are insoluble in their original state.

iii. By Chemical Methods: There are four chemical methods by which colloids are prepared. They are

- i. By double decomposition.
- ii. By reduction
- iii. By oxidation
- iv. By hydrolysis

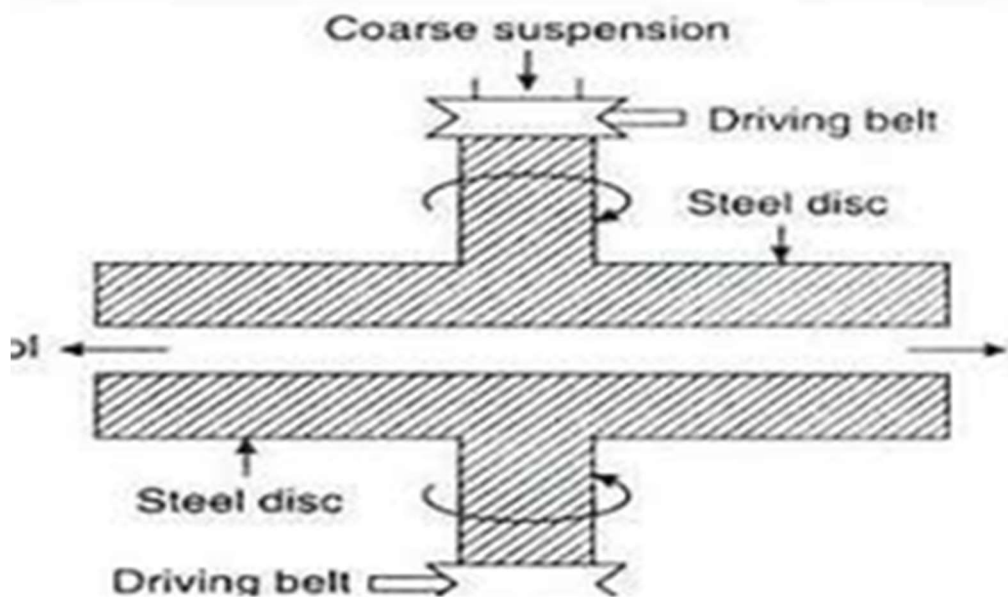
2. Dispersion or Disintegration Method: This is a direct method in which pulverized substance is dispersed in the dispersion medium. The important dispersion methods are

a) **By mechanical Dispersion:**

- The substance is finely ground and dispersed in a medium to form a suspension.
- The suspension is then passed between two oppositely rotating steel discs at high speed (7000rpm) with narrow distance.
- Then the metal discs break down the particles to colloidal size.

Ex: Paints, Black ink, Ointments, Varnishes etc. are prepared by this method.

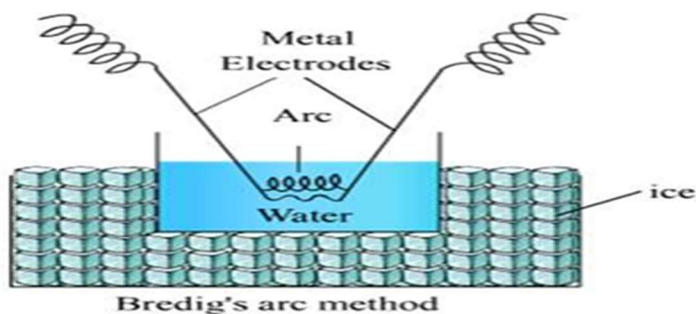
Preparation of Colloidal Solutions:



b) By electrical dispersion or Bredig's arc method:

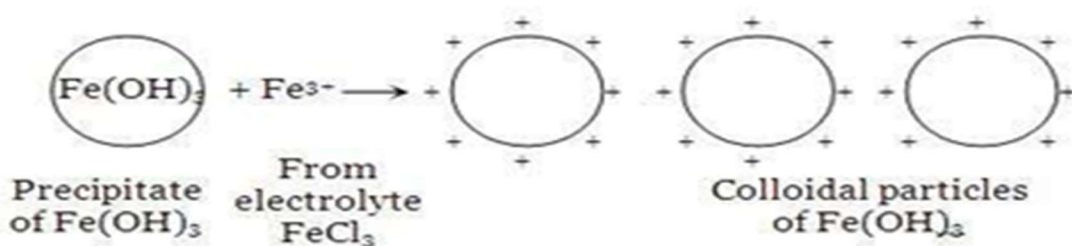
- This method is used to prepare sols of platinum, silver, copper or gold.
- The metal whose sol is to be prepared is made as two electrodes which immerse in dispersion medium such as water etc.

