NARASARAOPETA ENGINEERING COLLEGE
NARASARAOPET

(An Autonomous Institution – UGC, Govt. of India)

Approved by ACTE, New Delhi & Permanently Affiliated to JNTUK, Kakinada.

Twice Accredited by NBA & NAAC "A" Grade – ISO 9001:2008 Certified Institution.

ENGINEERING CHEMISTRY
LECTURE NOTES

B.Tech – I Year – I/II Semesters
DEPARTMENT OF CHEMISTRY

Student Name: ……………………………………………………………

Roll No: ……………………………………………………………………

Branch: ……………………………… **Section:** ………………………

Year: ……………………………… **Semester:** ………………………

NARASARAOPETA ENGINEERING COLLEGE:: NARASARAOPET (AUTONOMOUS)

DEPARTMENT OF CHEMISTRY

1ST B.TECH; ENGINEERING CHEMISTRY

(Macro Syllabus)

I B.TECH I & II SEMESTERS	L	T	P	INTERNAL MARKS	EXTERNAL MARKS	TOTAL MARKS	CREDITS
	3	0	0	30	70	100	3
Code: R20CC1103/ R20CC1204	**ENGINEERING CHEMISTRY (COMMON TO ALL BRANCHES)**						

COURSE OBJECTIVES:

- To analyze water for its various parameters and its significance in industrial and domestic allocations.
- To acquire the knowledge on types of polymers, fuels and their applications.
- To provide information on exciting advanced materials available in engineering.
- To apply the electrochemical principles, understand the fundamentals of corrosion and development of different techniques in corrosion control.
- To learn the importance of engineering materials used in daily life and industry.

COURSE OUTCOMES:

After successful completion of this course, the students will be able to:

CO 1: Analyze the suitable method of water treatment depending on the quality treatment.
CO 2: Compare different types of polymers and fuels and their importance.
CO 3: Utilize the advanced materials as engineering materials and apply them in domestic and industrial life.
CO 4: Distinguish electrical energy sources and importance of corrosion science.
CO 5: Identify different types of engineering materials and applications in engineering.

UNIT-I: WATER CHEMISTRY

Characteristics of water: Sources, Impurities–Hardness & its units–Industrial water characteristics–softening of water by external treatment methods (Lime soda process, Zeolite and Ion exchange process)–Numerical problems on lime soda process– Desalination of brackish water (Reverse osmosis and Electrodialysis).
Water analysis techniques: Alkalinity–hardness (Complexo-metric)–Break point chlorination–Free chlorine–DO–BOD and COD.

Characteristics of water:

1. Introduction
2. Sources of water
3. Impurities of water
    3.1. Sources of impurities
4. Hardness
    4.1. Types of hardness and its units
    4.2. Degree of hardness
5. Industrial water characteristics
6. Softening of water
    6.1. External treatment methods
        6.1.1. Lime-soda process
            6.2.1.1. Cold lime soda process
            6.2.1.2. Hot lime soda process
            6.2.1.3. Problems on lime soda process
        6.1.2. Zeolite or permutit process
        6.1.3. Ion exchange or deionization process
7. Desalination of brackish water
    7.1. Reverse osmosis
    7.2. Electrodialysis

Water analysis techniques:

8. Determination of alkalinity of water
9. Estimation of hardness by EDTA method
10. Free chlorine
    10.1. Break point chlorination
11. Dissolved Oxygen
12. Biological Oxygen Demand (BOD)
13. Chemical Oxygen Demand (COD)

UNIT-II: POLYMERS AND FUEL CHEMISTRY

Polymers: Introduction to polymers–chain growth (free radical, ionic)–step growth polymerization–coordination polymerization–copolymerization with specific examples–Thermoplastics and thermosets–Plastic moulding methods (Compression & Injection moulding)–Rubbers–Natural rubber–processing–Vulcanization.
Fuels-types of fuels–calorific value– numerical problems based on calorific value–analysis of coal–liquid fuels–refining of petroleum–cracking of heavy oil–knocking and anti knocking agents–octane and cetane values.

Polymers:

1. Introduction
2. Classification of polymers
3. Types of Polymerization
   - 3.1. Mechanism of polymerization
     - 3.1.1. Addition polymerization (Chain growth)
       - 3.1.1.1. Free radical chain polymerization
       - 3.1.1.2. Ionic chain polymerization
         - a) Cationic b) Anionic
     - 3.1.2. Condensation polymerization (Step growth)
     - 3.1.3. Coordination polymerization
     - 3.1.4. Copolymerization
4. Plastics
   - 4.1. Thermoplastics
   - 4.2. Thermo setting plastics
5. Plastic moulding methods
   - 5.1. Compression moulding
   - 5.2. Injection moulding
6. Rubbers
   - 6.1. Natural rubber processing
   - 6.2. Vulcanization of natural rubber

Fuels:

7. Introduction
8. Classification
9. Calorific value
   - 9.1. Higher calorific value
   - 9.2. Lower calorific value
   - 9.3. Problems on calorific value (Dulong's formule)
10. Analysis of Coal
    - 10.1. Proximate analysis
    - 10.2. Ultimate analysis
11. Liquid fuels
    - 11.1. Refining of petroleum
    - 11.2. Cracking
      - 11.2.1. Catalytic cracking
        - a) Fixed bed b) Moving bed
    - 11.3. Knocking
      - 11.3.1. Octane number
      - 11.3.2. Cetane number
      - 11.3.3. Anti knocking agents

UNIT-III: CHEMISTRY OF ADVANCED MATERIALS

Nano materials: Introduction–Sol-gel method & chemical reduction method of preparation –Characterization by BET method and TEM methods–Carbon nano tubes and fullerenes: Types–preparation–properties and applications.
Liquid crystals: Introduction–Types–Applications.
Composite materials: Introduction–Definition–Types–Applications–Cermets.

Nanomaterials

1. Introduction
2. Types
3. General methods of preparation
   - 3.1. Sol-gel method
   - 3.2. Chemical reduction method
4. Characterization
   - 4.1. Brunauer-Emmett-Teller (BET) method
   - 4.2. Transmission Electron Microscopic (TEM) method
5. Preparation of Carbon nanotubes
   - 5.1. Arc discharge method
   - 5.2. Laser ablation method
   - 5.3. Chemical vapour deposition method
   - 5.4. Properties and applications of CNT
6. Preparation, properties and applications of fullerenes

Liquid crystals

7. Introduction
   - 7.1. Types of liquid crystals
   - 7.2. Thermotropic and lyotropic liquid crystals
   - 7.3. Applications of liquid crystals

Composite materials

8. Introduction and definition
9. Classification
   - 9.1. Fiber reinforced plastics
   - 9.2. Cermets
10. Applications of composite materials

UNIT-IV: ELECTROCHEMISTRY AND CORROSION

Electrochemistry: Galvanic cells–Single electrode potential–Reference electrodes–Electrochemical series–Batteries (primary, secondary and fuel cells)–Applications of secondary batteries in E-vehicles.
Corrosion: Causes and effects of corrosion–Theories of corrosion (chemical and electrochemical corrosion)–Factors effecting corrosion–Corrosion control methods–Cathode protection–Sacrificial anodic, Impressed current methods–Surface coatings–Methods of application on metals (Hot dipping, Galvanizing, Tinning, Cladding, Electroplating, Electroless plating)–Organic surface coatings–Paints–Constituents and their functions–Pigment Volume Concentration.

Electrochemistry

1. Introduction
2. Galvanic cells
   2.1. Voltaic cell
   2.2. Daniel cell
3. Single electrode potential
4. Reference electrodes
   4.1. Gas electrode (Hydrogen electrode)
   4.2. Metal-metal ion electrode (Calomel electrode)
5. Electro chemical series
6. Batteries
   6.1. Primary cells
      6.1.1. Dry cell
   6.2. Secondary cells
      6.2.1. Lead-acid
      6.2.2. Nickel-cadmium
      6.2.3. Applications of secondary batteries in E-vehicles
   6.3. Fuel cells
      6.3.1. H_2-O_2 fuel cell
      6.3.2. CH_3OH-O_2 fuel cell

Corrosion

7. Introduction
8. Causes of corrosion
9. Effects of corrosion process
10. Theories of corrosion
    10.1. Chemical or Dry corrosion
    10.2. Electrochemical or wet corrosion
11. Factors effecting corrosion

12. Corrosion control methods
    - 12.1. Cathodic protection
        - 12.1.1. Sacrificial anode protection
        - 12.1.2. Impressed current cathodic protection
    - 12.2. Surface coatings
        - 12.2.1. Methods of applications on metals
        - 12.2.2. Hot dipping
            - a) Galvanizing b) Tinning
        - 12.2.3. Cladding
        - 12.2.4. Electroplating
        - 12.2.5. Electroless plating
    - 12.3. Organic surface coatings
        - 12.3.1. Paints
        - 12.3.2. Constituents and their functions
        - 12.3.3. Pigment Volume Concentration

UNIT-V: CHEMISTRY OF ENGINEERING MATERIALS

Lubricants: Introduction–Mechanism of lubrication–Classification of lubricants–Properties and Testing of lubricating oils.
Cement & Refractories: Manufacture–Setting and hardening of cement–failures of cement–Slag cement–Refractory: Introduction–classification and properties of refractories.

Lubricants:

1. Introduction
2. Classification flow chart
3. Mechanism of lubrication
    - 3.1. Fluid film (or) thick film (or) hydrodynamic lubrication
    - 3.2. Boundary (or) thin film lubrication
    - 3.3. Extreme pressure lubrication
4. Properties and testing of lubricating oils
    - 4.1. Viscosity
    - 4.2. Flash and fire point
    - 4.3. Oiliness
    - 4.4. Cloud and Pour point
    - 4.5. Emulsification
    - 4.6. Carbon residue
    - 4.7. Aniline point
    - 4.8. Acid value
    - 4.9. Saponifivation value
    - 4.10. Iodine value

Cement & Refractories

5. Introduction to cement
6. Classification
7. Preparation of Portland cement
8. Setting and hardening of cement
9. Failures of cement
    9.1. Effect of CO_2
    9.2. Effect of Chloride
10. Introduction to Refractories
11. Classification
12. Properties of refractories
    12.1. Refractoriness
    12.2. Strength (or) Refractoriness Under Load (RUL)
    12.3. Chemical inertness
    12.4. Porosity

TEXT BOOKS:

1. Shikha Agarwal, “**Engineering Chemistry**”, ISBN 1107476410, 2nd Edition, Cambridge University Press, New Delhi, (2019).
2. O.G. Palana, “**Engineering Chemistry**”, ISBN 0070146101, Tata McGraw Hill Education Private Limited, New Delhi, (2009).
3. B. Rama Devi, Ch. Venkata Ramana Reddy, Prashantharath, “**Text Book of Engineering Chemistry**”, ISBN 9789353500511, Cenage Learning India Pvt. Ltd, (2016).

REFERENCE BOOKS:

1. P.C. Jain and M. Jain “**Engineering Chemistry**”, ISBN 8187433175, 15/e, Dhanpat Rai & Sons, Delhi, (2015).
2. B.S Murthy and P. Shankar, “**A Text Book of NanoScience and NanoTechnology”**, University Press (2013).
3. K. Sesha Maheshwaramma and Mridula Chugh, “**Engineering Chemistry”**, Pearson India Edn services, (2016).
4. S.S. Dara, “**A Textbook of Engineering Chemistry”**, ISBN 8121932645, S.Chand Publisher, (2010)

Web References:

1. URL: https://www.youtube.com/watch?v=CWOJW4357Bg
2. URL: https://www.youtube.com/watch?v=H1Y1oxQ5eUA&t=627s
3. URL: https://www.youtube.com/watch?v=1xWBPZnEJk8
4. URL: https://www.youtube.com/watch?v=p9yPXdT0k48&t=225s
5. URL: https://www.youtube.com/watch?v=xb_xndPe4n0&t=390s

E-Books:

1. “**Engineering Chemistry**” (NPTEL Web-book), by B.L. Tembe, Kamaluddin and M.S. Krishnan.

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UNIT-I

WATER CHEMISTRY

CHARACTERSTICS OF WATER

Introduction

- Water is one of the few basic materials which are of prime importance for the preservation of life on earth.
- Water is not only essential for the lives of animals and plants but also occupies a unique position in industries.
- It's most important use as an engineering material.
- As engineering material water is used for producing steam in boilers to generate hydroelectric power, furnishing steam for engines, for refrigeration and air conditioning, for construction of concrete structures, for manufacturing purposes and as a solvent in chemical processes.

Sources of water

Rain water: It is the most important sources of water and the purest form of natural water. It is naturally distilled water.

River water: Water in the form of rivers comes from rain water which is not absorbed into the soil and melting of snow on the mountains.

Spring and well water: About one third of rain water falls on the surface of earth seeps inside the soil and goes down through it till it is prevented by impervious rock etc. After some time it then moves up and appears in the form of deep well water or spring water.

Sea water: Sea is the largest source of water. The river water which carries many dissolved and suspended impurities finally collects in to sea. The percentage of impurities in sea water is around 3.6 in which about 2.7% is the common salt.

Impurities of water

Chemically pure water is composed of two parts of hydrogen and one part of oxygen by volume and dissolves many substances. So natural water is not pure. It dissolves various impurities.

1. **Suspended impurities:** It is of two types:
    - Inorganic suspended impurities, like clay and sand.
    - Organic suspended impurities like animal and vegetable impurities. River water mainly contains suspended impurities, which is responsible for turbidity of water.

2. **Dissolved impurities:** The dissolved impurities are classified as:
    - Inorganic salts like bicarbonates, chlorides, sulphates of calcium and magnesium in the dissolved form causes hardness to water.
    - The dissolved impurities like salts of sodium, potassium causes alkalinity to water.
    - The other dissolved salts include iron, silica and alumina.
    - Dissolved gases like CO_2, N_2, O_2, H_2S are responsible for the odour and acidity in water. The presence of O_2 causes corrosion in boilers.
3. **Colloidal impurities:** The impurities which exists in very finely divided state such that their small quantities are not visible to naked eye is called colloidal impurities, which comprise of very finely divided silica, clay, aluminum hydroxide and micro-organisms.
4. **Organic impurities:** The organic impurities include algae, fungi and plant matter etc., which are vegetative by origin and microorganisms, bacteria and animal by their origin.

Sources of impurities

- When rain water floods to near stream it carries floating impurities along with it.
- Gases like CO_2, O_2 etc. are picked up from atmosphere.
- When water percolates through the layers of soil it dissolves the salts of calcium, magnesium, potassium, sodium etc. which remain as dissolved salts in the composition of water.
- The organic impurities are introduced into water due to the decomposition of plant and animal remains in water.

Hardness

Soap consuming character of water is known as hardness of water. It is the main characteristics of water which prevents the lathering of soap due to the presence of certain salt of Ca and Mg.

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

Sodium stearate (Hardness) Calcium stearate (insoluble)

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

Sodium stearate (Hardness) Magnesium stearate (insoluble)

Water can be divided into two types based on soap reaction.

1. **Soft water:** water which gives lather easily with soap is known as soft water. Soft water is free from all the minerals.

2. **Hard water:** Water which does not produce lather with soap solution readily is called hard water. Hard water contains high concentration of minerals. It contains bicarbonates, chlorides and sulphates of calcium and magnesium. Hence it does not produce lather with soap solution. Soap is sodium (Na) or potassium (K) salts of fatty acids. Example stearates, palmates and oleic acids etc. which gives cleaning action with soaps.

Types of hardness:

Temporary hardness: It is caused by the presence of dissolved bicarbonates of Ca and Mg. It can be easily removed by simple boiling of water, when bicarbonates are decomposed, yielding insoluble carbonates or hydroxides, which are deposited as a crust at the bottom of vessels.

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

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

Permanent hardness: It is present due to the presence of chlorides and sulphates of Ca and Mg. Unlike temporary hardness, permanent hardness is not destroyed on boiling.

$CaCl_2$, $MgCl_2$, $CaSO_4$, $MgSO_4$, $FeSO_4$, $Al_2(SO_4)_3$ etc.

But it can be removed by

i) Lime-soda process

$$\mathbf{CaCl_2 + Na_2CO_3 \rightarrow CaCO_3\downarrow + 2NaCl}$$

ii) Zeolite process:

$$\mathbf{CaSO_4 + Na_2Ze \rightarrow CaZe + Na_2SO_4}$$

iii) Ion exchange process:

$$\mathbf{2\ RCOO^- H^+ + Mg^+ \rightarrow (RCOO^-)_2Mg^+ + 2H^+}$$

$$\mathbf{RN^+(CH_3)_3\ OH^- + Cl^- \rightarrow RN^+(CH_3)Cl^- + OH^-}$$

Units of Hardness:

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

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

Mg/L: Milligram per liter is the number of milligrams of $CaCO_3$ equivalent hardness present per liter of water.

1 mg/L = 1 mg of $CaCO_3$ equivalent hardness of 1 L of water

Clark's degree (°Cl): It is the parts of $CaCO_3$ equivalent hardness per 70000 parts of water.

1°Cl = 1part of $CaCO_3$ equivalent hardness per 70000 parts of water

Degree French (°Fr): It is the parts of $CaCO_3$ equivalent hardness per 10^5 pars of water.

1°Fr = 1 part of $CaCO_3$ hardness equivalent per 10^5 parts of water

Relationship between various units of hardness

	ppm	**mg/L**	**°Fr**	**°C l**
ppm	1	1	0.1	0.07
mg/L	1	1	0.1	0.07
°Fr	10	10	1	0.7
°C l	1/0.07	1/0.07	1/0.7	1

Degree of hardness (Equivalents of Calcium Carbonate):

The concentrations of hardness as well as non-hardness constituting ions are usually expressed in terms of equivalent amount of $CaCO_3$, since this mode permit the multiplication and division of concentration, when required. The choice of $CaCO_3$ in particular is due to its molecular weight is 100 (equivalent weight is 50) and moreover, it is the most insoluble salt that can be precipitated in water treatment.

Name of the H.C.S	**Molecular weight**	**Multiplication factor in $CaCO_3$equivalents**
$Ca(HCO_3)_2$	162	100/162
$Mg(HCO_3)_2$	146	100/146
$CaCl_2$	111	100/111
$MgCl_2$	95	100/95
$CaSO_4$	136	100/136
$MgSO_4$	120	100/120
$Ca(NO_3)_2$	164	100/164
$Mg(NO_3)_2$	148	100/148

The method of calculating degree of hardness will be clear from the fallowing formula.

Hardness of the H.C.S (hardness causing salt) in terms of $CaCO_3$

$$= \frac{amount\ of\ the\ hardness\ causing\ salt\ X\ 100}{molecular\ weight\ of\ the\ hardness\ causing\ salt}$$

Industrial water characteristics

S.No.	Purpose	Characteristics of Water	Remarks
1	Boiler Feed water	Very soft, It contains small amount of nitrate and organic matter.	Hard water form scale on boiler walls, which reduce the working of the boiler. Hard water may cause priming and foaming.
2	Pharmaceutical industries	Very pure, free from any diseases causing bacteria, confirming to the standards of potable water.	Salts present in hard water may react with the chemicals to form unsuitable products.
3	Sugar Industries	Free from sulphates, carbonates and nitrates. Free from micro-organisms.	In the process of these anions the crystallization becomes difficult and sugar obtained in deliquescent. The micro-organisms may decompose the sugar partly.
4	Textiles	Free from hardness causing substances and Fe, Mn salts	Hard water precipitates basic dyes and decreases the solubility of acidic dyes. These salts produce insoluble precipitates which stain the cloth and cause uneven dyeing
5	Paper mills	Free from hardness and alkalinity, SiO_2, lime and magnesia.	Hardness producing ions may react with the chemicals used for paper. SiO_2 may produce cracks in paper.

Softening of water:

External treatment methods: It involves the removal of hardness causing salts from the water before feeding it into the boiler. The following are external treatment methods.

1. Lime –soda process
2. Zeolite or Permutit process
3. Ion- exchange process or Deionization

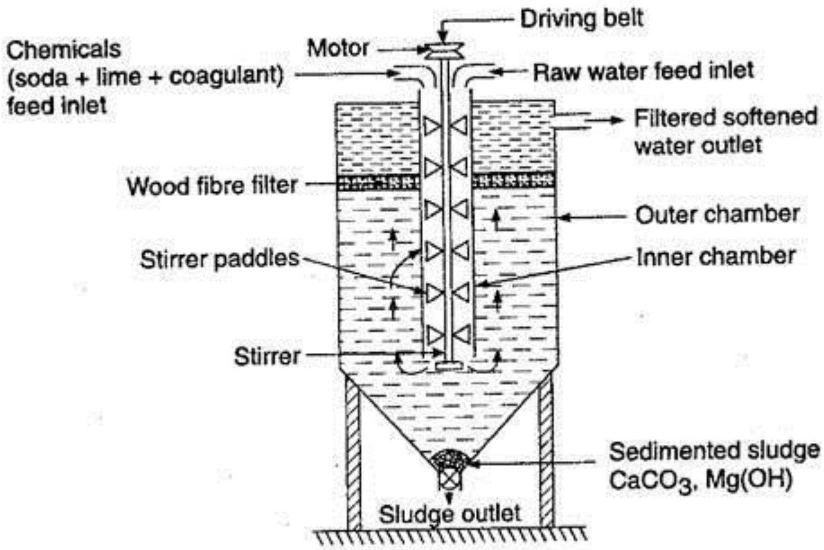
1. **Lime–soda process:** In this process the soluble calcium and magnesium salts in water are chemically converted into insoluble compounds, by adding calculated amounts of lime [$Ca(OH)_2$] and soda [Na_2CO_3]. Calcium carbonate and magnesium hydroxide so precipitates are filtered off. Lime -soda process is of two types.

- **Cold lime–soda process:** In this method calculated quantity of lime and soda are mixed with water at room temperature. The precipitates formed are finely divided, so they do not settle down easily. The coagulant is added which hydrolyze and form precipitate of aluminum hydroxide.

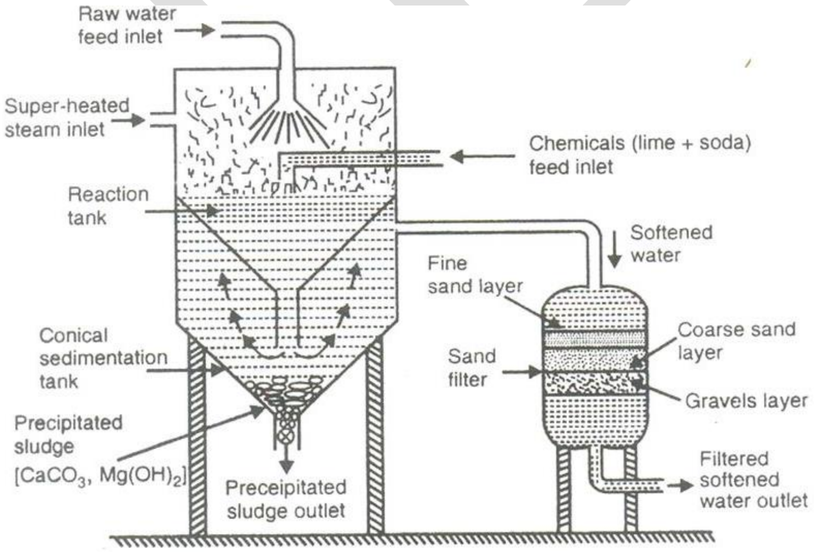
$$NaAlO_2 + 2H_2O \rightarrow NaOH + Al(OH)_3\downarrow$$

$$Al_2(SO_4)_3 + 3Ca(HCO_3)_2 \rightarrow 2Al(OH)_3\downarrow + 3CaSO_4 + 6CO_2\uparrow$$

Coagulant Hardness



Hot lime-soda process:



Essential parts of plant

(i) Reaction tank

(ii) Conical sedimentation vessel

(iii) Sand filter

- This process involves in treating water with softening chemicals at 80-150°C.
- Reaction proceeds faster.
- Softening capacity is increased.
- Precipitate and sludge settle down rapidly hence no coagulants are needed.
- Dissolved gases are also removed.
- Viscosity of softened water is lower so filtration of water becomes easier.

⦿ **Advantages:**

- Very economical
- Lesser amount of coagulants are need
- Minerals in water are reduced
- Pathogenic bacteria is considerably reduced (due to alkaline water)

⦿ **Disadvantages :**

- Careful operation and skilled supervision is required
- Disposal of sludge poses problem
- This process removes hardness only up to 15 ppm, which is not good for high pressure boilers.

2. Zeolite or Permutit process

The term zeolite stands for boiling stones (zeo-boiling, olite-stone). Zeolites are porous, when water passes through zeolite it gives the appearance as boiling. The chemical formula of zeolite is hydrated sodium aluminium silicate, represented as **$Na_2O.Al_2O_3.XSiO_2YH_2O$** where **X** = 2-10 and **Y**=2-6. The sodium ions which are loosely held in Na_2Ze are replaced by Ca^{2+} and Mg^{2+} ions present in water.

Types:

- **Natural zeolites: N**on-porous, $Na_2O.Al_2O_3.4SiO_2.2H_2O$
- **Synthetic zeolites:** Porous and possess gel structure. They are prepared by heating together china clay, feldspar and soda ash. Synthetic zeolites possess higher exchange capacity per unit weight than natural zeolite.

Process:

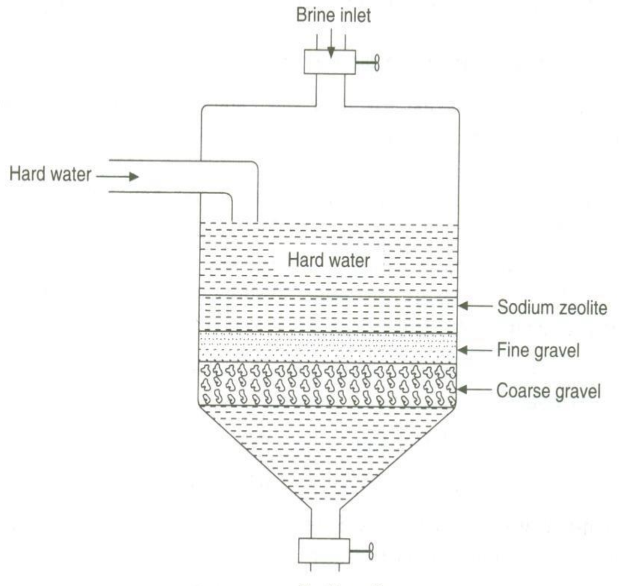
When hard water is passed through a bed of zeolite placed in a closed cylinder, the hardness causing ions like Ca^{2+} and Mg^{2+} ions are taken up by zeolite. Sodium salts are released during the reaction as byproduct. For softening of water by zeolite process, hard water is percolated at a specified rate through a bed of zeolite, kept in a cylinder. The hardness causing ions like Ca^{2+} and Mg^{2+} are retained by the zeolite as CaZe and MgZe. While the outgoing water contains sodium salts.

$$\mathbf{Na_2Ze + Ca(HCO_3)_2 \rightarrow CaZe + 2NaHCO_3}$$

$$\mathbf{Na_2Ze + Mg(HCO_3)_2 \rightarrow MgZe + 2NaHCO_3}$$

$$\mathbf{Na_2Ze + CaCl_2\ (or\ CaSO_4) \rightarrow CaZe + 2NaCl\ (or\ Na_2SO_4)}$$

$$\mathbf{Na_2Ze + MgCl_2\ (or\ MgSO_4) \rightarrow MgZe + 2NaCl\ (or\ Na_2SO_4)}$$



Zeolite softener.

Regeneration: After some time the zeolite is completely converted into calcium and magnesium zeolite and it stop to softening water. Zeolite is reclaimed by treating the bed with 10% NaCl.

$$\mathbf{CaZe/MgZe + 2NaCl \rightarrow Na_2Ze + CaCl_2/MgCl_2}$$

Advantages of Zeolite process:

- It reduces hardness up to 10 ppm.
- The equipment is quite compact.
- It requires less time for softening.
- It requires less skill for maintenance and operation.

Disadvantages of zeolite process:

- Highly turbid water cannot be treated by this method.
- This process removes only the cations (Ca^{2+} and Mg^{2+}).

3. Ion-exchange or de-ionization process:

In this process almost all the ions both anions (Cl^-, $SO4^{2-}$) and cations (Ca^{2+}, Mg^{2+}) present in hard water are removed. This process is also called "deionization process". In the deionization process, the ions present in water are removed by ion exchangers. 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. They are of two types.

(i) Cation exchangers. (ii) Anion exchangers.

i) **Cation exchangers:** Materials capable of exchanging cations are called cation exchangers. Cation exchanger resins containing acidic groups ($-COOH$,$-SO_3H$) are capable of exchanging their H^+ ions with other cations (Ca^{2+}, Mg^{2+}) of hard water. Cation exchange resin is represented as RH_2 (or) RH.

