TKR COLLEGE OF ENGINEERING AND TECHNOLOGY

AN AUTONOMOUS INSTITUTION

Accredited by NBA and NAAC with 'A+' Grade

(Sponsored by TKR Educational Society, Approved by AICTE, Affiliated to JNTUH)

Medbowli, Meerpet, Balapur, Hyderabad, Telangana–500097

LEARNING MATERIAL
of
ENGINEERING CHEMISTRY

I B.Tech I/II Semester

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ENGINEERINGCHEMISTRY

Common to CSE & CSE (AIML&DS), IT, ECE, EEE, CE

I Year B.Tech. Semester I/II

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Course Objectives:

1. Understand water quality parameters and apply suitable treatment methods for potable and industrial water.
2. Learn electrochemical principles for electrode potential measurement, pH determination, and corrosion prevention.
3. Understand various energy sources, including batteries, fuel cells, fossil fuels, and synthetic fuels, along with their applications.
4. Learn the classification, synthesis, properties, and applications of polymers, including conducting polymers.
5. Understand the properties, mechanisms, and engineering applications of smart materials, biosensors, cement, and lubricants.

Course Outcomes: At the end of the course, student would be able to -

CO1: Apply water quality analysis and treatment methods, including hardness removal, disinfection, Boiler feed water treatment, and desalination techniques.
CO2: Apply electrochemical principles to measure electrode potentials and pH, and analyze corrosion Mechanisms with appropriate prevention methods
CO3: Apply the concepts of conventional and alternative energy sources, including batteries, fuel cells, and fuels, for energy production and applications
CO4: Analyze polymer types, synthesis mechanisms, properties, and applications, including Conductingpolymers.
CO5: Analyze the properties, mechanisms, and applications of smart materials, biosensors, cement, and lubricants in engineering

UNIT-I: Water and its treatment:[8]

Introduction- Hardness,types, degree of hardness and units. Estimationofhardnessofwaterby complexometric method - Numerical problems. Potable water and its specifications (WHO) – Stepsinvolved in the treatment ofpotable water - Disinfection of potable water bychlorination and break-point chlorination.

Boiler troubles: Scales, Sludges and Caustic embrittlement. Internal treatment of boiler feed water - Calgon conditioning, Phosphate conditioning, Colloidal conditioning. External treatment methods - Softening of water by ion- exchange processes. Desalination of brackish water – Reverse osmosis.

Unit-II: Electrochemistry and Corrosion:[8]

Introduction- Electrode potential, standard electrode potential, Nernst equation (no derivation), electrochemical cell - Galvanic cell, cell representation, EMF of cell - Numerical problems. Types of electrodes, reference electrodes - Primary reference electrode - Standard Hydrogen Electrode (SHE), Secondary reference electrode - Calomel electrode,Construction, working and determination of pH of unknown solution using SHE and Calomel electrode.

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Corrosion: Introduction- Definition**,** causes and effects of corrosion – Theories of corrosion, chemical and electrochemical theories of corrosion, Types of corrosion: galvanic, water-line and pitting corrosion. Factors affecting rate of corrosion - Nature of the metal, Nature of the corroding environment. Corrosion control methods - Cathodic protection Methods - Sacrificial anode and impressed current methods.

UNIT–III: Energysources:[8]

Batteries: Introduction – Classification of batteries - Primary, secondary and reserve batteries with examples. Construction, working and applications of Zn-air and Lithium-ion battery. Fuel Cells – Differences between a battery and a fuel cell, Construction and applications of Direct Methanol Fuel Cell (DMFC).

Fuels: Introduction and characteristics of a good fuel, Calorific value–Units-HCV, LCV

Fossil fuels: Introduction, Classification, Petroleum - Refining of Crude oil, Cracking - Types of cracking - Moving bed catalytic cracking.LPG and CNG composition and uses.

Synthetic Fuels: Fischer-Tropschprocess.

UNIT–IV: Polymers:[8]

Definition-Classification ofpolymers:Basedon originandtacticity with examples –Typesof polymerization - Addition (free radical addition mechanism) and condensation polymerization. Plastics, Elastomers and Fibers: Definition and applications (PVC,Buna-S,Nylon-6,6). Differences between thermoplastics and thermosetting plastics.

Conductingpolymers: Definitionand Classification with examples-Mechanism of conduction in trans-poly-acetylene and applications of conducting polymers.

UNIT-V: Engineering materials:[8]

Smart materials: Introduction, Classification with examples - Shape Memory Alloys –Nitinol, Piezoelectric materials – quartz and their engineering applications.

Biosensor-Definition, Amperometric Glucose monitor sensor.

Cement: Portlandcement, its composition, setting and hardening.

Lubricants: Definition and characteristics of a good lubricant–thin film mechanism of lubrication, properties of lubricants - viscosity, cloud and pour point, flash and fire point.

SUGGESTEDTEXT BOOKS:

1. EngineeringChemistrybyP.C.Jain and M. Jain, Dhanpatrai PublishingCompany, 2010.
2. EngineeringChemistrybyRama Devi,Dr.P. AparnaandRath,Cengagelearning, 2025.

REFERENCETEXT BOOKS:

1. EngineeringChemistrybyThirumalaChary,Laxminarayana&Shashikala,Pearson Publications (2020).
2. EngineeringChemistrybyShashi Chawla, Dhanpatrai and Company(P)Ltd. Delhi 2011.
3. EngineeringChemistrybyShikhaAgarwal,CambridgeUniversityPress, Delhi 2015.
4. EngineeringAnalysisof SmartMaterialSystems byDonaldJ.Leo,Wiley,2007.
5. ChallengesandOpportunitiesinGreenHydrogenby**Editors:**ParamvirSingh,Avinash Kumar Agarwal, Anupma Thakur, R.K Sinha.
6. https://www.worldscientific.com/ doi/epdf/10.1142/13094
7. E-Content-https://doi.org/10.1142/13094|October2023
8. E-books: https://archive.org/details/EngineeringChemistryByShashiChawla/page/n11/mode/2up

UNIT- I

WATER AND ITS TREATMENT

Introduction:

Water is nature's most wonderful, abundant, useful compound and is an essential without it one cannot survive. It occupies a unique position in industries. Its most important use is as an engineering material in the steam generation. Water is also used as coolant in power and chemical plants. It is also used in other fields such as production of steel, rayon, paper, atomic energy, textiles, chemicals, ice and for air-conditioning, drinking, bathing, sanitary, washing, irrigation, etc.

Occurrence:

Water is widely distributed in nature. It has been estimated that about 75% matter on earth's surface consists of water. The body of human being consists of about 60% of water. Plants, fruits and vegetables contain 90-95% of water.

Sources of Water: Different sources of water are:

1. Surface Waters*:* Rain water (purest form of natural water), River water, Lake Water, Sea water (most impure form of natural water).

2. Underground Waters*:* Spring and Well water. Underground waters have high organic impurity.

Hardness of water: Hardness of water defined as which prevent the lathering of soap. This is due to presence of certain salts of Ca^{+2}, Mg^{+2} and other Heavy metals dissolved in it. Soaps are Sodium or Potassium salts of higher fatty acids like Oleic acid or Palmitic acid or stearic acids.

Hard water: Water which does not produce lather with soap solution is called hard water.

Soap with hard water reactions

$$2\,C_{17}H_{35}COONa + CaCl_2 \longrightarrow (C_{17}H_{35}COO)_2Ca + 2NaCl$$

Sodium sterate — Calcium sterate (insoluble)

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

Sodium sterate — Magnesium sterate (insoluble)

Soft water: Water which produce lather easily on shaking with soap solution is called soft water. Such water does not contain dissolved calcium and magnesium salts in it.

$$2\,C_{17}H_{35}COONa + H_2O \longrightarrow 2\,C_{17}H_{35}COOH + 2NaOH$$

Sodium sterate — Stearic acid (Lather)

Degree of hardness: Hardness of water is expressed in terms of calcium carbonate equivalents. The weights of different salts causing hardness are converted to weight equivalent to that of $CaCO_3$.

If a sample of water contains two or more than two salts, their quantities are converted in equivalent to that of $CaCO_3$ and then the sum will give the total hardness. $CaCO_3$ is selected for expression of the degree of hardness, because the mol.wt. of $CaCO_3$ is 100, which is easy for calculation and $CaCO_3$ is an insoluble salt in water. All the dissolved salts of calcium are precipitated as $CaCO_3$.

$$\text{Hardness of the water causing salts in terms of } CaCO_3 = \frac{\text{Amount of the hardness causing salt}}{\text{Mol wt hardness causing salt}} \times 100$$

Different types of water have different degrees of hardness:

Hardness	**Name of water**
0-70 mg/liter	Soft water
70-150 mg/liter	Moderate hard water
150-300 mg/liter	Hard water
300 mg/liter & above	Very hard water

Equivalents of $CaCO_3$: 100 parts by weight of $CaCO_3$ hardness must be equivalent

162 parts by weight of $Ca(HCO_3)_2$ hardness.

146 parts by weight of $Mg(HCO_3)_2$ hardness.

136 parts by weight of $CaSO_4$ hardness.

111parts by weight of $CaCl_2$hardness.

164 parts by weight of $Ca(NO_3)_2$ hardness.

120 parts by weight of $MgSO_4$ hardness.

95 parts by weight of $MgCl_2$ hardness

Units of hardness: -

1. **Parts Per Million (ppm): -** is the parts of $CaCO_3$ equivalent hardness causing salts present in10^6 (million) parts of water i.e., 1ppm= 1 part of $CaCO_3$ equivalent hardness in 10^6 parts of water.

2. **Milligrams Per Litre (mg/L): -** number of milligrams of $CaCO_3$ equivalent hardness causing salts present in liter of water. i.e.

1mg/L=1mg of $CaCO_3$ equivalent hardness of 1L of water= 1kg=1000g=10^6mg.

∴1mg/L=1mg of $CaCO_3$eq per 10^6mg of water=1ppm.

3. **Clarke's degree (^{0}Cl): -**is the no. of grains (1/7000lb) of $CaCO_3$ equivalent hardness causing salts present in per gallon (10lb) of water (or) it is parts of $CaCO_3$ equivalent hardness causing salts per 70,000 parts of water.

∴1^{0}Cl= 1 grain of $CaCO_3$eq hardness per gallon of water

=1 part of $CaCO_3$ hardness eq. per 10^5 parts of water.

4. Degree French (°Fr): parts of $CaCO_3$ equivalent hardness causing salts present in 10^5 parts of water.

$\therefore 1^0$Fr= 1 part of $CaCO_3$equivalent hardness per 10^5parts of water.

5. Milli-equivalent per liter (meq/L): - is the number of milli-equivalents of hardness causing salts present in per liter. i.e

1meq/L= 1meq of $CaCO_3$ per liter of water

= 10^{-3}x 50 g of $CaCO_3$ eq. per liter

= 50 mg of $CaCO_3$ eq. per liter = 50 mg/L of $CaCO_3$ eq. = 50ppm.

Relationship between various units of hardness:

1 ppm = 1 mg/L = 0.1°Fr = 0.07 °Cl = 0.02 meq/L

1 mg/L = 1 ppm = 0.1 °Fr = 0.07 °Cl = 0.02 meq/L

1 °Cl = 1.433 °Fr = 14.3 ppm = 14.3 mg/L = 0.0286meq/L

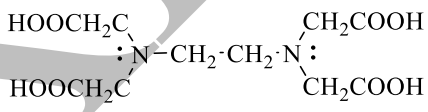
1 °Fr = 10 ppm = 10 mg/L = 0.7 °Cl = 0.2 meq/L

1 meq/L = 50 mg/L = 50 ppm = 5 °Fr = 0.35 °Cl

ESTIMATION OF HARDNESS BY EDTA METHOD:

The analysis is done by complexometric titration using standard EDTA and EBT as an indicator.

PRINCIPLE: In this complexometric Titration, the water sample is titrated with standard solution of Di sodium salt of EDTA using EBT indicator. EBT indicator when added to hard water at p_H = 10, forms weak complexes with calcium and magnesium present in hard water. It results in the formation of wine-red Ca-EBT or Mg-EBT complexes which are unstable. When hard water comes in contact with EDTA, at PH 9-10, Ca^{+2} and Mg^{+2} forms stable, colorless complex with EDTA, releasing the free indicator(blue) so, the colour changes from wine-red to blue at the endpoint.



Ethylene diamaine tetra acetic acid (EDTA)

EDTA can form 4 to 6 dative bonds with cations like Calcium Magnesium.

Ca^{+2} / Mg^{+2} + EBT $\xrightarrow{P_H\ 9\text{-}10\ \text{Buffer}}$ [Ca-EBT] or [Mg-EBT]

Colour less blue wine red colour

[Ca-EBT] or [Mg-EBT] + EDTA $\xrightarrow{P_H\ 9\text{-}10\ \text{Buffer}}$ [Ca-EDTA] or [Mg-EDTA] + EBT

wine red colour Blue colour

Procedure:

1. **Preparation of standard hard water:** Dissolve 1g of pure, dry $CaCO_3$ in minimum quantity of dil.HCl and then evaporate the solution to dryness on a water bath. Dissolve the residue in distilled water to make 1 Litre solution. Each ml of this solution thus contains 1mg of $CaCO_3$ equivalent hardness.

1 ml hard water solution = 1mg of $CaCO_3$ equivalent hardness.

$$\text{Molarity of standard hard water } (M_1) = \frac{\text{Weight of } CaCO_3}{\text{Mol wt } CaCO_3} \times \frac{1000}{100}$$

2. **Standardization of EDTA solution:** Pipette out 20 ml of standard hard water into a conical flask. Add 5ml of buffer solution and few drops of Eriochrome Black-T indicator, which is originally blue, would assume a wine-red colour. Titrate it with EDTA solution taken in the burette, till the wine-red colour changes to blue. This is the end point. Let the burette reading be V_2 ml.

$$\frac{M_1V_1}{n_1} = \frac{M_2V_2}{n_2} \qquad n_1 = n_2 = 1$$

$$\text{Molarity of EDTA } (M_2) = \frac{M_1V_1}{V_2}$$

3. Determination of total hardness: Pipette out 20 ml of tap water into a conical flask. Add 2ml of buffer solution and 2 to 3 drops of EBT indicator. Colour changes to wine red colour. Titrate with EDTA solution. Wine red colour changes to blue colour. Note burette reading. let the volume of the solution be V_2ml. Repeat the titration 2 or 3 times.

$$M_2V_2 = M_3V_3$$

$$\text{Molarity of Sample water } (M_3) = \frac{M_2V_2}{V_3}$$

Total hardness of sample water = M_3 x 100 x 1000 (ppm)

4. Determination of permanent hardness: Take 100ml of hard water into a conical flask and boil the water till the volume reduces to 50 ml. Add 50 ml of distilled water to it and pipette out 20 ml of this hard water into a comical flask and add 2ml of buffer solution, 3 drops of EBT indicator. Colour changes to wine red colour. Titrate with EDTA solution wine red colour changes to blue colour. Note the burette reading at the volume of EDTA solution, V_2 (zml). Repeat the titration 2 or 3 times.

$$M_2V_2 = M_4V_4$$

$$\text{Molarity of boiled filter water } (M_4) = \frac{M_2V_2}{V_4}$$

Permanent hardness of water = M_4 x 100 x 1000 (ppm)

Temporary hardness = Total hardness - Permanent hardness

$$M_2V_2 = M_3V_3$$

$$\text{Molarity of Sample water } (M_3) = \frac{M_2V_2}{V_3}$$

Advantages of EDTA method:

This method is definitely preparable to the other methods, because of the

1. Greater accuracy
2. Convenience

POTABLE WATER:

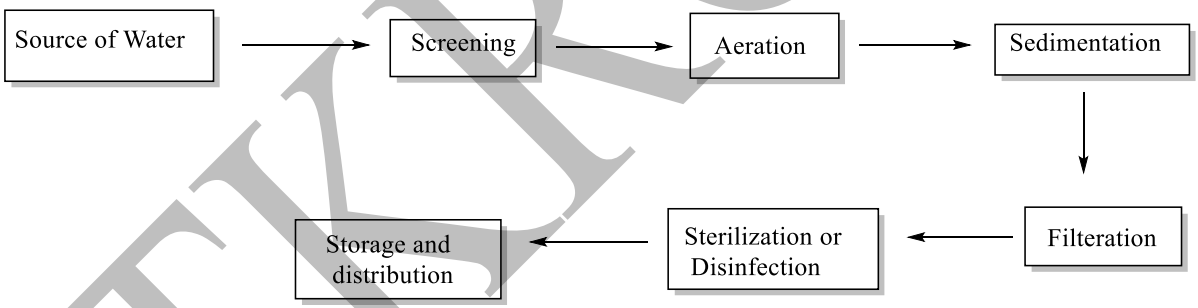
Specifications:

1. The water should be clear, colourless and odourless.
2. The water must be free from pathogenic bacteria and dissolved gases like H_2S.
3. The optimum hardness of water must be 125 ppm and pH must 7- 8.5.
4. The turbidity in drinking water should not exceed 25 ppm.
5. The recommended maximum concentration of total dissolved solids in portable water must not exceed 500 ppm.

Steps involved in the treatment of portable water:

The treatment includes the removal of suspended impurities, colloidal Impurities and harmful pathogenic bacteria, the following is the flow diagram of water treatment for domestic purposes and various stages involved in purification are given as:

Flow diagram of treatment of water for municipal supply



1. Screening: The water is passed through screens having large number of holes in it to remove floating impurities.

2. Aeration: The water is then subjected to aeration which

i) Helps in exchange of gases between water and air

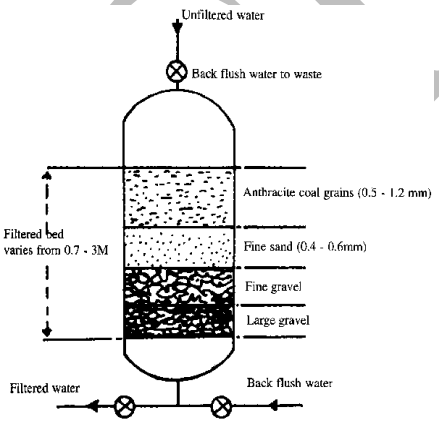
ii) Increase the oxygen content of water

Removes the impurities like Fe and Mn by precipitating as their hydroxides

3. Sedimentation with Coagulation: The suspended and colloidal impurities are allowed to settle under gravitation. The basic principle of this treatment is to allow water to flow at a very slow velocity, so that the heavier particles settle under gravitation. For settling of fine particles, coagulants like Alums, Sodium aluminate and salts of iron are added which produces gelatinous precipitates like floc. Floc attracts and helps accumulation of the colloidal particles resulting in setting of the colloidal particles. The following is the sedimentation tank used for the removal of colloidal impurities.

4. Filtration: It helps in removal of the colloidal and suspended impurities not removed by sedimentation. Usually sand filters are employed. There are 2 types of sand filters, slow sand filters and rapid sand filters or pressure filters. In slow sand filter the filter bed consists of 3 layers of sand of different particle size. A fine sand layer on the top supported by coarse sand layer, which is supported by gravel. The colloidal impurities are retained by the fine sand layer resulting a very slow filtration of water. The top layers of the fine sand layer is scraped off, washed, dried and introduced into the filter bed for reuse. Rapid sand filters make use of compressed air for fast filtration.

Rapid Sand Filter



1. Sterilisation and Disinfectation: Distruction of harmful pathogenic bacteria from drinking water is carried out by streilisation and disinfectation. The following are the methods adopted for this process.

a) Boiling: By boiling water for 15- 20 min, harmful bacteria are killed. This is not possible for the muncipal supply of water. This method of sterilization is adopted for domestic purpose.

b) Passing Ozone: Ozone when passed into water acts as disinfectant. Ozone is an unstable isotope of oxygen, produced nascent oxygen which is a powerful disinfectant.

$$O_3 \longrightarrow O_2 + (O)$$

This treatment is costly and ozone is unstable and cannot be stored for long time.

c) Chlorination: The process of utilizing chlorine as a powerful disinfectant is called chlorination. They is 3types of chlorinating reagents**.**

i) By passing Chloramines: Chlorine is mixed with ammonia in the ratio 2:1 by volume to form a stable chloramine which generates hypochlorous acid a powerful disinfectant.

$$Cl_2 + NH_3 \longrightarrow ClNH_2 + HCl$$

$$ClNH_2 + H_2O \longrightarrow HOCl + NH_3$$

Hypochlorous acid inactivates the enzymes of bacteria and kills bacteria. Chloramine is useful for disinfecting swimming pools.

ii) By bleaching powder: Bleaching powder contains 80% chlorine. When bleaching powder is used as disinfectant, it is called hypo chlorination because the disinfestations is due to Hypochlorous acid.