- The dispersion medium is kept cooled by ice.
- An electric arc is struck between the electrodes.
- The tremendous heat generated by this method gives colloidal solution.
- The colloidal solution prepared is stabilized by adding a small amount of KOH to it.



By peptization method:

- The process of converting a freshly prepared **precipitate** into **colloidal form** by the **addition of suitable electrolyte** is called peptization.
- Peptization occurs because of the **adsorption of the ions** of the electrolyte to the particles of the precipitate.
- The electrolyte used for this purpose is called **peptizing agent or stabilizing agent**.
- Important peptizing agents are sugar, gum, gelatin and electrolytes.



- S The colloid is stable when the particles remain suspended in the medium without settling down.
- Stability is hindered by aggregation and sedimentation.
- To stabilize the colloidal system, the interfacial tension between the colloidal particles must be reduced.
- This is done by adding suitable stabilizing agent.

Types of stabilization:

1. **Electrostatic Stabilization:** In this method, colloid particles are separated by developing like charges on the particles. Like charges repel each other hence the colloid particles remain suspended.
2. **Polymeric stabilization:** In this process, the colloid particles are covered with a polymer which prevents the particles to come near to one another.
3. **Adsorption of solvent:** In this method a layer of solvent is adsorbed on to the colloid particles to prevent from settling.
4. **Peptization:** Freshly formed precipitate is converted in to colloid by adding suitable electrolyte is called peptization method.

stabilization of Colloidal Solutions:

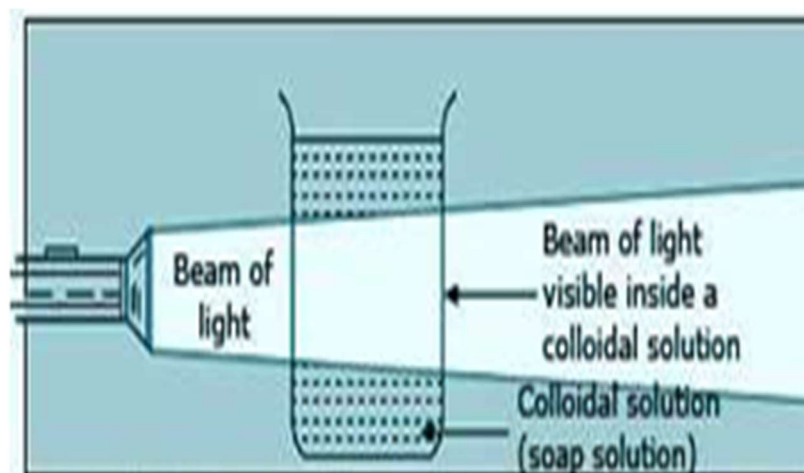
Properties of Colloidal Solutions:

1. **Heterogeneity:** Colloidal solutions consist of two phases dispersed phase and dispersion medium; hence they are heterogenous.
2. **Visibility of dispersed particles:** The dispersed particles present in them are not visible to the naked eye and they appear homogenous.
3. **Filterability:** The colloidal particles pass through an ordinary filter paper. However, they can be retained by animal membranes, cellophane membrane and ultrafilters.
4. **Stability:** Lyophilic sols in general and lyophobic sols in the absence of substantial concentrations of electrolytes are quite stable.
5. **Color:** The color of a colloidal solution depends upon the size of colloidal particles present in it. Larger particles absorb the light of longer wavelength and therefore transmit light of shorter wavelength.
6. **Tyndall Effect:**
 - When an intense beam of light is passed through a colloidal solution kept in dark, the path of the beam gets illuminated with a bluish light.
 - This phenomenon is called **Tyndall effect** and the illuminated path is known as **Tyndall cone**.
 - The Tyndall effect is due to the scattering of light by colloidal particles.
 - Tyndall effect is not exhibited by true solutions. This is because the particles present in a true solution are too small to scatter light.