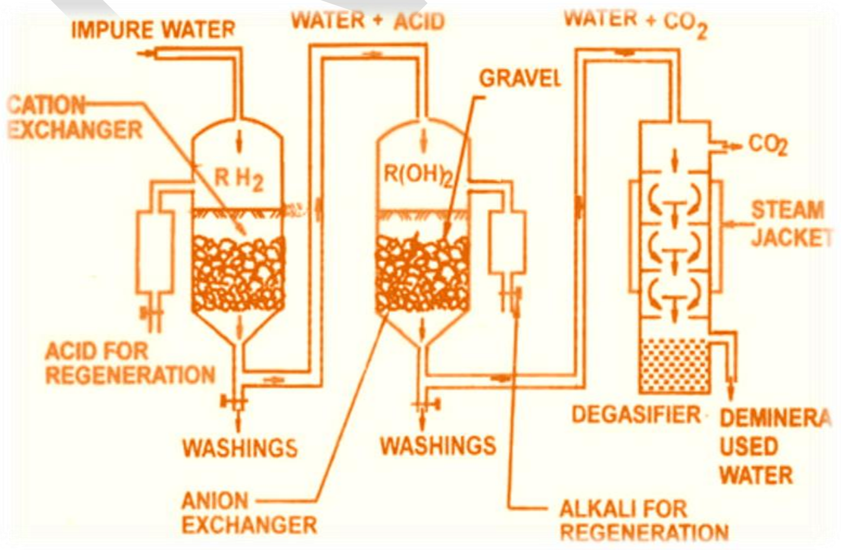
Eg: Styrene divinyl benzene.

ii) **Anion exchangers:** Materials capable of exchanging anions are called anion exchangers. Anion exchanger resins containing basic groups ($-NH_2$,$-OH$) are capable of exchanging their OH^- ions with the other anions of hard water. Anion exchange resin is represented as $R'(OH)_2$ (or) R/OH.

Eg: Phenol-formaldehyde resin.

Process:

The hard water is passed first through cation exchange column, which remove cations.



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

$$\mathbf{2RH^+ + Mg^{2+} \rightarrow R_2Mg^{2+}\ 2H^+}$$

After cation exchange column, the hard water is passed through anion exchange column.

$$\mathbf{R'OH^- + Cl^- \rightarrow R'Cl^- + OH^-}$$

$$\mathbf{2R'OH^- + SO_4^{2-} \rightarrow R'_2SO_4^{2-} + 2OH^-}$$

$$\mathbf{2R'OH^- + CO_3^{2-} \rightarrow R'_2CO_3^{2-} + 2OH^-}$$

H^+ and OH^- ions get combined to produce water molecules.

Regeneration: When capacity of cation and anion resin to exchange ions are lost then they are said to be exhausted. The regenerated ion exchange resins are then used again.

$$\mathbf{R_2Ca^{2+} + 2H^+\ (dil\ HCl/H_2SO_4) \rightarrow 2RH^+ + Ca^{2+}}$$

$$\mathbf{R_2SO_4^{2-} + 2OH^-\ (dil\ NaOH) \rightarrow 2R'OH^- + SO_4^{2-}}$$

Advantages:

- The process can be used for highly acidic or alkaline waters.
- It produces water of very low hardness (2ppm).
- It is very good for treating water for used in high pressure boilers.

Disadvantages:

- The equipment is costly and more expensive chemicals are needed.
- If water contains turbidity, then the output of process is reduced. The turbidity must be below 10 ppm.

Desalination of brackish water:

Brackish water: The water containing high concentrations of dissolved salts with a salty or brackish taste is called brackish water, which contains about 3.5% of dissolved salts. This water cannot be used for domestic and industrial applications unless the dissolved salts are removed by desalination.

Desalination: The process of removal of dissolved salts like NaCl from saline water is known as desalination of water.

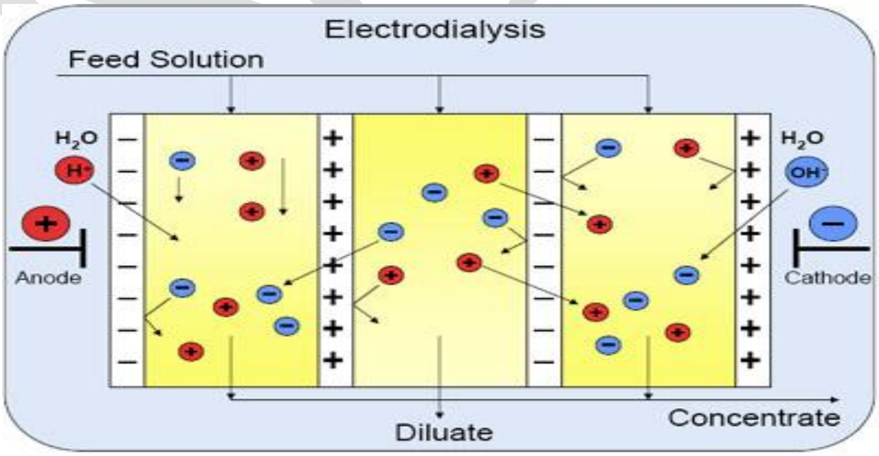
The methods used for desalination of brackish water are:

1. Electrodialysis
2. Reverse osmosis

1. Electrodialysis

Electrodialysis is based on the principle that the ions in saline water migrates towards their respective electrodes through ion selective membranes under the influence of applied e.m.f.

- The unit consists of a chamber with two electrodes.
- The chamber is divided into three compartments with the help of thin, rigid, ion-selective membranes which are permeable to either cation or anion.
- The anode is placed near anion selective membrane while the cathode is placed near cation selective membrane.
- The *anion selective membrane* is containing positively charged functional groups such as R_4N^+ and is *permeable to anions only*.
- The *cation selective membrane* consists of negatively charged functional groups such as RSO^-_3 and is *permeable to cations only*.
- Under the influence of applied e.m.f. across the electrodes the cations move towards cathode through the membrane and the anions move towards anode through the membrane.
- The net result is depletion of ions in the central compartment while it increases in the cathodic and anodic compartments.
- Desalinated water is periodically drawn from the central compartment while concentrated brackish water is replaced with fresh sample.



Advantages of electro dialysis:

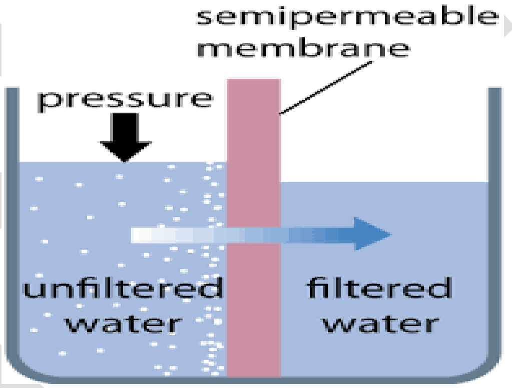
- The unit is compact.
- The process is economical as for as capital cost and operational expenses are concerned.

2. Reverse osmosis

- When two solutions of *unequal concentration* are separated by a *semipermeable membrane* which does not permit the passage of dissolved solute particles, (i.e. molecules and ions) flow of solvent takes place from the dilute solution to concentrated solution is called Osmosis.
- If a hydrostatic pressure in excess of osmatic pressure is applied on the concentrated side of the solvent, the solvent flow is reversed hence this method is called reverse osmosis. Thus in reverse osmosis pure water is separated from the contaminated water. This membrane filtration is also called "super filtration" or "hyper filtration".

Method of purification:

- The reverse osmosis cell consists of a chamber fitted with a semi permeable membrane, above which sea water/impure water is taken and a pressure of 15 to 40 kg/cm^2 is applied on the sea water/impure water.
- The pure water is forced through the semi permeable membrane which is made of very thin films of cellulose acetate. However superior membrane made of polymethacrylate and polyamide polymers have come to use.



Advantages:

- Ionic and non-ionic, colloidal and high molecule weight organic matter is removed from the water sample.
- Cost of purification of water is less and maintenance cost is less. This water can be used for high pressure boilers.

WATER ANALYSIS TECHNIQUES

Determination of alkalinity of water

Alkalinity of water, which is a measure of the ability of water to neutralize the acids, is due to presence of bicarbonates, carbonates & hydroxides of Ca & Mg. Determination of alkalinity due to different ions is based on the titration of the water sample against a standard acid making selective use of indicators. The indicators used are phenolphthalein & methyl orange.

The reaction taking place is as follows:

$$\left.\begin{array}{l}\left.\begin{array}{l}\textbf{i) } OH^- + H^+ \rightarrow H_2O \\ \textbf{ii) } CO_3^{-2} + H^+ \rightarrow HCO^-_3\end{array}\right\} P \\ \textbf{iii) } HCO^-_3 + H^+ \rightarrow H_2O + CO_2\end{array}\right\} M$$

Procedure:

1. Take 50ml of water sample in a 250ml conical flask. Add 2-3 drops of phenolphthalein indicator.
2. The colour of the solution will become pink. Now titrate this solution against 0.1 N HCl taken in a burette till colour of the solution disappears.
3. It shows all the carbonates have been converted in to bio-carbonates. Note the titrate value of the phenolphthalein and point [P].
4. Add 2-3 drops of Methyl orange indicator to the same solution and continue the titration until the sharp colour changes from yellow to rose red takes place.
5. Note the total titre value from the beginning of the experiment as methyl orange end point [M].

$$\text{Phenolphthalein alkalinity [P]} = \frac{E\ x\ N\ x\ V\ x1000}{volume\ of\ water\ sample}\ \text{ppm}$$

$$\text{Methyl orange alkalinity [M]} = \frac{E\ x\ N\ x\ V\ x1000}{volume\ of\ water\ sample}\ \text{ppm}$$

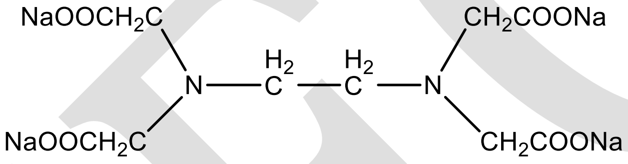
Case	**OH-**	**CO3^{-2}**	**HCO$^-_3$**	**Case**
P=0	NIL	NIL	M	**P=0**
P=M	P or M	NIL	NIL	**P=M**
P=½ M	NIL	2P	NIL	**P=½ M**
P>½ M	(2P-M)	2(M-P)	NIL	**P>½ M**

Estimation of hardness by EDTA Method

Water hardness is generally caused by the presence of Ca^{+2} and Mg^{+2} ions present in water. An excellent way to determine water hardness is to perform a complexometric titration using standard solution of EDTA (ethylene diamine tetra acetic acid) a weak acid forms a soluble complex with Ca^{+2} and Mg^{+2}. Hence the amount of EDTA consumed in the reaction gives the amount of calcium and magnesium salts present in the hard water.

Ethylene diamine tetra acetic acid (EDTA)

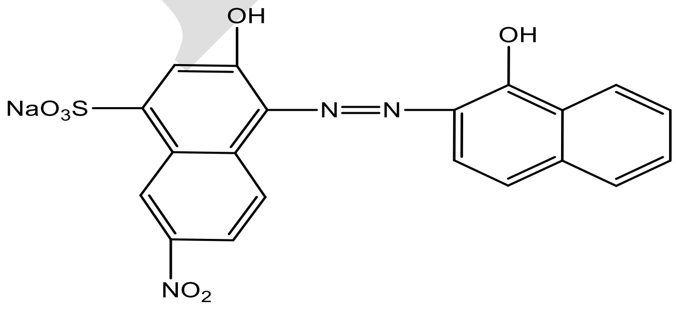
For simplicity it is represented by symbol H_4y. Because of its limited solubility, it is not used directly. It is usually used as its disodium salt dihydrates $Na_2H_2y.2H_2O$, because it can be obtained in high state of purity and is primary standard. The solution of EDTA is very valuable titrant because the reagent combines with metal ion in 1:1 ratio.



Structure of Na_2 EDTA

Eriochrome Black T (EBT) is used as indicator

It is a typical metal ion indicator chemically it is sodium 1-(1-hydroxy-2-napthylazo)-6-nitro-2-napthol-4-sulphonate. The indicator Eriochrome Black T (a dye stuff) is effective between the pH (8-11). It is therefore, essential while performing the titration of hard water with EDTA solution, the pH of the solution must be made (pH = 10) by adding a suitable buffer solution.



sodium 1-(1-hydroxy-2-napthylazo)-6-nitro-2-napthol-4-sulphonate

Buffer solution: The optimum pH for the experiment is 10 and is adjusted by NH_4OH and NH_4Cl buffer solution (Alkaline buffer).

Take 17.5 gms of NH_4Cl and add 14.2 ml. conc. NH_3 solution to it. Dilute the solution to 250 ml with distilled water.

Necessary Requirement:

Glasswares, Burette, Pipette, Conical flask, EDTA solution, Standard water sample, Buffer solution, Eriochrome Black-T, Unknown water sample.

Procedure:

1. Wash the burette with water, rinse it with given EDTA solution and then fill with EDTA solution.
2. Wash the pipette with water, pipette out 20 ml of water sample & transfer it in the conical flask.
3. Add 5ml of buffer solution and 2 drops of Eriochrome Black-T indicator.
4. Titrate the solution with EDTA solution from the burette until the colour changes from wine red to clear sky blue at the end point.
5. Repeat the same procedure till we get the concordant reading.

Metal- indicator unstable complex (wine red color)

When a small amount of the indicator is added to a hard water sample, whose pH has been controlled by the addition of the buffer solution. The indicator reacts with Ca^{+2} / Mg^{+2} ions produce wine red colour. As EDTA is added, combines free Ca^{+2} / Mg^{+2} ions to give very stable, colourless and water soluble Metal-EDTA complex.

$$\mathbf{Ca^{+2}/\ Mg^{+2} + EBT \xrightarrow[PH=10]{titration} [Ca^{+2}/\ Mg^{+2} - EBT]}$$

Metal- EDTA stable complex

After all the free metal ions are consumed the next drop of EDTA solution displaces the indicator EBT from M-EBT Complex.

$$\mathbf{[Ca^{+2}/\ Mg^{+2} - EBT] + EDTA \xrightarrow[PH=10]{titration} [Ca^{+2}/\ Mg^{+2} - EDTA] + EBT}$$

Thus, at the equivalence point, there is change in color from wine red to blue. Completion of the above reaction makes the end point of the titration.

Dissolved oxygen (DO)

The amount of oxygen present in water is called dissolved oxygen. It is expressed in ppm or mg/lit. DO is needed for living organisms to maintain biological process. Determination of DO is important for boiler feed water

Theory:

It is usually determined by "Winkler's method". The method is based on the fact that in presence of $MnSO_4$ (act as O_2 carrier to bring about the reaction between KI & O_2) dissolved oxygen, oxidises KI to Iodine. And the liberated iodine is titrated against standard hypo solution using starch as indicator.

$$\mathbf{2KOH+MnSO_4 \longrightarrow Mn(OH)_2+K_2SO_4}$$

$$\mathbf{2Mn\ (OH)_2+O_2 \longrightarrow 2MnO\ (OH)_2}$$

$$\mathbf{MnO(OH)_2+H_2SO_4 \longrightarrow MnSO_4+2H_2O+[O]}$$

$$\mathbf{2KI+H_2SO_4+[O] \longrightarrow K_2SO_4+H_2O+I_2}$$

$$\mathbf{I_2+2Na_2S_2O_3 \longrightarrow 2NaI+Na_2S_4O_6}$$

(Sodium tetrathionate)

$$\mathbf{Starch+I_2 \longrightarrow \text{Starch iodide complex}}$$

(**Blue colour**)

Procedure:

1. Take 300ml of water in a BOD bottle. Now add 2ml of alkaline iodide-azide reagent and 2 ml of $MnSO_4$ solution.
2. Stopper the bottle and shake it well. Keep the bottle in dark for 5 min and add conc. H_2SO_4 till the brown precipitates are dissolved.
3. Take 100 ml of the above solution in a conical flask. Titrate against N/100 hypo till the color changes to light Yellow.
4. Add 3-4 drops of starch in to it and the color changes to blue. The blue color solution is titrated against hypo solution till blue color disappeared. This is end point of the titration. The titer value V is noted.

Calculation of DO: The DO content of the water sample can be calculated as follows..

$$DO = V \times N \times \frac{1}{200} \times 8 \times 1000 \frac{mg}{lit} \text{ or ppm}$$

Where V is titer value, N is Normality of Hypo solution

Biological Oxygen Demand (BOD)

BOD is defined as the quantity of dissolved oxygen required by aerobic bacteria for the oxidation of organic matter under aerobic conditions. BOD is considering as the major characteristic used in stream pollution control. It gives valuable information regarding the self-purification capacity of the streams and serves as guide line for the regulatory authorities to check the quality of the effluents discharged in to water bodies. The demand for O_2 is proportional to the amount of organic waste to degrade aerobically. When the BOD is high DO become low. Hence greater the BOD, grater is the pollutants.

S.No	Source of Effluent	BOD(PPM)
1	Domestic sewage	320
2	Cow shed sewage	3010
3	Paper mill	8190
4	Tannery effluent	12360

Procedure:

1. The BOD test essentially consists of measurement of DO content of water sample, before and after incubation at 20^0C for 5 days.
2. Take the diluted sample in two stoppered bottles. The DO content of one of the bottles is determined. The bottle is incubated at 20^0C for 5 days.
3. Then it's DO content is determined. The depletion in DO caused is used as measure of BOD.

Calculation of BOD:

$$\text{BOD (mg/lit)} = \frac{(DO_0 - DO_5 - B)X100}{\%\ of\ the\ sample\ used}$$

Where

DO_0= initial DO content in mg/lit

DO_5= DO content after incubation at 20^0c for 5 days in mg/lit

B= dilution factor

Chemical Oxygen Demand (COD)

COD is defined as the amount of oxygen consumed under specified conditions in the oxidation of organic and oxidisable inorganic matter, corrected for the influence of chlorides.

The COD is a measure of the O_2 equivalent to the portion of organic matter present in the waste water sample that is susceptible to oxidation by $K_2Cr_2O_7$. This is an important and quickly measurable parameter for streams, sewage and industrial waste samples to determine their pollution strength.

The principle involved in the determination of COD is that when a waste water sample is refluxed with a known excess of $K_2Cr_2O_7$ in a 50% of H_2SO_4 in presence of $AgSO_4$(as catalyst) and $HgSO_4$ to eliminate interference due to chloride, the organic matter, present in the sample is oxidized to CO_2, H_2O and NH_3. The excess dichromate remaining unreacted in the solution is titrated against a solution of Mohr's salt. The COD of waste water sample is calculated as follows.

$$\text{COD} = \frac{(V1 - V2) \text{ X } N \text{ X } 8}{x} \text{ X } 1000 \text{ mg/lit}$$

Where V_1& V_2 are the volumes of Mohr's salt of the normality N, rundown in the blank and test experiments respectively, and x is the volume of sample taken for the test. Since in the COD test, both biologically oxidisable and the biologically inert matter are oxidized, the COD value for a sample is always higher than the BOD value.

Free chlorine:

Chlorine is widely used for disinfection of potable water to remove bacteria, fungus and other pathogenicmicro-organisms. The sterilising action of chlorine is due to its reaction with water, producing hypo chlorous acid and nascent oxygen both of which have powerful germicidal properties.

$$\mathbf{CaOCl_2 + H_2O \rightarrow Ca(OH)_2 + Cl_2}$$

$$\mathbf{Cl_2 + H_2O \rightarrow HCl + HOCl} \textbf{ (Hypochlorous acid)}$$

Germs + HOCl → Germs are killed

However, excess of free chlorine in drinking water is undesirable not only because of unpleasant taste but also because it is injuries to human metabolism. Hence, free chlorine present in municipal water is generally estimated prior to the domestic supply for adjusting the chlorine dose rate.

Procedure:

When the water sample containing free chlorine is treated with KI, free chlorine oxidises KI and liberates I_2 in equivalent amount. The liberated I_2 is titrated against Hypo solution using starch indicator. At the end point blue colour disappeared.

$$\mathbf{Cl_2 + 2KI \longrightarrow 2KCl + I_2}$$

$$\mathbf{I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI}$$

(Hypo) (Sodium tetrathionate)

The free chlorine present in the water sample can be calculated as follows..

$$\text{Free chlorine} = \frac{V1 \text{ X } N1}{V2} \text{ X } 35.5 \text{ X } 1000 \text{ ppm}$$

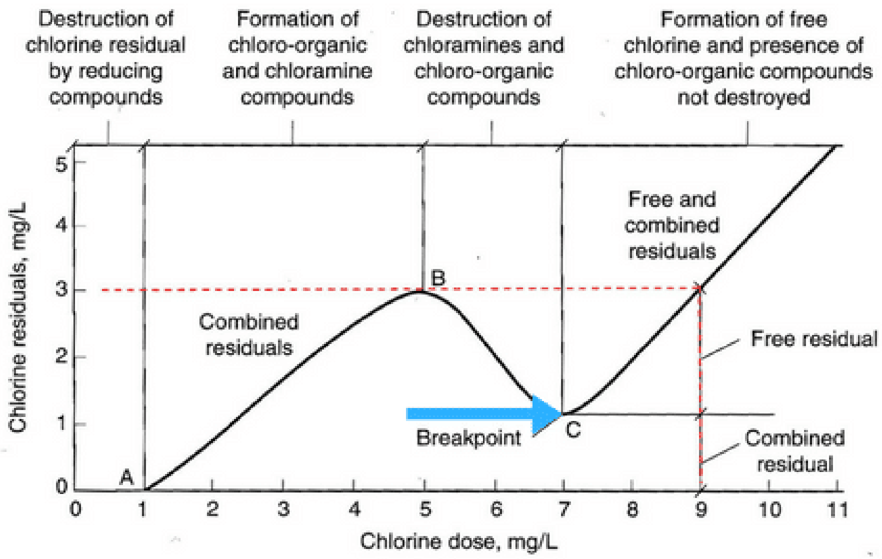
Where V_1 = Volume of standard hypo solution rundown at the end point

N_1 = Normality of hypo solution (N/20) and

V_2 = Volume of water sample used for the test (100 ml)

Breakpoint of chlorination (Free residual chlorination):

- It involves the addition of sufficient amount of chlorine to Oxidize: a) organic matter b) reducing substances c) free ammonia in raw water leaving behind mainly free chlorine, which possesses disinfecting action against disease-producing (pathogenic) bacteria.



- The addition of chlorine at the break is called “break-point”. This indicates the point at which free residual chlorine begins to appear. All tastes, odours (chlorines and others) disappear at break-point, resulting in appearance of water free from bad tastes and odours.

Advantages of break-point chlorination:

1) It oxidizes completely organic compounds, ammonia and other reducing compounds.
2) It removes colour in water, due to presence of organic matters.
3) It destroys completely (100%) all the disease-producing bacteria.
4) It removes both odour and taste from the water.
5) It prevents the growth of any weeds in water.

UNIT-1

WATER CHEMISTRY

IMPORTANT QUESTIONS

1. How do you estimate the hardness of water by EDTA method?
2. Describe the zeolite (Permutit) process used for softening of water.
3. With neat diagram explain the Ion–exchange (de ionization) process for the purification of water. Discuss the merits and demerits of the process.
4. Explain the different methods used for the desalination of brackish water.
5. Describe the Lime-Soda (Cold & hot) process used for softening of water.
6. Give an account of industrial water characteristics. Explain break point chlorination.
7. Write a brief note on determination of free chlorine present in water.
8. How would you estimate the amount of dissolved oxygen present in water?
9. Explain the determination BOD & COD and its significance.
10. How do you estimate the alkalinity of water?

UNIT-II

POLYMERS AND FUEL CHEMISTRY

POLYMERS

Introduction

Polymers are large class of materials consisting of many small molecules called monomers that can be linked together to form long chains. Thus, they are known as macromolecules.

The overall reaction leading to the formation of polymers from monomers (Ethylene) is called "**Polymerization**".

Ex: $nCH_2 = CH_2 \longrightarrow -[CH_2-CH_2]_n-$

Ethylene polythene

Classification of polymers

Polymers are classified into various types depending on:

i) Origin **ii)** Chemical nature **iii)** Thermal property

iv) Nature of monomers **V)** Mechanisms

i) Origin of the polymers: Based on the origin polymers are of two types:

- **Natural polymers:** The polymers which are isolated from natural resources are called natural polymers. **Ex:** Starch, Natural rubber, Cellulose etc.
- **Synthetic polymers:** The polymers which are isolated from low molecular weight compounds are called synthetic polymers. **Ex:** Teflon, PVC, Polyethylene, etc.

ii) Chemical nature of polymers: Based on chemical nature, polymers are of two types:

- **Organic polymers:** In organic polymers, the polymer chains are made up of carbon atoms. **Ex:** Styrene
- **Inorganic polymers:** In inorganic polymers, the polymeric chains are made up of inorganic elements. **Ex:** Silicon rubber

iii) Thermal property: Based on thermal property polymers are classified into two types:

- **Thermoplastic polymers:** Polymers which become soft on heating and becomes hard on cooling. **Ex:** PVC, Polyethylene etc.
- **Thermo setting polymers:** During moulding, these polymers get hardened and once they have solidified, they cannot be softened. **Ex:** Bakellite

IV) Nature of monomers: Based on nature of monomers polymers are of two types:

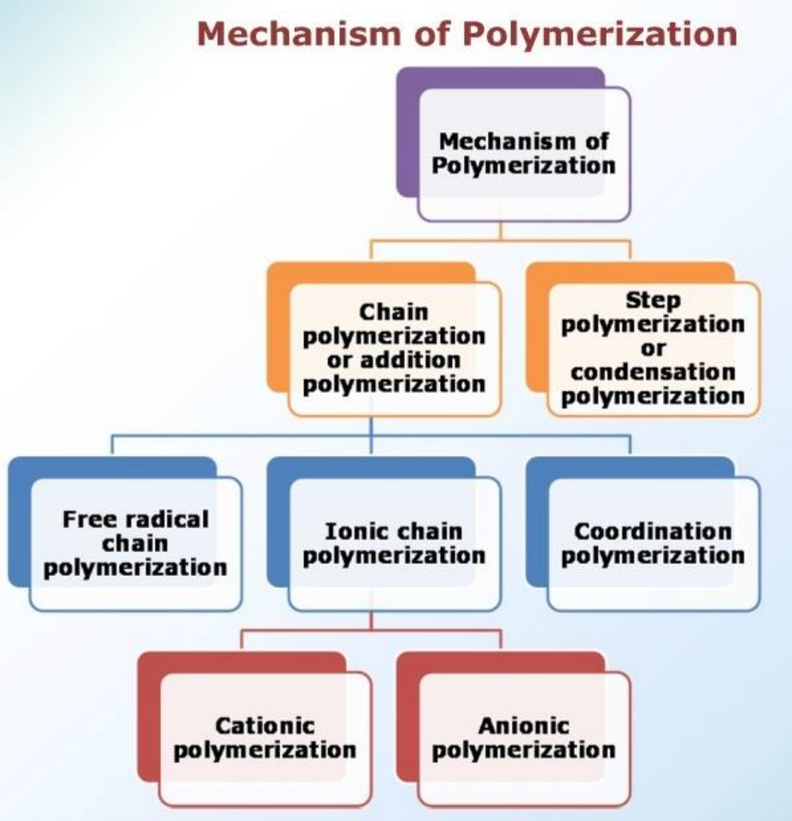
- **Homo polymers:** These polymers are derived from identical monomer unit.
  Ex: Polyethylene
- **Copolymers:** These polymers are derived from two or more different monomer units in the chain are called copolymers. **Ex:** Nylon 6,6

V) Mechanisms: Based on mechanisms polymers are classified into:

- **Addition polymers/Chain polymers:** The polymers which are formed by the addition of monomeric units repeatedly. **Ex:** PVC, Polyethylene
- **Condensation polymers/Stepwise:** The polymers which are formed by the process of condensation. **Ex:** Polyester, Nylon 6,6 etc.

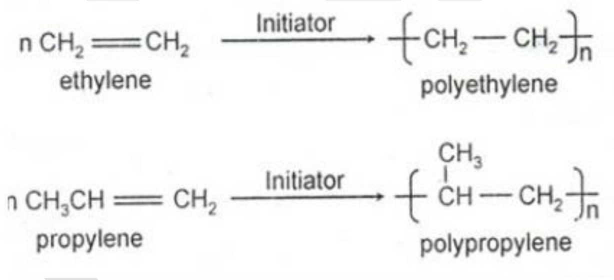
Types of Polymerization

Mechanism of polymerization

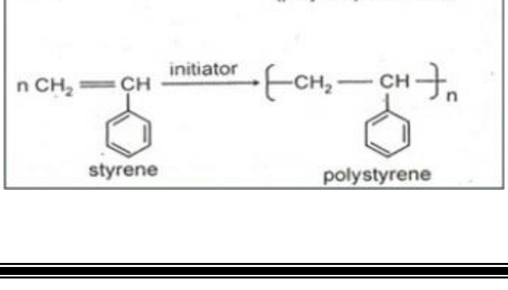


Addition/Chain polymerization

- A chain polymerization is a reaction that yields a polymer product which is the exact multiple of monomers. Thus the mechanism is also called addition polymerization. The following are the characteristics.
- The functionality of the monomer is a double bond and it is bifunctional.
- The polymerization takes place by self-addition of the monomer molecules to each other through a chain reaction.
- No biproducts like H_2O, CH_3OH etc. are produced.
- The polymer has the same chemical composition as that of monomer.
- The molecular weight of the polymer is the exact multiple of the monomers.
- The mechanism is carried out in three steps, i.e. initiation, propagation and termination.
- The mechanism is rapid.
- The conversion of p bond to s bond takes place during the polymerization, liberating 20 Kcal/mole of energy. Hence highly exothermic reactions.
- An initiator is required to start the polymerization reaction.
- The following compounds containing double bonds undergo chain polymerization, For example: **1)** Olefins, **2)** Vinyl, **3)** Allyl **4)** Dienes



2) Vinyl compounds: The general representation of vinyl compounds is CH_2=CHX, where X = halide, acid, alcohol, amine, phenyl etc.