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

(Bleaching powder)

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$

(Disinfectant)

iii) Chlorination: The process of applying calculated amount of Chlorine to water in order kill the pathogenic bacteria is called chlorination. Chlorine also reacts with water and generates Hypochlorous acid, which kills bacteria. Chlorine is a powerful disinfectant than chloramine and bleaching powder.

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$

(Disinfectant)

Break point of Chlorination:

Calculated amount of chlorine must be added to water because chlorine after reacting with bacteria and organic impurity or ammonia remains in water as residual chlorine, which gives bad taste, odor and is toxic to human beings. The exact amount of chlorine required to kill bacteria and to remove organic matter is called break-point chlorination.

Water contains the following impurities.

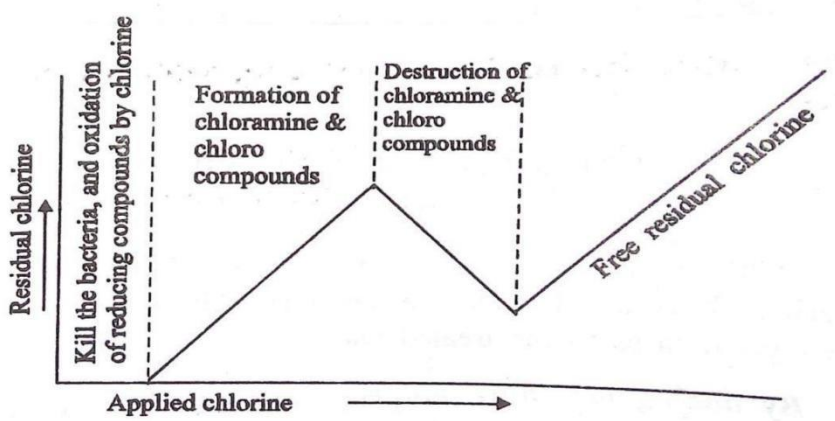
i) Bacteria

ii) Organic impurities

iii) Reducing substances (Fe^{2+}, H_2S etc)

iv) Free ammonia

Water sample is treated with chlorine and estimated for the residual chlorine in water and plotted a graph as shown below which gives the break-point chlorination:



From the above graph, it is clear that "A" grams of chlorine added oxidizes reducing impurities of water and kill the bacteria present in the water and there is no free residual chlorine. If further chlorine is added up to point "B" that forms chloramine and other chloro compounds with ammonia and organic impurities present in water. After the point 'B' further chlorine is added cause to the destruction of chloramines, organic chlorides and other impurities. Thus the combined residual chlorine decreases to a minimum point "C" is the breakpoint for addition of chlorine to water.

Advantages of Break point Chlorination:

1. It removes taste, color, and oxidizes completely organic compounds, ammonia and other reducing impurities.
2. It destroys completely all disease producing bacteria.
3. It prevents growth of any weeds in water.

Dechlorination: over chlorination after 'Break point' produces unpleasant taste, odor, and toxicity to water. The over chlorination is removed by passing the water through a bed of granular carbon and also by the addition of SO_2 and sodium thiosulphate.

$$SO_2 + Cl_2 + 2H_2O \longrightarrow H_2SO_4 + 2HCl$$

$$Na_2S_2O_3 + Cl_2 + H_2O \longrightarrow Na_2SO_4 + 2HCl$$

Boiler Troubles

Water finds a great use in various industries for generation of steam in boilers. When water is continuously evaporated to generate steam, the concentration of the dissolved salts increases progressively causing bad effects for steam boilers. The boiler troubles that arise are

1. Scale formation
2. Sludge formation
3. Caustic embrittlement

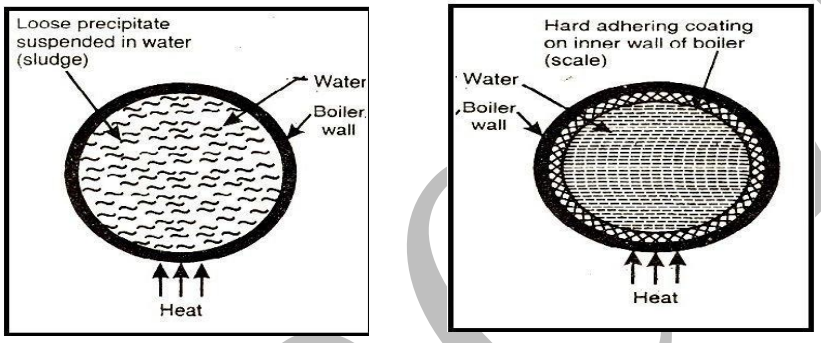
Scale and sludge formation in boilers

Boilers are employed for the generation of steam in power plants, where water is continuously heated to produce steam. As more and more water is removed from water in the form of steam, the boiler water gets concentrated with dissolved salts progressively reaches the saturation point. At this point the dissolved salts are precipitated out and slowly settle on the inner walls of the boiler plate. The precipitation takes place two ways

i) Scale ii) Sludge

i) Scale formation:

Scales are hard, adhering precipitates formed on the inner walls of the boilers. They stick very firmly to the inner walls of the boilers.



Causes of scale formation:

Following are the causes:

a. Decomposition of calcium bicarbonate

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$

In low pressure boilers,$CaCO_3$ causes scale formation. In high pressure boilers, $CaCO_3$ becomes soluble.

$$CaCO_3 + H_2O \longrightarrow Ca(OH)_2 + CO_2$$

b. Decomposition of calcium sulphate:

$CaSO_4$ is more soluble in cold water, hence its solubility decreases as the temperature of the boiler increases and precipitates out to produce hard scale on the surface of the bolier. The solubility of $CaSO_4$ is 3200ppm at15^Oc, reduces to 27ppm at 320^0c and completely insoluble in super-heated water in high pressure boilers. This is the main reason for the formation of scales in high pressure boilers. $CaSO_4$ scale is very hard, highly adherent and difficult to remove

c. Hydrolysis of Magnesium salts:

Dissolved Magnesium salts undergo hydrolysis forming $Mg(OH)_2$ precipitate causing scales.

d. Presence of Silica: Silica presents in small quantities deposits as silicates like $CaSiO_3$and $MgSiO_3$. These are very difficult to remove.

Disadvantages:

a. Wastage of fuel:

The scale formation causes decreases of heat transfer. As a result, over heating is required this causes consumption of fuel.

b. Lowering of boiler safety:

The hot scale cracks because of expansion and water suddenly comes in contact with overheated iron plates. This causes in formation of large amount of steam suddenly. This results in high pressure, causing the boiler to burst.

c. Decrease in efficiency:

Deposition of scales in the valves and condensers of the boiler, choke them partially. This results in a decrease in efficiency of the boiler.

d. Danger of explosion:

Because of the formation of the scales the boiler plate faces higher temperature outside and lesser temperature inside due to uneven heat transfer resulting the development cracks in the layers of scales. Water passes through the crack and comes in contact with boiler plates having high temperature. This causes formation of large amount of steam suddenly developing sudden high pressure which causes explosion of the boiler.

Removal of scales:

1. Scales can be removed by applying thermal shocks

2. Using scrapers, wire brush etc. scales can be removed.

3. Using certain chemicals scales can be removed. For example, using 5-10% HCl. Calcium carbonate scales can be removed. Calcium sulphate scales can be removed using EDTA solution.

4. By blow down operation the scale formation can be avoided.

ii) Sludge formation: If the precipitate is loose and slimy it is called sludge. Sludges are formed by substances like $MgCl_2$, $MgCO_3$, $MgSO_4$ and $CaCl_2$. They have greater solubilities in hot water than cold water. Formed at comparatively colder portions of the boiler and are collected at the bends. Easily removed with wire brush.

Disadvantages of sludge formation:

Sludges are poor conductors of heat, so they tend to waste a portion of heat generated.
Excessive sludge formation disturbs the working of the boiler.
Sludge can be removed by using softened water or by blow down operation i.e., drawing off a portion of the concentrated water.

3. Caustic embrittlement:

Caustic embrittlement is a term used for the appearance of cracks inside the boilers particularly at those places which are under stress such as riveted joints due to the high concentration of alkali leading to failure of the boiler.

$$Na_2CO_3+H_2O \rightarrow NaOH+ CO_2$$

Internal treatment: Suitable chemicals are added to the boiler water either to precipitate or to convert the scale into sludge.

1. Colloidal conditioning
2. Phosphate conditioning
3. Calgon conditioning

Some of the internal treatment methods used for the removed of scale formation in boilers are

1. Colloidal conditioning: The addition of organic substances such as Kerosene, tannin, Gel etc., to the surface in low pressure boilers may prevent the scale formation. These substances gets coated over the scale forming precipitates and gives a loose and non-sticky precipitates which can be removed by using blow-down operation.

2. Phosphate Conditioning: The addition of sodium phosphate in hard water reacts with the hardness causing agents and gives calcium and magnesium phosphates which are soft and non-adhere and can be removed easily by blow-down operation. In this way, scale formation is removed in high pressure boilers.

$$3\ CaCl_2 + 2\ Na_3PO_4 \longrightarrow Ca_3(PO_4)_2 + 6\ NaCl$$

3. Calgon conditioning: Involves in adding calgon to boiler water. It prevents the scale and sludge formation by forming soluble complex compound with $CaSO_4$.

Calgon = Sodium hexa Meta phosphate

$$Na_2[Na_4(PO_3)_6] \longrightarrow 2\ Na^+ + [Na_4(PO_3)_6]^{-2}$$

$$2\ CaSO_4 + [Na_4(PO_3)_6]^{-2} \longrightarrow [Ca_2(PO_3)_6]^{-2} + 2\ Na_2SO_4$$

Ion exchange process:

Ion exchange process also known as demineralization or de-ionization process. Ion-Exchange resins are insoluble. Cross linked long chain organic polymers with a micro porous structure, and the "functional Groups" attached to the chains are responsible for the ion-exchanging properties. In De-ionization process all the ions present in water are eliminated by using ion-exchange resins.

Resins are classified as

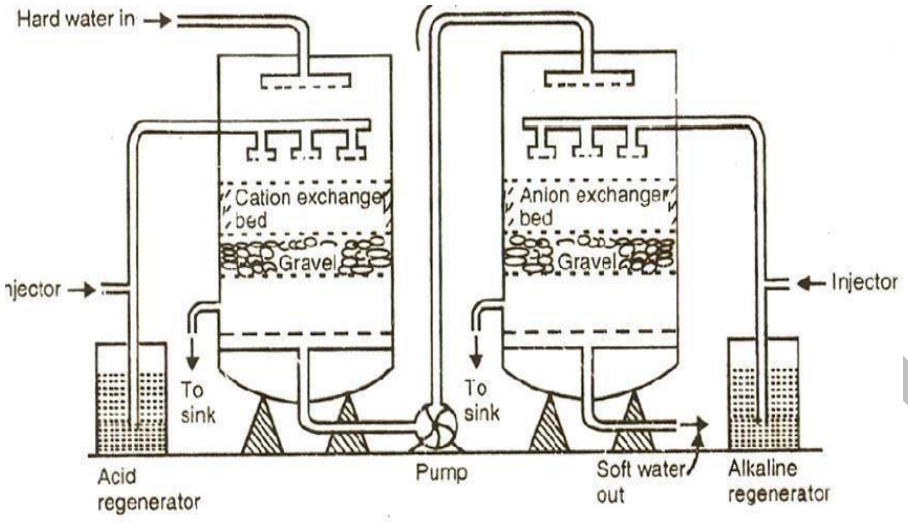
1. Cation Exchange Resins

2. Anion Exchange Resins

1. **Cation Exchange Resins:** These are mainly styrene divinyl benzene co-polymers, which on sulphonation or carboxylation. These are capable of exchanging their hydrogen ions with cations in water.

2. **Anion Exchange Resins:** Anion exchange resins are styrene-divinyl benzene or amine formaldehyde copolymers, which contains amino, quaternary ammonium groups as an internal part of the resin matrix. These after treatment with dilute NaOH solution. Become capable of exchanging their OH^- ions with anions in water.

In ion-exchange process, hard water is allowed to pass through cation exchange resins, which remove Ca^{+2} and Mg^{+2} ions and exchange equivalent amount of H^+ ions. Anions exchange resins remove bicarbonates, chlorides and sulphates from water exchange equivalent amount of OH^- ions.



Thus by passing hard water through cation and anion exchange resins, hardness is observed by the following reactions.

Cation Exchange Resins

$$2\ R\text{-}H + Ca^{+2} \longrightarrow R_2Ca + 2\ H^+$$

$$2\ R\text{-}H + Mg^{+2} \longrightarrow R_2Mg + 2\ H^+$$ **(R-H = Cation exchange resin)**

Anion Exchange Resins

$$R'\text{-}OH + Cl^+ \longrightarrow R'\text{-}Cl + OH^-$$

$$2\ R'\text{-}OH + SO_4^{-2} \longrightarrow R'_2SO_4 + 2\ OH^-$$

$$2\ R'\text{-}OH + CO_3^{-2} \longrightarrow R'_2CO_2 + 2\ OH^-$$ **(R'-OH) = Anion exchange resin)**

H^+ and OH^- ions, thus released in water from respective cation and anion exchange columns, get combined to produce water molecules.

$$H^+ + OH^- \longrightarrow H_2O$$

The water coming out from the exchanger is ion free i.e., free from anions and cations. Thus, water of zero hardness is obtained.

Regeneration: When cation exchanger losses capacity of producing H+ ions and exchanger losses capacity of producing OH^- ions, they are said to be exhausted. The exhausted cation exchanger is regenerated by passing it through dilute sulphruric acid.

$$R_2Ca^{+2} + 2H^+ \rightarrow 2RH^+ + Ca^{+2}$$

The exhausted anion exchanger is regenerated by passing a dilute solution of NaOH.

$$R_2SO_4^{-2} + 2OH^- \rightarrow 2R'OH^- + SO_4^{-2}$$

Merits of Ion-exchange process:

a. The process can be used to soften highly acidic or alkaline water.

b. It produces water of very low hardness (2 ppm)

c. So it is very good for treating water for use in high-pressure boilers.

Demerits of Ion-exchange process:

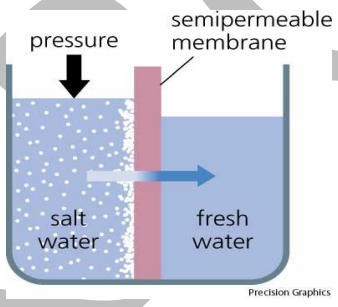
a. The equipment is costly and more expensive chemicals are needed.

b. If water contains turbidity, the output of the process is reduced. The turbidity must be below 10 ppm; else it has to be removed by coagulation and filtration.

Desalination of Brackish water: The process of removing common salt from the water is known as desalination. The water containing dissolved salts with a peculiar salty taste is called brackish water. Sea water, containing on an average about 3.5% salts, comes under this category. Commonly used methods for the desalination of brackish water is:

1. Reverse Osmosis 2. Electrodialysis.

1. Reverse Osmosis: Osmosis is the phenomenon by virtue of which flow of solvent takes place from a region of low concentration to high concentration when two solutions of different concentrations are separated by a semi-permeable membrane. The flow continues till the concentration is equal on both the sides. The driving force for osmosis is osmotic pressure. However, if a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the flow of solvent reverses as it is forced to move from concentrated side to dilute side across the membrane. This is the basis of reverse osmosis.



Method of purification:

The reverse Osmosis cell consists of a chamber fitted with a semi-permeable membrane which is made of thin films of cellulose acetate, polymethyl acrylate and polyamide polymers. Above the semi permeable membrane sea water or impure water is taken and a pressure of the order of 15-40 kg/cm^2 is applied on the sea water for separating the water from its contaminants. Pure water is forced through semi permeable membrane. The process is also known as super or hyper filtration.

Advantages:

a. Colloidal SiO_2 can be removed by reverse osmosis which even cannot be removed by demineralization.

b. It is simple and reliable process.

c. Capital and operating expenses are low.

d. The life of the semi-permeable membrane is about 2 years and it can be easily replaced within a few minutes; thereby nearly uninterrupted water supply can be provided.

UNIT-II

ELECTROCHEMISTRY AND CORROSION

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

Redox Reactions:

Oxidation: addition of O_2 / removal of H_2 / loss of electrons/increase in oxidation number.

Reduction: addition of H_2 / removal of O_2 / gain of electrons/ decrease in oxidation number.

If a substance loses electrons, some other substance must be involved in the reaction to accept these electrons and vice versa. Thus, oxidation and reduction must always go side by side. Reaction, in which loss of electrons takes place, is called oxidation half reaction, while the other reaction, in which gain of electrons takes place, is called reduction half reaction.

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

Anode: Anode is the electrode at which oxidation takes place

Cathode: Cathode is the electrode at which reduction takes place

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

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

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

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

Single electrode potential:- Each electrochemical cell is made up of two electrodes, at one electrode electrons are liberated and at other electrode they are used up. The potential of half

cell i.e. the potential difference between the metal and its salt solution in which it is dipped is called single electrode potential. It cannot be directly measured.

$$Zn \mid ZnSO_4 \parallel CuSO_4 \mid Cu$$

← half cell → ← half cell→

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

Types of Cells

Electrolytic cell: A cell which converts electrical energy to chemical energy.

Electro chemical cell: A cell which converts chemical energy to electrical energy. These are also called as Galvanic cells (or) Voltaic cells. Daniel cell is example of galvanic cell.

Differences between Electrolytic cell and Electro chemical cell:

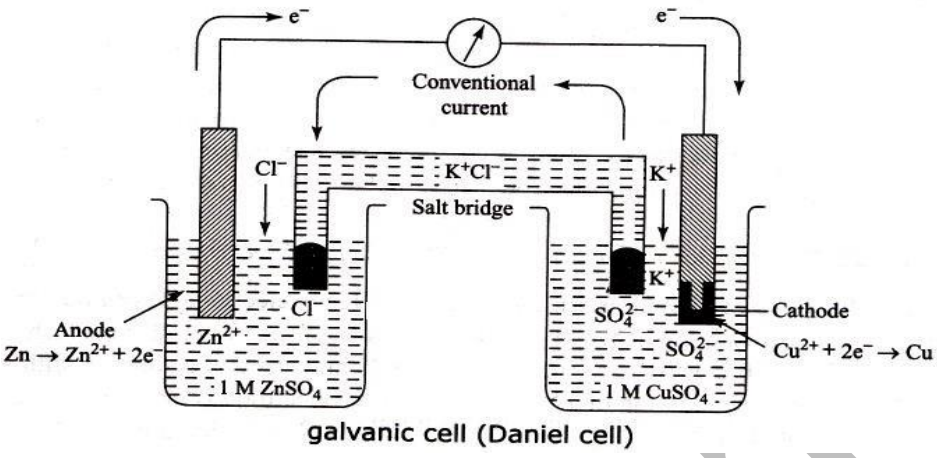
DANIEL CELL:

Electrolytic cell	Electro chemical cell
Electrical energy converted to Chemical energy.	Chemical energy converted to electrical energy.
Anode carries + ve charge	Anode carries - ve charge
Cathode carries – ve Charge	Cathode carries + ve Charge
Electrons are supply to the cell from external source.	Electrons are drawn from the cell.

DANIEL CELL:

- The Daniel cell is a typical example of Galvanic cell.
- Daniel cell consists of a beaker containing copper rod dipped in $CuSO_4$ solution which is connected to another beaker containing zinc rod dipped in $ZnSO_4$ solution by a salt bridge.