Tyndall effect can be used to distinguish a colloidal solution from a true solution. The phenomenon has also been used to devise an instrument known as **ultra-microscope**. This instrument is used for the detection of the particles of colloidal dimensions

7. Electrical Properties:

- The sol particles carry an electrical charge. The most important property of colloidal dispersion is that all the suspended particles carry either positive or negative charge.
- The mutual force of repulsion between charged particles prevents them from coagulation and settling under the force of gravity.
- This gives stability to the solution.
- The particles acquire +ve or -ve charges by adsorption of +ve or -ve from the dispersion medium.



Applications of Colloids:

- Colloids have very important application in our daily life starting from food products to the medicines to industries like rubber. Some of the applications of colloids are mentioned below.

1. Food and medicines:

- Colloids have great application in food industries and food stuffs.
- Many of the food materials which we eat are of colloidal nature.
- Milk and also many milk products like cheese, cream butter etc. are colloids i.e milk is an emulsion (liquid in liquid colloidal system). In milk, butter and fat are dispersed in water.
- Bread is colloidal system in which air is dispersed in baked dough.
- Colloids also have applications in the form of medicines. Colloidal medicines are competitively more effective as they are easily absorbed by the body. That is why many medicines are emulsion.

- Some major antibiotics like penicillin and streptomycin are injected in the body in the form of colloidal sol so that they would be absorbed by the body easily.

2. Water Purification:

- One of the very popular methods used for water purification is the addition of electrolytes like potash alum.
- Addition of these electrolytes is based on the fact that the impure water is usually a colloidal system.
- It usually contains dispersed colloidal particles which cannot be removed by filtration.
- Addition of these electrolytes results in coagulation of the impurity which can be separated by filtration then.

3. Sewage disposal:

- The sewage water contains impurities like mud and dirt of colloidal size which are dispersed in the water.
- Like any other colloidal system, the colloidal particles (impurities) of sewage are also charged particles.
- These charged particles of impurities present in sewage may be removed by electrophoresis.
- For this purpose, the sewage water is passed through a tunnel which is fitted with metallic electrodes and is maintained at a high potential difference.

The charged particles of impurity present in the sewage water migrate to the oppositely charged electrodes which results in their coagulation.

4. Smoke precipitation:

- Smoke is also a colloidal system which mainly consists of charged particles of carbon dispersed in air.
- Smoke is a big problem for environment as it is the major source for air pollution. Removal of the dispersed colloidal particles from the air will solve the problem.
- For this, the process of electrophoresis is used.
- This is done in Cottrell precipitator. Smoke is passed through a chamber which contains a number of metal plates attached to a metal wire connected to high potential source.
- The electrically charged colloidal particles of carbon present in air get discharged when they come in contact with the oppositely charged plates and fall down to the bottom.
- The clean hot air leaves the precipitator from an exit near the top.

5. Artificial rain:

- Clouds are also colloidal system. In clouds, water vapors are present in mixture with the dust particles.
- The water molecules present in cloud have electric charge on them and are of colloidal size. So, if the charged on the molecules is neutralized somehow, they will start raining.
- Sometimes it is done by spraying some electrolytes over the clouds and the rain resulted from this is called artificial rain.

• **6. Rubber industry:**

- Rubber is synthesized from the latex obtained from the rubber trees.
- This latex is an emulsion in which negatively charged particles of rubber are dispersed in water.
- For obtaining rubber, this latex is boiled because of which the rubber particles get coagulated.
- This coagulated mass is then vulcanized to solidify as natural rubber.

• **7. Leather tanning:**

- Tanning is the process of treating the skins of animals to obtain the leather.
- Skin of animals is also a colloidal system in which the colloidal particles are positively charged.
- During the process, the charged particles of skin are coagulated using negatively charged material like tannin and some compounds of aluminum and chromium.