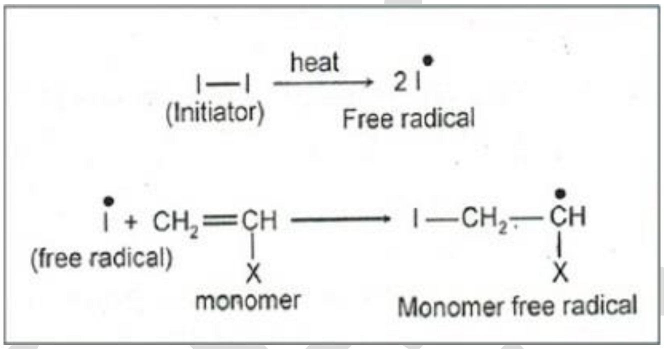
Chain polymerization is initiated by initiators and carried out in three different types of mechanism.

i) Free radical chain polymerization **ii)** Ionic mechanism **iii)** Coordination mechanism

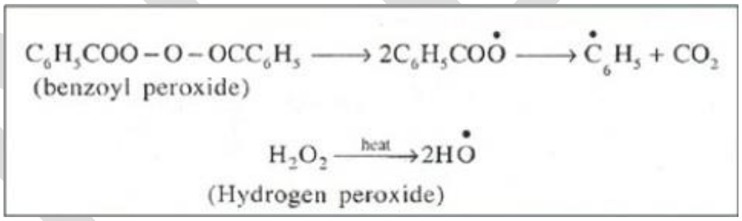
i) Free radical chain polymerization

The initiator undergoes homolytic fission to produce free radicals, which initiates and propagates (rapid chain growth) the polymerization reaction.

a) Initiation: Initiators are unstable compounds and undergo homolytic fission to produce free radicals which react with electrons of the monomer to produce monomer free radical.



Benzoyl peroxide, hydrogen peroxide are good initiators for free radical chain polymerization.



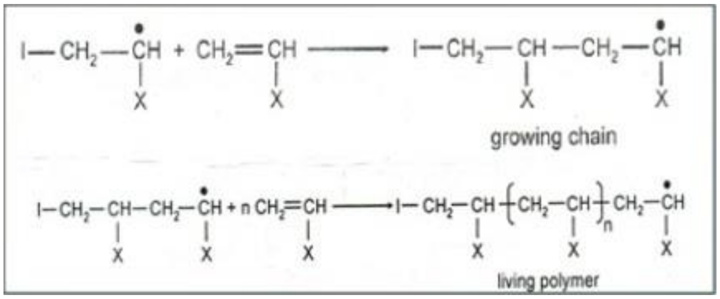
$$C_6H_5COO-O-OCC_6H_5 \longrightarrow 2C_6H_5CO\dot{O} \longrightarrow \dot{C}_6H_5 + CO_2$$

(benzoyl peroxide)

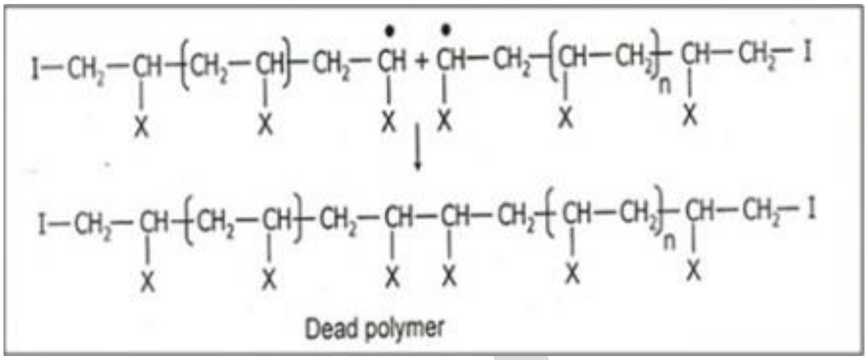
$$H_2O_2 \xrightarrow{heat} 2H\dot{O}$$

(Hydrogen peroxide)

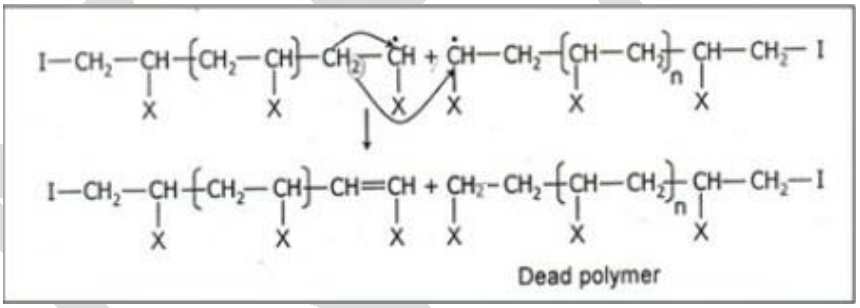
b) Propagation: The monomer free radical reacts with a number of monomers rapidly resulting in the chain growth with free radical site at the end of the chain producing a living polymer. By adding fresh monomer to the living polymer with free radical site, again chain growth starts. Hence it is known as living polymer.



c) **Termination:** Termination (to stop chain growth) of the growing polymer chain is carried by "coupling" and "disproportionation" resulting in the dead polymer. **Termination by coupling:** In coupling the collision of two growing chains causes the union of the two chains at their free radical site producing a dead polymer.



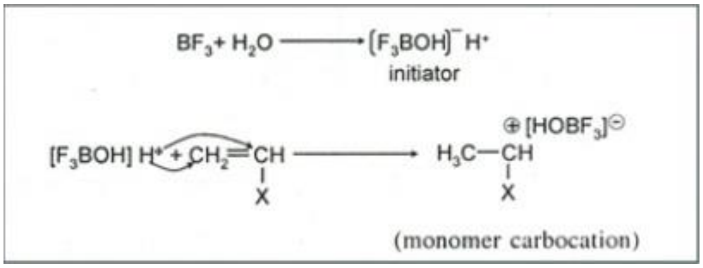
Termination by disproportionation: In termination by disproportionation, H from growing chain is abstracted by the other growing chain, utilizing the lone electron for getting stabilized, while the chain which has donated the H gets stabilized by the formation of a double bond.



ii) Ionic chain polymerization

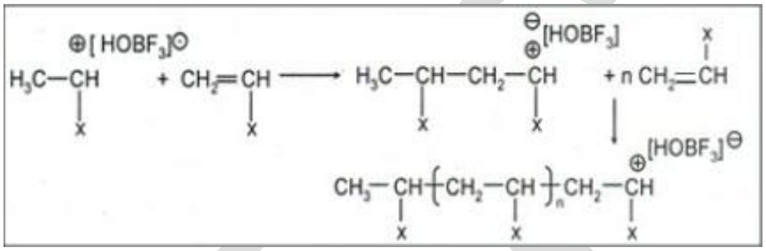
- **Cationic chain polymerization:** The heterolytic fission of the initiator results in cationic and anionic chain polymerization.

a) Initiation: In cationic chain polymerization the cation produced by the initiator attacks the electrons of the monomer forming a monomer carbonium ion. The strong lewis acids like BF_3, $AlCl_3$ etc. in presence of small amount of water initiates the reaction as follows.

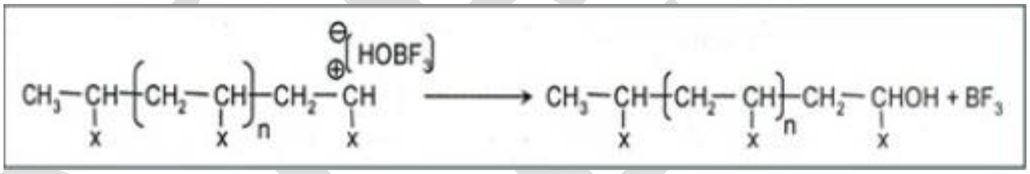


$[HOBF_3]^-$ is called counter ion, because it is always with carbonium ion of the monomer.

b) **Propagation:** The monomer carbocation attacks electrons of the other monomers resulting the chain growth with carbocation at the end of the chain.

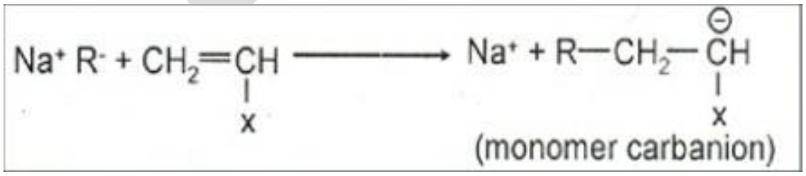


c) **Termination:** Termination of cationic chain polymerization is done by coupling where the OH^- ion from the counter ion terminates the polymerization.

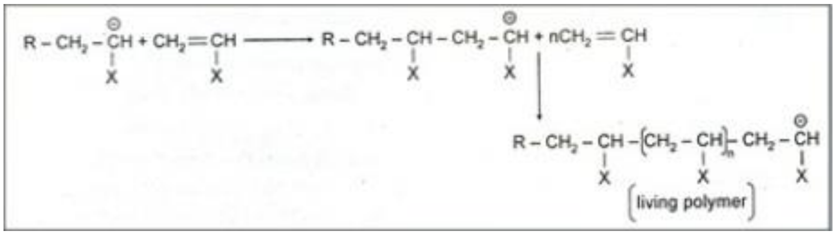


- **Anionic chain polymerization:** An anion produced by organo-alkali compounds like ethyl sodium, methyl potassium, butyl lithium etc. initiates the chain polymerization.

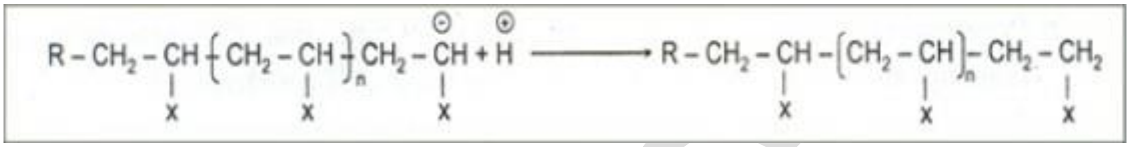
a) **Initiation:** An anion produced by the initiator will react with the monomer to produce monomer carbanion.



b) **Propagation:** Attack of the monomers by monomer carbanion results in chain growth.



c) Termination: Termination of the chain is carried out by H^+ ion.



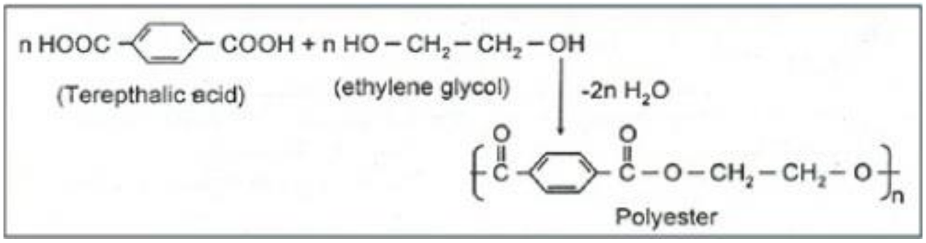
Condensation or step polymerization

Step polymerization takes place by condensation reactions of the functional groups of the monomers, with the elimination of biproducts like H_2O, HCl etc. hence known as condensation polymerization. The following are the characteristics of condensation polymerization.

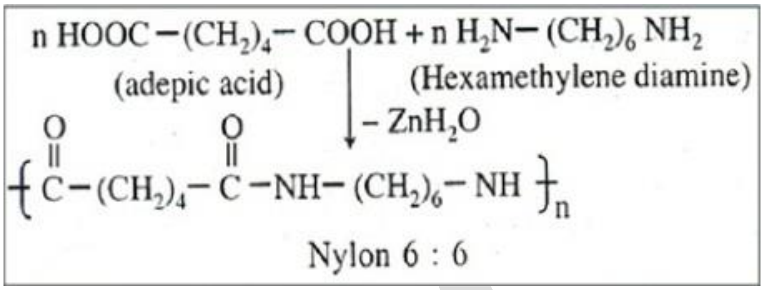
- The monomers contain functional groups like OH, -COOH, NH_2, RCOOR', halides etc.
- The functionality of the monomer must be two or more than two. The monomers must be dibasic acids, dioles, diamins or triols etc.
- The polymer is built up by a slow step wise condensation reaction of the functional groups of the monomer.
- The polymerization reaction is accompanied by the elimination of biproducts like HCl, CH_3OH, H_2O etc.
- The reactions are not exothermic.
- The molecular weight of the polymer is not the sum of the molecular weights of the monomers.
- The polymers produced are living polymers containing functional groups at the end of the chain.
- It is not a step mechanism of initiation, propagation and termination.
- The reactions are catalyzed by catalysts.

Examples of step polymerization:

- The polymerization of a diacid with diol produces polyester.



- The polymerization of a diamine with diacid gives Nylon a polyamide.



$$n\,HOOC-(CH_2)_4-COOH + n\,H_2N-(CH_2)_6\,NH_2 \xrightarrow{-\,ZnH_2O} \left[\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-NH-(CH_2)_6-NH\right]_n$$

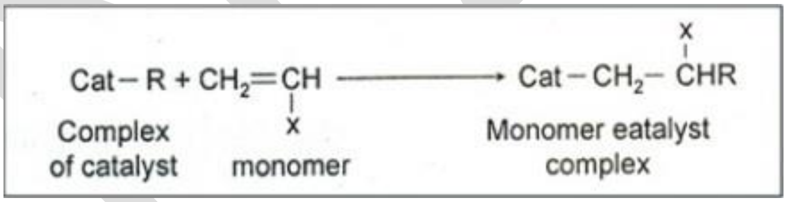
(adepic acid) (Hexamethylene diamine)

Nylon 6 : 6

Co-ordination polymerization or Zeigler-Natta polymerization

Zeigler (1953) and Natta (1955) discovered that in the presence of a combination of transition metal halides like $TiCl_4$, $ZnBr_3$ etc. with organometallic compounds like triethyl aluminium or trymethyl aluminium, stereospecific polymerization can be carried out. **Combination of metal halides and organometalic compounds are called "Zeigler Natta catalysts".** The mechanism is as follows.

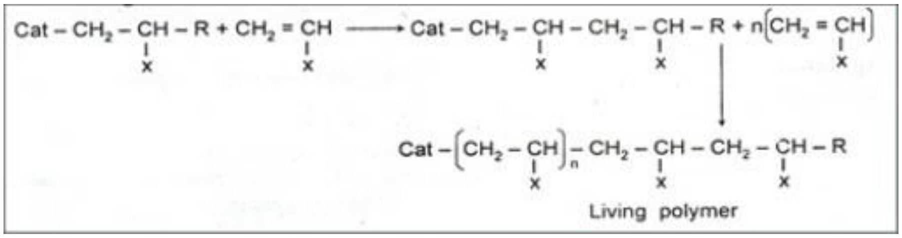
a) **Initiation:** The catalyst form monomer catalyst complexes by reacting with monomer molecules.



$$Cat-R + CH_2=\underset{X}{\underset{|}{CH}} \longrightarrow Cat-CH_2-\overset{X}{\overset{|}{C}}HR$$

Complex of catalyst — monomer — Monomer eatalyst complex

b) **Propagation:** The monomer catalyst complex reacts with fresh monomers resulting the chain growth.



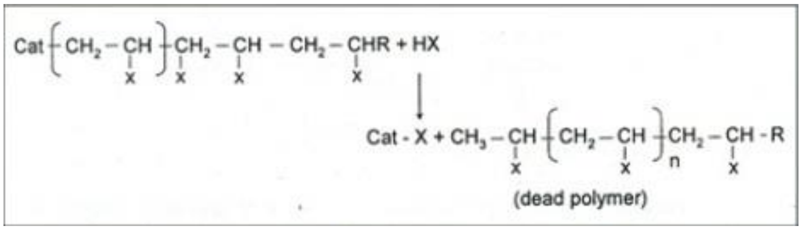
$$Cat-CH_2-\underset{X}{\underset{|}{CH}}-R + CH_2=\underset{X}{\underset{|}{CH}} \longrightarrow Cat-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{CH}}-R + n\left[CH_2=\underset{X}{\underset{|}{CH}}\right]$$

$$\downarrow$$

$$Cat-\left[CH_2-\underset{X}{\underset{|}{CH}}\right]_n-CH_2-\underset{X}{\underset{|}{CH}}-CH_2-\underset{X}{\underset{|}{CH}}-R$$

Living polymer

c) **Termination:** Termination is carried out with an active halogen compound.



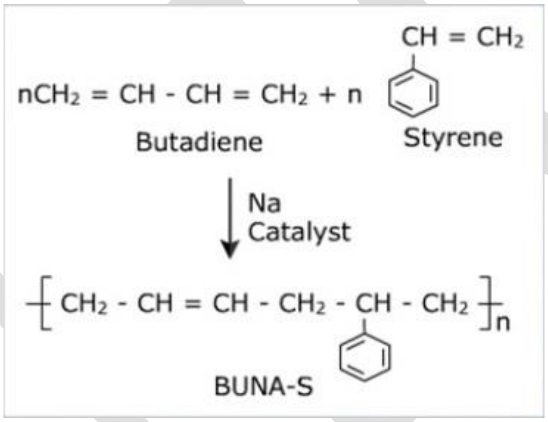
$$Cat-\left[CH_2-\underset{X}{CH}\right]-\underset{X}{CH_2}-\underset{X}{CH}-CH_2-\underset{X}{CHR}+HX \longrightarrow Cat-X+CH_3-\underset{X}{CH}-\left[CH_2-\underset{X}{CH}\right]_n-CH_2-\underset{X}{CH}-R$$

(dead polymer)

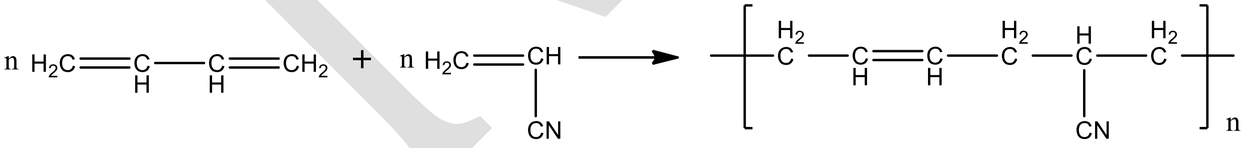
Copolymerization

It is the joint polymerization of two or more monomer species. High molecular weight compounds obtained by copolymerization are called copolymers. Preparation of Styrene rubber (BUNA-S) and Nitrile rubber (BUNA-N) are examples of this polymerization.

i) **Styrene rubber (BUNA-S) (GRS):** Styrene rubber is prepared by the copolymerization of butadiene with styrene using sodium as a catalyst.



ii) **Nitrile rubber/Acrylonitrile (BUNA-N) (GRA):** It is a polymer of butadiene and acrylonitrile (vinyl cyanide).



$$n\,H_2C=\underset{H}{C}-\underset{H}{C}=CH_2+n\,H_2C=\underset{CN}{CH}\longrightarrow\left[\overset{H_2}{C}-\underset{H}{C}=\underset{H}{C}-\overset{H_2}{C}-\underset{CN}{\overset{H}{C}}-\overset{H_2}{C}\right]_n$$

1,3-Butadiene Acrylonitrile Nitrile rubber

Plastics

- Plastics are high molecular weight organic compounds, which can be moulded or formed into stable shapes by the application of heat and pressure. The term plastic must be differentiated from resin.

- Resins are basic binding materials, which form a major part of the plastics and which actually has undergone polymerization and condensation reactions, during their preparation. Plastics are of two types. **1)** Theroplasts **2)** Thermosets.

1) **Thermoplasts:** Thermoplasts are those which can be softened on heating and harden on cooling. These are formed as a result of addition polymerization and have long molecular structure.
   Ex: PVC, Polyethelene, etc.

2) **Thermosets:** During fabrication process these resins are moulded. Once they are solidified they can't be softened.
   Ex: Bakelite, Nylon etc.

Differences between thermoplastic and thermosetting polymers

Thermoplastic polymers	Thermosetting polymers
1. They soften on heating readily.	**1.** They do not soften on heating. On prolong heating, however, they burn.
2. They consist of long-chain linear macromolecules.	**2.** The set of these polymers set molecules have three dimensional network structure, joined by strong covalent bonds.
3. They are formed mostly by addition polymerization.	**3.** They are formed by condensation polymerization.
4. By reheating to a suitable temperature, they can be softened, reshaped and thus reused.	**4.** They do not retain their shape and structure, even on heating. Hence, they cannot be reshaped and reused.
5. They are usually soft, weak and less brittle.	**5.** They are usually hard, strong and more brittle.
6. These can be reclaimed from wastes.	**6.** They cannot be reclaimed from wastes.
7. They are usually soluble in some organic solvents.	**7.** Due to strong bonds and cross linking, they are insoluble in almost all organic solvents.

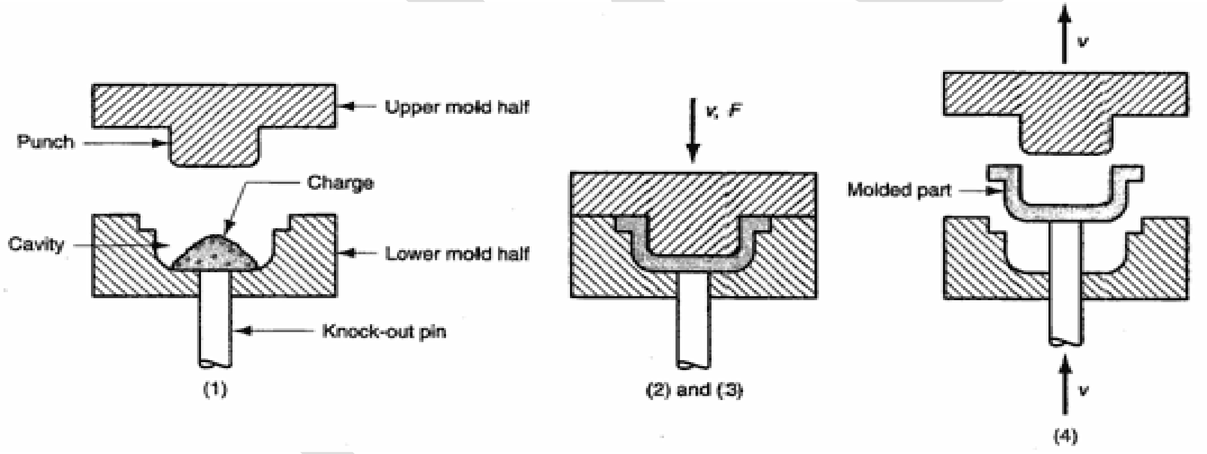
Plastic moulding methods

Depending on the type of resin, whether thermoplastic or thermoset the following fabrication of plastics are used.

1. Compression moulding
2. Injection moulding

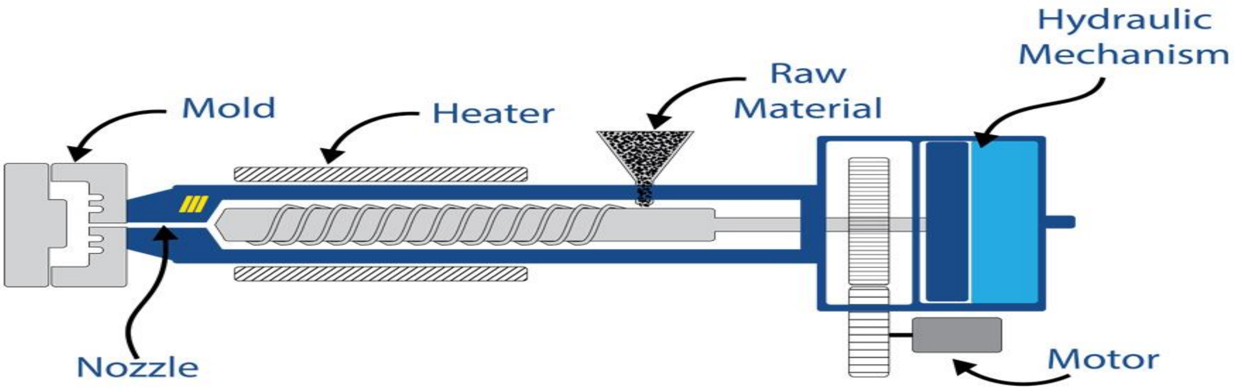
1. Compression moulding

- This method is applicable to both thermo plastics and thermo setting resigns. The predetermined quantity of plastics powder in proper proportions is filled between two halves pieces of mould which are moved relative to each other.
- Heat and pressure are then applied according to specification, and then cavity gets filled with fluidized plastics. Two halves are closed very slowly.
- Finally curing is done either by heating or cooling. Heating is applied in the case of thermo settings and cooling is applied in the case of thermo plastics.
- After curing the mould article is taken out by opening the mould parts.



2. Injection moulding

- It is applicable to thermo plastics polymers. In this the moulding plastics powder is introduced into hot cylinder heated by hot air jacket which is injected at a controlled rate into mould by using piston.
- The mould is kept cold to allow the hot plastics to cure and become rigid. After curing the mould article is taken out by opening the mould parts.

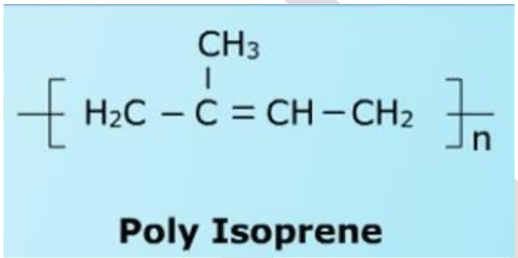


Rubbers and elastomers

Natural rubber:

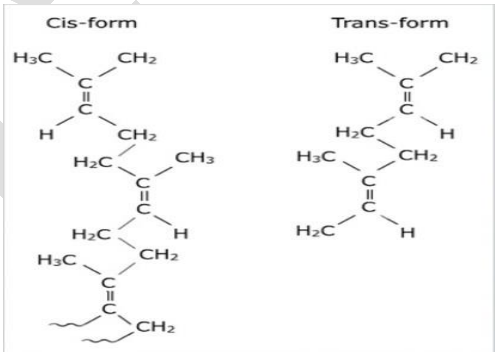
It is believed to be a polymer of isoprene.

- Rubber is obtained from the latex of Hevea tree.
- The main composition of natural rubber is polyisoprene
- Isoprene in natural rubber exists in two geometric forms, Cis and Trans.
- Cis-polyisoprene is present in Hevea rubber and trans polyisoprene in Guttapercha.



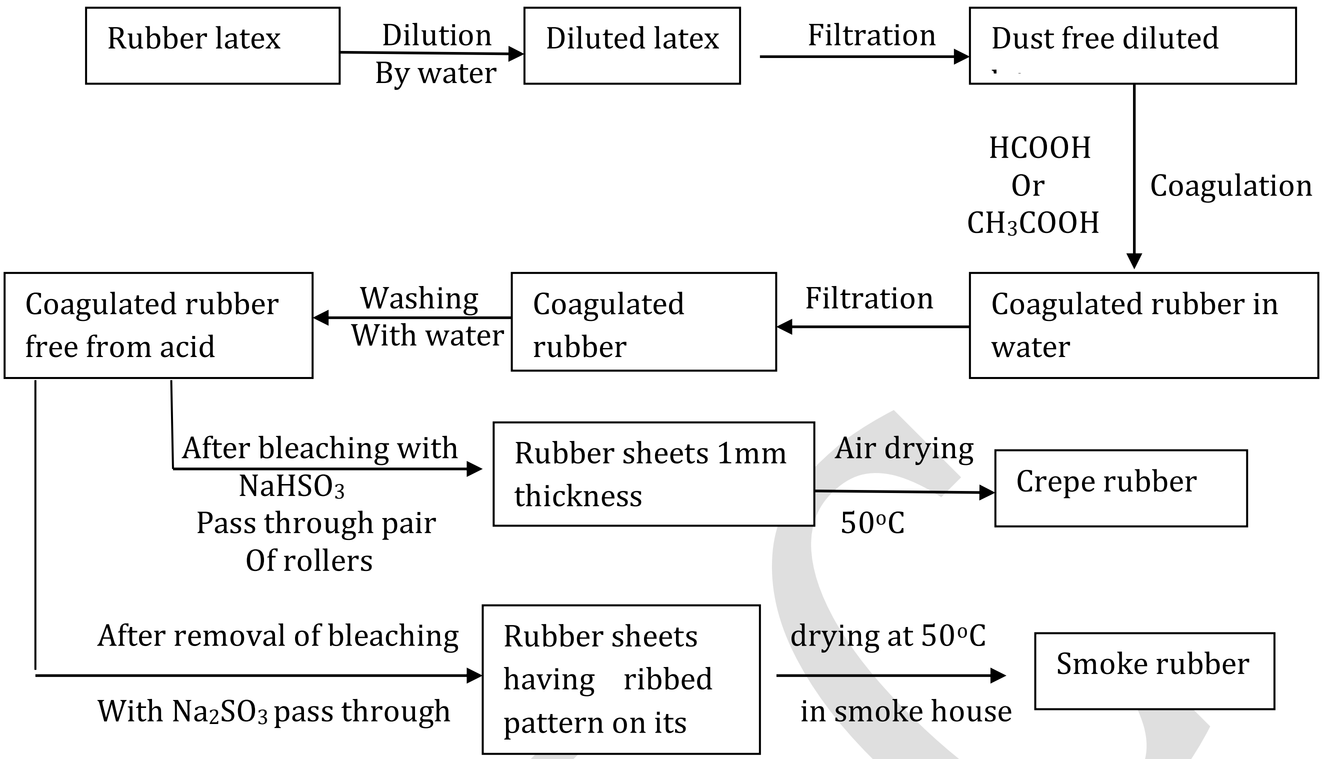
$$\left[H_2C - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH - CH_2 \right]_n$$

Poly Isoprene



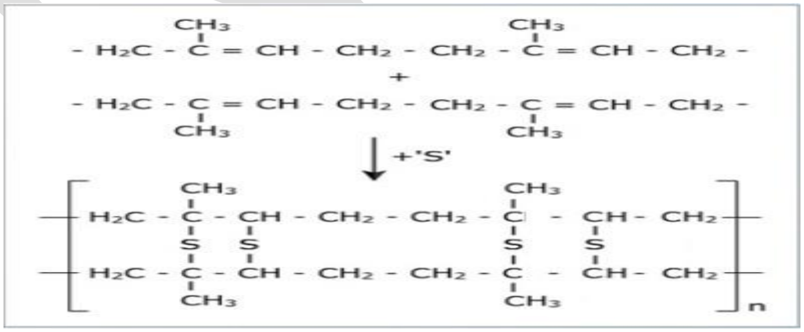
Processing of Natural Rubber:

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



Vulcanization of Rubber:

- The raw rubber possesses very undesirable properties such as low tensile strength and possesses elasticity over a limited range of temperatures.
- In this process natural rubber is heated with sulphur (or) sulphur compounds at 150^{0}C for few hours.
- Cross linked product is formed when sulphur combines chemically at double bonds of different rubber strips. This process is known as vulcanization.