Salt bridge is an inverted U-tube containing saturated solution of some electrolyte such as KCl, KNO_3, NH_4NO_3 which does not undergo chemical change during the process. The saturated solution is generally taken in agar-agar jelly or gelatin



galvanic cell (Daniel cell)

- The salt bridge allows the flow of ions to pass through it when the flow of electric current takes place. It completes the electrical circuit and maintains the electrical neutrality of two half cell solutions.
- When the circuit is completed, electric current flows through the external circuit as indicated by an ammeter. The following observations are made:

1. Zinc rod gradually loses its weight.
2. The concentration of $Zn^{+2}(aq)$ in the $ZnSO_4$ (aq) solution increases.
3. Copper gets deposited on the electrode
4. The concentration of $Cu^{+2}(aq)$ in $CuSO_4$ (aq) solution decreases.
5. The flow of electrons is from Zn-electrode (anode) to Cu-electrode (cathode).
6. The flow of electric current is from Cu-electrode to Zn-electrode

The above observations can be explained as follows:

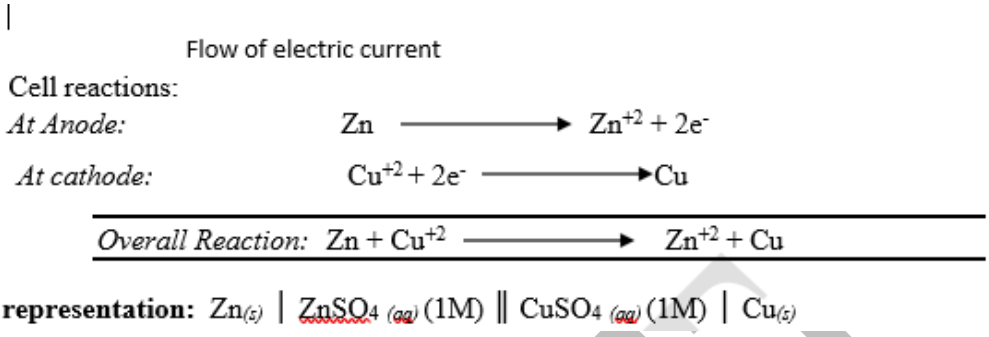
- Zn is oxidized to Zn^{+2} ions which go in the solution and therefore Zn rod gradually loses its weight (oxidation half cell).

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

- The electrons released at the Zn electrode move towards Cu electrode through external circuit.
- These electrons are accepted by the Cu^{+2} ions in the solution and get reduced to copper which gets deposited on the Cu-electrode (reduction half cell).

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

- The oxidation of Zn occurs at anode (negative terminal) and reduction of Cu^{+2} occurs at cathode (positive terminal).
- The flow of electrons is from negative terminal (anode) to positive terminal (cathode).



Cell representation: $Zn_{(s)} \mid ZnSO_{4\,(aq)}\,(1M) \parallel CuSO_{4\,(aq)}\,(1M) \mid Cu_{(s)}$

Electrodes

Electrode potential (or) Single Electrode potential (E): It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt.

Standard Electrode potential (E°): It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of 1M concentration at 25°C.

Reduction potential: The tendency of an electrode to gain electrons and to get reduced is called reduction potential.

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

Oxidation potential: The tendency of an electrode to lose electrons and to get oxidized is called oxidation potential.

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

Emf of electrochemical cell: The difference between potentials of the two half cells is known as emf of cell

$$E_{cell} = E_{right} - E_{left}$$
$$E_{cell} = E_{right} - E^o \text{ (if standard electrode is anode)}$$
$$E_{cell} = E^o - E_{left} \text{ (if standard electrode is cathode)}$$

Where E^o is the standard electrode potential.
Eg. Standard hydrogen electrode, Calomel electrode, Quinhydrone electrode.

Nernst Equation: The derivation of a mathematical relationship between the standard

electrode potentials, temperature and the concentration of ions is known as the Nernst equation. Consider a reaction

$$a\,A + b\,B \rightleftharpoons c\,C + d\,D$$

$$E_{cell} = E^{o}_{cell} - \frac{2.303RT}{nF} \log \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

R- Gas Constant = 8.314J/sec

n- No. of electrons involved in the reaction

T- Absolute temperature = 298K

F = Faraday = 96500c

$$E_{cell} = E^{o}_{cell} - \frac{2.303RT}{nF} \log \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

$$E_{cell} = E^{o}_{cell} - \frac{0.0591}{n} \log \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

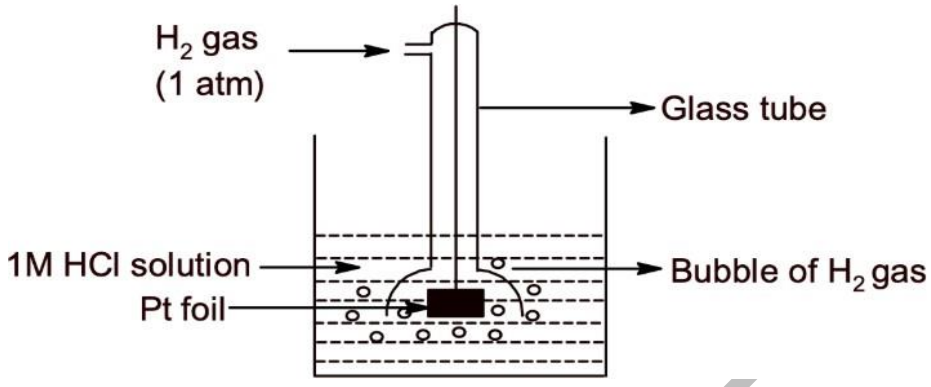
Types of Electrodes: An electrochemical cell consists of two electrodes, positive and negative. Each electrode constitutes a half cell or a single electrode.

The electrode of Standard potential, with which can compare the potentials of another electrode is called reference electrode.

Eg: Standard hydrogen electrode (Potential is zero at all temperatures)

STANDARD HYDROGEN ELECTRODE (OR) GAS ION ELECTRODE

It consists of a platinum wire which is the sealed in a glass tube. The lower end of the platinum wire is attached to the platinum foil which is plated by Platinum black. It helps with the adsorption of hydrogen and acts as a site for the reaction. This whole adjustment is dipped in to the beaker of 1M HCl solution with hydrogen gas 1 atm pressure at 25^0C which is constantly bubbled into a solution as below



If hydrogen gas is maintained at 1 atm pressure and 25^0C temperature and platinum foil is immersed into 1 M HCl solution., the electrode is called a **Standard hydrogen electrode**. Depending upon the nature of the counter electrode, the standard hydrogen electrode acts as a cathode as well as an anode.

If it acts as an anode: $H_2(g) \leftrightarrow 2\,H^+ + 2e^-$ (Oxidation half)

If it acts as a cathode: $2\,H^+ + 2e^- \leftrightarrow H_2(g)$ (Reduction half)

The electrode potential of a standard hydrogen electrode is taken as zero. In fact, the cell potential of the hydrogen electrode is neither zero nor independent of temperature. All other electrodes are calibrated with respect to standard hydrogen electrode. It is somewhat difficult to handle and cannot be used in the presence of oxidizing or reducing agents. The platinum black used is easily poisoned by mercury and H_2S. Therefore, other reference electrodes such as Calomel electrode are used. Such electrodes are called **Secondary reference electrode.**

Advantages of standard hydrogen electrode:

1. It can be used over the entire pH range.
2. It use no salt error.
3. It is highly accurate

Disadvantages of standard hydrogen electrode:

1. It is difficult to maintain one molar concentration of H^+ ion.
2. one atm pressure of H_2 gas cannot be maintained uniformly.
3. The hydrogen electrode gets poisoned even if traces of impurities are present.
4. Platinum used is expensive.

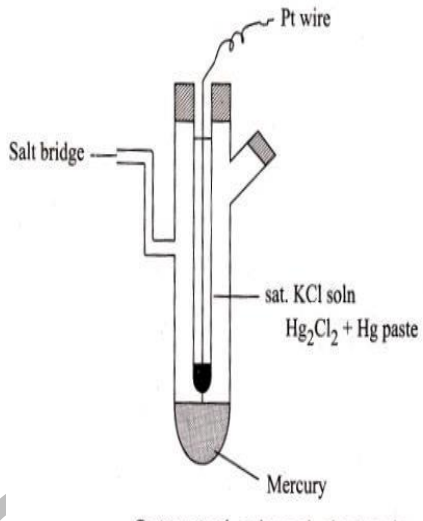
CALOMEL ELECTRODE

- It is a secondary reference electrode.
- It is a mercury-mercurous chloride (Hg-Hg_2Cl_2) electrode.

- The Calomel electrode is used as only reducing electrode

  i.e. as cathode only.

- It consists of a glass tube having a side tube on each side. One side tube acts as salt bridge and other is used to fill KCl solution.
- The high purity mercury is placed at the tip of this tube and connected to the circuit by the means of Pt-wire, sealed in a glass tube.



Saturated calomel electrode

- The surface of Hg is covered with a paste of mercurous chloride (calomel) and Hg in KCl solution.
- The electrolyte is the solution of KCl.
- The electrode is connected with the help of side tube on the left through salt bridge with the other electrode whose potential has to be determined.
- The potential of the calomel electrode depends upon the concentration of KCl.

Concentration of KCl	0.1N	1.0N	Saturated
Electrode potential (V)	0.3335	0.2810	0.2422

Representation of calomel electrode: Hg, $Hg_2Cl_{2(s)}$ | KCl (saturated solution)

Calomel electrode acts as secondary reference electrode. It acts as either anode or cathode depend the other electrode connected to it.

If the electrode acts as anode, oxidation takes place and the following reaction takes place:

$$2\,Hg(l) \rightarrow Hg_2^{2+} + 2e^- \text{ (Oxidation half reaction)}$$

$$Hg_2^{2+} + 2\,Cl^- \rightarrow Hg_2Cl_2$$

$$2Hg\,(l) + 2Cl^- \rightarrow Hg_2Cl_2\,(s) + 2e^-$$

Oxidation half reaction, which results in the decrease of concentration of Cl^- ions in the solution

If the electrode acts as cathode, reduction takes place and the following reaction takes place:

$$Hg_2^{2+} + 2e^- \rightarrow 2Hg\,(s) \text{ (Reduction half reaction)}$$

$$Hg_2Cl_2 \rightarrow Hg_2^{2+} + 2\,Cl^-$$

$$Hg_2Cl_2\,(s) + 2e^- \rightarrow 2Hg\,(s) + 2Cl^-$$

Reduction half reaction, which results in the increase of concentration of Cl^- ions in the solution

Nernst Equation: $E = E^0_{Hg2Cl2} - \frac{2.303RT}{2F} \log (Cl^-)^2$

$$E = E^0 - \frac{2.303RT}{F} \log (Cl^-)$$

$$\mathbf{E = E^0 - 0.0591 \log (Cl^-)}$$

Advantages of Calomel electrode:

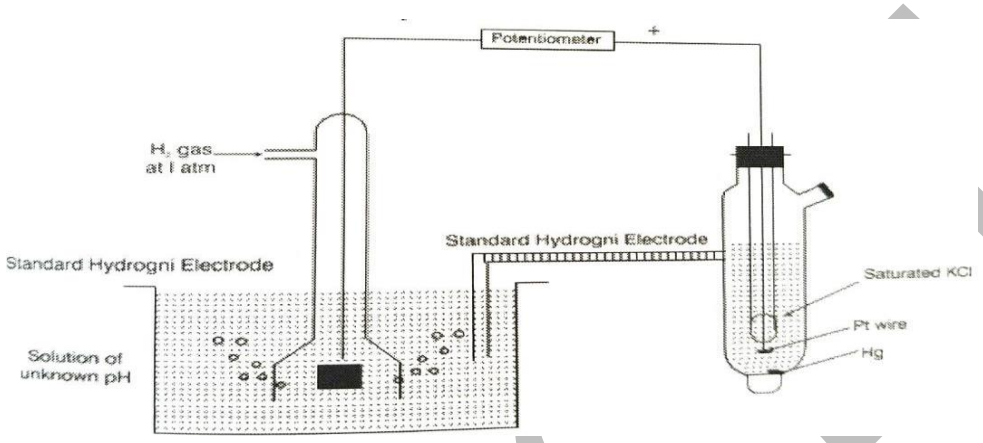
1. It provides a stable and reproducible potential over time, which is essential for accurate measurements.
2. The electrode potential remains stable even when a small current passes through it.

Disadvantages of Calomel electrode:

1. The electrode contains mercury, a hazardous substance that can pose a health risk and environmental concern.
2. The electrode's stability can be affected by temperatures above 50°C, and its temperature coefficient of potential is higher than that of silver/silver chloride electrodes.

DETERMINATION OF pH OF UNKNOWN SOLUTIONS USING CALOMEL ELECTRODE AND HYDROGEN ELECTRODE

When connected to SHE, the pH of an unknown solution can be determined using calomel electrode. When saturated calomel electrode is connected through potentiometer to standard hydrogen electrode dipped in the solution whose pH is to be determined.



$$Pt, H_2\ (1\ atm)\ |\ H^+\ (unknown)\ ||\ KCl\ (saturated)\ |\ Hg_2Cl_{2(s)}\ |\ Hg^+$$

$$E_{cell} = E_{cathode} - E_{anode}$$

$$E_{cell} = 0.2422 - (-0.0591\ pH)$$

$$E_{cell} = 0.2422 + 0.0591\ pH$$

$$pH = \frac{E_{cell} - 0.2422}{0.0591}$$

Uses

1. It is used as a secondary reference electrode in the measurement of single electrode potential.
2. It is commonly used reference electrode in all potentiometric determinations.

CORROSION

Definition: Corrosion may be defined as the disintegration or eating away of a metallic material from its surface by chemical or electrochemical reaction with its environment.

$$\text{Metal} \xleftrightarrow[\text{Metallurgy (Reduction)}]{\text{Corrosion (Oxidation)}} \text{Metallic compound} + \text{energy}$$

Example: Rusting of iron when exposed to atmospheric conditions.

$$2Fe^{2+} + \frac{3}{2} O_2 + 3H_2O \rightarrow Fe_2O_3.3H_2O \text{ (Rust is hydrated oxide } Fe_2O_3.xH_2O).$$

CAUSES OF CORROSION

In nature metals have a natural tendency to revert back to combined states. During this process mostly oxides are formed though in some cases sulphides, carbonates. Any process of deterioration and loss of solid metallic material by chemical or electrochemical attack by its environment is called corrosion. Corrosion is the reverse process of metallurgy.

Ore (Stable) → Metal (Unstable) → Corrosion Product (Stable)

EFFECT OF CORROSION

- Poor appearance
- Maintenance and operating costs
- Plant shutdowns
- Contamination of product
- Loss of valuable products due to leakage
- Effects on safety and reliability in handling hazardous materials
- Product liability
- Valuable metallic properties such as conductivity, malleability, ductility, etc. are lost due to corrosion.

THEORIES OF CORROSION

There are two theories of corrosion

1. Dry/Chemical theory
2. Wet/Electrochemical/galvanic theory

1.Dry (or) chemical Corrosion: According to this theory type of corrosion occurs mainly through the direct chemical action of atmospheric gasses (O_2, H_2S, SO_2, and N_2) with metal.

There are three main types of dry Corrosion:

i. Oxidation corrosion

ii. Corrosion of the other gases

iii. Liquid metal corrosion.

Oxidation corrosion: This is carried out by the direct action of oxygen low or high temperatures on metals in absence of moisture at ordinary temperature metals or very slightly attacked. The exceptions are Alkali metals and Alkaline earth metals. At high temperature all metals are oxidized. The exception is Ag, Au and Pt.

$$2M \rightarrow 2M^{n+} + 2n^{e-} \text{ (loss of electrons)}$$

(Metal ion)

$$nO_2 + 2n^{e-} \rightarrow 2nO^{2-} \text{ (gain of electrons)}$$

(Oxide ion)

$$2M + nO_2 \rightarrow 2M^{n+} + 2nO^{2-} \text{ (Metal oxide)}$$

Mechanism: During oxidation of a metal, metal oxide is formed as a thin film on the metallic surface which protects the metal from further corrosion. If diffusion of either oxygen or metal is across this layer, further corrosion is possible. Oxides of Pb, Al, Sn are stable, and hence inhibit further corrosion.

Corrosion of the other gases: Cl_2, SO_2, H_2S, NO_2 gases react with metal and form corrosion products which may be protective or non-protective. Dry Cl_2 reacts with Ag and forms AgCl which is a protective layer, while $SnCl_4$ is volatile in petroleum industries at high temperatures, H_2S attacks steel forming FeS scale which is porous and interferes with normal operations

Liquid metal corrosion: In several industries, molten metals pass through metallic pipes and causes corrosion due to dilution or due to internal penetration.

Example: Coolant (sodium metal) causes cadmium corrosion in nuclear reactor. Liquid metal mercury dissolves most metals by forming amalgams, there by cording them.

Wet (or) Electrochemical Corrosion:

Electrochemical theory of corrosion:

Wet or electro chemical corrosion is common type of corrosion which occurs under wet or moist conditions. It is observed when (i) a metal is in contact with a conducting liquid, and/or (ii) dissimilar metals are dipped partially in aqueous corrosive environment. According to this theory, there is a formation of galvanic cell on the surface of the metal. Some of the metal surface act as anode and rest as cathode. The chemical in the environment and humidity act as an electrolyte. Oxidation takes place at anode and its results in corrosion, while reduction takes place at cathode.

Mechanism: Electrochemical corrosion involves flow of electrons between anode and cathode. The anodic reaction involves dissolution of metal liberating free electrons.

$$M \rightarrow M^{n+} + ne^-$$

The cathodic reaction consumes electrons with either **evolution of hydrogen** or **absorption of oxygen** which depends on the nature of corrosive environment

i. **Evolution of hydrogen:** This type of corrosion occurs in acidic medium.

Ex: Considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with liberation of electrons.

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

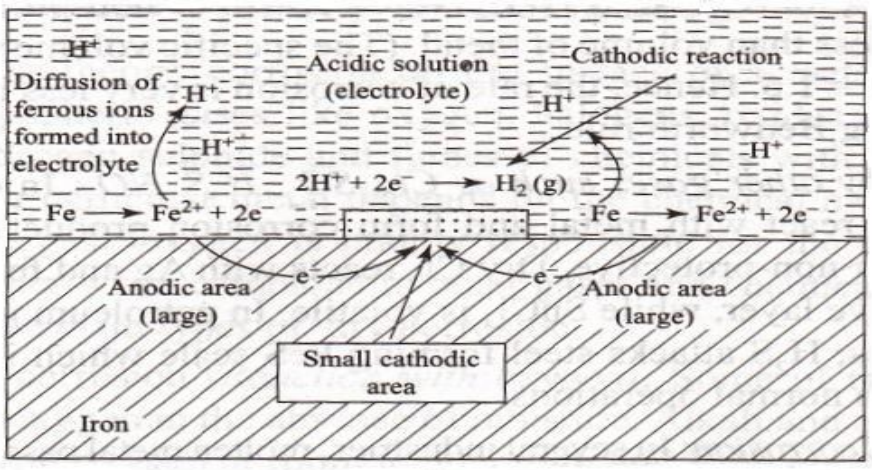
At Anode: $Fe \rightarrow Fe^{2+} + 2e^-$ (Oxidation)

At Cathode: $2H^+ + 2e^- \rightarrow H_2$ (Reduction)

Overall reaction: $Fe + 2H^+ \rightarrow Fe^{2+} + H_2$

This type of corrosion causes displacement of hydrogen ions from the solution by metal ions. All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of H_2 gas.

The anodes are large areas, whereas cathodes are small areas.



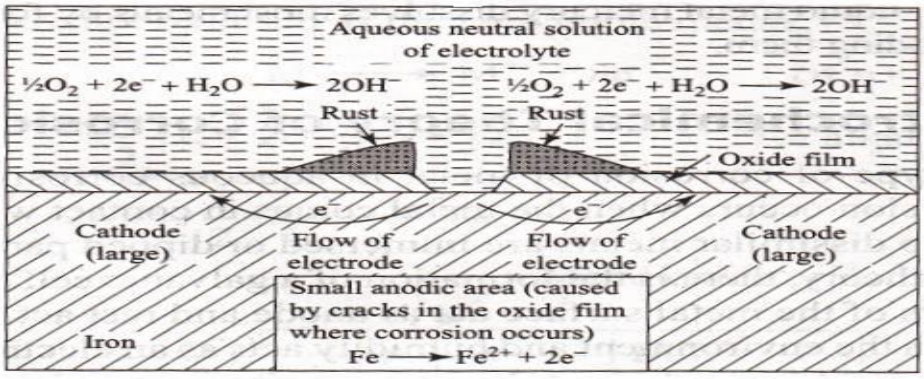
(a)

ii. Absorption of oxygen:

This type of corrosion occurs in neutral (or) basic medium.