• **8. Cleansing action of soaps:**

- As we have discussed earlier also, the soap solution is a colloidal system and it removes the oil and dirt by forming water soluble emulsions.

• **9. Smoke screen:**

- Smoke screens are used to hide something by a layer of smoke. In generally it is used to hide the movement of troops.
- The smoke screens are also colloidal system in which the particles of titanium oxide are dispersed in air.

Nano metals & Nanometal Oxides

• Introduction-Nanometals:

- Metal Nanoparticles are the particles having a size ranging from **1-50nm**.

- They are obtained as **colloids**. These colloidal particles have a tendency to remain as **single crystals** so they are also called as **metal nanocrystals**.
- These nanocrystals possess better magnetic, electronic and optical properties than the metals.

Advantages of Nanometals:

- Metal nano particles have size less than 100nm, so their surface area is more than the metal.
- They have 5 times more hardness than the parent metal.
- Strength of the metal nano particles is 3-10 times higher than the metal.
- They possess very good corrosion resistance property than the metal.
- Because of their small size, they show good optical properties.
- Nanometals have low melting point than the parent metals.
- Electrical properties of nanometals are increases by 3 times than the corresponding metals.
- Suspensions of nanometals can be prepared because of their high surface area.
- Nanometals have 170 times more water resistance than the normal metals.
- Nano metal oxides play an important role in chemistry, physics & material science as they have many applications in micro electric circuits, sensor fuel cells, corrosion resistance coatings and as a catalyst.

Properties:

- Oxide nanoparticles exhibit good physical and chemical properties due to their limited size and high density of surface sites.
- They possess good transport property than the bulk metal oxides.
- They show redistribution of charge.
- They have very good conductivity.
- They show good acid & base properties, so they have many applications in many industries.

Synthesis of Nanometal & Nano metal Oxides:

- There are two main methods for the preparation of Nanometal & Nanometal oxides.
- 1.Solvothermal Synthesis method

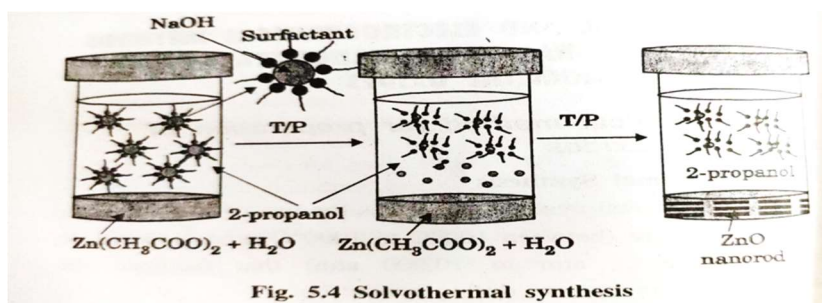
- 2. Electro deposition method

Solvothermal Synthesis method:

- This method uses solvent under high temperature (between 100°C to 1000°C) and high pressure (1atm to 10000atm) to synthesise nanometal oxides and nanometals from metal precursors.
- Solvent is mixed with metal precursors and the mixture is placed in an autoclave kept at high temperature and pressure in an oven.
- Then the pressure generated in the vessel due to solvent vapour increases the boiling point of the solvent.
- Then the precursor dissolves in the solvent to form particles of nano size.
- The common solvents used are Ethanol, Methanol, Toluene, Cyclohexane etc.
- Ex: Synthesis of ZnO nanocrystals.