Advantages:

- Vulcanized rubber has good tensile strength.
- It has good resistant to organic solvents.
- Posses high chemical resistance.
- Posses low water absorption tendency.

FUELS

Introduction

- Fuel is a combustible substance, containing carbon as main constituent, which on proper burning gives large amount of heat, which can be economically for domestic and industrial purposes.
- The main sources of fuels are coal and petroleum oils, natural gas etc.
- During the combustion process of fuels, a redox reaction takes place between fuel and oxygen which is accompanied by a large amount of heat. Hence these fuels are termed as chemical fuels.
- The energy liberated is due to the rearrangement of valance electrons in the atom of reactants, which results in the formation of compounds like CO_2, H_2O etc.
- The products of combustion have less energy than the reactants and therefore, the energy released during the combustion process is the difference in the energy of reactants and products that are formed.
- The primary or main sources of fuels are coal, natural gas and petroleum. These are stored fuels available in the earth's crust and are called fossil fuels.

Classification of fuels

Fuels are classified into two types

- Occurrence
- State of Aggregation

- **Occurrence:**
  - On the basis of occurrence, fuels are classified in to two types.

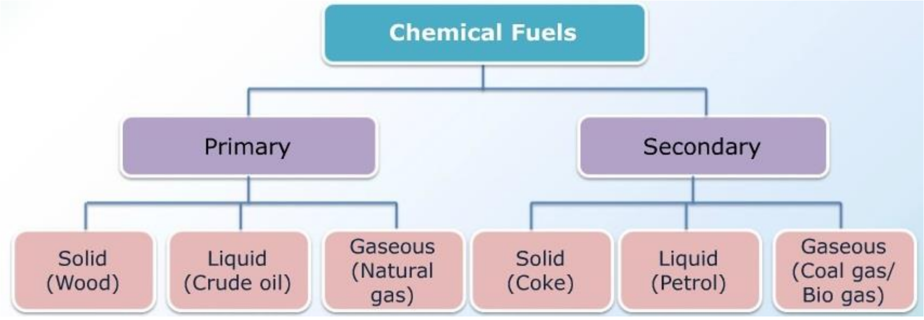
Natural (or) primary fuels:

- Fuels which are found in nature are called natural or primary fuels.
- **Ex:** Wood, Coal, Crude oil.

Artificial (or) secondary fuels:

- Fuels which are prepared from the primary fuels are called Artificial or secondary fuels.
- **Ex:** Kerosene, LPG, CNG, Coke.

- **State of aggregation:**
  - On the basis of the physical state of aggregation, fuels are classified in to solids, liquids and gases.



Calorific Value

Calorific value of a fuel is the total quantity of heat liberated when a unit mass of the fuel burnt completely.

Units

Calorie: The amount of heat required to raise the temperature of 1g water through 1^0C.

Kilocalorie: The quantity of heat required to raise the temperature of 1kg of water through 1^0C. 1K. Cal = 1,000 Calories.

B.T.U (British Thermal Unit): Defined as the quantity of heat required to raise the temperature of one pound of water through 1^0F. 1B.T.U = 252 cal.

Centigrade Heat Unit (C.H.U): The quantity of heat required to raise the temperature of 1 pound of water through 1^0C. 1K.cal = 3.968 B.T.U = 2.2 C.H.U.

- **Higher (or) gross calorific value (HCV or GCV):**

HCV is the total amount of heat produced, when unit mass/volume of the fuel is burnt completely and the products of combustion have been cooled to room temperature.

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

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

Characteristics of Good Fuel

A good fuel should possess the following characteristics:

High calorific value:

- A fuel should possess high calorific value which results in the liberation of a large amount of heat per unit mass/volume of the fuel.

Moderate Ignition temperature:

- It is the lowest temperature to which the fuel is to preheat so that it burns smoothly. Low ignition temperature is dangerous for storage, since it causes fire hazards.
- Whereas, high ignition temperature causes difficulty in ignition of the fuel. Hence, a good fuel should possess moderate ignition temperature.

Low ash content:

- An ideal fuel should possess low ash content.
- Ash is non-combustible when a sample of coal, with high ash content is used in a furnace, the ash produced in the furnace, fuses due to high temperature and forms hard masses called clinkers.
- Clinkers are bad conductors of heat and causes loss of heat. Further, ash does not contribute to calorific value.

Low moisture content:

- The moisture content of a coal sample reduces the heating value of the fuel. Hence, samples of coal possess low moisture content.

Moderate velocity of combustion:

- If the rate of combustion is low, then the required high temperature may not be possible, because a part of the heat liberated may get radiated, instead of raising the temperature. On the other hand, too high combustion rates are not required.

Low cost:

- A fuel should be available at a cheaper rate.

Combustion nature:

- A good fuel should undergo combustion easily and should controllable when required.

SOLID FUELS

Coal

- Coal is highly carbonaceous matter that has been formed as a result of alteration vegetable matter under certain favorable conditions.
- It is composed of C, H, N and O, besides non-combustible in organic matter.

Analysis of Coal

To determine quantity of coal, the following two types of analysis are

- Proximate analysis
- Ultimate analysis

Proximate analysis

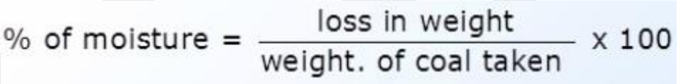
- The data varies with the procedure adopted and hence it is called proximate analysis.

Proximate analysis of coal determines:

- Moisture content
- Volatile matter
- Fixed carbon
- Ash

Moisture Content

- About 1 gm of finely powdered air-dried coal sample is weighed in a crucible.
- The crucible is placed inside an electric hot air-oven, maintained at 105^0C-11^0C for 1hr.
- The crucible is then taken out and cooled in desiccators and weighed. Loss in weight reported as moisture.

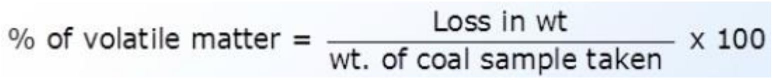


$$\% \text{ of moisture} = \frac{\text{loss in weight}}{\text{weight. of coal taken}} \times 100$$

Importance: Moisture in coal evaporates when the coal is burnt and it takes some of the heat liberated in the form of latent heat of evaporation. Therefore moisture lowers the calorific value.

Volatile matter:

- The dries of coal left in the crucible is covered with a vented lid and placed in a muffle furnace maintained at 925-970^0C for 7 min.
- Crucible is first cooled in air, then inside desiccators and weighed again.
- Loss in weight is reported as volatile matter. The percentage of volatile matter is,



$$\% \text{ of volatile matter} = \frac{\text{Loss in wt}}{\text{wt. of coal sample taken}} \times 100$$

Importance: High volatile matter escapes unburnt and hence a high volatile matter containing coal burns with a long flame, high smoke and has low calorific value. Therefore, lesser the volatile matter, better the rank of coal.

Ash:

- The residual coal left in the crucible is then heated without a lid in a muffle furnace at 700-750^{0}C for half an hour.
- The crucible is then taken out, cooled first in air, then in desiccators and weighed.
- Heating, cooling and weighing is repeated, till a constant weight is obtained.
- The residue is reported as ash. Thus the percentage of ash is,

$$\% \text{ Ash} = \frac{\text{wt. of ash left}}{\text{wt. of coal taken}} \times 100$$

Importance: Ash is a non-combustible matter, which reduces the calorific value of coal. Ash causes the hindrances to the flow of air and heat, which lowers the temperature. Also, it often causes trouble during firing by forming clinkers. Hence, lower the ash content, better the quality of coal.

Fixed Carbon:

- The percentage of fixed carbon is given by:

% of Fixed Carbon = 100-(% of moisture + volatile matter + ash)

Importance: Higher the percentage of fixed carbon, greater will be its calorific value and better the quality of coal. Hence, a high percentage of fixed carbon is desirable.

Ultimate analysis

- It is carried out to ascertain the composition of coal.
- Ultimate analysis includes estimation of the following:
- Carbon and hydrogen
- Sulphur
- Nitrogen
- Oxygen

Carbon and hydrogen

- About 1g of accurately weighed coal sample is burnt in a current of oxygen in a combustion chamber.
- C & H of the coal are converted in to CO_2 and H_2O.

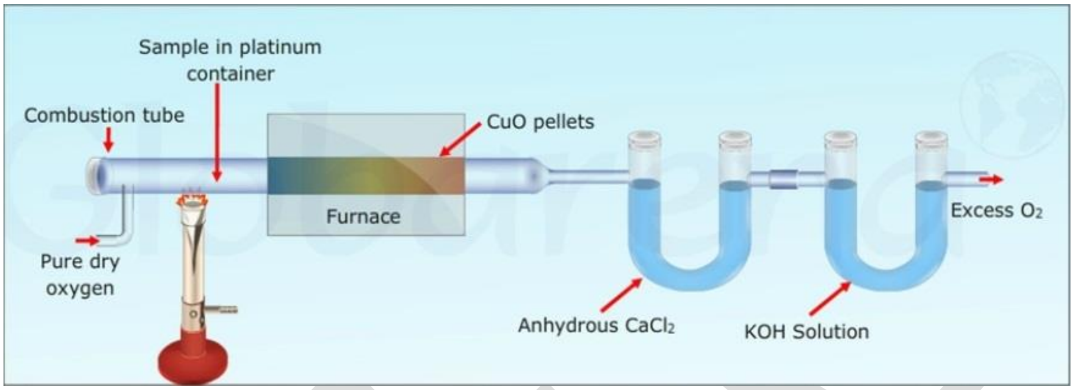
$$\mathbf{C + O_2 \longrightarrow CO_2; \qquad H_2 + 1/2O_2 \longrightarrow H_2O}$$

- The products of combustion CO_2 and H_2O are absorbed respectively by KOH and $CaCl_2$ tubes of known weights.
- The increase in weight of these tubes are then determines.

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

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

Estimation of carbon and hydrogen



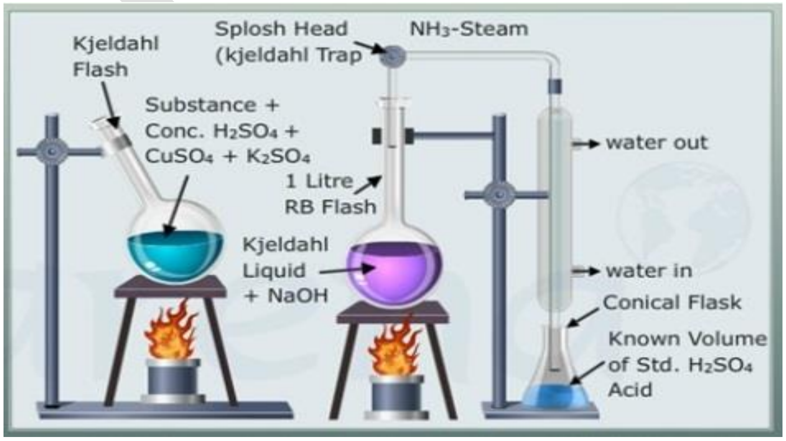
$$\% C = \frac{\text{Increases in wt of KOH tube} \times 12 \times 100}{\text{wt . of coal taken} \times 44}$$

$$\% H = \frac{\text{Increase in wt . of } CaCl_2 \text{ tube} \times 2 \times 100}{\text{wt . of coal taken} \times 18}$$

Importance:

Greater the percentage of carbon and hydrogen, better is the coal in quality and calorific value.

Nitrogen



Nitrogen present in coal sample can be estimated by Kjeldahl's method;

- About 1 g of accurately weighed powered coal is heated with concentrated H_2SO_4 in the presence of a small quantity of K_2SO_4 (catalyst), in a long-necked flask called Kjeldahl's flask.
- After the solution becomes clear it is treated with an excess of KOH (solution) and liberated ammonia is distilled and absorbed in a known volume of the standard acid solution.
- After the solution is clear i.e., when the entire is converted into ammonium sulphate, it is treated with an excess of NaOH to liberate ammonia. The liberated ammonia is distilled into a measured amount of standard acid.
- The volume of unused acid (H_2SO_4) is then determined by back titration with standard NaOH solution.
- The amount of acid neutralized by the liberated ammonia is determined from which the nitrogen present in the sample is calculated.

$$\text{Nitrogen} + H_2SO_4 \xrightarrow{\text{Heat}} (NH_4)_2SO_4$$

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow 2NH_3\uparrow + Na_2SO_4$$

$$\%\ N = \frac{\text{volume of acid used x normality of acidx } 1.4}{\text{wt . of coal taken}}$$

Importance: Nitrogen has no calorific value and hence, its presence in coal is undesirable. Thus a good quality coal should have very little nitrogen content.

Sulphur

- Sulphur present in coal is determined from the washings obtained from the known mass of coal used in a bomb calorimeter for determination of calorific value.
- During combustion, suphur is converted into sulphate.
- The washings are treated with barium chloride, whereby $BaSO_4$ is precipitated.
- The precipitate is filtered, washed and heated to constant weight.
- Sulphate washings from bomb calorimeter + $BaCl_2 \longrightarrow BaSO_4$

$$\%\text{ of S} = \frac{\text{wt. of } BaSO_4 \times 32 \times 100}{\text{wt. of coal taken} \times 233}$$

Importance: Presence of sulphur is highly undesirable in coal and is used for making coke in the iron industry, as it transfer to the iron metal and badly affect the quality and properties of steel. Moreover, oxides of sulphur pollute the atmosphere that leads to corrosion of combustion apparatus.

- **Ash**
  - Ash determination is carried out as in proximate analysis.
- **Oxygen**
  - It is obtained by difference

% of O = 100 - % (C + H + S + N + ash)

Importance: Oxygen content decreases the calorific value of coal. High oxygen-content coals are characterized by high inherent moisture, low calorific value and low coking power. Hence, oxygen is undesirable. Thus, a good quality coal should have a low percentage of oxygen.

Theoretical calculation of Calorific value of a fuel (Dulong's formula)

- The calorific value of fuel can be approximately computed by noting the amounts of the constituents of the fuel. The higher the calorific values of some of the chief combustible constituents of fuel are tabulated below:

Table:1 Calorific values of fuel constituents

Constituent	**Hydrogen**	**Carbon**	**Sulphur**
HCV (Kcal/Kg)	34,500	8,080	2,240

- The oxygen, if present in the fuel, is assumed to be in combined with hydrogen, i.e., in the form of fixed carbon [H_2O]. So, the amount of hydrogen available for combustion = Total mass of hydrogen in fuel – fixed hydrogen

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

  (8 parts of oxygen combine with one part of hydrogen to form H_2O.

Dulong's formula for calorific value from the chemical composition of fuel is:

$$\mathbf{HCV = 1/100[8{,}080C + 34{,}500\ (H\text{-}O/8) + 2{,}240\ S]\ Kcal/Kg}$$

- Where C, H, O and S are the percentages of carbon, hydrogen, oxygen and sulphur in the fuel respectively.

$$\mathbf{LCV = [HCV\text{-}9/100H \times 587]\ Kcal/Kg = [HCV\text{-}0.09H \times 587]\ Kcal/Kg}$$

- This is based on the fact that 1 part of H by mass gives 9 parts of H_2O and latent heat of steam is 587 Kcal/Kg.

LIQUID FUELS

Petroleum

- Petroleum is dark greenish-brown viscous oil found deep in earth's crust.
- It is composed mainly of hydrocarbons together with small amounts of organic compounds containing oxygen, N_2 and sulphur.
- The average composition of crude petroleum is

C	-	79.5 to 87.1%
H	-	11.5 to 14.8%
S	-	01. To 3.5%
N + O	-	0.1 to 0.5%

Refining of crude oil

- The crude is separated into various useful fractions by fractional distillation and finally converted into desired specific products.
- The process is called refining of crude oil and the plants set up for the purpose called refineries.
- Refining of petroleum is done in different stages such as
  - **Step-1:** Separation of water
  - **Step-2:** Removal of harmful sulphur compounds
  - **Step-3:** Fractional distillation

Step-1: Separation of water

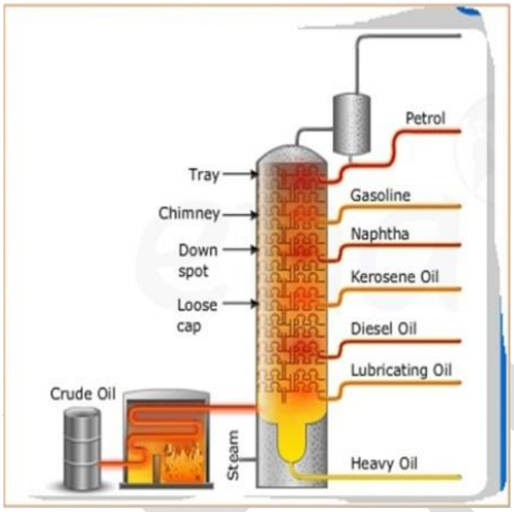
- The crude oil acquired from the earth's crust is in the form of stable emulsion of oil and salt water.
- When this mixture is passed between the two highly charged electrodes they destroy the emulsion films and the colloidal water droplets coalesce into bigger drops and they get separated from the oil.

Step-2: Removal of harmful sulphur compounds

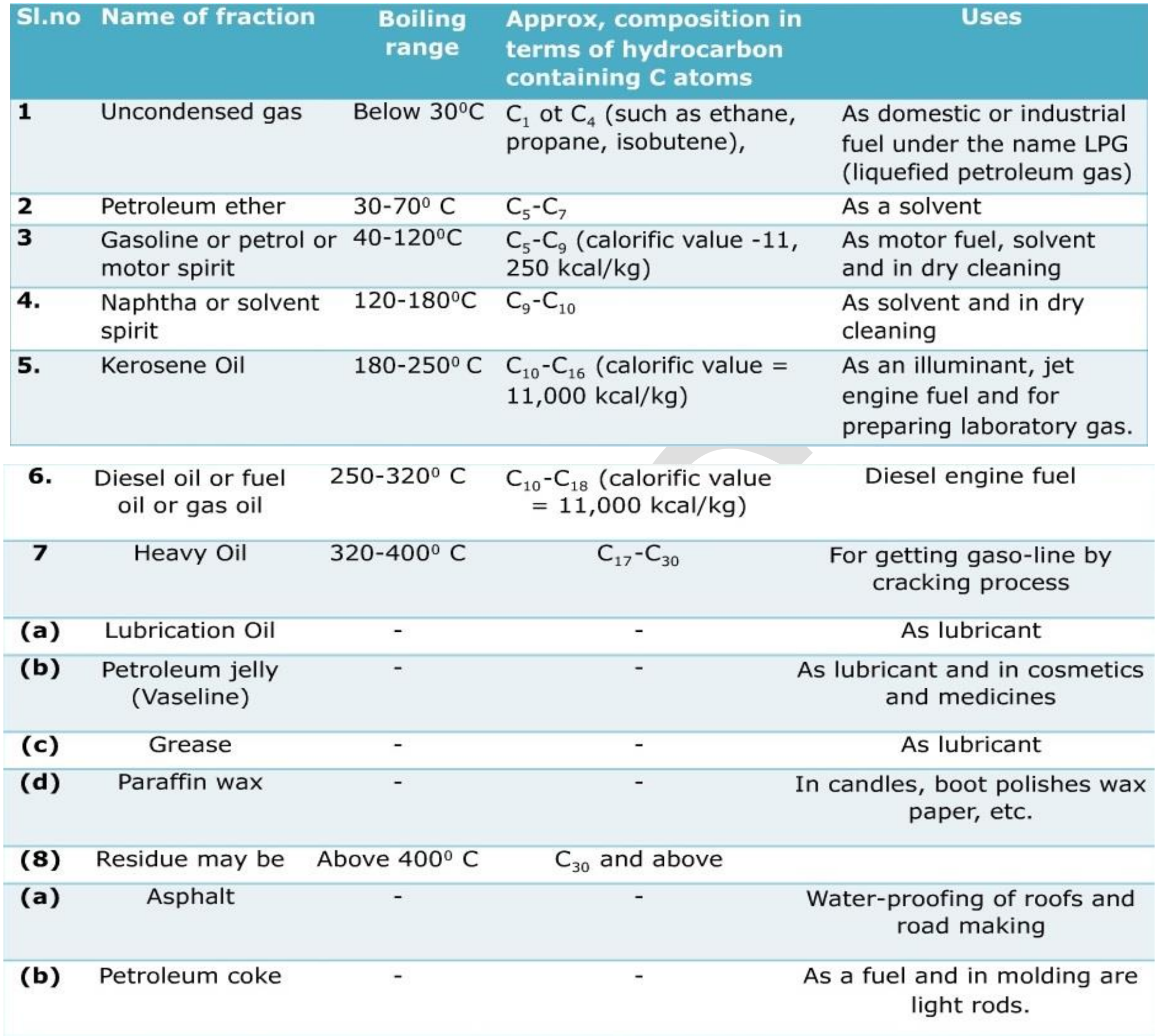
- To remove the sulphur compounds in the crude oil, the crude oil is treated with copper oxide.

- The sulphur compounds convert into the insoluble copper sulphide and can be removed by the process of filtration.
- Substances like sodium chloride and magnesium chloride present will corrode the refining equipment and result in the formation of scale.
- These can be removed by techniques like dehydration and electric desalting.

Step-3: Fractional distillation



- The crude oil enters through the bottom of the still by an inlet. The crude oil is heated with steam, inside the still to a temperature of about 400^0C
- All volatile constituents except the residue are evaporated. The vapours are then passed up a fractionating column.
- Fractional column is a tall cylindrical tower containing a number of the stainless steel trays at short distances.
- Each tray is provided with a small chimney, covered with a loose cap.
- As the vapour goes up, they become gradually cooler and fractional condensation takes place at different heights of column.
- The constituents of fraction and the temperature at which they are obtained are given in the table below.



Sl.no	Name of fraction	Boiling range	Approx, composition in terms of hydrocarbon containing C atoms	Uses
1	Uncondensed gas	Below 30⁰C	C_1 ot C_4 (such as ethane, propane, isobutene),	As domestic or industrial fuel under the name LPG (liquefied petroleum gas)
2	Petroleum ether	30-70⁰ C	C_5-C_7	As a solvent
3	Gasoline or petrol or motor spirit	40-120⁰C	C_5-C_9 (calorific value -11, 250 kcal/kg)	As motor fuel, solvent and in dry cleaning
4.	Naphtha or solvent spirit	120-180⁰C	C_9-C_{10}	As solvent and in dry cleaning
5.	Kerosene Oil	180-250⁰ C	C_{10}-C_{16} (calorific value = 11,000 kcal/kg)	As an illuminant, jet engine fuel and for preparing laboratory gas.
6.	Diesel oil or fuel oil or gas oil	250-320⁰ C	C_{10}-C_{18} (calorific value = 11,000 kcal/kg)	Diesel engine fuel
7	Heavy Oil	320-400⁰ C	C_{17}-C_{30}	For getting gaso-line by cracking process
(a)	Lubrication Oil	-	-	As lubricant
(b)	Petroleum jelly (Vaseline)	-	-	As lubricant and in cosmetics and medicines
(c)	Grease	-	-	As lubricant
(d)	Paraffin wax	-	-	In candles, boot polishes wax paper, etc.
(8)	Residue may be	Above 400⁰ C	C_{30} and above	
(a)	Asphalt	-	-	Water-proofing of roofs and road making
(b)	Petroleum coke	-	-	As a fuel and in molding are light rods.

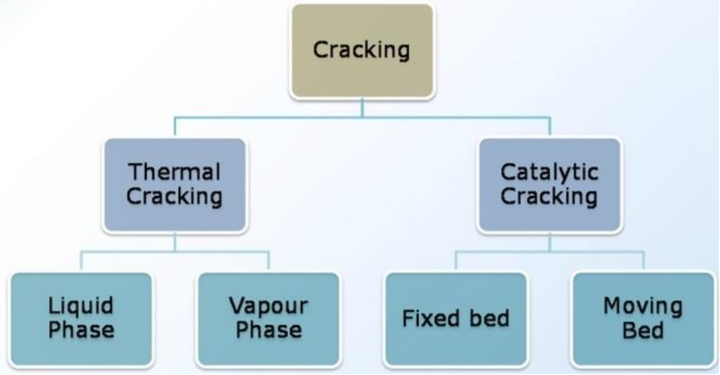
Cracking

- The process of breaking bigger hydrocarbon molecular to simpler, low boiling hydrocarbons of low molecular weight is called cracking.

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

Decane **n-pentane** **Pentene**

Cracking is carried out in different ways is given below



Thermal cracking

Thermal cracking is the breaking of bigger hydrocarbons into simpler, low boiling, lower molecular weight hydrocarbons making use of high temperature and pressure.

Catalytic cracking

In catalytic cracking, a catalyst is used at low pressure and moderate temperature. The catalyst like aluminum oxide, aluminium metasilicate, etc. is used as catalyst.

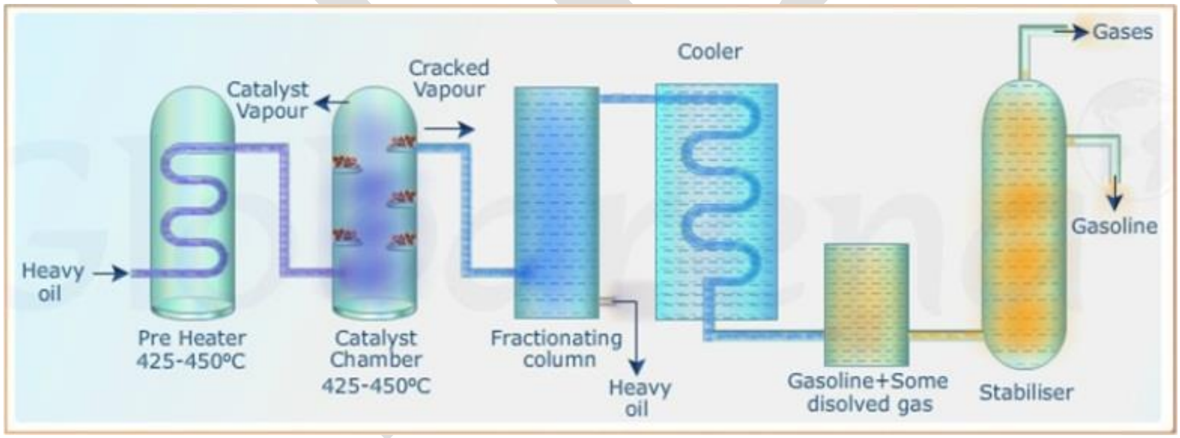
Advantages of catalytic cracking over thermal cracking

- The yield of petrol is higher.
- Quality of petrol is produced is better.
- A much lower pressure is needed in catalytic cracking.
- The product contains very little amount of undesirable 'S'

Types of catalytic cracking

- Fixed bed catalytic cracking
- Moving bed catalytic cracking

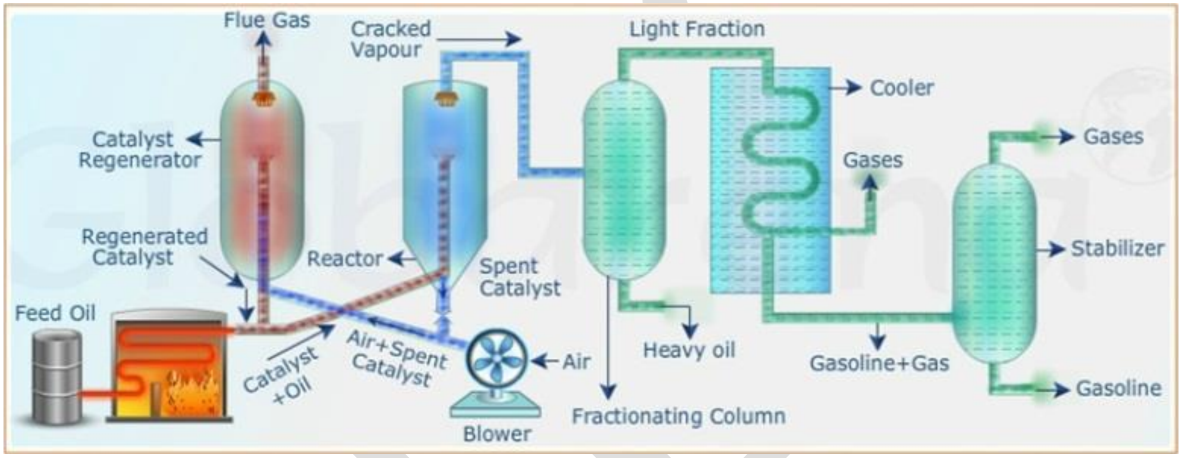
Fixed bed catalytic cracking



- Zirconium oxide mixed with artificial clay is used as catalyst which is placed in the catalytic chamber at fixed places in shelf's. Therefore, it is called fixed-bed catalytic process.
- The oil vapours are heated in a preheater to cracking temperature 425-450^{0}C and forced through a catalytic chamber maintained at 425-450^{0}C temperature and 1.5 Kg/cm^2 pressure.