Ex: Rusting of iron in neutral aqueous solution of electrolytes in presence of atmospheric oxygen. Usually the surface of iron is coated with a thin film of iron oxide. If the film develops cracks, anodic areas are created on the surface. While the metal parts act as cathodes. It shows

that anodes are small areas, while the rest metallic part forms large cathodes.



(b)

At anode: $Fe \rightarrow Fe^{2+} + 2e^{-}$ (Oxidation)

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

Overall reaction: $Fe + \frac{1}{2} O_2 + H_2O \rightarrow Fe^{2+} + 2OH^{-}$ $(Fe(OH)_2)$

If oxygen is in excess, ferrous hydroxide is easily oxidized to ferric hydroxide

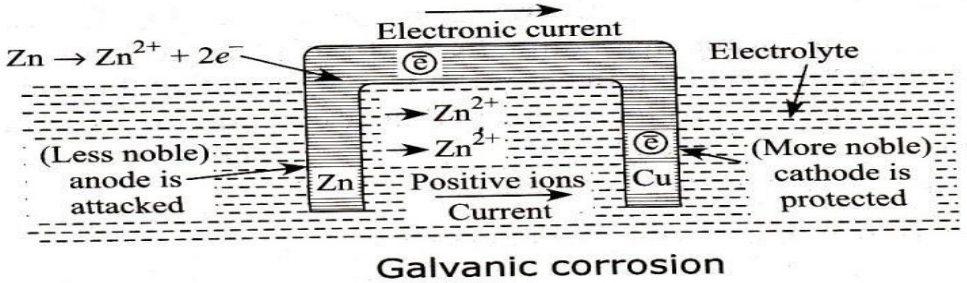
$$4\,Fe^{2+}(OH)_2 + O_2 + 2\,H_2O \rightarrow 4\,Fe(OH)_3$$

The product called yellow rust corresponds to $Fe_2O_3 . xH_2O$

TYPES OF CORROSION

Galvanic Corrosion: When two dissimilar metals are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion. This type of corrosion is called galvanic corrosion

Galvanic corrosion can be avoided by coupling metals close to the electrochemical series, fixing insulating material between two metals, by using larger anodic metal and smaller cathodic metal.

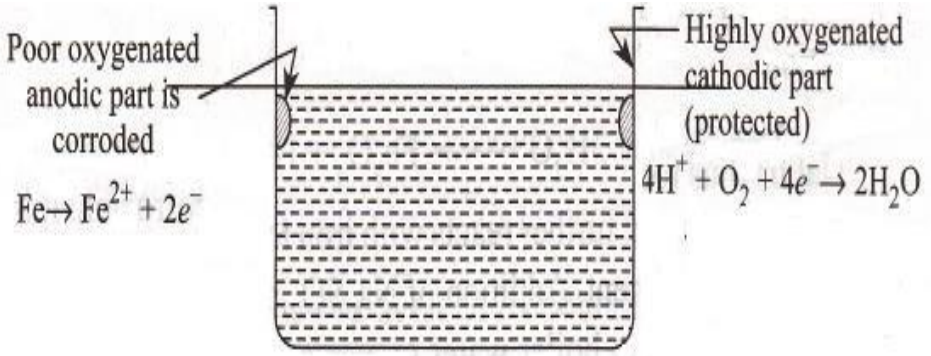


Galvanic corrosion

At anode: $Zn \rightarrow Zn^{++} + 2e^{-}$ [Oxidation] corrosion

At cathode: $Cu^{++} + 2e^{-} \rightarrow Cu$ [Reduction] unaffected

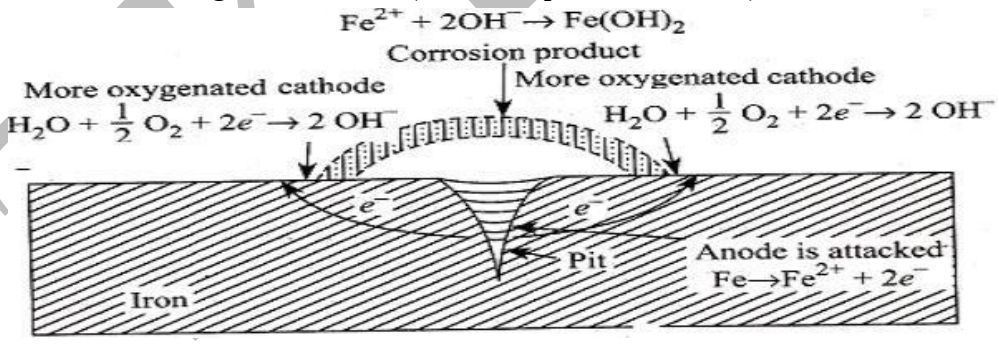
Waterline Corrosion: This is also known as *differential oxygen concentration corrosion*. It has been observed in the case of iron tank containing water, that the portion of iron tank just below the water level undergoes corrosion. It is due to the difference in oxygen concentration.



At anode: $Fe \rightarrow Fe^{2+} + 2^{e-}$
At cathode: $2H^+ + \frac{1}{2}O_2 + 2^{e-} \rightarrow H_2O$ ($H_2O \rightarrow H^+ + OH^-$)
Overall reaction: $Fe + \frac{1}{2} O_2 + H_2O \rightarrow Fe^{2+} + 2OH^-$ ($Fe(OH)_2$)

The area above the waterline (highly oxygenated) acts as cathodic and is not affected by corrosion. However, if the water is relatively free from acidity, little corrosion occurs. This type of corrosion is prevented to a great extent by painting the sides of the ships by antifouling paints

Pitting corrosion: Pitting corrosion is due to crack on the surface of a metal, there is a formation of a *"local galvanic cell''* (Pinholes, pits and cavities) in the metal



Pitting is usually the result of the breakdown or cracking of the protective film on a metal at specific points. This gives rise to the formation of small anodic and large cathodic areas. In the corrosive environment this produces corrosion current.

FACTORS AFFECTING OF CORROSION

The rate and extent of corrosion depends on the nature of the metal and nature of corroding environment.

Those are **1.** Effect of metal

2. Effect of environment

1. **Effect of metal:** Different properties of a metal are responsible for corrosion. These properties are given below.

a. Position of metal in galvanic series **b.** Hydrogen over voltage

c. Nature of surface/oxide film **d.** Volatility of corrosion product

a. Position of metal in galvanic series: It decides the corrosion rate. A metal having higher position in galvanic series undergoes corrosion when connected to another metal below it.

b. Hydrogen over voltage: In case of Zinc metal placed in a normal solution of H_2SO_4, reaction takes place forming bubbles of hydrogen gas on zinc surface. The process is slow due to high overvoltage of zinc metal (0.7 V) which reduces the effective potential to a small value. In presence of $CuSO_4$ the corrosion rate of zinc is accelerated.

c. Nature of surface/oxide film: In aerated atmosphere, all metals get covered with a thin surface film of metal oxides. The ratio of the volumes of metal oxides to the metal is known as specific volume ratio. Greater is this value lesser is the oxidation corrosion rate. Specific volume ratios of Ni, Cr and W are 1.6, 2.0 and 3.6 respectively suggesting Tungsten has least corrosion. Further the corrosion depends on nature of oxide film. Metals like Al have a firm oxide film in comparison to Fe and hence Al in less corrosive means it follows ***Pilling-Bed worth Rule.*** The iron oxide is porous in nature and this leads to extension of corrosion to inner surface.

D.Volatility of corrosion products: If the corrosion product is volatile, then the underlying surface is exposed for further attack. This causes rapid and continuous corrosion. E.g. MoO_3 is volatile

2. **Effect of environment:** Different properties of an environment are responsible for corrosion. These properties are given below.

a. Effect of pH **b.** Temperature

c. Humidity of air

a. Effect of pH:

In the corrosion reaction described H^+ or OH^- are also involved. Therefore the effect of pH is obvious. It can be easily seen from the chemical equation for a reaction the direction in which it will shift by change in concentration of H^+ or OH^-. As a general rule, acids are more corrosive than neutral or alkaline solutions.

b. Temperature:

As the temperature of environment is increased the reaction rate is increased thereby accelerating corrosion. The effect of temperature on the corrosion rate is complicated because of the fact that it affects the various factors in different ways. The rate of chemical reaction increases, with rise in temperature but the solubility of gases, like oxygen which affect corrosion, decreases. The temperature may affect the protective coatings in different ways. In general, the rate of corrosion due to oxygen or oxidizing agents is decreased with rise in temperature but the rate of hydrogen type corrosion is increased.

c. Humidity of air:

Corrosion of a metal is furnished in humid atmosphere because gases (CO_2, O_2) and vapours present in atmosphere furnish water to the electrolyte essential to establish an electrochemical corrosion cell. The oxide film on the metal surface has the property to absorb moisture. In presence of this absorbed moisture, corrosion rate is enhanced. Rain water may also wash away the oxide film from the metal surface. This leads to enhanced atmospheric attack. The exceptions are Cr, Al.

CORROSION CONTROL METHODS

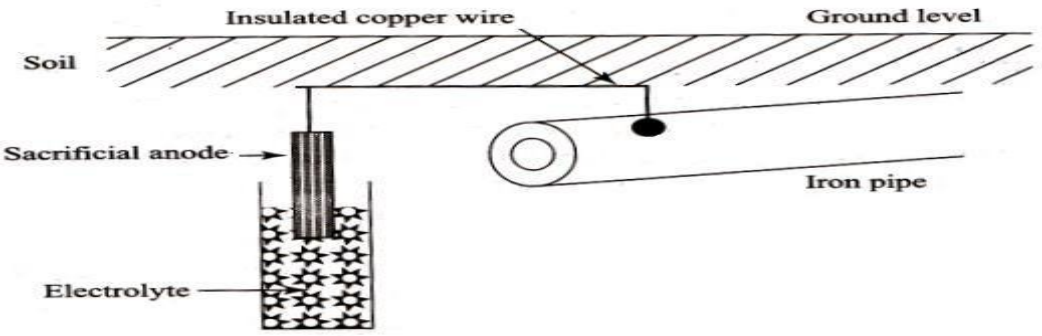
1. Cathodic Protection:

The cathodic protection of metals is used to control corrosion metals where it is impartibly to alter the nature of the corrosion medium. The principle involved in this method is to protect metals and alloys from corrosion by making them completely cathodic. Since there will not be any anodic area on the metal, therefore corrosion does not occurs. The following are **two types** of cathodic protections.

a. Sacrificial anodic protection **b.** Impressed current cathodic protection

a. Sacrificial anodic protection:

In this method, the metal structure can be protected from corrosion by connecting it with wire to a more anodic metal. As this more active metal is sacrificed in the process of saving metal from corrosion, it is known as sacrificial anode. The metals which are commonly used as sacrificial anodes are Mg, Zn, Al and their alloys.

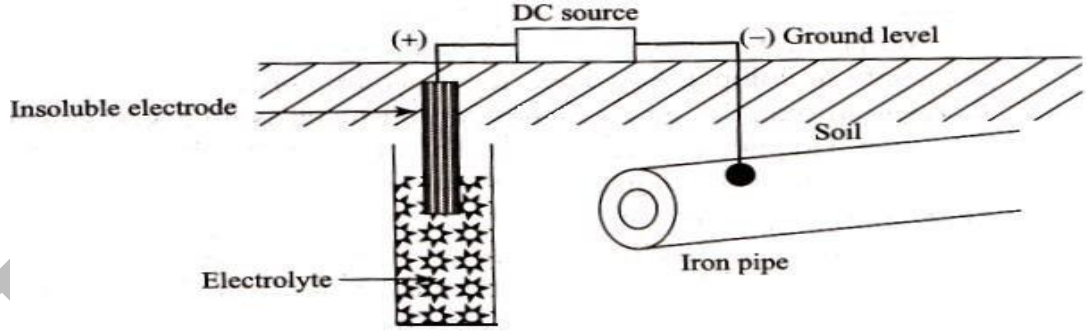


The important applications of this method are:

- Protection of underground cables and pipelines from soil corrosion.
- Protection of ships and boat hulls from marine corrosion.
- Prevention of rusty water by inserting Mg sheets or rods into domestic water boilers or tanks.

b. Impressed current cathodic protection:

As the name implies, an impressed current is applied to convert the corroding metal from anode to cathode. The applied current is in opposite direction since to nullify the corrosion current. This can be accomplished by applying sufficient amount of direct current source like battery or rectifier to an anode like graphite, high silica iron, stainless steel or platinum buried in the soil or immersed in the corrosion medium, and connected to the corroding metal structure which is to be protected as shown in the diagram below.



In impressed current cathodic protection, electrons are supplied from an external cell, so that the object itself becomes cathodic and not oxidized. This type of cathodic protect ion has been applied to buried structures such as tanks and pipelines, transmission line-towers, marine piers, laid-up ships etc. since, their operating and maintenance costs are less, they are well suited for large structures and long term operations.

UNIT – III

ENERGY SOURCES

INTRODUCTION

Battery Chemistry

Electrochemical Cell:

An electrochemical cell is a device in which chemical energy is converted into electrical energy.

Battery:

A battery is an arrangement of several electrochemical (galvanic) cells connected in series.

A single cell contains only one anode and one cathode.

A battery contains multiple anodes and cathodes because it consists of several cells.

Types of Batteries:

1) Primary Batteries / Primary Cells:

- These are non-rechargeable batteries.
- In these cells, the electrode and electrolyte reactions cannot be reversed by supplying external energy.
- The reactions occur only once, and after that the battery becomes dead.

Examples:

- Zinc–air battery
- Dry cell
- Mercury cell

2) Secondary Batteries:

- These are rechargeable batteries.

• In these cells, the electrode reactions can be reversed by supplying external electrical energy.

• They can be recharged by passing electric current and used repeatedly.

• They are also called storage cells or accumulators.

Examples: Lithium-ion batteries, Sodium-ion batteries.

Differences between Primary and secondary battery cell:

S.No	Primary Battery Cells	Secondary Battery Cells
1	Used only once; cannot be recharged.	Can be recharged and used repeatedly.
2	Chemical reactions are irreversible.	Chemical reactions are reversible.
3	Discarded after complete discharge.	Can be recharged after discharge and reused.
4	Lower initial cost.	Higher initial cost.
5	Higher running cost due to frequent replacement.	Lower running cost due to repeated use.
6	Generally lighter and compact.	Usually heavier because of rechargeable components.
7	Lower self-discharge rate; suitable for long-term storage.	Higher self-discharge rate than primary cells.
8	Used in low-power devices such as remote controls, clocks, flashlights, calculators, and toys.	Used in high-power devices such as mobile phones, laptops, electric vehicles (EVs), UPS, and power tools.
9	Not environmentally friendly because they are disposed of after use.	More environmentally friendly due to multiple recharge cycles.
10	Examples: Dry cell (Leclanché cell), Alkaline battery, Zinc-air battery.	Examples: Lead-acid battery, Lithium-ion battery, Nickel-Cadmium (Ni-Cd) battery, Nickel-Metal Hydride (Ni-MH) battery.

Lithium-ion batteries (or) Lithium-ion cells

Lithium-ion battery is a secondary battery. As the name suggests, the movement of lithium ions are responsible for charging & discharging. Lithium-ion cell has the following three components.

- A positive electrode (Layers of lithium-metal oxide) (cathode)
- A negative electrode (Layers of porous carbon) (anode)
- An electrolyte (Polymer gel) (separator)

Construction

The positive electrode is typically made from a layered chemical compound called lithium-cobalt oxide ($LiCoO_2$).

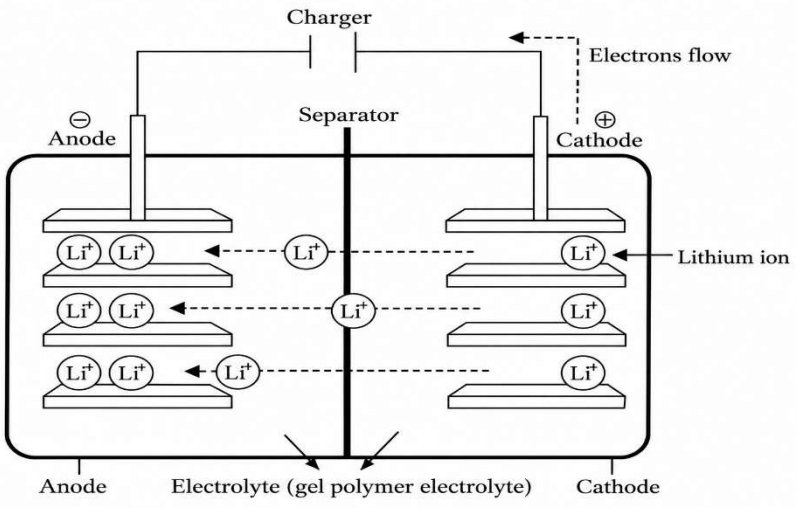
The negative electrode is made from layers of porous carbon (C) (graphite).

Both the electrodes are dipped in a polymer gel electrolyte (organic solvent) and separated by a separator, which is a perforated plastic and allows the Li^+ ions to pass through.

Working Principle:

Charging:

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



Lithium-ion cell during charging

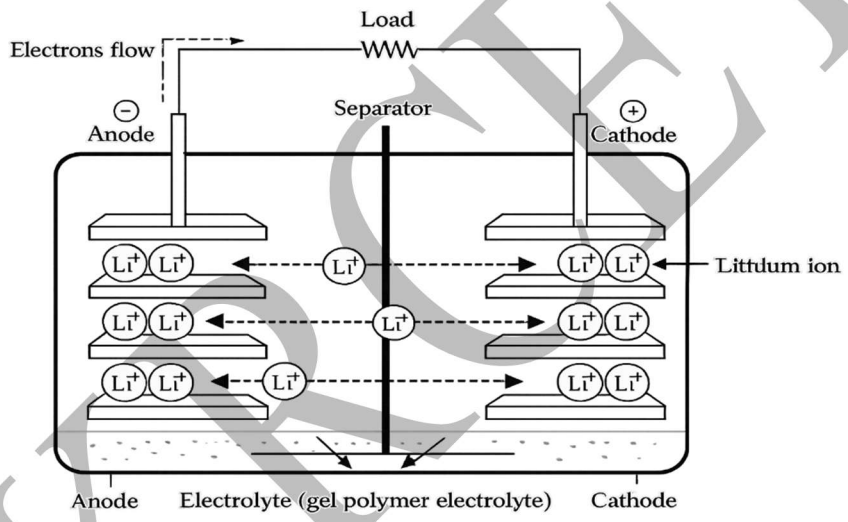
to the negative electrode. The electrons and Li^+ ions combine at the negative electrode and deposit there as Li.

$$LiCoO_2 + C \rightarrow Li_{1-x}CoO_2 + CLi_x$$

Discharging

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

$$Li_{1-x}CoO_2 + CLi_x \rightarrow LiCoO_2 + C$$



Lithium-ion cell during discharging

Advantages (or) Characteristics

1. Lithium-ion batteries are high voltage and light weight batteries.
2. It is smaller in size.
3. It produces three times the voltage of Ni-Cd batteries.
4. It has none of the memory effect seen in Ni-Cd batteries.

Uses

It is used in cell phones, notebooks, PCs, portable LCD TVs, semiconductor-driven audio, etc.

Zinc-Air Battery

It is a primary cell battery.