Synthesis of ZnO nanocrystals:

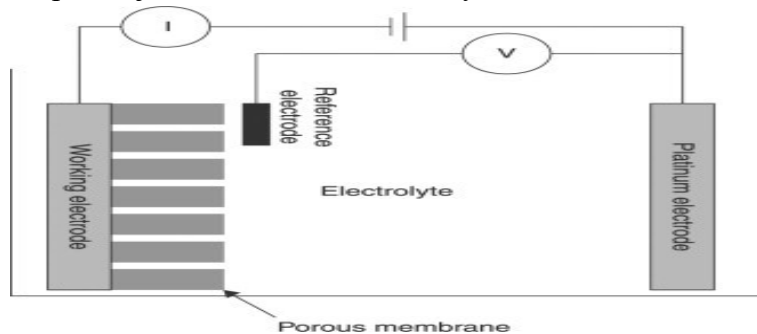
- Zinc acetate dihydrate is dissolved in 2-propanol at 50°C.
- The solution is cooled to 0°C and NaOH is added to precipitate ZnO.
- Then the solution is heated to 65°C. Then rod shaped ZnO nanocrystal is obtained.



. Electro deposition method:

- It is an electrochemical method in which ions from the solution are deposited at the surface of the cathode.
- Template is used for preparation of nanometals of desired size & shape.
- Many nano-structured materials with specific arrangements can be prepared by this method using an active template as a cathode.
- **Process:**
- This is done in an electrochemical cell.
- The cell consists of a reference electrode, specially designed template as cathode and metal whose nano crystals are to be prepared as anode.

- All the electrodes are connected with the battery through an voltmeter dipped in metal electrolyte.
- When the current is passed through the electrodes of template, the metal ions from the solution enter in to the pores and gets reduced at the cathode.
- Then based on the structure of template, nanowires or nanocrystals develop inside the pores of the template.
- **Advantages of Electro-Deposition:** This method is fast and cost effective. Complex shaped objects also can be coated by this method.



The film or wire obtained will be uniform.

Stabilization of Nanomaterials:

- Most of the nano particles are unstable in the environment and aggregate to form big size particles and get sedimented.
- This occurs due to lowering of the surface energy of the nano particles.
- Hence nano particles should be protected by adding a desirable stabilizing agent or by surface coating or by avoiding aggregation.

Methods of stabilization:

1. Electrostatic stabilization
2. Steric stabilization
3. Stabilization by ionic liquid.
4. Stability against oxidation.
5. Stabilization by size
6. By using capping agents
7. **Electrostatic stabilization:** In this method, nano particles are separated by developing like charges on the particles. Like charges repel each other hence the nano particles remain suspended.
8. **Steric stabilization:** Stabilizer is added to nanoparticles which forms a layer on the surface of the particles there by prevents aggregation.

9. **Stabilization by ionic liquid:** Ionic liquids when added on to the nanoparticles, they get adsorbed on to the surface of the particles there by prevents the aggregation.
10. **Stability against oxidation:** Nanoparticles undergo easy oxidation when exposed to air and get aggregated. This can be prevented by adding protective agents. These agents modify the surface of the particles so that the oxygen does not adsorb on the surface of the molecule.
11. **5. Stabilization by size:** If the size of the particles is reduced, then the stabilization can be increased.
12. **6. By using capping agents:** Reducing agents are used to reduce the metal to zero oxidation state. These agents are called capping agents. These capping agents form bonding among themselves and acts as a cage around the nanoparticles. This prevents the interaction of nanoparticles with one another there by prevents the aggregation of nano particles.
13. **Ex: PVP (Poly Vinyl Propylidene)**
14. **Thiolate-** for stabilization of Au Nanoparticles
15. **Poly ethylene Glycol, EDTA, PVP-** for stabilization of Ag Nanoparticles

Applications of Nano Materials:

- Nanomaterials have very important application in our daily life as they are having better physical, chemical and mechanical properties.

1. Catalysis:

- As nano materials are having good surface area than the bulk metal, they possess good catalytic property. They can be used as catalysts when where normal catalysts cannot work very efficiently.

2. Medicine:

- Nano materials are used as nano drugs for cancer and TB therapy.
- They act as nano-medicos that release anti-cancer drug and treat cancer.
- Gold coated nano shells convert light in to heat and kill tumours
- They help in protein analysis and blood immune assay.
- Gold nano particles are used in slow and selective release of drugs to the targeted organs.
- Nano technology is used to repair neurological damage.

3. Sensors:

- Nano materials and nanostructures play an important role in the development of more sensitive and more specific sensing devices.