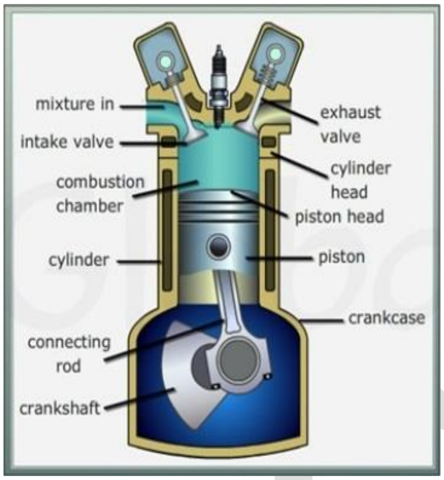
- About 40% of the charge converted into gasoline and about 2.4% carbon is formed. The carbon gets absorbed on the catalyst bed.
- Vapours produced, are then passed through a fractionating column, where heavy oil fractions condense.
- The vapours are then passed through a cooler, where some of the gases are condensed with gasoline and uncondensed gases move on.
- Gasoline containing some dissolved gases then sent to a stabilized, where the dissolved gases are removed and pure gasoline is obtained.

Moving bed catalytic cracking



- The solid catalyst is very finely powdered, so that it behaves almost as a fluid, which can move freely in the chamber.
- Vapours of cracking stock (heavy oil, gas oil etc.) mixed with fluidized catalyst are forced into a large reactor bed.
- Near the top of the reactor, there is a centrifugal separator (called cyclone), which allows only the cracked oil vapours to pass on to the fractionating column by retaining the catalyst.
- During cracking, carbon is deposited on catalyst and settles to the bottom from where it is forced by an air blast to the regenerator (maintained at 600^0C)
- In the regenerator, carbon is burnt and regenerated catalyst flows through a stand-pipe for mixing with the fresh batch of incoming oil.
- As the top of the regenerator there is a separator, which permits only gases (CO_2) to pass out, and hold catalyst particles.

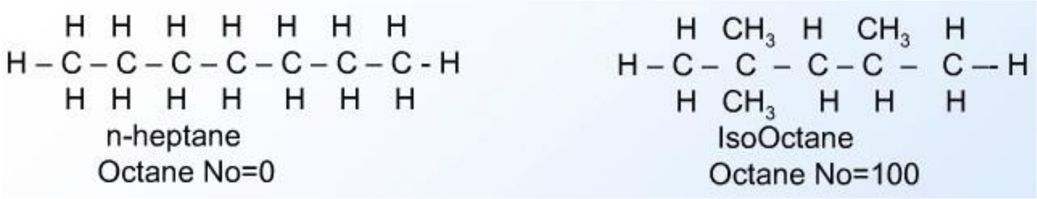
Knocking



- In the combustion of liquid fuel in internal combustion, a spark is struck in the cylinder containing petrol vapour mixed and air for the initiation of the combustion reaction.
- After striking the spark in the cylinder, the flame should spread rapidly and smoothly through the gaseous mixture. This leads to the combustion and expansion of the mixture of products combustion which pushes the piston down the cylinder.
- The ratio of the volume in the cylinder at the end of suction-stroke to the volume at the end of the compression-stroke of the piston is known the compression ratio.
- The efficiency of engine increases with the increase in the compression ratio and the compression ratio is influenced by the composition of petrol used.
- Under certain circumstances, the rate of oxidation becomes so large that the last portion of the fuel-air mixture gets ignited which is called pre-ignition, producing a large thumping sound called knocking. The knocking results in loss of efficiency.

Octane rating

- It has been found that n-heptane knock very badly and hence its anti-knocking value has been given zero.
- On the other hand isooctane given very little knocking. So its anti-knock value has been given as 100.
- Octane number of a gasoline is the % of isooctane in mixture of isooctane and n-heptane which matches the fuel under test in knocking characteristics



n-heptane
Octane No=0

IsoOctane
Octane No=100

Improvement of anti-knock characteristics of a fuel:

- The octane number of internal combustion fuels is increased by the addition of materials as tetra ethyl lead, $(C_2H_5)_4Pb$, MTB ether, benzene etc., however, the usage of tetra ethyl lead is stopped due to its environmental pollution hazards.

Unleaded petrol:

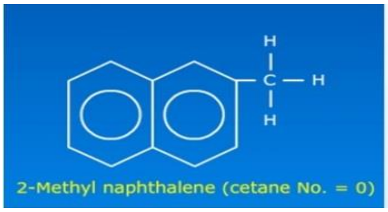
- The method of increasing the octane number of petrol is to add high octane compounds like isopenetene, isooctane, ethyl benzene, isopropyl benzene and methyl tertiary butyl ether (MTBE).
- Out of all these compounds, MTBE is preferred as it contains oxygen in the form of ether group and supplies oxygen for the combustion of petrol in an internal combustion engine. This reduces the extent of peroxy compound formation.
- Unleaded petrol is the enhancement of octane rating and is accomplished without the addition of lead compounds.

Uses of unleaded petrol:

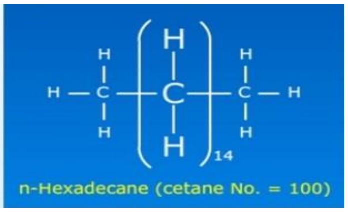
- It prevents the use of catalytic converter attached to the exhaust in automobiles.
- A catalytic converter contains a catalyst (Rhodium), which converts the toxic gases (CO and NO) to form gases (CO_2 and N_2 respectively). Moreover, it oxidizes unburnt hydrocarbons into CO_2 and H_2O.

Cetane Rating:

- The suitability of a diesel fuel is determined by its cetane value, which is the percentage of n-hexadecane in a mixture of n-hexadecane and 2-methyl naphthalene, which has the same ignition characteristics as the diesel fuel.
- The cetane number of a diesel fuel can be increased by the addition of a small quantity of “pre-ignition dopes” like ethyl nitrite, acetone peroxide etc.



2-Methyl naphthalene (cetane No. = 0)



n-Hexadecane (cetane No. = 100)

UNIT-II

POLYMERS AND FUEL CHEMISTRY

IMPORTANT QUESTIONS

1. What is polymerisation? Explain the chain growth & step growth polymerization with examples.
2. Explain about mechanism of Addition polymerization (Free radical, cationic, anionic).
3. Explain the difference between thermoplastics and thermosetting plastics
4. Explain the mechanism of co-ordination polymerization.(Z-N catalysis)
5. What is meant by moulding of plastics? Mention the moulding techniques of Compression and injection moulding with neat diagram.
6. Explain the procedures used in the processing of natural rubber. And how to overcome the drawbacks of natural rubber by vulcanization process?
7. Explain analysis of coal.
8. Describe refining of petroleum with diagram.
9. What is cracking? How gasoline is obtained from moving and fixed catalytic cracking?
10. What is meant by knocking? Explain how molecular structure will affect the Octane and cetane numbers.

UNIT-III

CHEMISTRY OF ADVANCED MATERIALS

NANO METERIALS

Introduction

- The materials like metals, non-metals, and ceramics, polymeric or composite which are made up of nano sized particles i.e. particles in the range of 1 nm to 100 nm are called nanomaterials.

Or

- Nanomaterials are those which have structure components with atleast one dimension less than 100 nm.

Examples:

Size of hydrogen atom	-	0.1 nm
Size of water molecule	-	<1 nm
Size of RBC	-	500 nm
Size of human hair	-	50000 nm
Diameter of carbon nanotube	-	1.3 nm

- The properties of materials like melting point, conductivity, colour, reactivity, reaction rate, catalytic activity are different for different sizes i.e. bulk and nano.

Examples:

- Bulk gold looks yellow but 12 nm nano sized gold particles look red.
- Bulk silver is inert but nano scale silver shows anti bacterial activity.
- Graphite possesses less mechanical strength, carbon nanotubes posses' high mechanical strength.
- The catalytic activity of materials at nano scale is much higher than large size.

- Nanomaterials can be effectively used for many specific applications which cause revolutionary changes in the field of electronics, medicine, energy, agriculture, space, security, defence, construction etc.
- Nano means 10^{-9}. A nanometer is one thousand millionth of a meter. Atoms are extremely small and the diameter of a single atom can vary from 0.1 to 0.5 nm depending on the type of the element. For example, one carbon atom is approximately 0.15 nm in diameter.

Nanomaterials: The materials in which the atoms are in the order of 1 to 100 nm and these atoms will not move away from each other, called as nanomaterials.

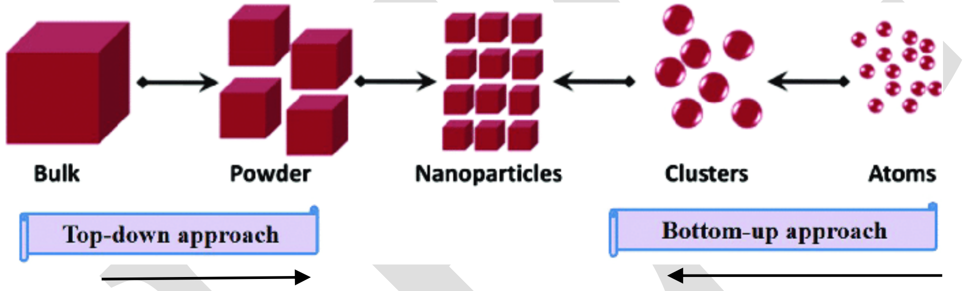
Ex: C, ZnO, Cu–Fe alloys, Ni, Pd, Pt etc.

1. Materials that are nanoscale in one dimension called as nano layers [Thin films, surface coatings].
2. Two dimensional nanomaterials are called as nano tubes and nanowires.
3. Three dimensional nanomaterials are called as nanoparticles. **Ex:** Precipitates, Colloids & Quantum dots, tiny particles of semi-conductor materials.

General methods of preparation:

There are basically two major types of approach for the preparation of nano materials.

1. **Top-down approach:** Top down approach refers to successive cutting of a bulk material to get nano sized particle. Attrition or milling is a typical top down method in making nano particles.



2. **Bottom-up approach:** Bottom up approach refers to the buildup of a material from the bottom *viz* atom by atom, molecule by molecule or cluster by cluster. Colloidal dispersion is a good example of bottom up approach in the synthesis of nano particles.

Sol-Gel method: It is a wet chemical process, widely used for the fabrication of nano structured ceramic materials and thin films. Sol-gel process involves the conversion of precursor solution (usually metal salts or metal alkoxides) into nano structured inorganic solid through inorganic polymerization reactions catalyzed by water. In general, metal alkoxides (M-OR) are widely used as precursors, because they are readily react with water. The reactions involved in sol gel process are

1. **Hydrolysis:**

   $M\text{-}OR + H_2O \longrightarrow M\text{-}OH + R\text{-}OH$

   (Metal Alkoxide) (Metal hydroxide)

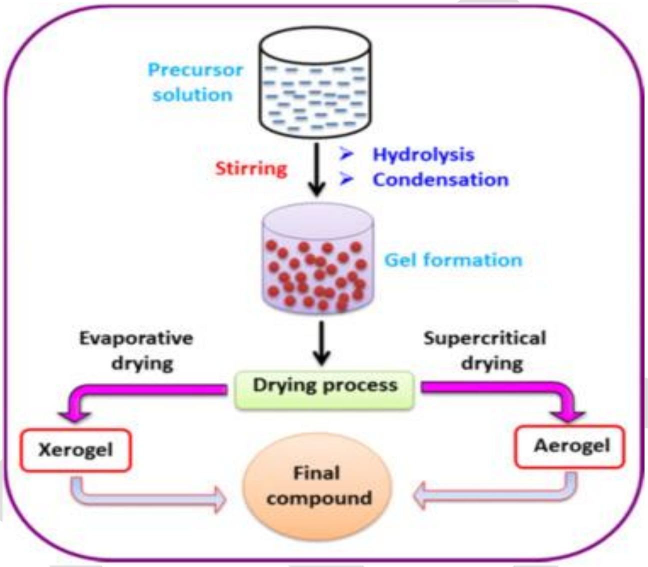
2. **Condensation:**

   $M\text{-}OR + M\text{-}OH \longrightarrow M\text{-}O\text{-}M + R\text{-}OH$

The M-O-M undergoes poly condensation reaction, results to form polymer network in all directions.

Process:

Step-1: Sol formation by Hydrolysis: Preparation of homogeneous solution either by dissolution metal salt in water or metal alkoxide in inorganic solvent (usually alcohol) i.e. miscible in water. It involves the conversion of homogeneous solution in to a sol due to hydrolysis reaction.



Step-2: Gel formation by Condensation: The colloidal solution is kept for few hours. During this condensation reaction between to metal hydroxyl and alkoxy species leads to M-O-M bonds with elimination of water. This condensation process continuous and finally results in gel an inter connected a rigid and porous network covered completely with liquid phase. This transformation is called Sol-Gel transition.

Step-3: Drying of Gel: It involves removal of liquid phase from gel network. There are different ways of drying gel.

- If the gel medium is dried by removing the liquid solvent without destroying the gel network, aerogel is produced.
- If the solvent is dehydrated by under ambient conditions (removal of R-OH groups) xerogels are produced.
- If the gel network is heated at high temperature (800°C), densification, decomposition of gel results in complete collapse of gel network in to powder.

Chemical reduction method of preparation:

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

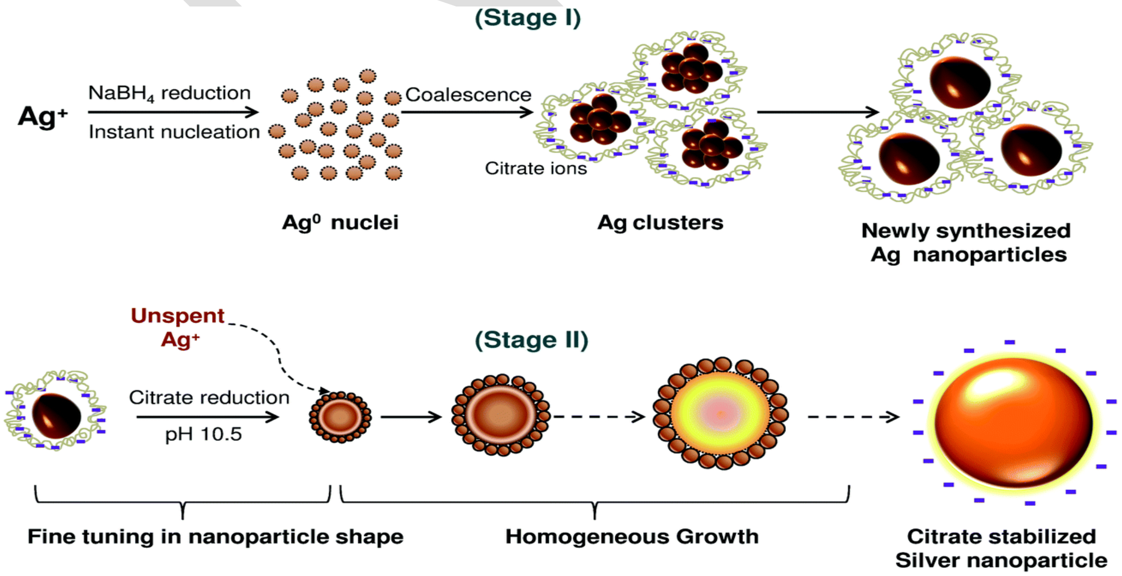
Synthesis of silver nanoparticles:

General preparation is carried out by mixing the metal salts with phase transfer agents and reducing reagents. Different phase transfer reagents are used for the preparation of different metal nanoparticles.

Metal salt solution + Metal salt precursor + Stabilizer + Reducing agent → Stand for some time → Nanoparticles separate → Purification → Centrifugation → Freeze drying → Metal nanoparticles.

Example:

- For the preparation of silver nano particles $AgNO_3$ solution (from 1 ppm to 6 ppm) and 8% w/w sodium dodecyl sulphate (SDS) are used as metal salt precursor and metal stabilizing agent respectively.
- Hydrizine hydrate (2-12ppm) and citrate solution (1ppm) are used as reducing agents.
- The transparent colorless solution will be converted to pale yellow and pale red colour which indicates the formation of silver nanoparticles.
- To remove the excess silver ions the solution is washed with deionizer water under nitrogen stream for three times.
- The nano particles are characterized by UV and X-ray crystallography.



Characterization of nanomaterials:

Brunauer–Emmett–Teller (BET) method:

- **Brunauer–Emmett–Teller** (**BET**) **theory** aims to explain the physical adsorption of gas molecules on a nano material surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of nano materials.
- The BET method applies to systems of multilayer adsorption and usually utilizes probing gases that do not chemically react with material surfaces as adsorbates to quantify specific surface area.
- Nitrogen is the most commonly employed gaseous adsorbate used for surface probing by BET methods. For this reason, standard BET analysis is most often conducted at the boiling temperature of N_2 (77 K).
- Further probing adsorbates are also utilized, albeit with lower frequency, allowing the measurement of surface area at different temperatures and measurement scales. These have included argon, carbon dioxide, and water.
- Specific surface area is a scale-dependent property, with no single true value of specific surface area definable, and thus quantities of specific surface area determined through BET theory may depend on the adsorbate molecule utilized and its adsorption cross section.

TEM (Transmission Electron Microscopy) method:

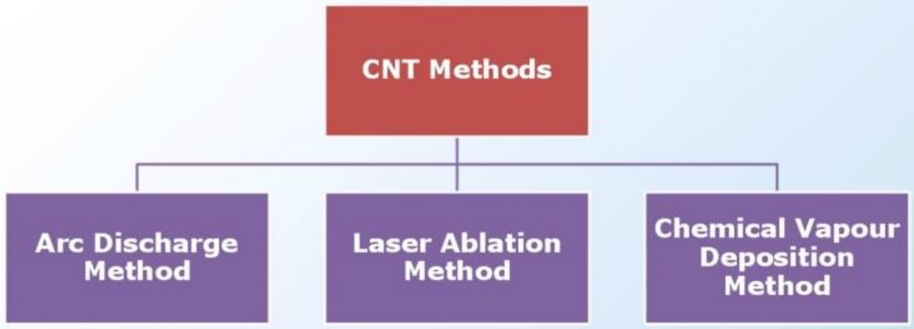
- **Transmission electron microscopy** is a microscopy technique in which a beam of electrons is transmitted through a nanomaterial to form an image. The nanomaterial is most often an ultrathin section less than 100 nm thick or a suspension on a grid.
- An image is formed from the interaction of the electrons with the sample as the beam is transmitted through the nanomaterial. The image is then magnified and focused onto an imaging device, such as a fluorescent screen, a layer of photographic film, or a sensor such as a scintillator attached to a charge-coupled device.
- Transmission electron microscopy is a major analytical method in the physical, chemical and biological sciences. TEMs find application in cancer research, virology, and materials science as well as pollution, nanotechnology and semiconductor research, but also in other fields such as paleontology and palynology.

Carbon Nano Tubes

CNT are sheets of graphite about 0.4 nm in diameter rolled up to make a tube of few nano meters in diameter. These are cyllendrical fullerenes and are also known as bucky tubes.

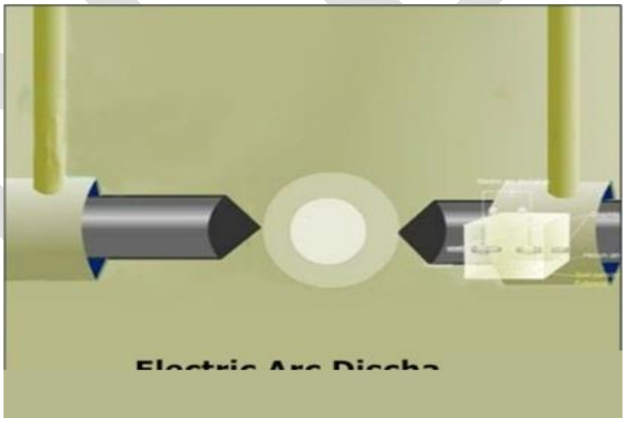
Preparation:

CNTs are prepared by three methods such as:



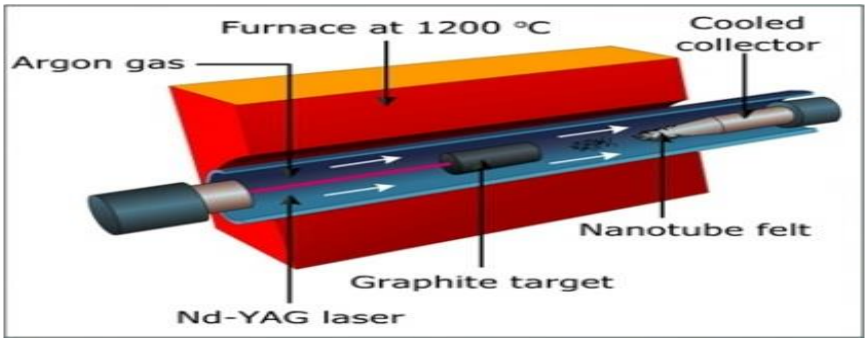
Arc Discharge Method:

- In this method CNT's are produced by the arc discharge of graphite electrodes in the presence of ionized gas at high temperature by using a current of 100 amperes.
- The carbon contained in the negative electrode sublimates during the process.
- In this method the yield is 30% and both the single and multiwall nanotubes are produced.



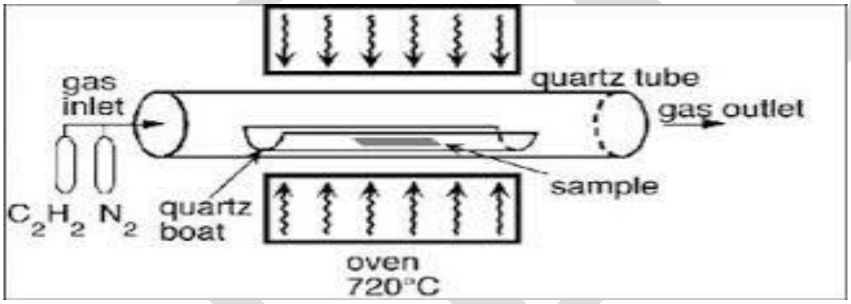
Laser Ablation Method:

- This method was developed by Dr. Richard Smalley. A pulsed laser vaporizes a graphite sheet in a high temperature reactor, through which an inert gas is sent. A mixture of cobalt and nickel is used as a catalyst.
- CNTs are obtained on the cooler surface of the reactor.
- In this process the yield is 70%. This is an expensive method.



Chemical Vapour Deposition method:

- It is a low cost method.
- In this method, a substance is prepared with a layer of catalyst nickel or cobalt nanoparticles.
- The substance is heated to 700^0C and a mixture of nitrogen and carbon containing acetylene or ethylene or methane is passed over it. The CNTs are produced on the surface of catalyst particles.



Properties:

- CNTs are posses high tensile strength upto 100 giga pascals (GPa)
- These are very hard and can withstand a pressure upto 25 Gpa without deformation.
- Multiwalled CNTs exhibit striking telescopic properties.
- CNT is semiconducting and involves quantum effects.
- CNTs show optical properties due to the absorption of photoluminescence.
- CNTs are very good thermal conductors and posses a thermal conductivity of 3500 $WM^{-1}K^{-1}$.
- CNTs are toxic and can induce harmful effects and can cause cell death.

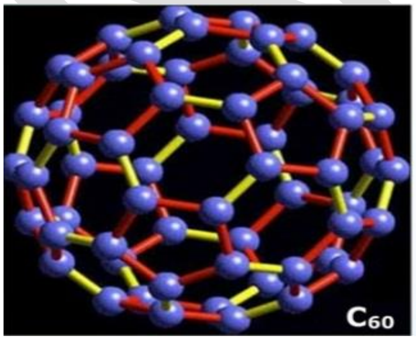
Applications:

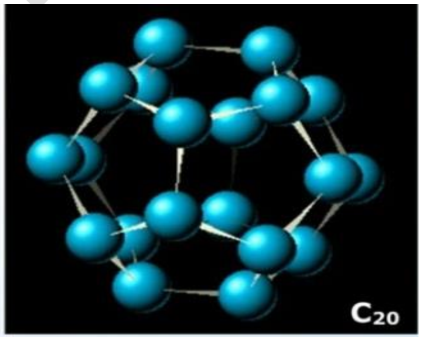
- CNTs are used to make space elevators, stab-proof, bullet-proof clothing.

- Semi conducting nanotubes are used for the preparation of CNT field effect transistor.
- These are also used in the making of nano-tube polymers used in the manufacturing of electrical cables and wires.
- CNTs are used in the preparation of paper batteries which can be used for stable power output.
- A mixture of CNT and fullerenes is used in solar panels.
- CNTs are used for the storage of hydrogen gas.
- Single walled CNT is used to cure cancer.
- CNTs are also used in textiles for the manufacture of fabrics which are antibacterial and electrically conductive.

Fullerenes

- Previously it is assumed that carbon is present in two crystal structures, such as diamond, graphite and in amorphous form.
- In 1985, Richard Smalley *et al.* at Rich University discovered new group of molecules, entirely made up of carbon atoms called fullerenes.
- A fullerene is any molecule composed entirely of carbon in the form of a hallow sphere, ellipsoid or tube.
- Speherical fullerene, are also called buckyballs as they resembles the balls used in football.





- Fullerenes are similar in structure to graphite which is composed of stacked graphene sheets of linked hexagonal, pentagonal or heptagonal rings.
- The smallest fullerene is dodecahedral C_{20} and the most common fullerene is C_{60}.
- 60 carbon atoms combine to form hollow sphere like structure indicated by C_{60} and 70 carbon atoms from ellipsoidal structure indicated by C_{70}.
- When a metal is used as an inclusion compound it is called metallo fullerene.

Preparation

- Fullerenes are prepared by a large current between two nearby graphite electrodes in an inert atmosphere.
- The resulting carbon plasma between the electrodes cools into sooty residue from which fullerenes can be isolated.
- The fullerenes are extracted from soot using the multi-step procedure.

Properties:

- Fullerenes are stable with sp^2 hybridized carbon atoms.
- Fullerenes are sparingly soluble in many solvents. Common solvents for fullerenes are like toluene, CS_2.
- Fullerenes show a wave practical duality due to which several sculptures symbolizing wave particle duality are created.
- Some fullerenes are inherently chiral because they are D_2-symmetric and have been successfully resolved.
- Fullerenes undergo:
- **Hydrogenation:** C_{60} posses little aromatic character and undergo addition with hydrogen to form polyhydro fullerenes.
- **Halogenation:** Addition of F, Cl and Br occur for C_{60} under various conditions, produce a vast number of halogenated derivatives. **Ex:** $C_{60}Br_8$ and $C_{60}Br_{24}$.

Applications:

A fuel:

- Buckyballs are an efficient medium to make hydrogen fuel.

Medicine:

- Buckminster fullerenes inhibit the HIV virus.
- C_{60} inhibits a key enzyme in the human immunodeficiency virus known as HIV-1 protease which could inhibit the reproduction of HIV virus in immune cells.
- When impregnated with He, C_{60} buckyballs can be used as chemical traces in human body.

Solar cells:

- The optical absorption of C_{60} match the solar spectrum, hence find its application in solar cells.

LIQUID CRYSTALS

- Liquid crystals are matter in a state that has properties between liquid and solid.
- Many organic materials exhibit liquid crystals state over a restricted temperature range.
- The material becomes a crystalline solid at the lower end of the temperature range and becomes a clear liquid at the upper end.

- The liquid crystalline state is obtained by raising the temperature of solid and or by lowering the temperature of a liquid.