It has three important components:

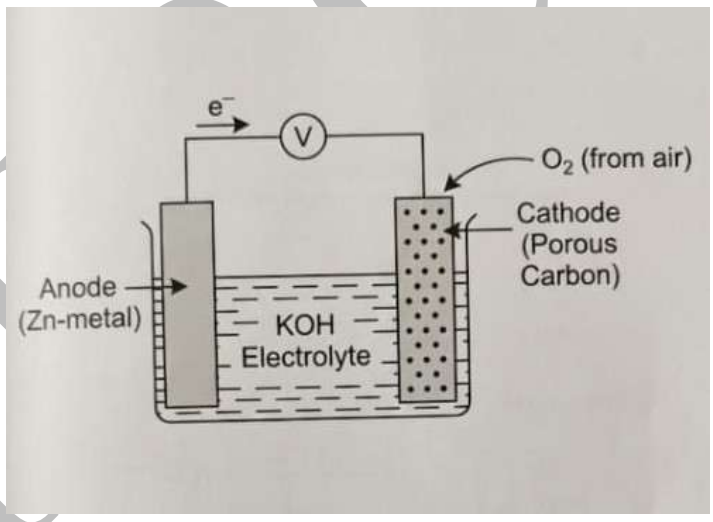
I. Anode: Zn Zinc metal plate.

II. Cathode: An air electrode, made of a porous Carbon.

III. Electrolyte: aq. KOH (Potassium hydroxide).

Working Principle:

A zinc–air battery is an electrochemical cell in which zinc is used as the anode and oxygen from atmospheric air acts as the cathode material. The electrolyte used is aqueous potassium hydroxide (KOH). During discharge, zinc undergoes oxidation at the anode, while oxygen is reduced at the cathode, producing electrical energy.



Cell Reactions

At anode:

$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$$

(or sometimes written as $Zn + 4OH^- \rightarrow Zn(OH)_4^{2-} + 2e^-$ in concentrated KOH)

At cathode:

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

Overall reaction:

$$Zn + \frac{1}{2} O_2 \rightarrow ZnO$$

Applications:

1. It is used in hearing aid devices.
2. It is used in pagers.
3. It is used in military transistors and voice transmitters.

FUEL CELLS

Definition

A fuel cell is a voltaic cell which converts the chemical energy of the fuels directly into electricity without combustion. It converts the energy of the fuel directly into electricity. In these cells, the reactants, products and electrolytes pass through the cell.

Fuel + Oxygen → Oxidation products + Electricity

Examples

Hydrogen-oxygen fuel cell

Methyl alcohol-oxygen fuel cell

Methanol–Oxygen Fuel Cell

Introduction

A **Methanol–Oxygen Fuel Cell (MOFC)** is a type of **Direct Methanol Fuel Cell (DMFC)** that converts the chemical energy of **methanol and oxygen** directly into electrical energy.

Construction

1. **Anode:**
   Porous Ni plate coated with Pt block catalyst where methanol is oxidized.

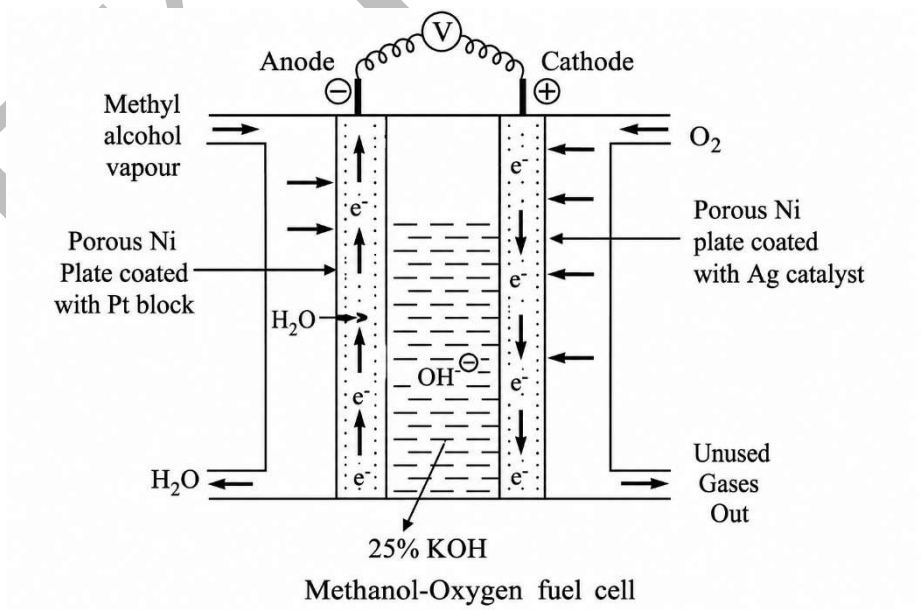
2. **Cathode:**
   Porous Ni plate coated with Ag catalyst where oxygen is reduced.

3. **Electrolyte:**
   Proton Exchange Membrane (PEM) such as **Nafion**, which allows **H^+ ions** to pass but blocks electrons.

4. **Fuel:**
   Methanol (CH_3OH) mixed with water.

5. **Oxidant:**
   Oxygen (O_2) from atmospheric air.

6. **External Circuit:**
   Electrons flow through the circuit to produce **usable power**.



Methanol-Oxygen fuel cell

Working Principle

The cell works on the principle of **redox reactions** where methanol undergoes oxidation at the anode and oxygen undergoes reduction at the cathode.

Cell Reaction

Anode Reaction (Oxidation)

Methanol is oxidized to carbon dioxide:

At anode: $CH_3OH + H_2O \longrightarrow CO_2\uparrow + 6H^+ + 6e^-$

- H^+ ions migrate through the PEM to the cathode.
- Electrons travel through the external circuit producing current.

Cathode Reaction (Reduction)

$$6H^+ + 6e^- + 3/2\ O_2 \longrightarrow 3H_2O\uparrow$$

Overall Cell Reaction

$$CH_3OH + 3/2\ O_2 \longrightarrow CO_2\uparrow + 2H_2O\uparrow$$

Advantages

- High energy density.
- Simple liquid fuel handling (methanol is easy to store & transport).
- Environment-friendly and efficient.
- It produces electric current directly from the reaction of a fuel and an Oxidiser.

Disadvantages

Not store electrical energy

- Pt catalysts are expensive.
- Methanol crossover through the membrane reduces efficiency.
- Slower reaction kinetics compared to H_2 fuel cells.

Applications

- Portable power supplies.

- Military communication devices.
- Backup power for remote stations.
- Small electronic gadgets.

Here is the transcribed text from the photocopy (corrected for spelling, grammar, and scientific accuracy where obvious):

FUELS

Introduction

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

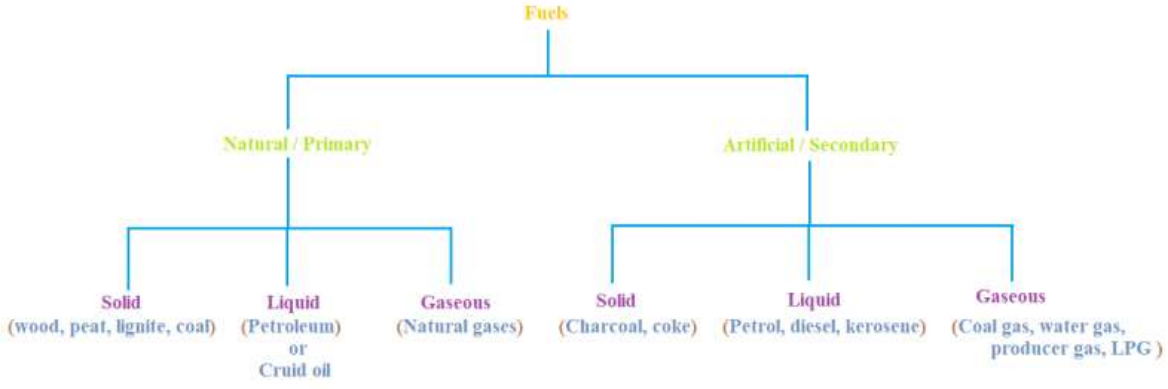
$$\text{Fuel} + O_2 \rightarrow CO_2 + H_2O + \text{Energy (Heat)}$$

Classification of Fuel

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

i) **Natural/primary fuels**: These fuels are naturally present.

ii) **Artificial/ secondary fuels**: They are synthesized by primary fuels.



Characteristics of a good fuel:

While selecting an ideal fuel for domestic or industrial purpose we should keep in mind that the fuel selected must possess the following characteristic properties.

1. It should possess high calorific value. If the calorific value of the fuel is high, the fuel is said to be more efficient.

2. It should not produce harmful combustion products like CO, SO_2, NO, H_2S, smoke and clinkers during combustion. In other words, it should not cause pollution on combustion

3. It should have low moisture and volatile content.

4. Fuel must be easily available in abundant and its cost must be minimum.

5. It should be easy to handle and transport.

6. It must have moderate ignition temperature and should leave less ash after combustion. (Ignition temperature is the minimum temperature to which the fuel is to be heated to start combustion.)

7. Combustion should be easily controllable i.e., combustion of fuel should be easy to start or stop as and when required.

8. Uniform size: In the case of a solid fuel, the size should be uniform so that the combustion is regular.

9. The combustion of a good fuel should not be explosive.

Calorific value:

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

There are different units for measuring the quantity of heat.

They are:

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

Inter conversion of various units of heat:

1 k.cal = 1000 cals = 3.968 B.Th.U = 2.2 C.H.U

Fuel calorific value is two types:-

• Gross calorific (or) higher calorific value (H.C.V)

• Net calorific value (or) lower calorific value (L.C.V)

Higher calorific value (HCV) or gross calorific value:

HCV is defined as "the total amount of heat liberated, when unit mass or unit volume of the fuel has been burnt completely and the products of combustion are cooled down to room temperature (60 0F or 15 0C)".

Lower calorific value (LCV) or Net calorific value (NCV):

LCV is defined as "the net heat produced, when unit mass or unit volume of the fuel is burnt completely and the combustion products are allowed to escape".

LCV = HCV – Latent heat of water vapour formed

N.C.V = gross calorific value – latent heat of vaporization.

latent heat of vaporization = [Mass of hydrogen per unit weight of fuel burnt ×9× latent heat of vaporization of water]

One part of H gives 9 parts of H_2O and latent heat of steam for water is 587 cal/g.

N.C.V = G.C.V- 9×(H/100) × 587

(Or)

N.C.V = G.C.V – 0.09×H×587 (Where H= % of Hydrogen in the fuel)

Fossil Fuels

Fossil fuels are non-renewable energy sources formed from the preserved remains of dead plants and dead animals that were buried under the Earth millions of years ago.

Due to high temperature and high pressure inside the Earth, these organic remains gradually transformed into coal, petroleum, and natural gas.

Liquid fuels:

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

Examples are: Petrol, Kerosene, diesel, cooking oil, etc.

On average the composition of petroleum is

C= 79.5-87.1% H= 11.5-14.8%

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

Refining of Petroleum:

The process of purification and separation of crude oil or petroleum into different fractions on the basis of their boiling points is known as refining or fractionation of petroleum. Refining is done in oil refineries.

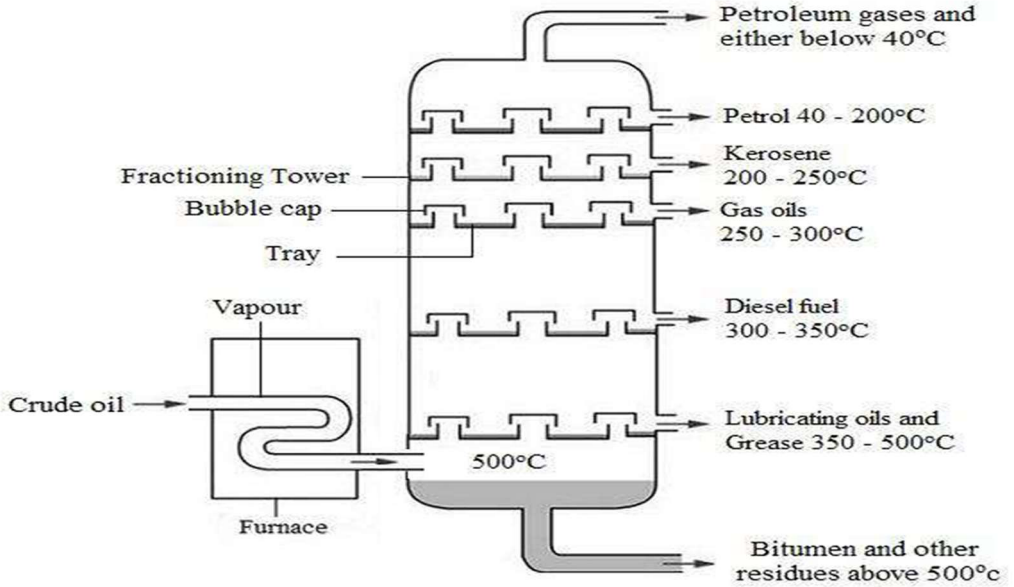
Refining of petroleum is done in different stages:

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

b. **Removal of water (Cottrell's process):**
The crude oil obtained from the earth's crust is in the form of stable emulsion of oil and brine (salt water). To separate water from crude oil, the crude oil is allowed to flow between two highly charged electrodes. The colloidal water droplets combine to form large drops and get separated from oil.

c. **Removal of sulphur compounds:**
To remove sulphur from the crude oil or petroleum, the crude oil is treated with copper oxide. The sulphur gets precipitated as copper sulphide and is separated by filtration.

d. **Fractional distillation:** Heating of crude oil around 400 0C in an iron retort, produces hot vapours which is allowed to pass through fractionating column. It is a tall cylindrical tower containing a number of horizontal stainless trays at short distances and is provided with small chimney covered with loose cap. As the vapours go up they get cooled gradually and fractional condensation takes place.



The vapours of the liquid having the highest boiling point are the first to condense and go out, and those which have the lowest boiling points go last, along with the uncondensed gases. The constituents of each fraction and the temperature at which they are obtained is given in Table 1 below:

Table – 1: Details of fractions obtained on distillation

Fraction	**Boiling Point Range (°C)**	**Number of Carbon Atoms**	**Uses**
Petroleum gas	< 40	1–4	Fuel; feedstock for petrochemicals
Gasoline / Naphtha	40–170	5–10	**Gasoline:** Fuel for automobiles; **Naphtha:** Feedstock for petrochemical industry
Kerosene	200–250	10–16	Jet fuel; domestic heating and cooking fuel
Diesel	300–350	11–18	Fuel for trucks, buses, tractors, and agricultural machinery
Fuel oil	350–450	20–25	Fuel for ships, industrial furnaces, and power plants
Residue	> 500	> 25	Lubricating oils, paraffin wax, bitumen (asphalt) for road construction

Cracking

Cracking is defined as the process of decomposition of higher molecular weight hydrocarbons (higher boiling) into lower molecular weight hydrocarbons (low boiling).

Example: Decane is cracking into pentane and pentene

$$C_{10}H_{22} \longrightarrow C_5H_{12} + C_5H_{10}$$

Cracking is mainly divided into two types –

1.Thermal cracking 2. Catalytic cracking Thermal cracking:

If the cracking takes place at high temperature, then it is thermal cracking.

Catalytic Cracking:

In this type of cracking catalysts are used. The suitable catalysts used are Al_2O_3 and $Al_2(SiO_3)_3$.

Catalytic cracking is of 2 types.

(i) Fixed bed cracking (ii) Moving bed catalytic cracking

Moving bed catalytic cracking or Fluid bed catalytic cracking

In this method the finely divided catalyst bed is fluidized by passing heavy oil or gas oil vapours, in a cracking chamber. The cracked vapours are sent into fractionating column to separate into gases, gasoline and un-cracked gases**.**

- In this process the solid catalyst (Al_2O_3 +SiO_2) is finely powered which act as a liquid and is circulated in gas stream.
- Heavy oil vapours and catalyst fluid are allowed into reactor at 500°c, cracking takes place , near top of the reactor there is centrifugal separator, which can allow only cracked vapours but not catalyst powder and carbon dust
- Cracked vapours passed through fractionating column and products are fractionated into gases, gasoline, gas oils and residual oils (unconverted).

- The un-cracked oils are further subjected to cracking.
- The deactivated catalyst is reached at bottom of reactor and regenerated by burning off (at 600°c), the carbon deposited and is mixed with fresh heavy oil and returned to the cracking chamber.

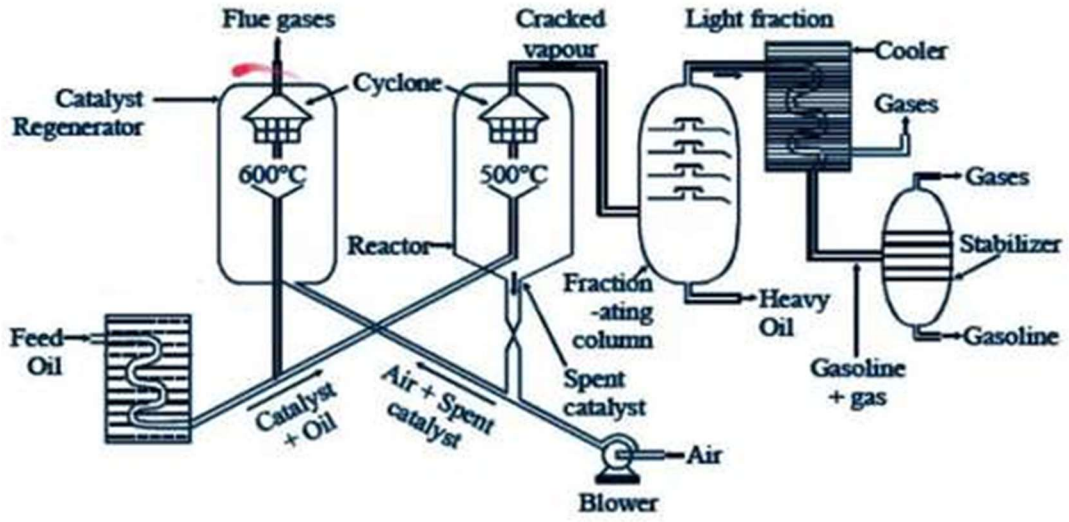


Figure: moving bed catalytic cracking.

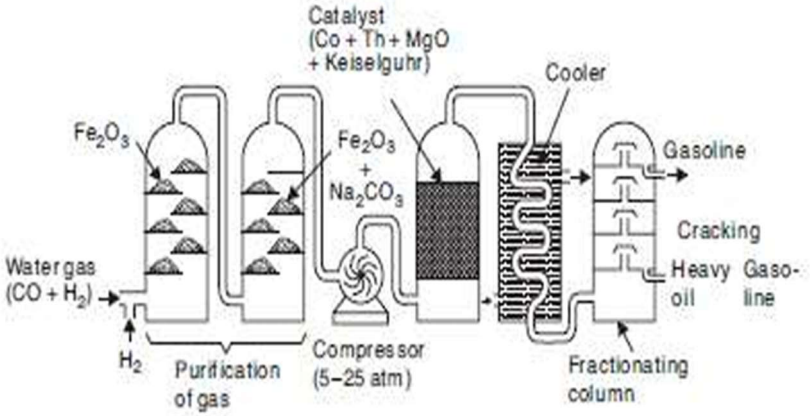
Synthetic petrol - Fischer-Tropsch's process

Fischer-Tropsch's process This method was developed by two German scientists Franz Fischer and Hans Tropsch.

The raw material i.e. hard coke is converted into water gas ($CO + H_2$) by passing steam over red hot coke**.**

$$C + H_2O \rightarrow CO + H_2 \text{ (water gas)}$$

A mixture of hydrogen and water gas is first purified by passing through Fe_2O_3 (to remove H_2S) and then into a mixture of $Fe_2O_3 + Na_2CO_3$ (to remove organic sulfur compounds).



The purified gas is compressed to 5-25 atm and then passed through a converter maintained at about 200-300^{0}C. The converter is packed with a catalyst consisting of a mixture of cobalt (Co, 100 parts), thoria (5 parts), magnesia (MgO, 8 parts) and keiselguhr earth (200 parts). Mixtures of saturated and unsaturated hydrocarbons are formed.

$$n\,CO + 2n\,H2 \rightarrow C_nH_{2n} + n\,H_2O$$

$$n\,CO + (2n+1)\,H_2 \rightarrow C_nH_{2n+2} + n\,H_2O$$

The reaction is exothermic as such the hot gaseous mixture is led to a cooler, where a liquid resembling crude oil is obtained. The crude oil obtained is then fractionated to yield: (i) Gasoline, and (ii) high- boiling heavy oil. The heavy oil is reused for cracking to get more gasoline

Gaseous fuels

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

a) Primary fuels Ex:- Natural gas

b) Secondary fuels ex: - Coal gas, producer gas, water gas.

Composition and uses of LPG (Liquefied Petroleum Gas)

Nowadays LPG has been a common fuel for domestic work and also in most of the industries. The main components of LPG are **n-butane, isobutane, butene and propane.**

The gas can be compressed under pressure in container and sold trade flames like Indian, hp, bharat gas etc---

LPG has special odour due to the presence of organic sulphides which are added specially for safety measure

- It has high calorific value: 27,800 kcal/m^3
- It gives less CO and least un-burnt hydrocarbons. So it causes least pollution
- It gives moderate heat which is very useful for cooking
- It has a tendency to mix with air easily, it is colourless
- Even though it is toxic, on combustion it gives no toxic gases
- It neither gives ash or smoke content
- It is cheaper than gasoline. Hence used as motor fuel
- It is dangerous when leakage is there. It is highly knock resistant
- LPG is used as domestic fuel and as a fuel in internal combustion engines

Composition and uses of CNG

Natural gas contains mainly CH_4. When natural gas is compressed at high pressure (1000atm) or cooled to -160^0C, it is converted to CNG.
It is stored in cylinder made of steel
It is now replacing gasoline (petrol) as it releases less pollutants during combustion c.n.g vehicles are used to reduce the pollution

Advantages of CNG:

- Due to higher temperature of ignition, CNG is better fuel than petrol and diesel.
- Operating cost of CNG is less. Cost of production is less. It can be easily stored.
- It releases least pollutants like CO and unburnt hydrocarbons.
- It undergoes regular combustion.
- The calorific value of CNG is 900KJ/mole
- It was used to generate electricity, heat buildings, fuel vehicles, power industrial furnaces and air conditioners.
- CNG vehicles are used to reduce pollution.

UNIT – IV

Polymers

Polymer:

The word "**poly**" means many and "**mer**" means unit

A polymer is a large molecule formed by repeating units of small molecules through covalent bonds.

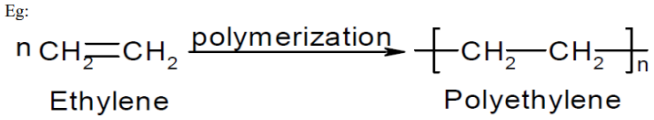
Monomer:

The simple molecule from which the polymer is formed is called monomer.

Degree of polymerization:

The number of monomeric units available in the polymer is known as degree of polymerization.

Eg:



n =Degree of polymerisation

Classification of Polymers:

1. Classification based on source of origin
2. Classification based on source of tacticity
3. Classification based on structure of monomer chain
4. Classification based on variety of monomers
5. Classification based on polymerization
6. Classification based on molecular forces

1. Classification of Polymers based on source of origin

a. Natural polymers: These are obtained from nature found in plants and animals. The polymers having **biological origin** are called natural polymers
Eg: Cotton, Wool, Silk, Natural Rubber, Starch, Cellulose, Protein etc.
b. Synthetic polymers: These have been prepared by humans in laboratories

(Manmade polymers).

Polymers which are **made in industry** from chemical substances are called synthetic polymers.

Eg: Polyethylene, Polyvinyl chloride (PVC), Bakelite, Teflon, Nylon-6,6 etc.

2. Classification of Polymers Based on Tacticity

Tacticity refers to the stereo chemical arrangement of side groups (substituents) along the polymer backbone. Based on tacticity, polymers are classified into three types.

i. Isotactic polymers,
ii. Syndiotactic polymers
iii. Atactic polymers

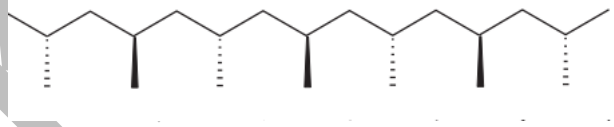
I. Isotactic Polymers

All the side groups are arranged on the same side of the polymer chain. The structure is highly regular. These polymers are generally highly crystalline.

Isotactic Polymer

II. Syndiotactic Polymers

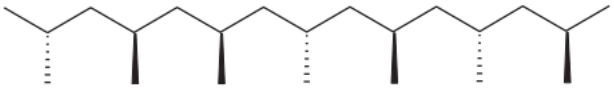
The side groups are arranged on alternate sides of the polymer chain. The structure is regular, but less than isotactic polymers.



Syndiotactic Polymer

III. Atactic Polymers

The side groups are arranged in a random manner along the polymer chain. The structure is irregular.



Atactic Polymer

3. Classification of Polymers based on structure of monomer

a. Linear Polymers: Monomers join with each other to form long straight chains.

Eg: Polyvinyl chloride, High-density polyethylene (HDPE), polystyrene and polypropylene.

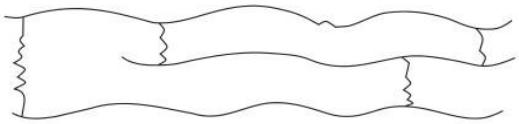
b. Branched Chain Polymers: In these polymers, monomers are joined to form long chains with side chains or branches of different lengths. They have low melting points and low densities.

Eg: Low-density polyethylene (LDPE).

c. Cross-linked Polymers/Network Polymers:

These polymers are formed by bifunctional and tri-functional monomers with a strong covalent bond between the various linear polymer chains.

Eg: Bakelite, melamine and formaldehyde resin.



4. Classification of Polymers based on variety of the monomers

a. Homo-polymer: When the same monomer is repeated throughout the chain of the polymer, it is called homo-polymer.

Eg: Polyvinyl chloride, Polyethylene and Teflon.

b. Hetero-polymer or Co-polymer: When there are at least two different monomers along the entire chain, it is called co-polymer.

Eg: Nylon 6, 6 and Terylene,

5. Classification of Polymers based on polymerization

a. Addition polymers Or Chain growth polymers:

Polymerization in which monomers are added together to form polymer without elimination of simple molecules is called addition polymerization and polymers are called addition polymers.

Eg: Polyvinyl chloride and Teflon

b. Condensation polymers:

Polymerization in which monomers are added together to form polymers with elimination of simple molecules like water, NH_3, HCl etc. is called condensation polymerization and polymers are called condensation polymers

Eg: Nylon-6,6 and Poly ethylene terephthalate (PET)

6. Classification of Polymers based on molecular forces

a. Thermoplastics: plastics which are softened on heating and harden on cooling are known as thermoplastics

Eg: Polyethylene, polystyrene, polypropylene.

b. Thermosets: Thermosets are the polymers that undergo chemical changes and crosslinking on heating and become permanently hard, rigid and infusible. They will not soften on heating, once they are set.

Eg: Bakelite, melamine.

c. Elastomers: Polymer chains that are elastic and can be stretched like rubber. They have weak intermolecular forces between the chains and may have cross bonds.

Eg: Vulcanized rubber.

d. Fibres: Fibres are long, thin, flexible materials composed of polymer chains that are highly oriented and arranged along the fibre axis, giving them high tensile strength and durability. They have Strong intermolecular forces between the chains.

Eg : Nylon, Polyesters, terylene etc

Types of polymerizations

a. Addition polymerization Or Chain growth polymerization:

Polymerization in which monomers are added together to form polymer without elimination of simple molecules is called addition polymerization and polymers are called addition polymers.

Eg: Polyethylene, Polyvinyl chloride (PVC)

$$n\,(CH_2{=}CH_2) \rightarrow (-CH_2-CH_2-)_n$$

Ethylene Polyethylene

$$n\,(CH_2{=}CHCl) \rightarrow (-CH_2-CHCl-)_n$$

Vinyl chloride Polyvinyl chloride

- Monomers must have either a double bond or triple bond (unsaturated compounds)
- Molecular weight of the resulting polymer product is the exact multiple of monomers molecular weight.
- In addition polymerization, no by products will be formed.

Mechanism of Addition Polymerisation (or) Free Radical Addition Mechanism

Mechanism of addition polymerisation can be explained by the free radical mechanism. Free radical polymerisation occurs in three major steps:

1. Initiation
2. Propagation
3. Termination

1. Initiation

Initiation involves two reactions.

a) Dissociation step:

First reaction involves production of free radicals by homolytic dissociation of an initiator to give a pair of free radicals (R•).

$$R-R \longrightarrow 2R^{\bullet}$$

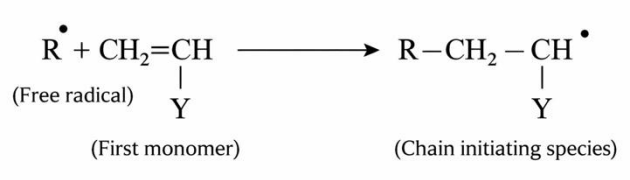
Initiator Free radicals

Initiators are the compounds which produce free radicals by homolytic dissociation.

Eg: Acetyl peroxide, Benzoyl peroxide are commonly used initiators

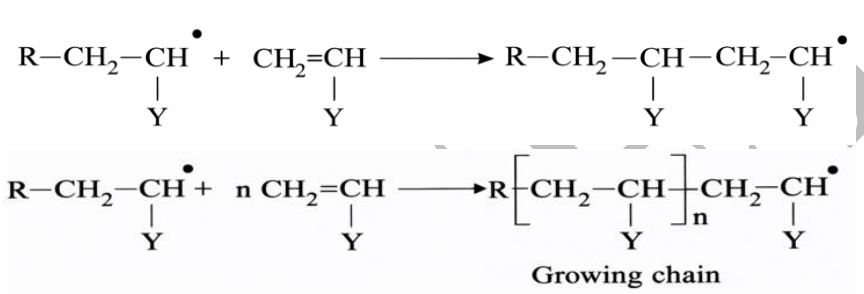
b) Association step:

Second reaction involves addition of this free radical to the first monomer to produce chain initiating species.



2. Propagation

It involves the growth of chain initiating species by the successive addition of large number of monomers.

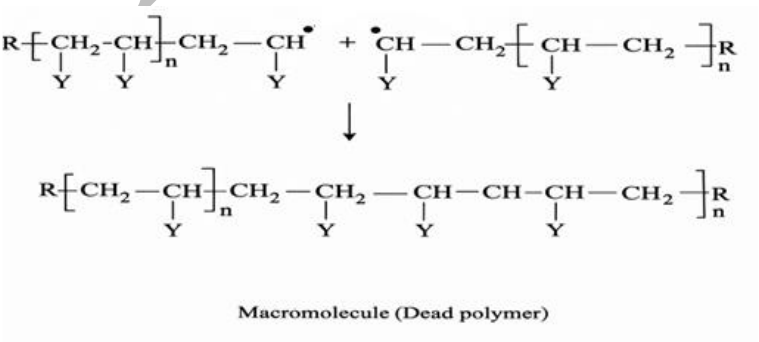


3. Termination

Termination of the growing chain of the polymer occurs either by coupling reaction or disproportionation.

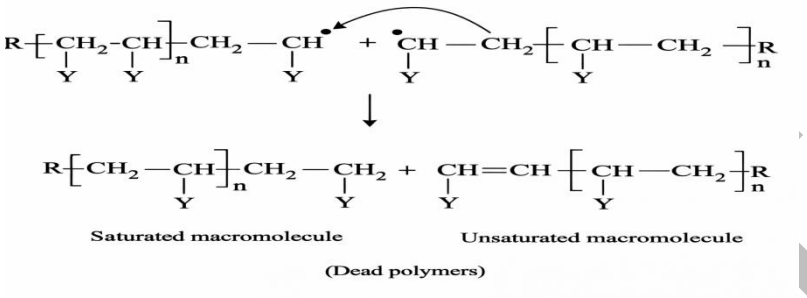
<u>Coupling (or) Combination:</u>

It involves coupling of free radical of one chain end to another free radical to form macromolecule (dead polymer).



Disproportionation:

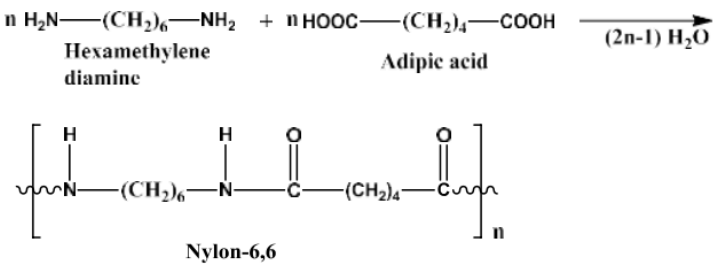
It involves transfer of a hydrogen atom of one radical centre to another radical centre forming two macromolecules, one saturated and another unsaturated.



b. **Condensation polymerization or Step growth polymerization:**

Polymerization in which monomers are added together to form polymers with elimination of simple molecules like water, NH_3, HCl etc. is called condensation polymerization and polymers are called condensation polymers

Eg: Nylon-6,6 and Bakelite



- Monomers must have two or more functional groups.
- The monomers contain functional groups like –COOH, -CHO, $-NH_2$, -OH, -COOR and halides etc
- In this polymerization by-products will be formed like H_2O, NH_3, HCl etc

Differences between addition and condensation polymerization:

S. No.	Addition polymerization	Condensation polymerization
1	It is also called as Chain growth polymerization	It is also called as step growth polymerization
2	Monomers are added together to form polymer without elimination of simple molecules	Monomers are added together to form polymers with elimination of simple molecules
3	Monomers must have either a double bond or triple bond	Monomers must have two similar or different functional groups
4	It results in no by-products.	It results in by-products such as ammonia, water and HCl.
5	Molecular weight of the polymer is an integral multiple of molecular weight of monomer	Molecular weight of the polymers need not be an integral multiple of monomer's
6	It follows three step mechanism of initiation, propagation and termination.	It not follows three step mechanism
7	Examples: Polyethene, polypropene, PVC, Teflon	Examples: Nylon-6,6, Bakelite

Plastics

- The word plastic was derived from the word **'Plastikos'** meaning **'to mould'** in Greek
- Plastics are high molecular weight organic materials which can be moulded into any desired shape by **the application of heat and pressure in the presence of catalyst**.

  Eg: Polyethylene, Polystyrene, Polyvinylchloride etc.

Characteristics of Plastics

- Lightweight, chemically stable.
- Poor conductors of heat and electricity
- Good insulation and low thermal conductivity.
- Easily moulded into different shapes and sizes.
- Resist corrosion and are resistant to many chemicals.
- Good impact resistance and they do not rust.

- Tensile strength, good transparency, and wear resistance.
- Waterproofing, low processing cost.

Classification of Plastics

Depending on thermal properties, the plastics are divided into two types.

1. Thermoplastic polymers:

Thermoplastics are the polymers that become soft on heating and hard on cooling and the process can be repeated for a number of times.
Eg: Polyethylene, Polystyrene, PVC, and Polypropylene.

2. Thermosetting polymers

Thermosetting polymers are polymers that, once heated, form a rigid, cross-linked structure that cannot be softened or reshaped on further heating.
Eg: Bakelite (Phenol formaldehyde resin), Urea formaldehyde resin, and Nylon-6,6.

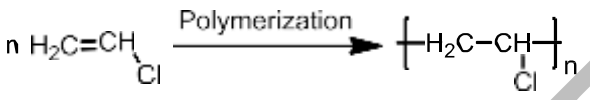
Differences between *Thermoplastics* and *Thermosetting* polymers:

	Thermoplastic polymers	**Thermosetting polymers**
1	These polymers become soft on heating and rigid on cooling	These polymers are moulded by heating. Once they are solidified, they cannot be softened by heating again
2	They are formed by addition (Chain) polymerization	They are formed by condensation (Step-growth) polymerization
3	They can be reclaimed from waste	They can't be reclaimed from waste
4	These are linear polymers without any crosslinking.	These are three dimensional crosslinked polymers.
5	They can be reshaped	They can't be reshaped
6	These resins are usually soluble in suitable organic solvents	Due to strong bonds and cross-links, they are insoluble in all organic solvents
7	Polymeric chains are held together by Weak vanderwaals forces	Polymeric chains are held together by strong Covalent bonds in the form of cross links.
8	They are weak, soft and less brittle.	They are usually hard, strong and more brittle.
9	Ex: Polyethylene, PVC, Polystyrene etc.	Ex: Nylon-6,6, Bakelite etc.

POLYVINYL CHLORIDE (PVC)

Preparation:

Polyvinyl chloride is a thermoplastic addition polymer. PVC is produced by heating vinyl chloride in the presence of benzyl peroxide or H_2O_2.



Vinyl Chloride **PVC**

Properties:

- PVC is colourless, odourless and non-flammable thermoplastic polymer.
- It is strong, durable, and lightweight.
- It is a chemically inert and highly resistant to acids, alkalis and oils.
- It has a melting point at **160^0C.**
- It is a good electrical insulator and exhibits high resistance to moisture.

Applications:

- PVC is used in the production of toys, food and beverage **packaging.**
- It is mainly used for making **sheets** used to line big containers, tanks etc.
- PVC is used as insulation for electrical **cables** and **wires**.
- Plasticized PVC is used for making rain coats, table-cloths, curtains, jackets and bags.
- Other materials like refrigerator components, tray, cycle and motor cycle mud guards, tubes, **pipes** etc are also manufactured.
- Soft PVC is used in medical devices such as IV tubing, blood bags.

Fibres

Fibres can be generally defined as the thread-like structures that are thin, long, and flexible strands. The two main sources of Fibres are plants and animals.

Fibres possess high tensile strength because the chains possess strong inter molecular forces such as hydrogen bonding.

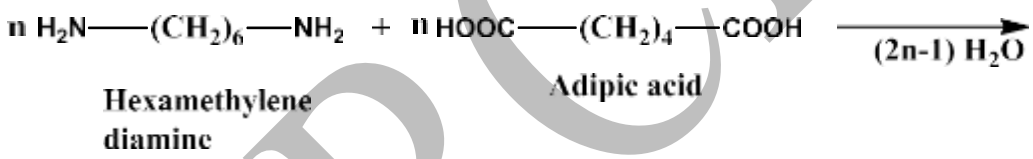
Eg: Nylon-6,6, terylene, wool, cellulose and polyesteretc.

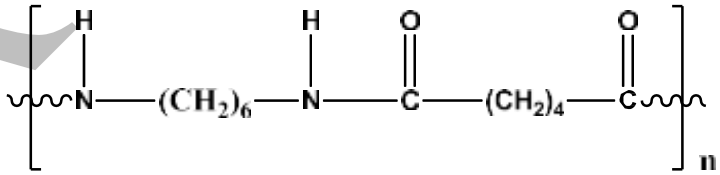
Characteristics of fibres

- Strong
- Good fibrE must be aninsulator
- Resistant to stretching and shrinkage
- Must absorb color easily, Washable or dry-cleanable
- Quick drying
- Resistant to corrosion
- Resistant to most chemicals

Nylon-6,6:

Preparation: It is a polyamide. It is prepared by the condensation of hexamethylenediamine and adipic acid.





Nylon-6,6

Properties:

- They are insoluble in common solvents and dissolve only in phenols and formicacid.
- They possess high temperature stability and high melting point (>500 ^{o}C).
- They have low density and absorb moisture.
- They have good mechanical strength and self-lubricating properties.
- They are light, flexible and retain their original shape after use.

Applications:

1. The major application is in textile industry.
2. They are used in making socks, dresses, nets, carpets and ropes.
3. They can be blended with wool.
4. Because of its high thermal & abrasion resistance nylons are used in automobile industry (gears, bearings, radiator parts).
5. Nylons are used as electrical insulators.
6. They are also used for making bristles for tooth brushes, films, carpet fibres and airbags.

Elastomers

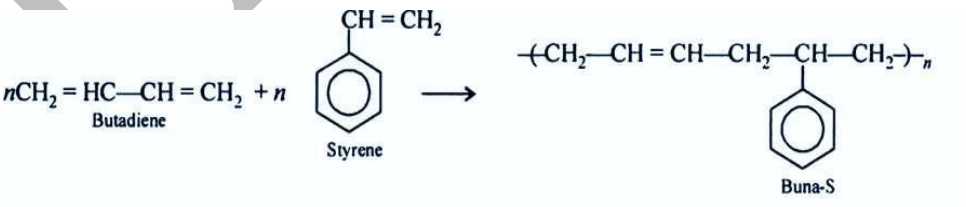
Elastomers are a class of polymers that exhibit high elasticity, meaning they can be stretched significantly and return to their original shape when the applied force is removed.
Eg: Natural Rubber, Buna-S, Buna-N, Neoprene

Characteristics

- ❖ Highly elastic and flexible
- ❖ Can undergo large deformation and recover their original shape
- ❖ Have low intermolecular forces compared with rigid polymers
- ❖ Usually possess light cross-linking between polymer chains
- ❖ Generally have a low glass transition temperature (Tg)

Styrene rubber (Buna-S):

Preparation:
It is prepared by the co-polymerization of emulsion of butadiene (about 75% by weight) and styrene (about 25% by weight) in the presence of peroxide or Na.