  Example: Cholesterol myristate is a crystalline solid below 71^{o}C and above 71^{o}C it becomes a cloudy liquid and at 86^{o}C becomes a clear liquid. The intermediate state i.e. from 71^{o}C to 86^{o}C is said to be liquid crystal state.

Types of Liquid Crystals:

1. Thermotropic liquid crystals:

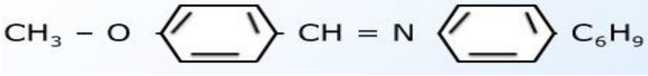
a) Nematic Crystals b) Cholestric Crystals c) Smectic Crystals

2. Lyotropic liquid crystals

Nematic Crystals:

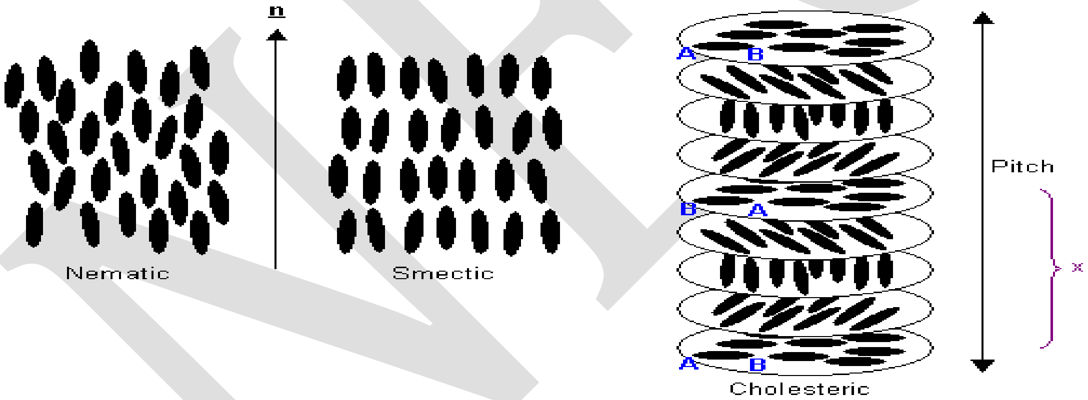
- In crystalline state, liquid crystal state and liquid state of an organic substance posses different arrangement of molecules.
- Solid state posses orderly arrangement and liquid state posses arrangement of molecules random in some directions and regular in others.
- The molecules exist in layers and within layers the molecules can slide around each other and layers can slide over one another. This molecular produces the fluidity characteristic of a liquid.
- Liquid crystals have the mobility of liquids and optical properties of solids.

- The most widely used ones twisted nematic liquid crystals which contain long axes of molecules which rotate by a small angle from one layer to the next.
- The nematic liquid crystal is made of MBBA molecule i.e. 4-methoxy-Benzylidine,4-butylaniline in which two benzene rings are linked in a single group.
- The molecular formula of MBBA molecule is



Cholestric Crystals

- In cholestric phase, the molecules are orderly arranged similar to nematic phase, but in planes. Here the only difference is the orientation will differ from one plane to another.
- The distance between the similar planes i.e., the planes in which the molecules has same direction is called 'pitch'.
- The cholestric liquid crystal has a special property that, if white light is allowed to pass through the crystal it appears coloured.



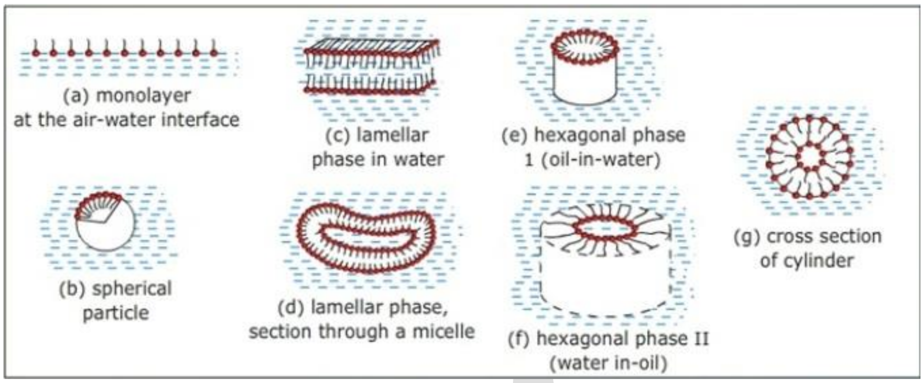
Smectic Crystals:

The word smectic is derived from the Greek word soap. In smectic state, the molecules posses a general orientation order like nematic but also tend to align themselves in layers or planes. The smectic state is more 'solid like structure' then nematic.

Lyotropic Crystals

- This crystal state occurs in concentrated solution of rod like molecules in isotropic solvents usually in water. This is shown in soaps, gels and colloids.

- Lyotropic liquid crystals transitions occure due to the influence of solvent. These are amphiphillic i.e., they consists of lyophilic (solvent attracting) and lyophobic (solvent repelling) parts and from micellar strctures.



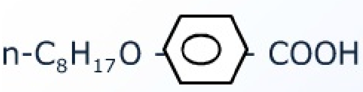
Examples of Liquid Crystalline Compounds

The liquid crystalline state is obtained by raising the temperature of a solid and or by lowering the temperature of a liquid.

Liquid crystalline compounds

P-azonyanisole (PAA)

P-n-octyloxy Lengoic acid



Sodium stearete

$CH_3\ (CH_2)_{16}\ COO^-\ Nat$

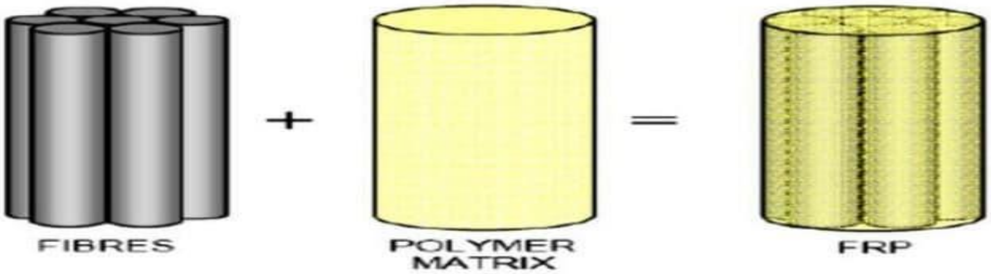
Applications of Liquid Crystals:

- Liquid crystals are used as display devices in TVs, watches, calculators and flat panel displays.
- Liquid crystals are used in gas liquid chromatography because their mechanical and electrical properties lie between solid and liquids.
- Cholesteric liquid crystals vary their colours depending in the temperature. They can be used to detect veins, arteries and tumors which are warmer than surrounding tissue.
- Liquid crystals are used as electro optical materials.
- Liquid crystals are used as radiation and pressure sensors.

COMPOSITES

- Composites, also known as Fibre-Reinforced Polymer (FRP) composites, are made from a polymer matrix that is reinforced with an engineered, man-made or natural fibre (like glass, carbon or aramid) or other reinforcing material.
- The matrix protects the fibres from environmental and external damage and transfers the load between the fibres. The fibres, in turn, provide strength and stiffness to reinforce the matrix-and help it resist cracks and fractures.

Fibre Reinforced Plastics (FRP): Fibre Reinforced Polymer (FRP) composite is defined as a polymer that is reinforced with fibre.



Types of Fibre Reinforced Polymer (FRP)

1. Glass Fibre Reinforced Polymer (GFRP)

In this type glass material is incorporated in plastic materials. Glass FRPs used because of durability, acid proof, water proof and fire proof nature of glass. Glass is drawn into threads in the form of fine cotton threads. Then these threads are woven in the form of mats. This mat is filled with plastic materials. The common plastics used are polyesters, polyamides and poly vinyl chlorides.

Properties:

- Good dimensional stability.
- High service temperature.
- Excellent chemical resistance.
- Excellent corrosion resistance.
- Good tensile strength.
- Posse’s good thermal resistance.

Applications:

Fibre reinforced plastics are used in

- Auto motive parts
- Storage times
- Industrial flooring
- Plastic pipes
- Transportation industries to reduce vehicle weight.

2. Carbon Fibre Reinforced Polymer (CFRP)

Carbon Fibre Reinforced Polymer (CFRP) is a polymer matrix composite material reinforced by carbon fibres. The reinforcing dispersed phase may be in form of either continuous or discontinuous carbon fibres of diameter about 0.0004" commonly woven into a cloth. Carbon fibres are very expensive but they possess the highest specific (divided by weight).

Properties:

- Very high modulus of elasticity exceeding that of steel.
- High tensile strength, which may reach 1000 ksi (7 GPa).
- Low density: 114 lb/ft^3 (1800 kg/m^3).
- High chemical inertness.

Applications:

- It is widely used in aerospace and aircraft industries.
- It is used in sports industry (light weight badminton rockets and golf sticks).
- It is used in automobile industry (bonnet, bumper, car body parts and engine cover).

Cermets:

Composite materials composed of ceramic (cer) and metal (met). Cermet's deliver the benefits of both metal and ceramic in engineering material which can't be obtained from either one material. Ceremets are hot pressed or sintered materials, consisting of combination of ceramics and metals.

Properties:

- High refractoriness of ceramics
- High thermal conductivity of metals
- High thermal shock resistance of metals
- High shapability.

Applications:

- Used as cutting tool materials involving titanium carbide or titanium carbonitrides as the hard refractory phase.
- Cermets based on SiC & B_4C used in wear and corrosion resistance or antifriction applications and also in nuclear reactor applications.
- TiN & ZrN bonded with their respective metallic elements developed for special heat and corrosion resistant purposes.
- UO_2 or ThO_2 based cermets found application as a major fission component in nuclear reactor fuel elements.
- Combinations of Al_2O_3 with TiC are suitable for hot machining tools.
- Combination of ZrB_2 and SiC is resistant to erosion from the propulsion gases of chemical rockets.
- ZrB based cermets used in liq. Metal pumping system and also thermocouple sheathes.

UNIT-III

CHEMISTRY OF ADVANCED MATERIALS

IMPORTANT QUESTIONS

1. What are nano materials? Explain the preparation of nanomaterials by Sol-Gel and Chemical reduction method.
2. How to characterize nano materials by BET and TEM methods.
3. Explain preparation properties and applications of CNTs.
4. Explain preparation properties and applications of Fullerenes.
5. Discuss the types and applications of liquid crystals
6. What is FRP? Explain the properties and applications of FRP?
7. Write a short note on cermets.

UNIT-IV

ELECTROCHEMISTRY AND CORROSION

ELECROCHEMSTRY

Introduction

- Electrochemistry is a branch of chemistry which deals with the relationship between electrical energy and chemical energy.
- Some applications in which electrical energy is converted into chemical energy are:
    - Electrolysis
    - Electroplating
    - Extraction and purification of metals and some non-metals (F_2, Cl_2) etc.
    - Recharging of secondary batteries etc.
- Batteries and electro analytical techniques to find the concentration of solutions are some applications in which chemical energy is converted to electrical energy.

Classification

Depending on the ability to conduct electricity substances are divided as

- Conductors
- Non-Conductors
- Semi Conductors
- Super Conductors

Conductors:

Substances which allow the electric current to pass through them are called conductors.

Ex: Acids, Bases and salt solutions, fused salts etc.

Non-Conductors:

Non-conductors do not allow the electricity to pass through them.

Ex: Wood, Rubber, Cloth, Plastic, Pure water, Paper, Non-metals except Carbon.

Semi Conductors:

- Possess properties between the metals and non-metals
- Partially allow the current
- Conducting property is increased by the addition of impurities called doping agents.

Depending on doping material, semiconductors are of two types:

- n-type semiconductors - Addition of V group elements
- p-type semiconductors - Addition of III group elements

Super conductors:

The compounds which allow the flow of current with zero resistance are called Super Conductors.

Ex: Mixture of Cu, Ba and rare earth metal oxides show zero resistance and exhibit super conductivity.

Types of Conductors

Conductors are of two types

Metallic or Electronic Conductors

- Metallic or electronic conductors conduct electricity without undergoing any chemical change.
- In these substances, conduction is due to the movements of electrons.

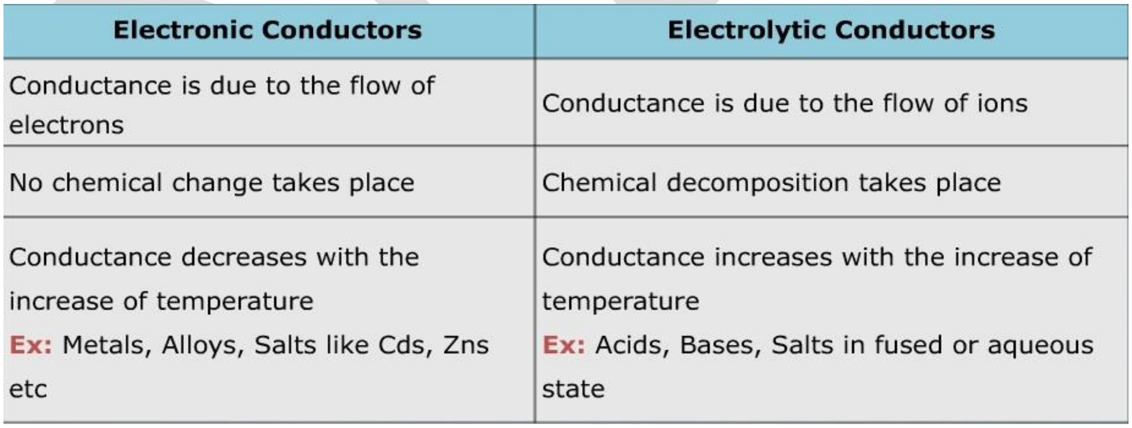
  Ex: Metals-Cu, Fe, Al, Ag, Graphite etc.

Electrolytic Conductors or Electrolytes

- Electrolytic conductors undergo decomposition when electric current is passed through them.
- In these conductors, the flow of electricity or conductance is due to the movement of ions.

  Ex: Solutions of acids, bases, salts in aqueous medium and in fused state.

Differences between Electronic and Electrolytic conductors



Electronic Conductors	**Electrolytic Conductors**
Conductance is due to the flow of electrons	Conductance is due to the flow of ions
No chemical change takes place	Chemical decomposition takes place
Conductance decreases with the increase of temperature **Ex:** Metals, Alloys, Salts like Cds, Zns etc	Conductance increases with the increase of temperature **Ex:** Acids, Bases, Salts in fused or aqueous state

Classification of Electrolytes

Electrolytes can be classified into two types depending on their value of their equivalent conductance

- Strong Electrolytes
- Weak Electrolytes

Strong Electrolytes:

The electrolytes possess a high value of equivalent conductance even at high concentration.

Ex: Mineral acids like HCl, H_2SO_4

Alkalies like NaOH, KOH etc.

Alkaline earth hydroxides like $Ca(OH)_2$, $Ba(OH)_2$ etc.

Salts like NaCl, KCl etc.

Weak Electrolytes:

These electrolytes possess a low value of equivalent conductance at ordinary concentration.

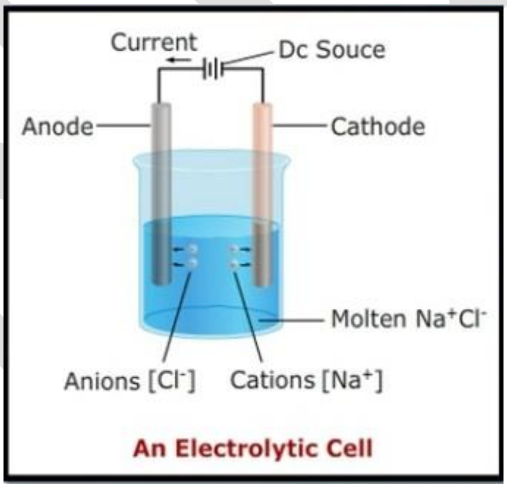
Ex: CH_3COOH, NH_4OH etc.

Electrolytic Cell

- The cell which converts electrical energy into chemical energy is called electrolytic cell.
- In this cell, electrical energy induces chemical reactions.

  Ex: Electrolysis of molten NaCl using graphite electrodes.

Cell Reactions: NaCl dissolves when current is passed through it.



An Electrolytic Cell

Electrochemical or Galvanic or Voltaic cells

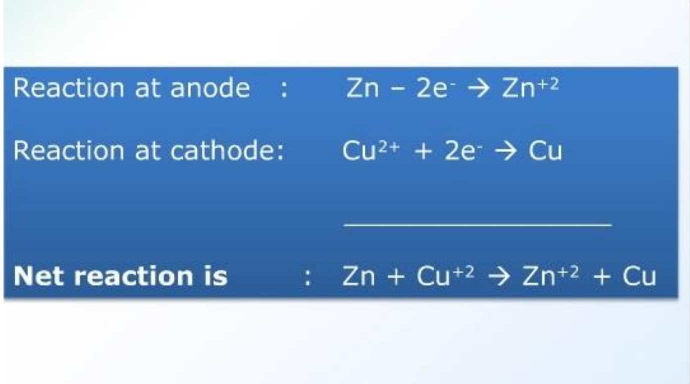
The device which converts chemical energy into electrical energy due to spontaneous redox reaction is called Galvanic Cell

Ex: Daniel cell, Laclenche cell, Fuel cell

Note: Daniel cell is a typical example of a galvanic cell.

Daniel Cell

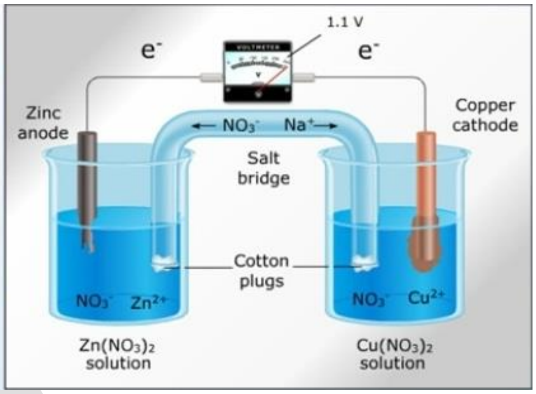
It consists of two half cells or single electrodes one is oxidation half cell in which oxidation takes place and the other is reduction half cell in which reduction tales place. These two half cells are connected by a salt bridge.



Reaction at anode : $Zn - 2e^- \rightarrow Zn^{+2}$

Reaction at cathode: $Cu^{2+} + 2e^- \rightarrow Cu$

Net reaction is : $Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu$



Working of Salt Bridge:

- Salt bridge is an inverted U-shaped glass tube filled with a paste of KCl or KNO_3 with agar-agar gel.
- Salt bridge maintains electrical neutrality in the Galvanic cell by providing anions and cations of almost same speed.
- It prevents accumulation of charges.

Differences between electrolytic and Galvanic Cells

Electrolytic Cell	Galvanic Cell
In this cell electrical energy is converted into chemical energy	In this cell chemical energy is converted into electrical energy
It involves non-spontaneous reaction	It involves spontaneous reaction
$\Delta G > 0$	$\Delta G < 0$
E.M.F < 0	E.M.F > 0
In this cell anode is +Ve and cathode is –Ve.	Anode is –Ve and cathode is +Ve
Electricity is consumed	Electricity is produced

Electrode Potential

- It is the potential difference that exists at the surface of separation of a metal or a non-metal and its own ions which are in equilibrium in electrons.
- It is a measure of tendency of an electrode to loose or gain of electrons. (OR)
- It is the ability of a metal either to undergo oxidation or reduction.
- It is indicated by 'E' and its units are volts (V)

Electrode Potential Equation

- Electrode potential is two types

Oxidation Potential:

- It is the measure of tendency of electrode to lose electrons

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

Reduction Potential:

- It is the measure of tendency of electrode to gain electrons.

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

Standard Electrode Potential

- The electrode potential of given electrode at 25^0C at unit activity (1molar concentration of an electrolyte and 1 atm pressure in case of gas) is known as "Standard Electrode Potential"

SEP is of two types

- SOP - Standard Oxidation Potential
- SRP - Standard Reduction Potential

According to IUPAC conversion, SRP is taken as SEP

SOP and SRP of an electrolyte are equal in magnitude but opposite in sign.

Electrodes

The various types of electrodes in an electrochemical cell are as follows

1. Metal-Metal ion electrode
2. Gas electrode
3. Metal-Amalgam electrode
4. Redox electrode
5. Metal-Metal insoluble salt electrode

Reference Electrode

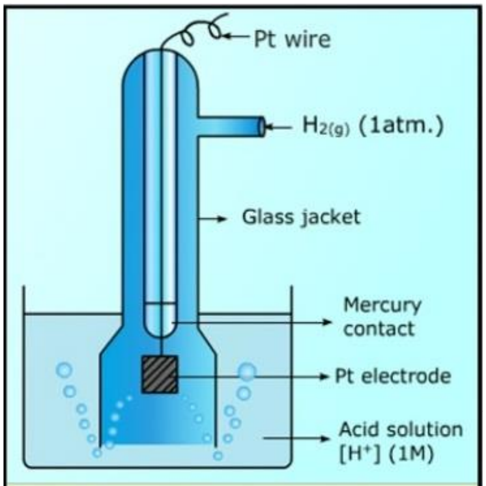
There are two types of reference electrodes

1. Primary reference electrode

   Ex: Standard Hydrogen electrode
2. Secondary reference electrode

   Ex: Saturated calomel electrode, Quinhydrone electrode, Glass electrode

Gas Electrode



Standard Hydrogen Electrode (SHE)

It is also called gas ion electrode

Ex: Hydrogen electrode

Introduction

- It is an electrode possessing stable and constant potential
- It is used as one of the half cell of electrochemical cell for determining the potential of the other half cell.
- The standard reduction potential of this electrode is assumed as zero and this electrode is used to measure the SRP of other electrodes.
- In a cell when this electrode acts as anode, the H_2 has undergoes oxidation as

$$H_2 \longrightarrow 2H^+ + 2e^-$$

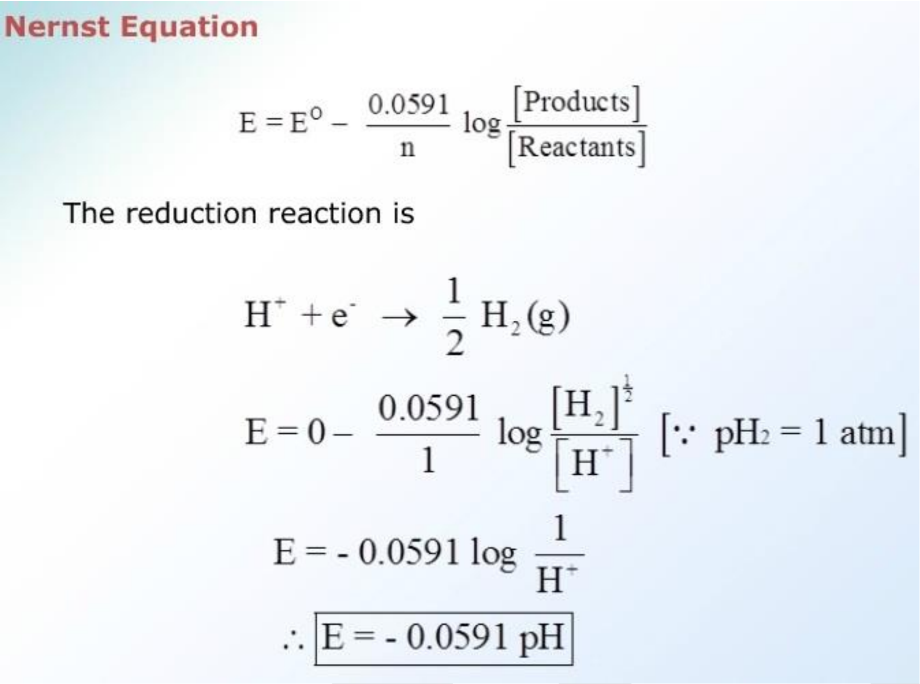
- When this electrode acts as cathode the reduction reaction takes place is

$$2H^+ + 2e^- \longrightarrow H_2$$

Construction

It is a primary reference electrode (S.H.E or N.H.E).

- It consists of a platinum electrode coated with platinum black immersed in a 1M solution of H^+ ions (HCl) maintained at 25^0C.
- Hydrogen gas at 1 atm pressure is bubbled through the electrode.
- The electrode notation for hydrogen electrode is Pt H_2 (g) / H^+ (aq).



Nernst Equation

$$E = E^{0} - \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$$

The reduction reaction is

$$H^{+} + e^{-} \rightarrow \frac{1}{2} H_2(g)$$

$$E = 0 - \frac{0.0591}{1} \log \frac{[H_2]^{\frac{1}{2}}}{[H^{+}]} \quad [\because pH_2 = 1 \text{ atm}]$$

$$E = -0.0591 \log \frac{1}{H^{+}}$$

$$\therefore \boxed{E = -0.0591\ pH}$$

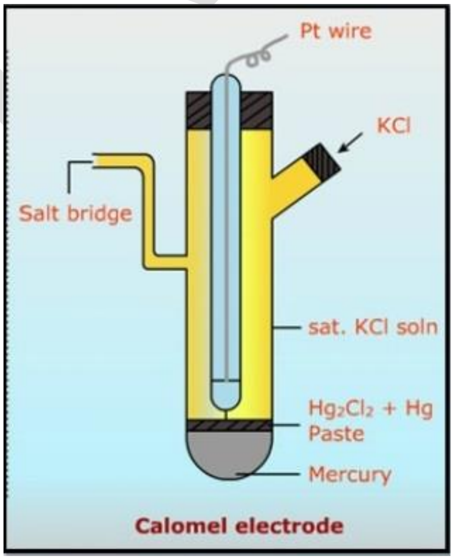
Advantages:

- Results are highly accurate.
- It can be used over entire range of pH.

Drawbacks:

- It is cumbersome to step up and maintain the hydrogen gas pressure.
- It has to be carefully handled as Hydrogen forms explosive mixture with air.
- It cannot be used in presence of oxidizing agents such as Fe^{+3}, MnO_4^{-}, $C_2O_4^{-2}$ etc.
- It gets easily poisoned by cyanide, mercury, arsenic, sulphate etc.

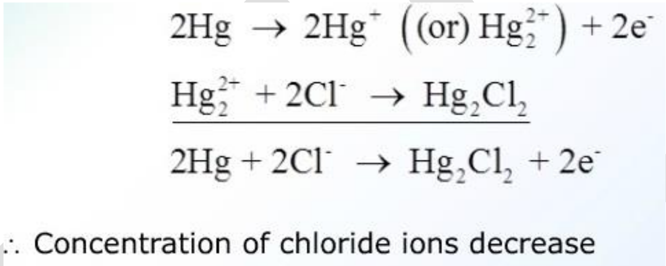
Calomel Electrode



- It is a secondary reference electrode.
- It consists of a wide glass tube. Pure mercury is taken at its bottom and above this Hg & Hg_2Cl_2 (Calomel) paste is placed.
- The remaining portion of the tube is filled with a solution of KCl.
- A platinum wire sealed through a glass tube is dipped into mercury and makes contact with the circuit.
- This tube has two side tubes one for introducing KCl solution and the other for connecting to a salt bridge and other half cell.
- The electrode notation is Pt, $Hg_{(L)}$, $Hg_2Cl_{2(S)}$/KCl.

Working:

When this electrode acts as anode, mercury undergoes oxidation



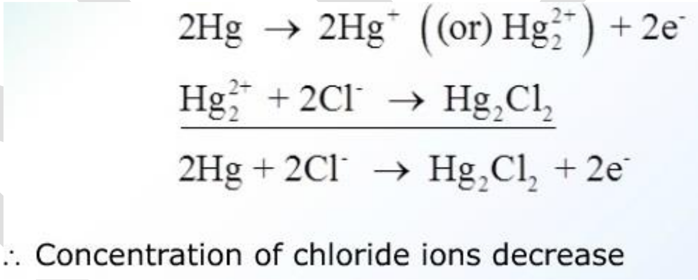
$$2Hg \rightarrow 2Hg^{+} \left((or)\, Hg_2^{2+}\right) + 2e^{-}$$

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

$$2Hg + 2Cl^{-} \rightarrow Hg_2Cl_2 + 2e^{-}$$

∴ Concentration of chloride ions decrease

When this electrode acts as cathode, Hg_2Cl_2 is reduced to mercury



$$2Hg \rightarrow 2Hg^{+} \left((or)\, Hg_2^{2+}\right) + 2e^{-}$$

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

$$2Hg + 2Cl^{-} \rightarrow Hg_2Cl_2 + 2e^{-}$$

∴ Concentration of chloride ions decrease

Hence calomel electrode is reversible w.r.t. chloride ion concentration

Standard E.M.F. Values (E^0)

E^0 values of calomel electrode depend on the concentration of KCl solution.

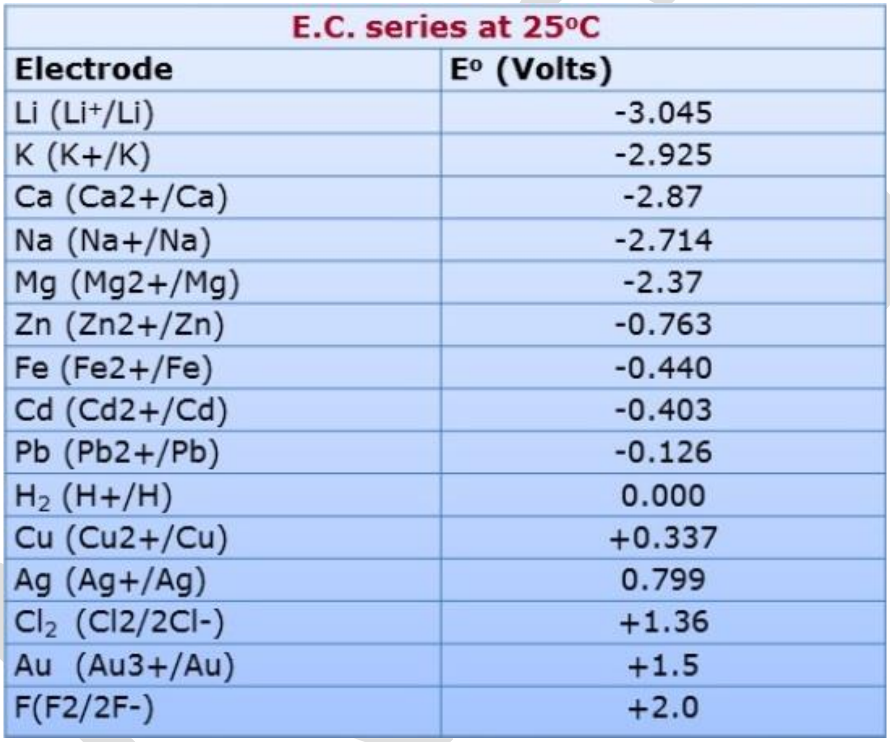
- Saturated Calomel Electrode (SCE) : 0.2422V
  (Saturated KCl)
- Nornal Calomel Electrode (NCE) : 0.2800V
  (1N, KCl)
- Deci-Normal Calomel Electrode (DCE) : 0.3335V
  (0.1N, KCl)

Advantages:

- It is simple to construct.
- Results of cell potential measurements are reproducible and stable over a long period and do not vary with temperature.

Electro Chemical Series

- The series in which elements are arranged in increasing order of standard reduction electrode potential as compared to that of standard hydrogen electrode is called electrochemical series.



E.C. series at 25°C

Electrode	E^o (Volts)
Li (Li^+/Li)	-3.045
K (K+/K)	-2.925
Ca (Ca2+/Ca)	-2.87
Na (Na+/Na)	-2.714
Mg (Mg2+/Mg)	-2.37
Zn (Zn2+/Zn)	-0.763
Fe (Fe2+/Fe)	-0.440
Cd (Cd2+/Cd)	-0.403
Pb (Pb2+/Pb)	-0.126
H_2 (H+/H)	0.000
Cu (Cu2+/Cu)	+0.337
Ag (Ag+/Ag)	0.799
Cl_2 (Cl2/2Cl-)	+1.36
Au (Au3+/Au)	+1.5
F(F2/2F-)	+2.0

Features:

- Electrodes present above hydrogen have –ve S.R.P values and those below H_2 have +ve S.R.P values.
- Li is at the top most position of the series with S.R.P -3.045V and F_2 is at the bottom most with S.R.P +2.87V.
- The element present above in the series act as anode and below in the series act as cathode.
- The reactivity of elements decrease down the series.
- The metals above the hydrogen in the series can be easily oxidized and hence undergo corrosion easily.

Applications:

- To know the relative reducing or oxidizing abilities of given system.
- Replacing ability of metals can be predicted.
- The feasibility of given redox reaction can be predicted.
- The E^0 cell can be calculated.
- The corrosion tendency of the metal can be predicted.

Batteries

A Battery is an electrochemical cell or often several electrochemical cells connected in series that can be used as a source of direct electric current at constant voltages.

Or

A device which converts chemical energy into electrical energy is called Battery.

Advantages of Battery

- Batteries act as a portable source of electric energy.
- The portability of electronic equipment s in the form of hand sets are made possible by batteries.
- Rechargeable batteries have better shelf life tolerance. These batteries have increased the usage of electronic gadgets in recent times.
- Batteries are used in all commercial applications.
- **Ex:** Batteries for automobiles, aircrafts etc.

Classification

Batteries are classified into three types

1. Primary cells
2. Secondary cells
3. Fuel cells

1. Primary Cells

- The cell in which the cell reactions are not reversible are said to be primary cells.
- Non rechargeable and meant for single use and can be discarded after use.
- Can generate electricity as long as the reactants are present in the cell.
- When all the reactants are converted into products, the battery is dead.

- Cannot be recharged because the cell reaction cannot be reversed by applying internal e.m.f. in opposite direction.

Dry Cell

Dry cell

- Invented by Georges Laclenche in 1886.
- The Battery contains a conducting solution of NH_4Cl, a cathode of carbon, a depolarizer of MnO_2 and an anode Zinc.

Working

- The chemical process which produces electricity in the cell begins when the zinc atoms on the surface of the anode oxidize, as the Zn^{+2} moves away from the anode, leaving these electrons on the surface, the anode becomes more negatively charged than the cathode.
- When the cell is connected in an external electrical circuit, the excess electrons of zinc flow through the circuit to the carbon rod, due to which the movement of electrons form an electric current.
- After passing through the circuit, electrons enter the cathode and combine with MnO_2 and water which react with each other to produce Mn_2O_3 and OH^- ions.
- The OH^- ions react with NH_4Cl to produce ammonia, which is not liberated as has but immediately combines with Zn^{+2} and Cl^- ions to form a complex salt $[Zn(NH_3)_2Cl_2]$

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

$$2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^-$$

$$2NH_4Cl + 2OH^- \rightarrow 2NH_3 + Cl^- + 2H_2O$$

$$Zn^{+2} + 2NH_3 + 2Cl^- \rightarrow [Zn(NH_3)_2Cl_2]$$

Diamine dichloro zinc

- A dry cell battery is a subtype of battery. It stores energy in an immobilized electrolyte paste which minimizes the need of water.
- The dry cell finds its applications in flashlights, transistor radios, calculators etc.

2. Secondary Cells:

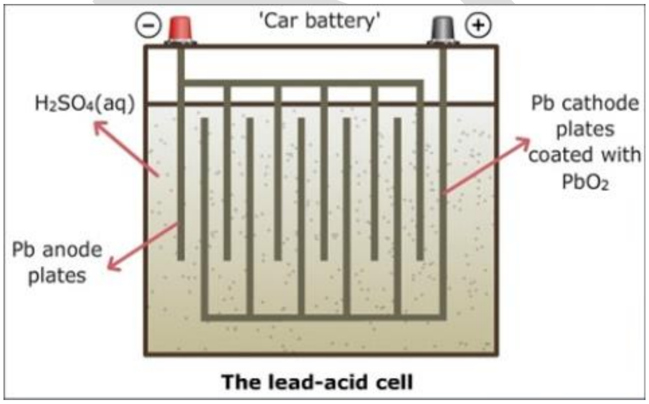
- The batteries in which cell reaction can be reversed by applying external e.m.f. in opposite direction are called secondary batteries or accumulators.
- These batteries are used for multi-cycle purpose (discharging and recharging).
- Cycle is reversed till the capacity fades or lost due to internal short circuit or leakage.
- These batteries have large capacitance and low-current rate discharge.

  Ex: Lead acid storage cell, Nickel-Cadmium cell and Lithium cell.

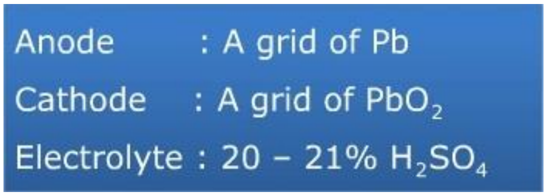
Lead Acid Storage Cell

It is a secondary battery because the cell reaction can be reversed by applying external e.m.f. on opposite direction.

- The Pb and PbO_2 plates are arranged alternatively and this arrangement is immersed in H_2SO_4 taken in a container made up of hard rubber.
- The battery acts as Galvanic cell while discharging and electrolytic cell while recharging.



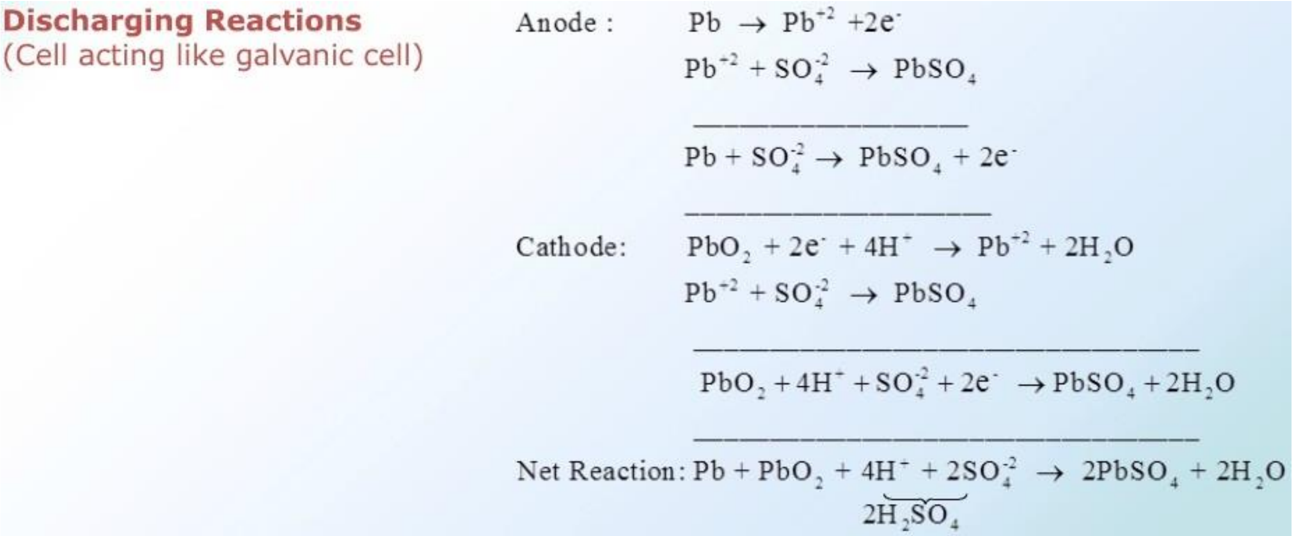
The lead-acid cell



Anode : A grid of Pb

Cathode : A grid of PbO_2

Electrolyte : 20 – 21% H_2SO_4



Discharging Reactions
(Cell acting like galvanic cell)

Anode :

$$Pb \rightarrow Pb^{+2} + 2e^-$$
$$Pb^{+2} + SO_4^{-2} \rightarrow PbSO_4$$
$$Pb + SO_4^{-2} \rightarrow PbSO_4 + 2e^-$$

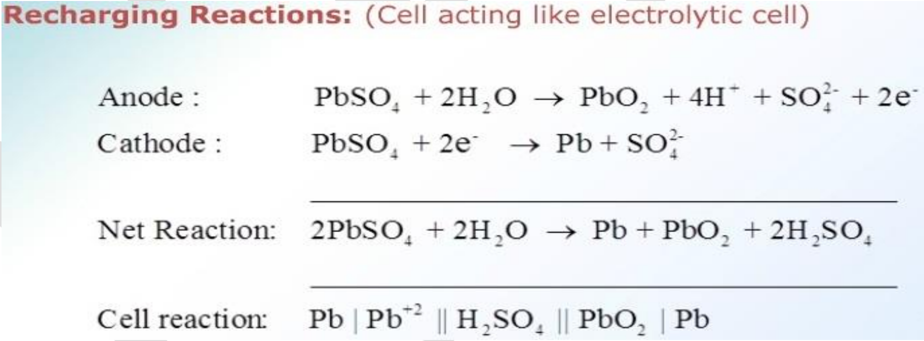
Cathode:

$$PbO_2 + 2e^- + 4H^+ \rightarrow Pb^{+2} + 2H_2O$$
$$Pb^{+2} + SO_4^{-2} \rightarrow PbSO_4$$
$$PbO_2 + 4H^+ + SO_4^{-2} + 2e^- \rightarrow PbSO_4 + 2H_2O$$

Net Reaction: $Pb + PbO_2 + \underbrace{4H^+ + 2SO_4^{-2}}_{2H_2SO_4} \rightarrow 2PbSO_4 + 2H_2O$

- Due to anodic and cathodic reactions, the Pb and PbO_2 are covered with $PbSO_4$ and the specific gravity of H_2SO_4 decreases.
- If it reaches a voltage less than 1.2V, the cell can be recharged by applying external e.m.f.

E_{cell} = 2V. The commercial lead acid storage cells used in automobiles consists 6(12V) cells connected in series



Recharging Reactions: (Cell acting like electrolytic cell)

Anode : $PbSO_4 + 2H_2O \rightarrow PbO_2 + 4H^+ + SO_4^{2-} + 2e^-$

Cathode : $PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$

Net Reaction: $2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$

Cell reaction: $Pb \mid Pb^{+2} \parallel H_2SO_4 \parallel PbO_2 \mid Pb$

Applications:

- Used in automobiles and power inverters.
- Also used to supply current for electric vehicles, telephone exchanges, electric trains, mines, laboratories, hospitals, broadcasting stations, power stations etc.

Advantages:

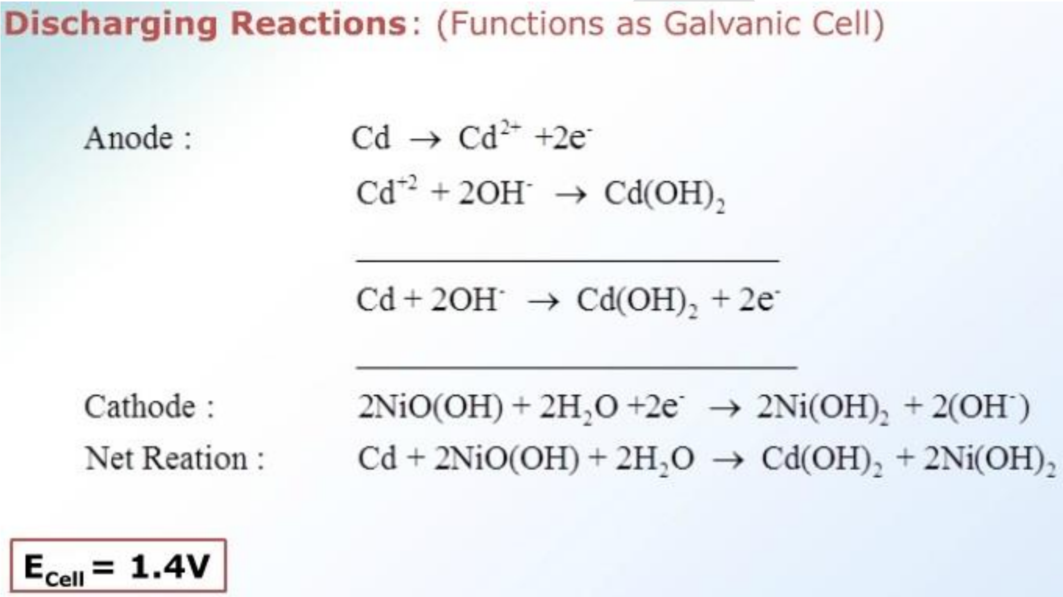
- It is rechargeable.
- It is less expensive and has long life.
- Ability to withstand mistreatment.
- It can generate electricity at constant voltage.
- Perform well in high and low temperature and in high-drain applications.

Drawbacks:

- Use of H_2SO_4 is dangerous
- Use of Pb and PbO_2 is harmful to environment.

Nickel Cadmium Battery

- It is also known as Ni-Cd cell or Ni-Cd battery.
- It is a secondary battery
- It is an alkaline battery



Discharging Reactions: (Functions as Galvanic Cell)

Anode : $Cd \rightarrow Cd^{2+} + 2e^-$

$Cd^{+2} + 2OH^- \rightarrow Cd(OH)_2$

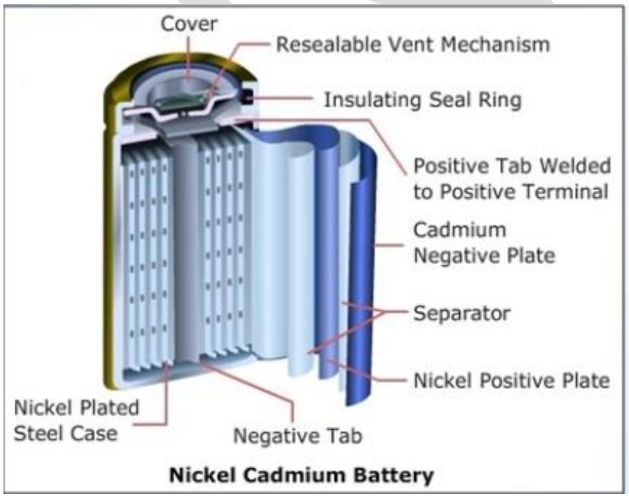
$Cd + 2OH^- \rightarrow Cd(OH)_2 + 2e^-$

Cathode : $2NiO(OH) + 2H_2O + 2e^- \rightarrow 2Ni(OH)_2 + 2(OH^-)$

Net Reation : $Cd + 2NiO(OH) + 2H_2O \rightarrow Cd(OH)_2 + 2Ni(OH)_2$

$\boxed{E_{Cell} = 1.4V}$

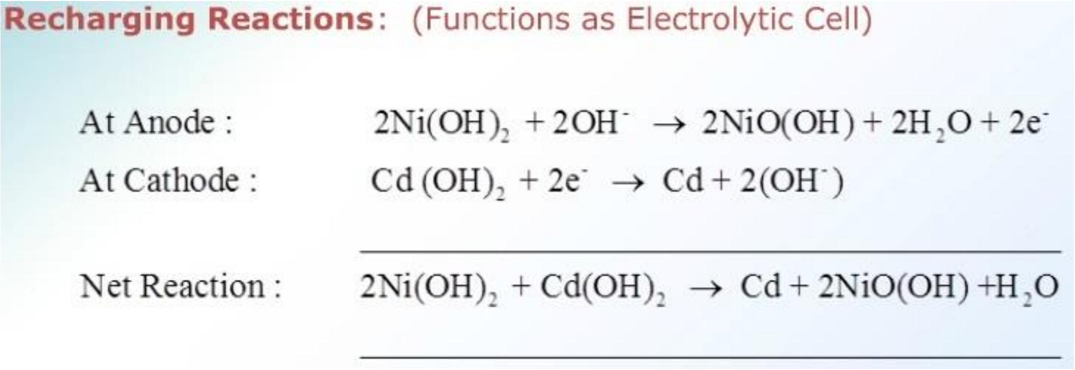
Cell Notation: Cd/CdO//6MKOH//NiO(OH), $Ni(OH)_2$/Ni



Anode : Spongy Cd/CdO

Cathode : NiO(OH)/Ni

Electrolyte : 6M KOH



Recharging Reactions: (Functions as Electrolytic Cell)

At Anode : $2Ni(OH)_2 + 2OH^- \rightarrow 2NiO(OH) + 2H_2O + 2e^-$

At Cathode : $Cd(OH)_2 + 2e^- \rightarrow Cd + 2(OH^-)$

Net Reaction : $2Ni(OH)_2 + Cd(OH)_2 \rightarrow Cd + 2NiO(OH) + H_2O$

Since the net reaction does not consume electrolyte, small amount of electrolyte is sufficient which reduces the weight of the battery.

Advantages:

- Light weight
- Rechargeable
- Compact
- Long shelf life
- Long cycle life and sturdy.

Drawbacks:

- Expensive
- Lower power density

Applications of secondary batteries in E-vehicles

- There are two basic types of EVs: All-Electric Vehicles (AEVs) and plug-in hybrid electric vehicles (PHEVs). AEVs include Battery Electric Vehicles (BEVs) and Fuel Cell Electric Vehicles (FCEVs).
- In addition to charging from the secondary batteries, both types are charged in part by regenerative braking, which generates electricity from some of the energy normally lost when braking.
- All-electric vehicles (AEVs) run only on electricity. Most have all-electric ranges of 80 to 100 miles, while a few luxury models have ranges up to 250 miles.
- When the battery is depleted, it can take from 30 minutes (with fast charging) up to nearly a full day (with Level 1 charging) to recharge it, depending on the type of charger and battery.

3. Fuel Cells

- A fuel cell converts the chemical energy of the fuels directly to electricity. The essential process in a fuel cell is:

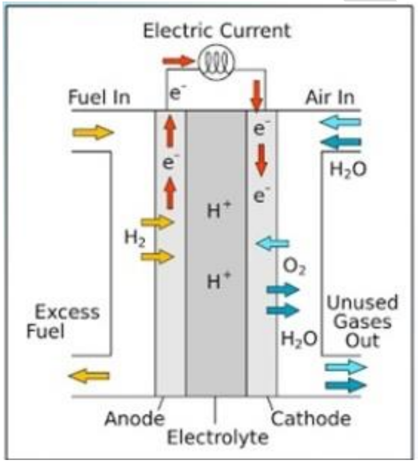
  Fuel + Oxygen $\longrightarrow$ Oxidation process + Electricity

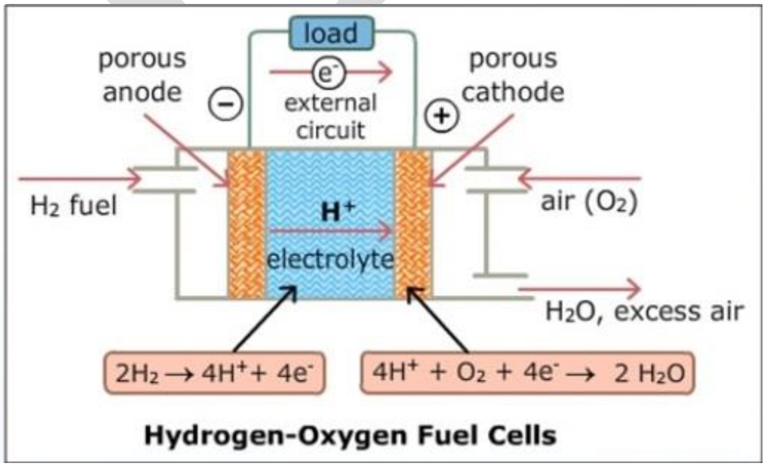
- These are special type of galvanic cells which convert free energy of a chemical reaction between the fuel and oxidant directly into electrical energy.
- In these cells, electricity is generated continuously as long as the fuel and oxidant are supplied continuously and separately at the two electrodes.
- The fuel cell system may be represented as:

  Fuel/electrode/electrolyte/electrode/oxidant

- Fuel undergoing oxidation at the anode releases electrons and the oxidant gets reduced at the cathode by the electrons flowing through the external circuit to the cathode.
- **Anode:** Fuel = Oxidation products + ne^-
- **Cathode:** Oxidant + ne- = Reduction products
- One of the simplest and most successful fuels is hydrogen-oxygen fuel cell.

Hydrogen-oxygen fuel cell





- It consists of an electrolytic solution such as 25% KOH solution and two inert porous electrodes.
- Hydrogen and oxygen gases are bubbled through the anode and cathode components respectively, where the following reactions takes place:

  Anode : $2H_2\,(g) + 4OH^-(aq) \longrightarrow 4H_2O + 4e^-$

  Cathode : $O_2\,(g) + 4H_2O + 4e^- \longrightarrow 4OH^-(aq)$

- Electrodes are made up of porous graphite. Platinum is used as the catalyst in low temperature and nickel in high temperature.
- The electrolyte is 25% KOH.
- Here, hydrogen gas is bubbled at anode and oxygen gas is bubbled at cathode.

Cell Reactions

Anode : $2H_2 (g) + 4OH^- (aq) \longrightarrow 4H_2O + 4e^-$

Cathode : $O_2 (g) + 2H_2O + 4e^- \longrightarrow 4OH^- (aq)$

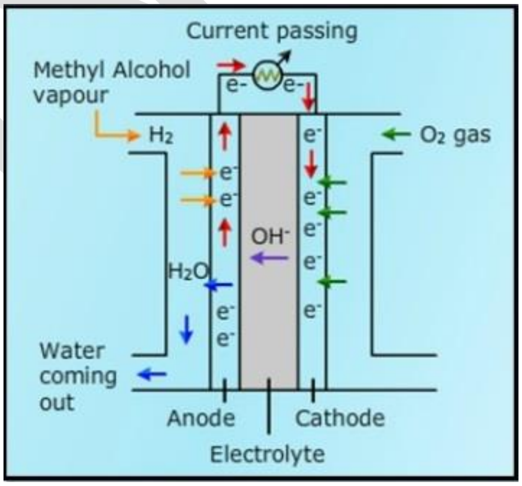
Net Reaction: $2H_2 (g) + O_2 (g) \longrightarrow 2H_2O$

Uses

- Used as auxiliary energy sources in space vehicles (space craft), submarines and other military vehicles.
- For space craft, they are preferred due to their lightness and product water is available as a source of fresh water for the astronauts.

Methyl Alcohol-Oxygen Alkaline Fuel Cell

- The methyl alcohol-oxygen fuel cell has two electrodes.
- The anode is porous nickel electrode impregnated with Pt/Pd catalyst.
- Cathode is porous nickel electrode coated with silver catalyst.
- The electrolyte KOH, is taken in between the two electrodes.
- CH_3OH and O_2 are sent continuously into their electrodes and electrical energy is produced due to the following cell reactions:



At Anode : $CH_3OH + 6OH^- \longrightarrow CO_2 + 5H_2O + 6e^-$

At Cathode : $3/2\ O_2 + 3H_2O + 6e^- \longrightarrow 6OH^-$

Net Reaction: $CH_3OH + 3/2\ O_2 \longrightarrow CO_2 + 2H_2O$

Advantages:

- Methanol fuel cells are reasonably stable at all environmental conditions
- Easy to transport
- Because of high hydrogen concentration in methanol, it is an excellent fuel.
- Methanol poses less risk to aquatic plants, animals and human beings than gasoline.
- Due to its low inflammability limit, methanol has less risk than gasoline
- There is zero emission by the cells. Hence the fuel cells are eco-friendly.

Applications:

- Methyl alcohol oxygen fuel cells are used in motor vehicles like NECAR in Japan, USA etc.

Advantages of Fuel Cells

- Eco-friendly, high efficient and offer an excellent use of our renewable energy sources.
- Low maintenance cost, compact and transportable.
- Less corrosive and can be operated up to 200^0C.
- Fuel cell energy is economical and safe.
- These are good storage devices for future nuclear and solar energy economies.

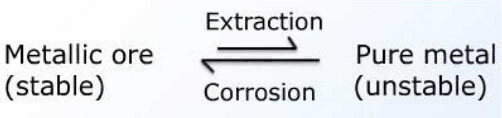
Limitations of Fuel Cells

- High initial cost.
- Large weight and volume of hydrogen gas fuel storage system
- Lack of infrastructure for distribution and marketing of hydrogen gas
- High cost of hydrogen cost.
- Most of the cells suffer from carbon dioxide leakage.

CORROSION

Why metals corrode: Reason

- All metals except gold and platinum corrode when exposed to atmosphere.
- Metals exist in the form of ores, which are in the combined form.
- Metals are extracted from their ores by reduction process.
- Corrosion is the reverse process of extraction of metals from ores by oxidation.



- Greater is the amount of energy required to separate the metal from its mineral, higher will be the tendency of the metal to revert back to its natural state resulting in the degradation of the metal.

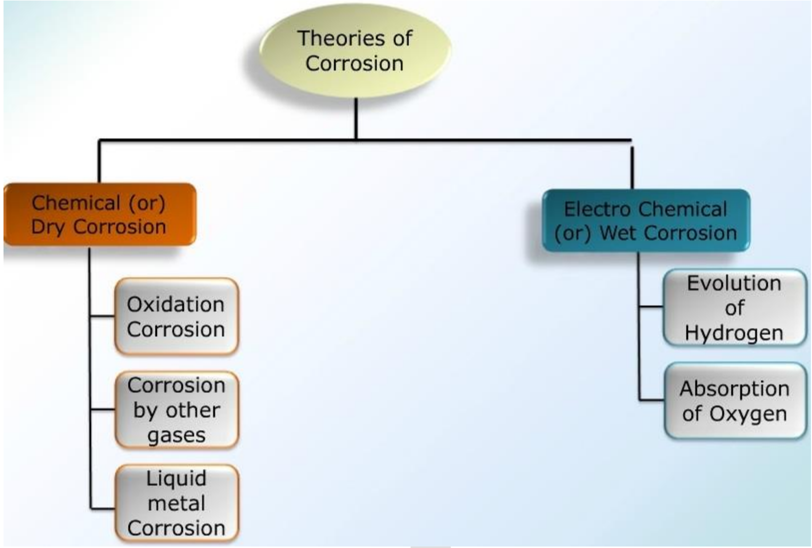
Consequences of Corrosion

- Leads to an enomorous loss of metallic material such as machines, equipments, tools, structures etc.
- It leads to unpredictable machinery failure.
- It leads to decrease in the efficiency of equipment and machinery.
- Health due to a corrosion product or due to an escaping chemical from corroded equipment.
- Necessity for overdesign to allow for corrosion.
- Plant shutdown due to failure.
- Preventive maintenance.
- Losses, to the tune of millions of rupees or dollars per annum.

Theories of Corrosion

Chemical (or) Dry Corrosion

- It is the simplest cause of corrosion.
- Here corrosion takes place by direct chemical attack of atmospheric gases such as oxygen, halogen, hydrogen sulphide (H_2S), SO_2 etc. on metal surface.