BUNA-S stands for the composition of the monomers and catalyst.

"Bu" stands for the Butadiene – monomer

"Na" Stands for the sodium–Catalyst.

"S" stands for the Styrene– monomer.

Properties:

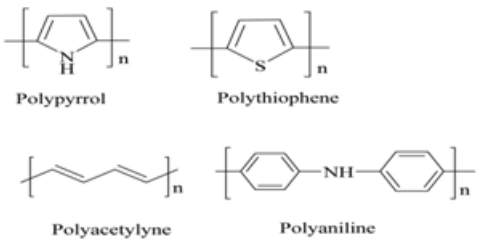
- ❖ It possesses high abrasion resistance, high load bearing capacity.
- ❖ It gets readily oxidized especially in presence of traces of ozone present in the atmosphere.
- ❖ Relatively poor resistance to oils and organic solvents.
- ❖ It has good elasticity.
- ❖ It is a good electrical insulator.

Uses:

- ❖ It is used for the manufacture of car, bike and cycle tyres.
- ❖ Other uses of this elastomer are floor tiles, shoe soles, foot wear components, gaskets, wire and cable insulations, adhesives, tank-lining, carpet backing, conveyor belts, brake and clutch pads.

CONDUCTING POLYMERS

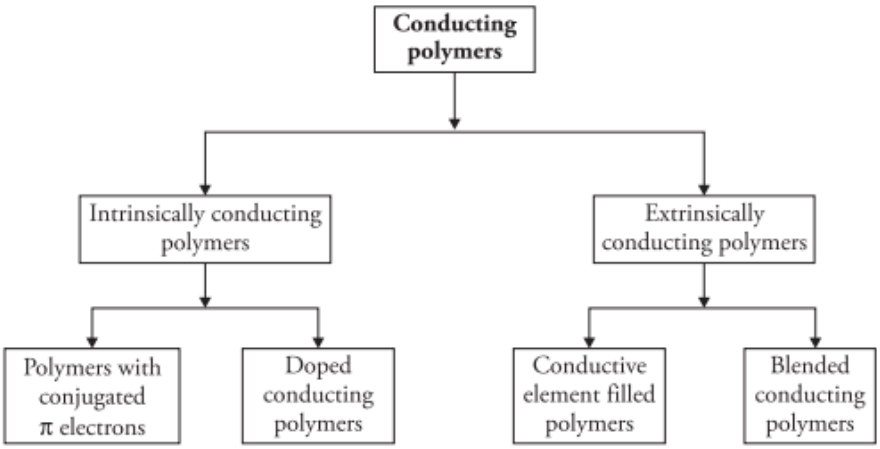
❖ Conducting polymers are organic polymers that can conduct electricity.
❖ They exhibit electrical and optical properties similar to metals and semiconductors, making them useful in various applications.
❖ These polymers achieve conductivity through a conjugated pi-electron system in their backbone, which allows for the movement of electrons when doped or under an electric field.
❖ Examples: Polyaniline, Polypyrrole, Trans polyacetylene.



Characteristics of Conducting Polymers:

1. Conductivity polymers have high melting and softening points
2. They are insoluble in many common solvents.
3. Conductivity polymers show excellent chemical, thermal, and oxidative stability due to low hydrogen content and aromatic structure.
4. They can be processed into a highly ordered crystalline thin film that is electrically conducting upon doping.

Classification of Conducting Polymers:



Intrinsically conducting polymers:

The polymers have extensive conjugation in the backbone which is responsible for conductance. They are further of two types.

a. **Conjugated π-electron conducting polymers**:

The conductivity of these polymers is due to the presence of conjugated π-electrons. The conjugated π-electrons are delocalized. Ex: polyacetylene, polyaniline, polypyrrole.

Explanation: Overlapping of conjugated π-electrons over the entire backbone results in the formation of valence bands as well as conduction bands that extends over the entire polymer molecule. The valence band and the conduction bands are separated by a significant band gap. Thus, electrical conduction occurs only after thermal or photolytic activation of electrons to give them sufficient energy to jump the gap and reach into the lower levels of the conduction band.

b. Doped conducting polymers:

The conducting polymers having conjugated π-electrons in their backbone structure can be easily oxidized or reduced. Hence the conductance can be increased by creating positive or negative charge on polymer backbone by oxidation or reduction. The polymers are doped by adding either electron donors or electron acceptors on the polymeric backbone. Doping can be of two types.

(i) **p-type doping:** When the polymer is treated with a Lewis acid, its oxidation takes place and holes (positive charges) are created on the polymer backbone. Commonly used p-dopants are I_2, Br_2, $FeCl_3$, AsF_5, etc.

(ii) **n-type doping:** When the polymer is treated with Lewis base, reduction takes place and negative charges are added on the polymeric chain. Some common n-type dopants are Li, Na, sodium naphthalide, etc.

Extrinsically conducting polymers:

The conductivity of these polymers is due to presence of externally added ingredients. They are of two types.

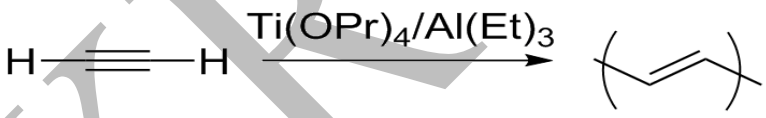
(a) Conductive element-filled polymers: When the polymer is filled with conducting elements like carbon black, metallic fibres, metal oxides, their conductivity rises. Here the polymer acts as the binder of the conducting elements. Ex: Carbon Black-Filled-Polymer Matrix: Polyethylene (PE), Polypropylene (PP), Polystyrene (PS).

(b) Blended conducting polymer: Conducting polymers are added to conventional polymers. The blended polymers have better physical, chemical and mechanical properties. Ex: Polyaniline (PANI) blends with Polyvinyl chloride (PVC).

POLYACETYLENE

Preparation:

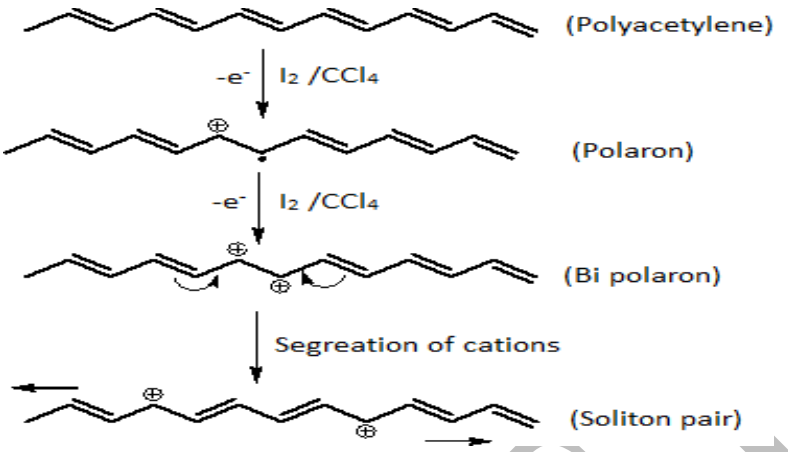
Polymerization of acetylene over Zeigler Natta catalysts (Titanium Isoprpoxide and Triethyl Aluminium) gives polyacetylene.



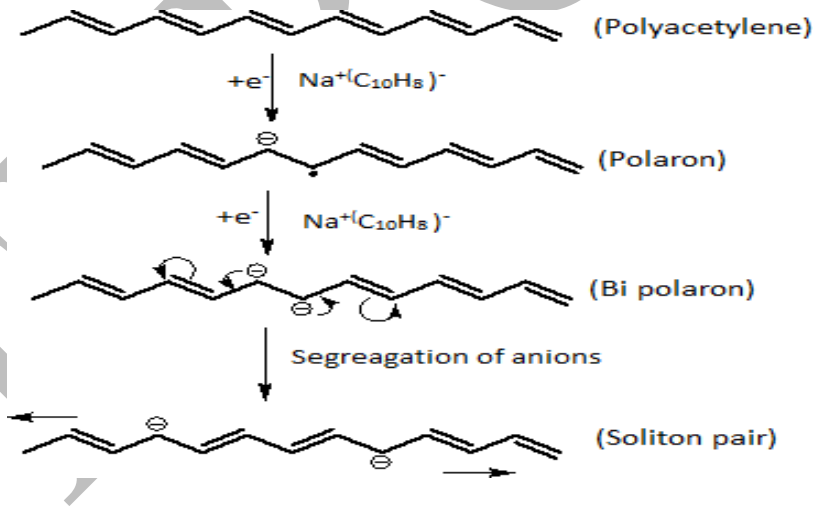
MECHANISM OF CONDUCTION IN TRANS-POLYACETYLENE

- Trans-polyacetylene exhibits a unique conducting mechanism due to its structure and the effects of doping. There are two types of doping
  p-doping (oxidation)
  n-doping (Reduction)

a) p-doping: In p-doping, conducting polymer having conjugation is partially oxidized using a suitable oxidizing agent like I_2 vapour or I_2 in CCl_4. This is called p-doping or oxidative doping. During the oxidation process the removal of pi electron from polymer backbone leads to the formation of delocalized radical cation called 'Polaron'. The second oxidation of the polaron results in two positive charges in each chain called bipolaron. These delocalized positive charges are current carriers for conduction.



b) n-doping: n-doping is done by reduction process. It involves the treatment of an intrinsically conducting polymer with a Lewis base like Na, Li, sodium naphthalide. n-doping leads to the formation of polaron and bipolaron in two steps. This followed by recombination of radicals yields two negative charge carriers on each chain of polyacetylene which are responsible for conduction.



UNIT – V

Advanced Functional Materials

Introduction to Smart Materials

Smart materials are advanced materials that can **sense changes in their surroundings and respond automatically** in a useful and controlled manner. They represent the latest development in material science, following the Plastic Age and Composite Age. Unlike conventional materials, smart materials possess the ability to adapt their properties when exposed to external or internal stimuli.

These stimuli may include **temperature, pressure, stress, strain, electric field, magnetic field, light, and chemicals**. Due to their adaptive behavior, smart materials are also known as **intelligent materials**. They combine sensing and actuation capabilities, making them multifunctional and highly efficient.

Smart materials are widely used in engineering applications such as **sensors, actuators, aerospace, biomedical devices, robotics, civil structures, and electronics**. Their ability to improve performance, reliability, and safety has made them one of the most important classes of modern engineering materials.

Smart materials:

Smart materials, also called intelligent or responsive materials, are designed materials that have one or more properties that can be significantly changed in a controlled fashion by external stimuli, such as stress, moisture, electric or magnetic fields, light, temperature, pH, or chemical compounds.

The several external stimuli to which the smart materials sensitive are:

- Stress
- Temperature
- Moisture
- pH
- Electric Fields
- Magnetic Fields

Three basic components of a smart system are:

- Sensor
- processor
- Actuator

Example: Smart concrete building (suitable to earthquake areas)
Sensor: optical fibers (embedded in concrete)
Processor: smart wires (automatic shrink/expand)
Actuator: chemically active smart materials (fillers preventing crack propagation**)**

External Stimulus	Smart Material	Resulting Response
Mechanical Stress / Electric Field	**Piezoelectric Material**	Produces electrical charge or mechanical deformation
Electric Field	**Electro-rheological Fluid**	Changes its viscosity (flow resistance)
Magnetic Field	**Magnetostrictive Material**	Undergoes mechanical deformation (strain)
Heat / Temperature	**Shape Memory Alloy (SMA)**	Recovers its original pre-set shape
Temperature / Pressure Mechanical Strain	**Optical Fiber Sensor**	Converts physical changes into optical signals

Table: Common smart materials and associated stimulus-response

Classification of Smart Materials

Smart materials are classified into **two types** based on their ability to respond to external stimuli.

1. Active Smart Materials

Active smart materials can **sense a change in the environment and produce a response by converting one form of energy into another**. They can change their shape, size, or other properties when exposed to **electric, magnetic, or thermal (heat) fields**. Since they can convert energy, they are used as **actuators** (to produce motion) and **transducers** (to convert one form of energy into another).

Examples: Piezoelectric materials, Shape Memory Alloys (SMAs), Magnetostrictive materials

2.Passive Smart Materials

Passive smart materials can **detect or sense changes in the environment but cannot convert energy or produce mechanical action**. They mainly function as **sensors** by monitoring changes such as temperature, pressure, or strain.

Example: Optical Fibres

Types of Smart Materials

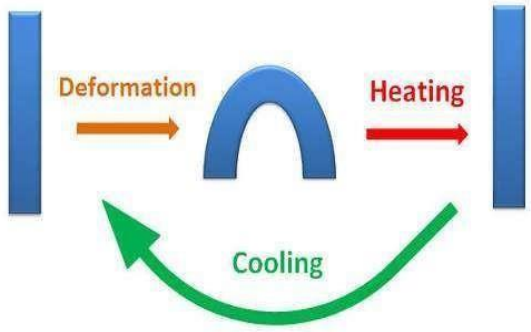
1. Piezoelectric Materials
2. Shape Memory Alloys
3. Magnetostrictive Materials
4. Electrostrictive materials

- **Shape Memory Alloys**

Shape Memory alloys are metals that exhibit the properties of pseudo-elasticity and the Shape Memory Effect.

- Shape memory alloys are smart materials
- A shape memory alloys (SMA) are metal alloys that can be deformed at one temperature but when heated or cooled, return to their "original shape".
- Shape Memory Alloys are materials that "remember" their original shape.
- If deformed, they recover their original shape upon heating.
- They can take large stresses without undergoing permanent deformation.
- They can be formed into various shapes like bars, wires, plates and rings thus serving various functions.
- SMA also exhibits super elastic (Pseudo elastic) behaviour.
  The high temperature causes the atoms to arrange themselves into the most compact and regular pattern possible.

Shape Memory Effect – unique ability of materials to be severely deformed and then return to their original shape through stimulus
SME occurs due to the change in the crystalline structure of materials.



Working Principle

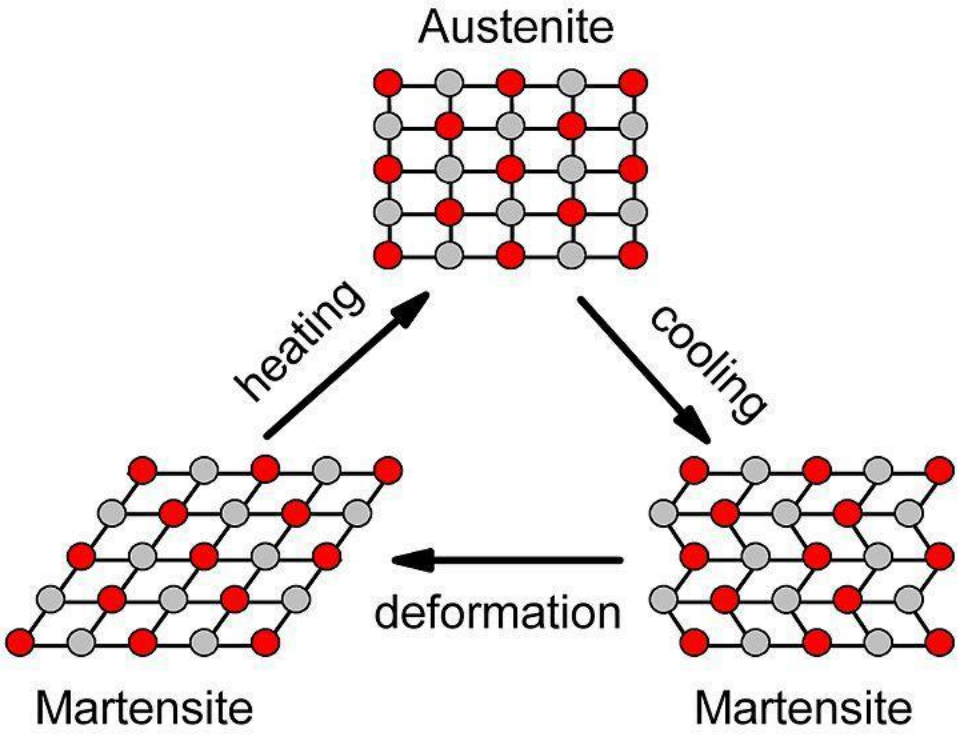
- SMAs have two stable phases are:
- Martensite: Low temperature phase, relatively weak
- Austenite: High temperature phase, relatively strong
- Martensite to Austenite transformation occurs by heating
- Austenite to Martensite occurs by cooling.

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

When subjected to a thermal field, this material will undergo phase transformations which will produce shape changes. It deforms to its **'martensitic'** condition with low temperature, and regains its original shape in its **'austenite'** condition when heated (high temperature).

Examples:

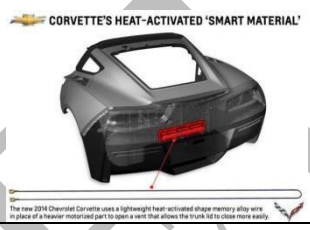
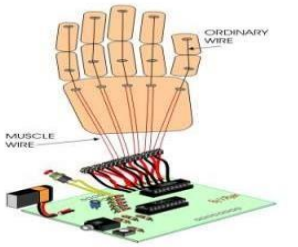
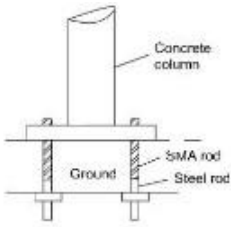
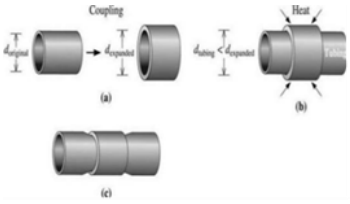
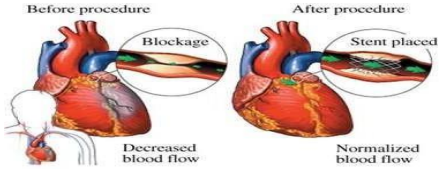
- **Nickel-Titanium alloys (NiTinol)**
- Copper -Aluminium- Nickel alloys
- Copper Zinc-Aluminium alloys
- Iron -Manganese-Silicon alloys



NiTinol: Nickel–titanium alloys have been the most used shape memory material. This family of nickel–titanium alloys is known as **Nitinol,** after the laboratory where this material was first observed (Nickel Titanium Naval Ordinance Laboratory).

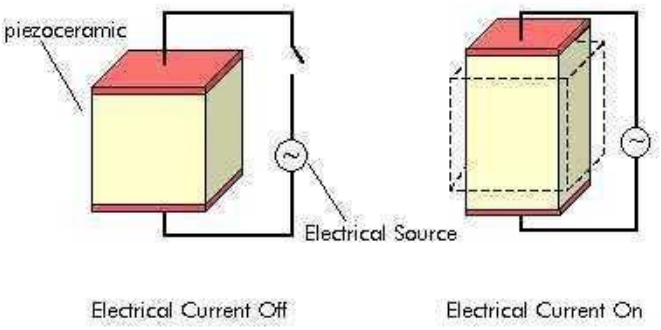
Applications of Smart memory alloys

Nitinol has been used in military, medical, safety, and robotics applications. Specific applications include hydraulic lines on F-14 fighter planes, medical tweezers and sutures, anchors for attaching tendons to bones, stents for cardiac arteries, eyeglass frames, and antiscalding valves in water faucets and showers

S.No	Application	Image
1)	**Aircraft:** Alloys can be used to create flexible wings in aircrafts using Shape Memory wires	
2)	**Automotive:** To reduces engine noise, some designers install chevrons onto engines to mix the flow of exhaust gases and reduces engine noise.	
3)	**Robotics: Muscle Wires:** SMAs are very good at mimicking human muscles and tendons so they can be used to create humanlike movements in robots	
4)	**Civil Structures:** SMAs find a variety of applications in civil structures such as bridges and buildings. One such application is Intelligent Reinforced Concrete (IRC), which incorporates SMA wires embedded within the concrete.	
5)	**Piping:** The first consumer commercial application was a shape-memory coupling for piping, e.g. oil line pipes for industrial applications, water pipe	
6)	**Medicine:** Stent-A reinforced grafts for vascular application to replace or repair damaged arteries (25mm diameter)	

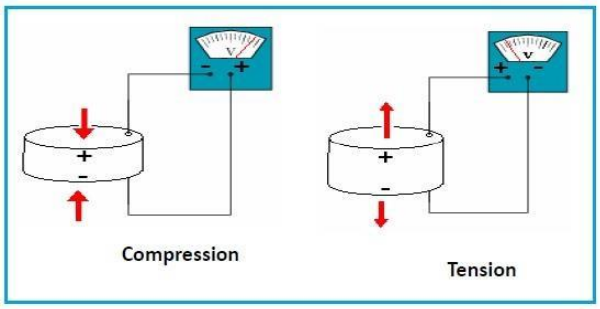
➢ Piezoelectric Materials

- The word originates from the Greek word **"piezein"**, which means **"to press".**
- Piezoelectrics are materials that can create **electricity** when subjected to a **mechanical stress.**
- They will also work in reverse, generating a **strain** by the application of **an electric field.**
- Piezoelectric effect: When subjected to an electric charge or a variation in voltage, piezoelectric material will undergo some mechanical change, and vice versa. These events are called the direct and converse effects.
- All piezoelectric materials are non-conductive in order for the piezoelectric effect to occur and work. They can be separated into two groups: crystals and ceramics.



Working Principle Piezoelectric effect

Piezoelectric effect is the ability of certain materials to generate an electric charge in response to applied mechanical stress



Piezoelectric material will generate electric potential when subjected to some kind of mechanical stress.

Devices that use the direct piezoelectric effect include microphones, pressure sensors, hydrophones, and many other sensing types of devices.

Piezoelectric Materials

Definition

Piezoelectric materials are **smart materials** that generate an **electric charge when mechanical stress (pressure, force, or vibration) is applied**. They also exhibit the **reverse piezoelectric effect**, in which they undergo mechanical deformation when an electric field is applied.

The word **piezo** comes from the Greek word *piezein*, meaning **"to press or squeeze."**

Piezoelectric Effect

The piezoelectric effect is of **two types**:

1. Direct Piezoelectric Effect

When mechanical stress is applied to a piezoelectric material, it produces an electrical voltage.

Mechanical Stress → Electrical Energy

Example: Pressure applied on quartz crystal generates electric charge.

2. Inverse (Reverse) Piezoelectric Effect

When an electric field is applied to a piezoelectric material, it changes its shape or dimensions.

Electrical Energy → Mechanical Strain

Example: Quartz crystal vibrates when an alternating voltage is applied.

- **Quartz (SiO_2) as a Piezoelectric Material**

Quartz is one of the most commonly used **natural piezoelectric materials**. It consists of **silicon dioxide (SiO_2)** arranged in a crystalline structure.

Properties of Quartz

- Naturally occurring piezoelectric crystal.
- High mechanical strength.
- Excellent electrical insulation.
- Chemically stable and corrosion resistant.
- High frequency stability.
- Durable and reliable over a wide temperature range.

Working Principle of Quartz

When a force is applied to a quartz crystal, the positive and negative charges inside the crystal become separated, producing a potential difference across its surfaces.

Similarly, when an electric voltage is applied, the crystal expands and contracts, producing mechanical vibrations.

Advantages of Piezoelectric Materials

- High sensitivity.
- Fast response.
- Compact size.
- High accuracy.
- No external power required for sensing.
- Long service life and high reliability.

Limitations

- Produce only a small electrical output.
- Suitable mainly for dynamic (changing) forces.
- Brittle in nature.
- Performance decreases at very high temperatures.

Applications of Piezoelectric Materials (Quartz)

1. **Pressure Sensors** – Used to measure pressure, force, and strain.
2. **Ultrasonic Transducers** – Used in ultrasonic cleaning, welding, and medical imaging.
3. **Microphones** – Convert sound vibrations into electrical signals.
4. **Buzzers and Speakers** – Convert electrical energy into sound.
5. **Quartz Watches and Clocks** – Quartz crystals provide accurate timekeeping by vibrating at a constant frequency.
6. **Medical Equipment** – Used in ultrasound scanners for diagnostic imaging.
7. **Vibration Sensors** – Used in industrial machinery for condition monitoring.
8. **Sonar Systems** – Used for underwater navigation and depth measurement.
9. **Ignition Systems** – Used in gas lighters and gas stoves to generate sparks.
10. **Energy Harvesting Devices** – Convert mechanical vibrations into electrical energy for low-power electronic devices.

Biosensors

Definition

A biosensor is an analytical device that converts a biological reaction into an electrical signal. It is used to detect specific substances accurately.

Biosensors are modern analytical devices used for fast and accurate detection of substances.

They play an important role in healthcare, industries, and environmental monitoring.

Biosensors combine a biological sensing element with a transducer. They are more sensitive and selective than many conventional diagnostic devices.

They are widely used in medical field, food industry, agriculture, and environmental monitoring.

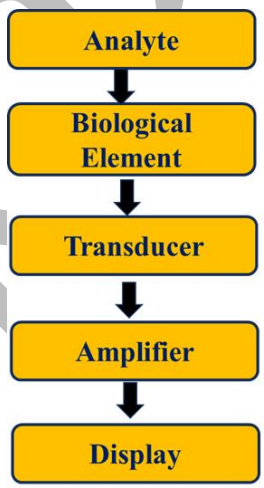
Main Components of a Biosensor

1. Biological Element (Sensor): Recognizes the analyte. Examples: enzymes, antibodies, nucleic acids, cells.

2. Transducer: Converts the biological response into an electrical signal.

3. Signal Processor / Display: Amplifies the signal and displays the result.

Block Diagram



Working Principle

1. The analyte comes in contact with the biological element.

2. A biochemical reaction takes place.

3. This reaction produces changes like electrons, heat, ions, or gas.

4. The transducer converts these changes into an electrical signal.

5. The signal is amplified and displayed as output.

- **Types of Biosensors**
  - **Based on Transducer:**
  1. Electrochemical Biosensors
  2. Optical Biosensors
  3. Thermal Biosensors
  4. Piezoelectric Biosensors

- **Electrochemical Biosensors are of four types:**
  - Amperometric Biosensors
  - Potentiometric Biosensors
  - Impedimetric Biosensors
  - Voltammetric Biosensors

- **Amperometric Biosensor**

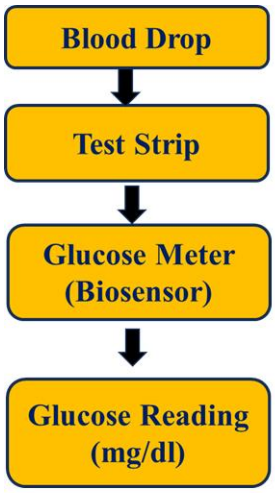
Definition

An amperometric biosensor measures the **current produced during oxidation or reduction reaction**.

Working

- Uses working, reference, and counter electrodes.
- When analyte reacts, electrons are produced.
- Current generated is proportional to analyte concentration.

Example: Glucose meter



- A **glucose meter** is a device used to measure sugar level in blood.
- It is mainly used by people with **diabetes**.
- It helps to monitor blood glucose regularly.
- A small drop of blood is placed on a **test strip**.
- The strip is inserted into the glucose meter.
- The meter uses a **biosensor** to detect glucose level.
- It shows the result on the screen within a few seconds.
- It is small, portable, and easy to use at home.
- Regular checking helps control diabetes and avoid complications.
- Glucose meters are widely used in hospitals and homes

Advantages of Biosensors

- High sensitivity
- High selectivity
- Fast response
- Portable size
- Low cost
- Reproducible results

Applications of Biosensors

- Blood glucose monitoring
- Disease diagnosis
- Food quality testing
- Pollution control
- Agriculture testing

- Marine analysis

Biosensors are modern analytical devices used for fast and accurate detection of substances. They play an important role in healthcare, industries, and environmental monitoring.

CEMENT

Cement is a dirty greenish powder which finds its importance as a building material.

It is described as a material which possesses adhesive property to bind rigid masses like stones, bricks, building blocks etc.

Cement is hydraulic in nature i.e., it possesses the property of setting and hardening in the presence of water.

Classification of cement

1. **Natural cement:** it is prepared by the reaction between clay and lime stone, during the reaction calcium reacts with silicates and aluminum present in clay to form calcium silicates and calcium aluminates.
2. **Puzzalona cement:** It is prepared from ash of lava. This ash contains silica and alumina which is on reaction with lime (CaO) forms calcium silicates and aluminates.
3. **Slag cement:** It is prepared from slag which is obtained from furnace ash. This slag contains silica and alumina which is on reaction with lime (CaO) forms calcium silicates and aluminates.
4. **Portland cement:** It is made by calcining (at 1500^{o}C) an intimate mixture of clay and lime containing raw materials in correct proportion. After calcinations gypsum is added.

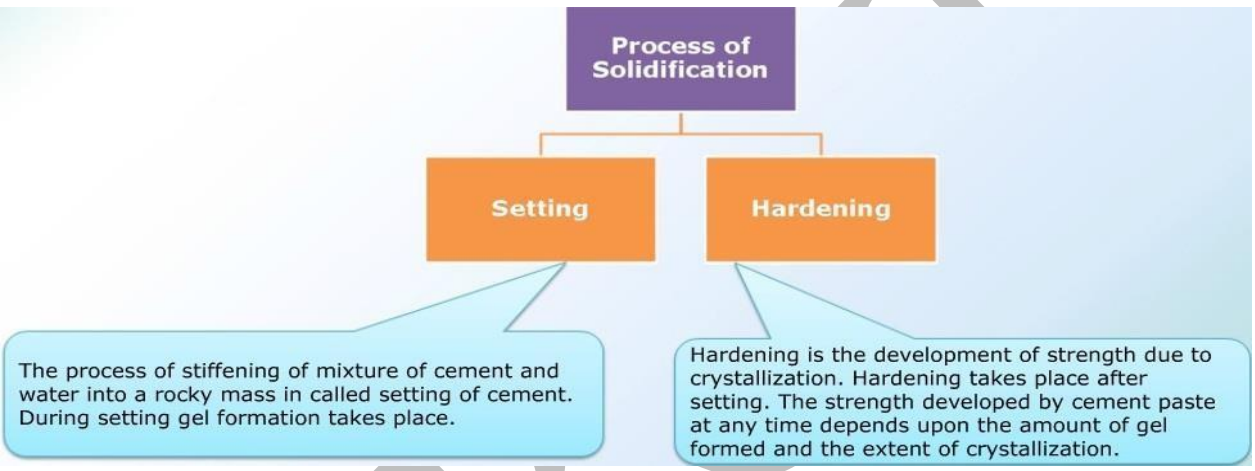
Composition of Portland cement

Calcium Oxide or Lime (CaO)	=	60-70%
Silica SiO_2	=	20-24%
Alumina (Al_2O_3)	=	5-7.5%
Magnesia (MgO)	=	2-3%
Ferric Oxide (Fe_2O_3)	=	1-2.5%
Sulphur Trioxide (SO_3)	=	1-1.5%
Sodium Oxide (Na_2O)	=	1%

Potassium Oxide (K_2O) = 1%

Setting and Hardening of Cement

- When cement is mixed with water, a plastic mass known as cement paste is formed. This results in the formation of gel and crystalline products which surround sand, crushed stones and other inert materials and bind them very strongly.
  - The process of solidification of cement comprises of:



The chemical reactions that take place during setting and hardening are:

- Initial setting of cement involves the hydration of tricalcium aluminate resulting in the formation of crystalline hydrated tricalcium aluminate. This is called set or flash set.

$$3CaO.Al_2O_3 + 6H_2O \longrightarrow 3CaO.Al_2O_3.6H_2O + 880\ KJ/Kg$$

- Tetra calcium alumino ferrite present in cement reacts with water forming gels and crystalline compounds.

$$4CaO.Al_2O_3.Fe_2O_3 + 7H_2O \longrightarrow 3CaO.Al_2O_3.6H_2O + CaO.Fe_2O_3.H_2O + 420\ KJ/Kg$$

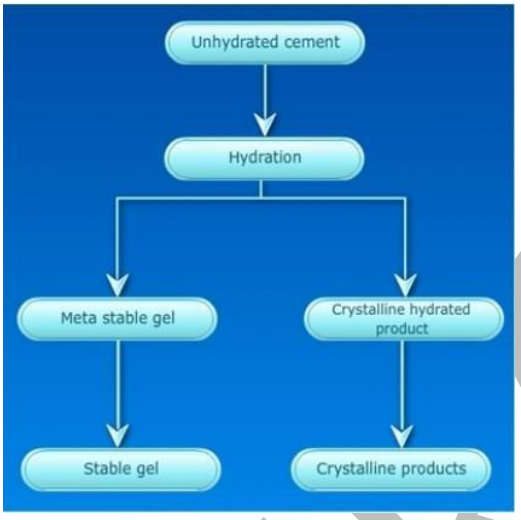
- In the second step gelation takes place in which tobermonite gel is formed.

- $2[2CaO.SiO_2] + 4H_2O \longrightarrow 3CaO.2SiO_2.6H_2O + Ca(OH)_2 + 250\ KJ/Kg$

- In this reaction dicalcium hydrolyses to give tobermonite gel which shows high adhesive property due to high surface area.
- Final setting and hardening of cement paste is due to the formation of tobermonite gel and crystalline of calcium hydroxide and hydrated tricalcium aluminate.

$$2[2CaO.SiO_2] + 6H_2O \longrightarrow \underset{\text{Tobermonite gel}}{3CaO.2SiO_2.3H_2O} + Ca(OH)_2 + 500\ KJ/Kg$$

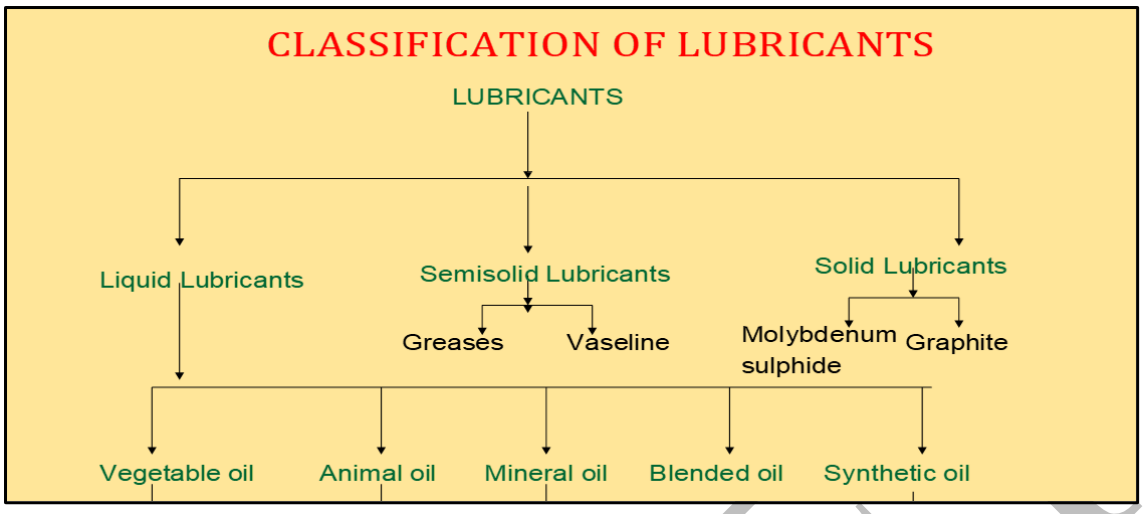
The setting and hardening of cement can be shown as



Lubricants

Introduction

- When one solid surface is sliding past over another solid surface, friction and wear is developed due to relative motion of two contacting surfaces which results in loss of energy as heat.
- As the equipment gets heated up it is damaged and sometimes results in welding or seizure.
- Any substance introduced between two moving or sliding surface with a view to reduce the frictional resistance between them is known as lubricants.
- The process of reducing frictional resistance between moving or sliding surface by the introduction of lubricants in between them is called lubrication.



➢ **Characteristics of a good Lubricant**

- It reduces frictional resistance between moving or sliding surface.
- It reduces surface deformation, wear and tear, because the direct contact between the rubbing surfaces is avoided.
- It reduces loss of energy in the form of heat in other words it acts as a coolant.
- It reduces waste of energy, so that efficiency of machine is enhanced.
- It reduces expansion of metal by local frictional heat.
- It avoids seizure of moving surfaces.
- It reduces the maintenance and running cost of the machine.
- It also, sometimes, acts as a seal. For example, lubricant used between piston and the cylinder wall of an internal combustion engine acts as seal

➢ **Mechanism of lubrication**

1. Fluid-film or Thick-film or Hydrodynamic lubrication
2. Boundary lubrication or Thin-film lubrication
3. Extreme-Pressure lubrications

- **Boundary lubrication or thin-film lubrication:**

Boundary lubrication or thin-film lubrication is done when a continuous film of lubricant cannot persist and direct metal-to-metal contact is possible due to certain reasons.

This happens when:

- A shaft starts moving from rest
- The speed is very low
- The load is very high, and
- Viscosity of the oil is too low.

- Under such conditions, the clearance space between the moving/sliding surfaces is lubricated with an oil lubricant, a thin layer of which is adsorbed, (surface attached) by physical or chemical forces or both on both the metallic surfaces.
- These adsorbed layers avoid direct metal-to-metal contact. The load is carried by the layers of the adsorbed lubricant on the both metal surfaces.
- Vegetable and animal oils (glycerides of higher fatty acids) and their soaps possess property of adsorption (or surface attachment), either physically adsorbed to metal surfaces or react chemically at the metal surfaces, forming a thin film of metallic soap, which acts as lubricant.
- The load is carried by the two layers of absorbed lubricant. Although the fatty oils possess a greater linkage property (called oiliness) than mineral oil.
- In order to improve the oiliness of mineral oils, small amounts of fatty oils or fatty acids are added. Graphite and molybdenum disulphide either alone or as stable suspension in oil are used for boundary lubrication.
- These materials form films on the metal surfaces, which possess low internal friction and can, bear compression as well as high temperatures.
- For boundary lubrication thlubricant should have
- Long hydrocarbon chains
- Polar group to promote spreading over the surface,

- lateral attraction between the chains,
- Active functional groups & good oiliness
- Resistance to heat & oxidation
- High viscosity index

Properties of Lubricants

1. Viscosity

- Viscosity is the property of a liquid or fluid by virtue of which it offers resistance to its own flow. Any two layers will move with different velocities. Top layer moves faster than the next lower layer, due to viscous drag (i.e., internal friction). The unit of viscosity is poise.
- Viscosity is the most important single property of any lubricating oil, because it is the main determinant of the operating characteristics of the lubricant, if the viscosity of the oil is too low, a liquid oil film cannot be maintained between two moving/sliding surfaces, and consequently, excessive wear will take place. On the other hand if the viscosity is too high, excessive friction will result.

2. Flash Point & Fire Point

- **Flash point** is "the lowest temperature at which the oil lubricant gives off enough vapours that ignite for a moment, when a tiny flame is brought near it." While **Fire point** is the lowest temperature at which the vapours of oil burns continuously for at least five seconds when a tiny flame brought near it.
- A good lubricant should have flash point at least above the temperature at which it is to be used. In most of cases the fire point is 5 to 40^{o}C higher than flash point.

  The Flash point & Fire point are usually determined by
  - Pensky-Marten's Apparatus
  - Abel's Apparatus

3. Cloud and Pour point

- The lubricating oil is derived from petroleum. It contains dissolved paraffin wax and other resinous impurities. These impurities tend to separate out of oil at lower temperatures.
- The temperature at which the impurities begin to separate out from the solution and

lubricating oil becomes cloudy or hazy in appearance is called "**cloud point**" while the temperature at which the oil ceases to flow or pour is called "**pour point**".

- Cloud point and pour points indicate the suitability of lubricants in cold conditions. Machines working with low temperatures like refrigerator plants, aircraft engines, lubricants with low cloud and pour points are preferred.