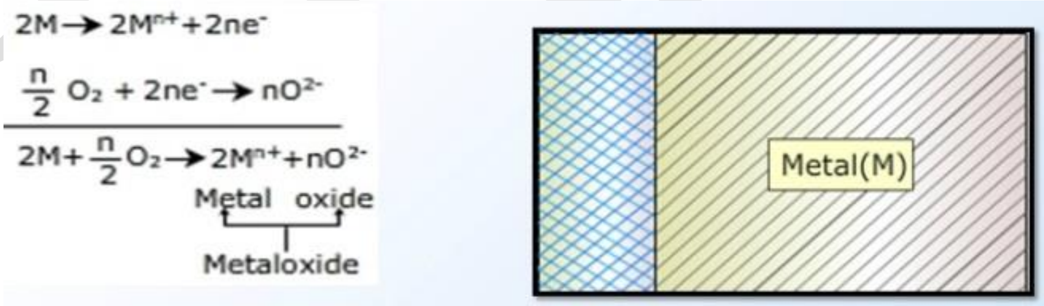


Dry corrosion is of three types:

1. Oxidation corrosion
2. Corrosion by other gases
3. Liquid metal corrosion

1. Oxidation Corrosion

- Oxidation corrosion takes place by direct action of oxygen on metals, at low or high temperature forming oxides of the metal. It generally takes place in the absence of moisture.



- Oxidation first occures at the surface of the metal and the resulting metal oxide scale forms a barrier that tends to restrict further oxidation.

Mechanism

- Oxygen is adsorbed at the surface of the metal by physical adsorption.
- When the temperature rises, the physical adsorption turns into chemical adsorption and the gets oxidized to metal ions.

$$\mathbf{M \longrightarrow M^{+n} + ne^-}$$

- The electrons are taken up by the oxygen which gets reduced to oxide ion.

$$n/2\ O_2 + 2ne^- \longrightarrow nO^{-2}$$

- The metal oxide scale so formed forms a barrier between the metal and the oxygen and restricts further oxidation or corrosion of the metal.
- For oxidation to continue either the metal must diffuse outwards through the scale to the surface or oxygen must diffuse through the scale to the underlying metal.
- As the metal cation is much smaller in size, the outward diffusion of the metal ion is much more rapid than inward diffusion. Hence, corrosion continues by rapid diffusion of highly mobile cations.
- The extent of corrosion depends upon the nature of the corrosion product formed.
- Nature of the oxide film formed plays an important role in corrosion process. The nature of the oxide film decides further corrosion process.

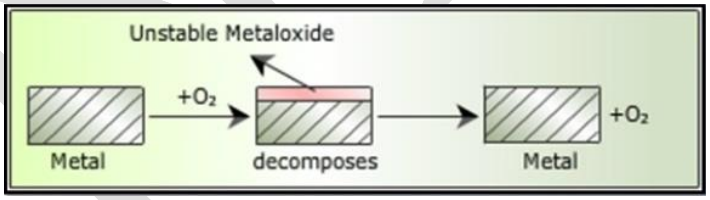
Stable:

- If metal oxide is stable in nature, it acts as a protective barrier between metal and oxygen, so further corrosion doesn't takes place.

  Ex: Al_2O_3, Cr_2O_7, Pb_2O_3

Unstable:

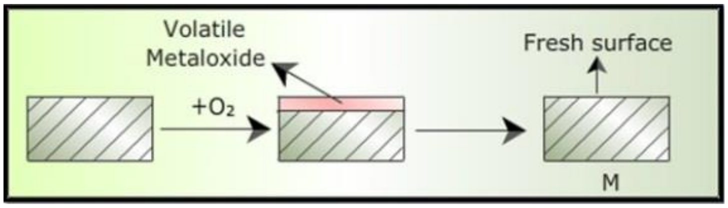
- The oxide layer formed decomposes back into the metal and oxygen. Hence further corrosion is possible.
- Metal Oxide $\longrightarrow$ Metal + Oxygen



Volatile:

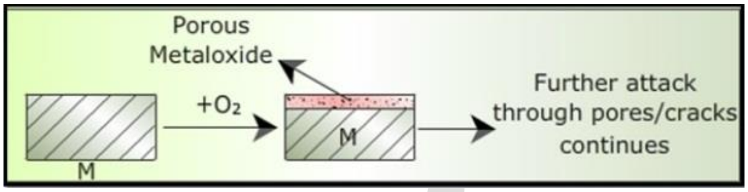
- The oxide layer volatizes as soon as it is formed, there by leaving underlying metal for further attack.

  Ex: MoO_3



Porous:

- Have pores or cracks.
- In such case, the atmospheric oxygen has access to the underlying surface of metal through the pores or cracks.
- Further corrosion takes place continuously till the entire metal is converted in to its oxide.



Pilling-Bed worth Rule (or) Ratio:

- The oxide layer can be protective or non-protective depending on the ratio of the volume of the metal oxide formed to the volume of metal consumed. This is known as "Pilling-Bed Worth ratio"

Pilling Bed worth ratio = Vol.of metal oxide formed/Vol. of metal consumed

According to the Pilling Bed worth rule

- If the volume of the oxide film is less than the volume of the respective metal from which it is formed and the ratio is less than the unity (1), then the oxide film will be non-protective in nature.

  Ex: Alkali and alkaline earth metals such as Na, Ca, Mg (except Al).

  Consequently the oxide film develops cracks and pores on its surface
- If the metal oxide film formed is equal or greater than the respective metal from which it is formed and the ratio is more than the unity (1), the metal oxide film is protective in nature. In such case, the oxide film formed is continuous, adhering and nonporous.

  Ex: Al, Cr etc.

2. Corrosion by other gases

- In addition to oxygen, a number of other gases such as CO_2, SO_2, Cl_2, H_2S, F_2 etc. also have corrosion effect on metals.

- The extent of corrosion depends on the chemical affinity between the metal and the gas involved. In this case also the film so formed may be protective or non-protective in nature.
- If the film formed is protective in nature, the extent of attack of corrosion decreases.

  Ex: Chlorine gas attacks silver metal.
- If the metal film formed is non-protective in nature, then it destroys the whole metal eventually.

  Ex: Chlorine attacks Sn to form $SnCl_4$ film which is volatile.

  H_2S attacks steel forming FeS layer which is porous in nature.

3. Liquid Metal Corrosion:

- Liquid metal corrosion is due to the chemical action of flowing liquid metal at high temperature on solid metal or alloy.
- Such corrosion in devices is used for nuclear power.
- The corrosion reaction involves either of the following.
  - Dissolution of a solid metal by a liquid metal.
  - Internal penetration of the liquid metal into the solid metal.
- Both these modes of corrosion cause weakening of the solid metal.

Electro Chemical (or) Wet Corrosion

- The corrosion of metals in aqueous medium is electrochemical in nature.
- This type of corrosion occurs:
  - **i.** Where a conducting liquid is in contact with metal (or)
  - **ii.** When two dissimilar metals or alloys are either immersed or dipped in a solution.
- The corrosion occurs due to the existence of separate anodic and cathodic areas, between which current flows through the conducting solution.

Cell Reactions:

a) Anodic Reactions: At anodic area oxidation takes place

$$\underset{\text{(Metal)}}{\mathbf{M}} \longrightarrow \underset{\text{(Metal ion)}}{\mathbf{M^{n+}}} + \mathbf{ne^-}$$

Thus, anodic metal is destroyed by either dissolving or assuming combined state.

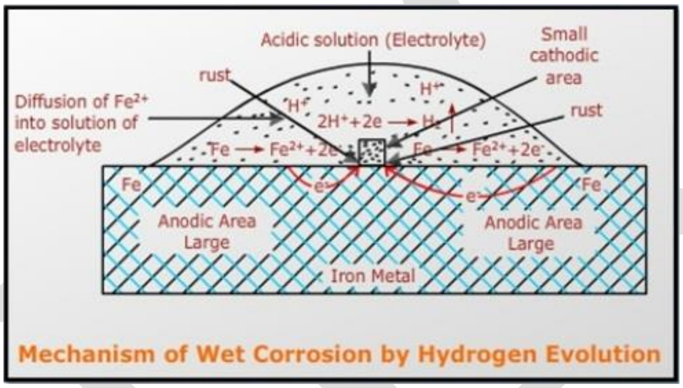
b) Cathodic Reactions:

- The electrons released at the anodic area are consumed in the reaction at the cathodic area forming ions like OH^-, O^{-2} etc.
- The metallic ions (at anodic part) and non-metallic ions (formed at cathodic part) diffuse towards each other through conducting medium and form a corrosion product between anode and cathode.

Wet corrosion takes place in two ways

- ❖ Evolution of hydrogen
- ❖ Absorption of oxygen

Evolution of hydrogen



Mechanism of Wet Corrosion by Hydrogen Evolution

- It occurs in acidic environment.

  Ex: Rusting of iron in acidic medium in the absence of oxygen.
- At anode, iron undergoes oxidation by releasing electrons and dissolves.

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

- The electrons flow from anode to cathode and absorbed by H^+ ions of acidic solution to form hydrogen gas. Thus H_2 gas evolved.

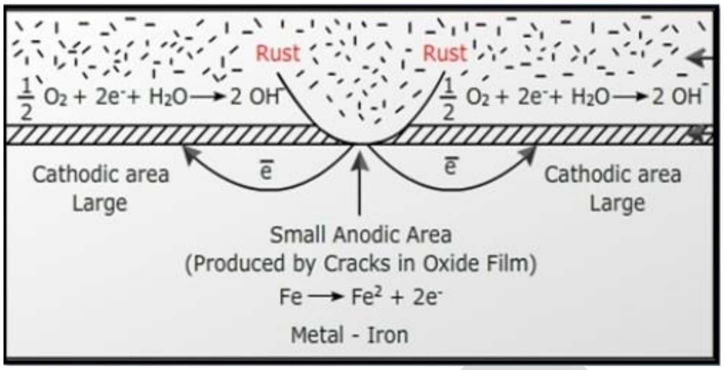
$$\mathbf{2H^+ + 2e^- \longrightarrow H_2\uparrow}$$

- Overall reaction is

$$\mathbf{Fe + 2H^+ \longrightarrow Fe^{+2} + H_2\uparrow}$$

- Hence, in this type of corrosion, hydrogen ions are displaced from the acidic solution by metal ions.

Absorption of Oxygen



- This type of corrosion reaction takes place in the presence of atmospheric oxygen.
- In neutral aqueous or weakly alkaline solution oxygen gets reduced as

$$2H_2O + O_2 + 4e^- \longrightarrow 4OH^-$$

Ex: Rusting of iron in neutral solution in the presence of oxygen.

- Anodic reaction is

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

- The electrons are moved to the cathode and accepted by water oxygen to form OH- ions by reduction.

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

- The Fe^{+2} ions at anode and OH^- ions at cathode diffuse towards each other forming rust. i.e. $Fe(OH)_2$

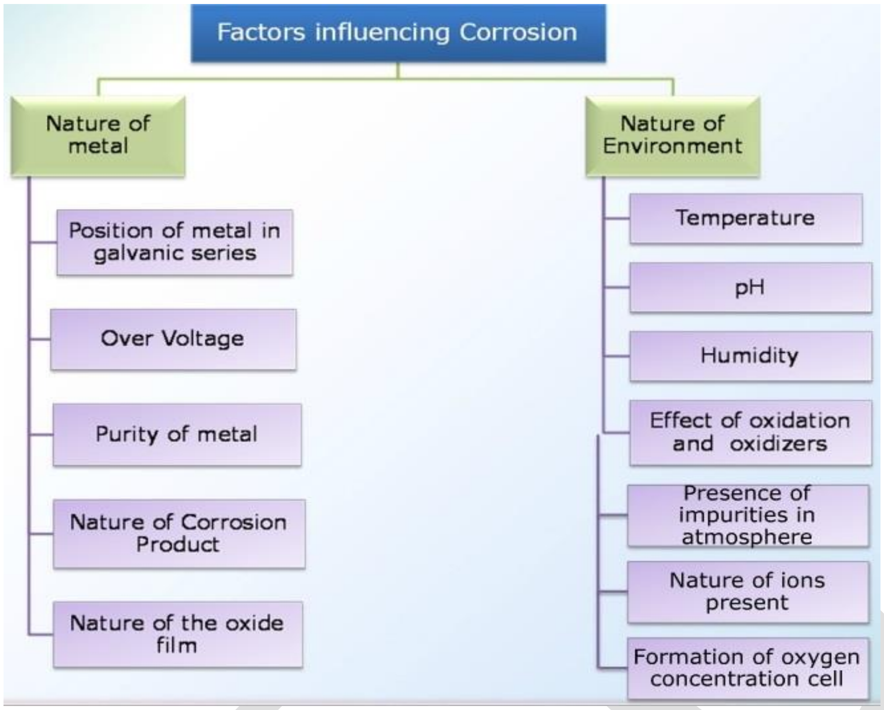
$$Fe^{+2} + 2OH^- \longrightarrow Fe(OH)_2 \downarrow$$

- If enough oxygen is present $Fe(OH)_2$ is easily oxidized to $Fe(OH)_3$

$$Fe(OH)_2 + O_2 + 2H_2O \longrightarrow 4Fe(OH)_3 \text{ or } 3Fe_2O_3.3H_2O \text{ (rust)}$$

- Though corrosion occurs at the anode, the rust formed near the cathode because of smaller Fe^{+2} ions produced at the anode diffuse faster towards the cathode than the larger OH^- ions towards the anode.

Factors influencing Corrosion



Nature of Metal

Position of metal in galvanic series

- When two metals or alloys are in electric contact in the presence of an electrolyte, the metal high in series (more anodic) undergoes corrosion faster than the metal below it.
- Greater the difference, faster is the corrosion.

  Ex: Li corrodes faster than Mg.

Over voltage

- Over voltage occurs when the voltage in a circuit or part of it is raised above its upper limit.

  Ex: When Zn is placed in 1N H_2SO_4, it undergoes corrosion forming a film and evolving hydrogen gas. The initial rate of corrosion is slow, due to high over voltage i.e. 0.76 volts.
- On addition of copper sulphate, the corrosion rate of Zinc is accelerated due to the deposition of copper, where the overvoltage of hydrogen is 0.33v. Thus, reduction in overvoltage of the corroding metal/alloy accelerates the corrosion rate.

Purity of metal:

- Heterogeneity is produced if impurities are present in a metal and form tiny electrochemical cells at the exposed parts.
- As the extent of exposure and impurities increases, corrosion increases.

  Ex: Zinc metal containing impurity such as Pb or Fe undergoes corrosion due to the formation of local electrochemical cells.

Nature of corrosion product:

- If the corrosion product is volatile and soluble in both the cases, the corrosion will be faster. MnO_3, $SnCl_4$ are volatile, so the corrosion of Sn is faster in Cl.
- In case of soluble corrosion product, it is enhanced by water and the metal surface is exposed for further corrosion.

Nature of oxide film

- All metals when exposed to atmosphere produce a thin film of metal oxide. The ratio of the volumes of the metal oxide to the metal is called specific volume ratio.
- If the volume is more, the rate of corrosion is less, because the surface of the metal is completely covered by the film which protects the metal surface.

Nature of Environment

Temperature

- The rate of corrosion reaction and diffusion with increase in temperature, causing the increase in rate of corrosion.

pH

- pH has greater effect on corrosion. When pH is lowered, the rate of corrosion increases.

Humidity

- Corrosion of metals becomes faster in humid atmosphere.
- It provides water, which is essential for setting up an electrochemical corrosion.

Effect of oxidation and oxidizers

- When oxidizer is added, some metals achieve passivity due to the formation of oxide film which is protective in nature.

Presence of impurities in atmosphere

- Atmosphere, in the vicinity of industrial areas, contains corrosive gases like CO_2, H_2S, SO_2 and fumes of HCl, H_2SO_4, etc.
- In presence of these gases, the acidity of the liquid, adjacent to the metal surfaces, increases and its electrical conductivity also increases.
- This consequently, results in an increase of corrosion current flowing in the local electrochemical cells on the exposed metal surfaces.
- Similarly, in the marine atmosphere, the presence of sodium and other chlorides (of sea water) lead to increased conductivity of the liquid layer in contact with the metal surface, thereby corrosion is speeded up.

Nature of ions present

- Presence of anions like silicate in the medium, leads to the formation of insoluble reaction products (**Ex.** Silica gel), which inhibit further corrosion.
- On the other hand, chloride ions, if present in the medium, destroy the protective and passive surface film, thereby exposing the metal/alloy surface for fresh corrosion.
- Many metals, including iron, undergo corrosion rapidly, if corroding medium contains ammonium salts.
- Presence of even traces of copper (or any noble metal) in mine waters, accelerates the corrosion of the iron pipes, used for carrying such waters.

Formation of oxygen concentration cell

- With the increase in the supply of oxygen/air to the moist-metal surface, the corrosion is formed.
- Less oxygen concentration (**Ex.** Oxide-coated part or less-exposed part) parts becomes anodic, while the more-oxygenated regions (or parts more exposed to oxygen) becomes cathodic, thereby leading to the formation of oxygen concentration cell in which the anodic part suffers corrosion.

Corrosion controlling Methods

There are many corrosion control methods like; Proper designing, Using pure metal, Using metal alloys, Cathodic protection, Modifying the environment, Use of inhibitors and Application of protective coatings etc.

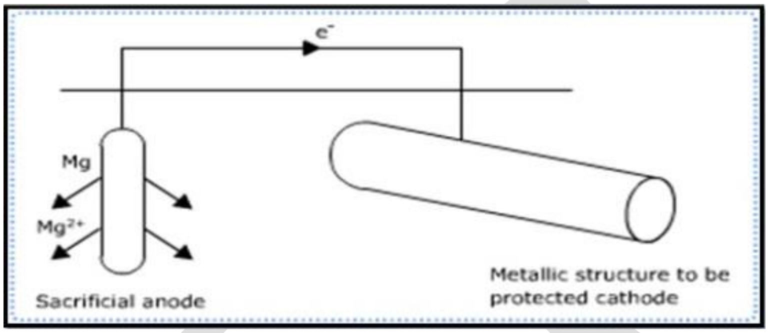
Cathodic protection

Principle: The metal to be protected is forced to act as cathode, so that the metal can be protected from corrosion.

There are two types of cathodic protection:

1. Sacrificial Anode protection
2. Impressed current cathodic protection

1. Sacrificial Anode protection

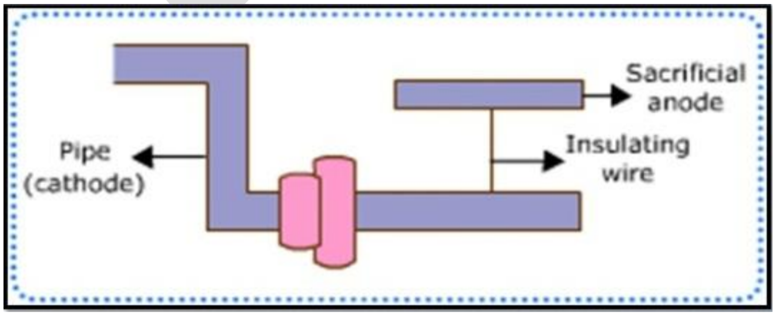


- In this method the metallic structure to be protected is connected to a more active metal through an insulated wire, so that active metal acts as an anode and gets corroded, the metallic structure acts as a cathode and gets protected.
- Since the anode is sacrificing itself, it is called sacrificial anodic. The corroded sacrificial anode block is replaced by a fresh one, when consumed completely. The commonly used sacrificial anodes are Mg, Alloys of Mg, Zn, Al, etc.

Important applications of sacrificial anodic method

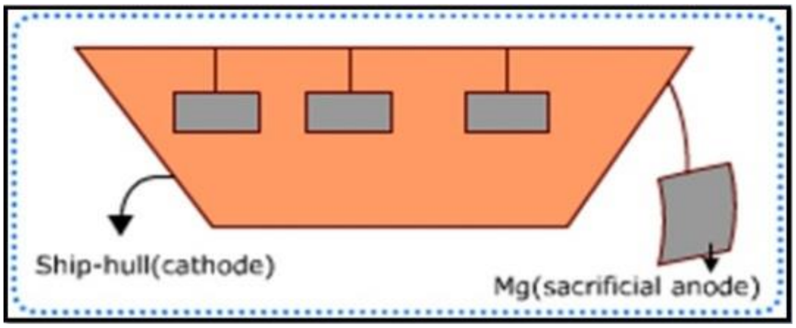
- Buried pipe lines, underground cables, marine structure, ship-hulls, water-tanks etc. are protected by this method.

  Ex: 1. For the protection of underground cables.

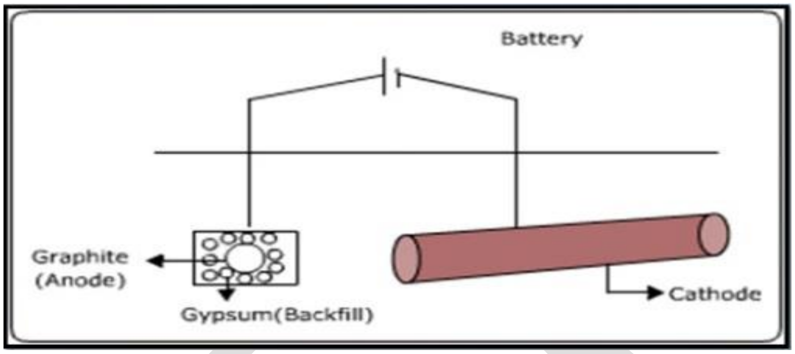


Ex: 2. For the protection of ships or boats

The sheets of Mg or Zn are hung using an insulating wire.



2. Impressed current cathodic protection



- In this method, an impressed current is applied in the opposite direction to nullify the corrosion current and to convert the corroding metal from anode to cathode.
- Generally anode is made up of insoluble materials such as graphite, platinum etc. which is buried in a black electric conductivity.
- This method is used for the long term protection of large structures like electrical transmission towers, underground pipes, water box coolers etc.

Surface Coatings

- The surface of the structure to be protected is covered with another material which forms a coating and acts as a barrier between the metal and its environment and offers protection to the metal.
- There are three types of surface coatings:
    1. Metallic coating (**Example:** Galvanization and Tinning)
    2. Organic coating (**Example:** Paint and varnish)
    3. Non-metallic coatings (**Example:** Enamel coating)

1. Metallic Coatings

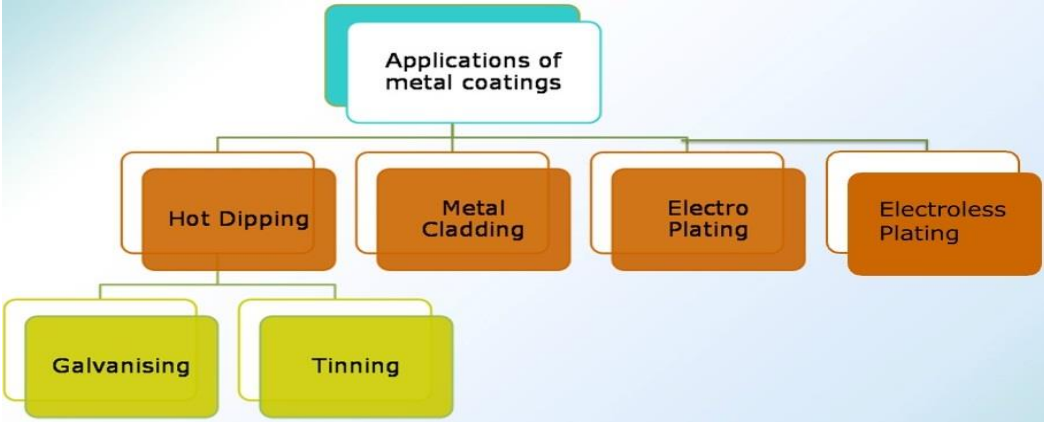
The surface of the metal coated with another metal is called metal coating. It is of two types.

    - Anodic Coating
    - Cathodic Coating

- **Anodic Coating**
    - The surface of the base metal (to be protected) is coated with another more anodic metal.
    - The coating metal acts as an anode and the base metal acts as cathode.
    - **Example:** Galvanization of Fe/Steel
    - Let us consider the surface of Fe/Steel coated with Zinc. Here, Zinc acts as anode and the base metal Fe acts as cathode.
    - Anodic coating of Zinc protects the base metal iron sacrificially.
    - Protection continues even if there are cracks or pin holes in the coating, in such a case, the exposed part of the base metal (Fe) acts as a cathode and its is protected.

- **Cathodic Coating**
    - In this method the base metal is coated with a more noble metal that is a metal present below it in the galvanic series.
    - Here, the coating metal acts as a cathode and the base metal acts as anode.
        - **Ex:** Coating of the surface of iron with metals like Sn, Ni, Cr etc.
    - Cathodic coating protects the base metal due to its noble character.
    - Cathodic coating can protect the base metal only as long as the coating is continuous.
    - In the case of any discontinuity, the exposed part of the base metal (for **Ex:** iron) becomes anodic and the coating metal (for **Ex:** Sn) becomes cathodic in the galvanic cell formed. Severe corrosion occurs and iron gets corroded very badly.

Methods of Application of Metal Coatings

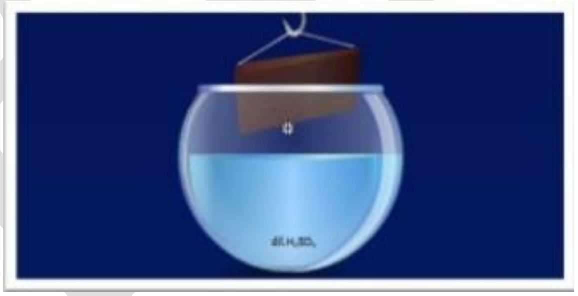


Hot Dipping

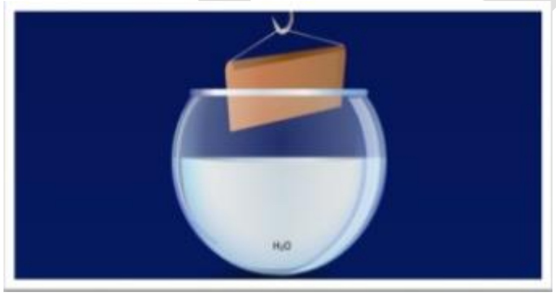
- Hot dipping is used for producing a coating of low melting metal such as Zn (M.P-419^{0}C), Sn (M.P = 230^{0}C) Pb, Al etc., on iron and steel, which have relatively higher melting points.
- The process in general, consists of immersing the base metal in a bath of the molten coating metal covered by a molten flux layer.
- The flux cleans the base metal surface and prevents the oxidation of molten coating metal.

Galvanizing

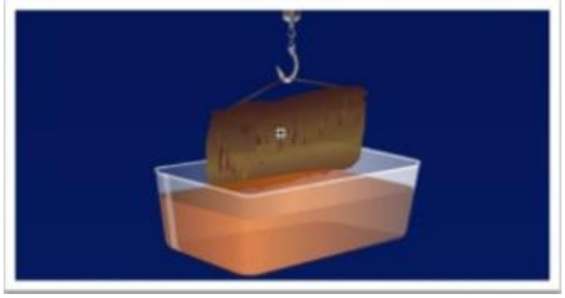
- The process of the coating of iron or steel with a thin layer of zinc to prevent them from rusting.
- Metal piece is carried by a spring balance.
- A metal piece is dipped in a solution of dil. H_2SO_4 (at 60^0-90^{0}C temp. for 15-20 min.). It removes scale, rust and impurities.

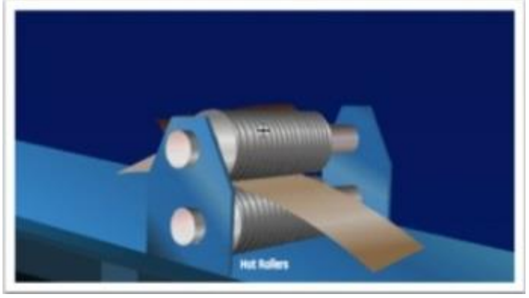


- Again it is dipped in water.
- Metal piece is dried by using a drier.



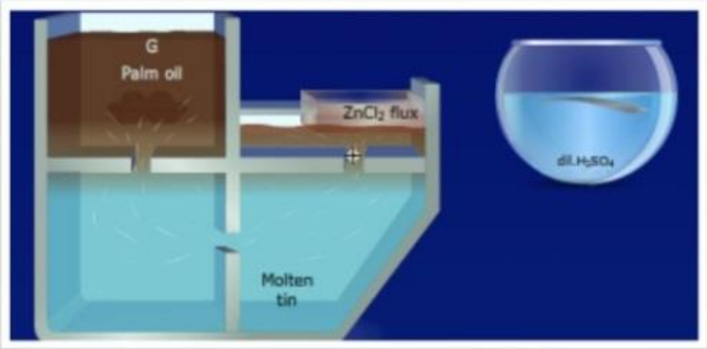
- Metal piece is dipped in a zinc bath (metal will be in irregular shape)
- It is maintained at 425^{0}C-435^{0}C and covered by NH_4Cl flux to avoid oxidation of Zinc.
- Metal is placed in between the rollers to get a regular shape and the excess of zinc will be melting down.



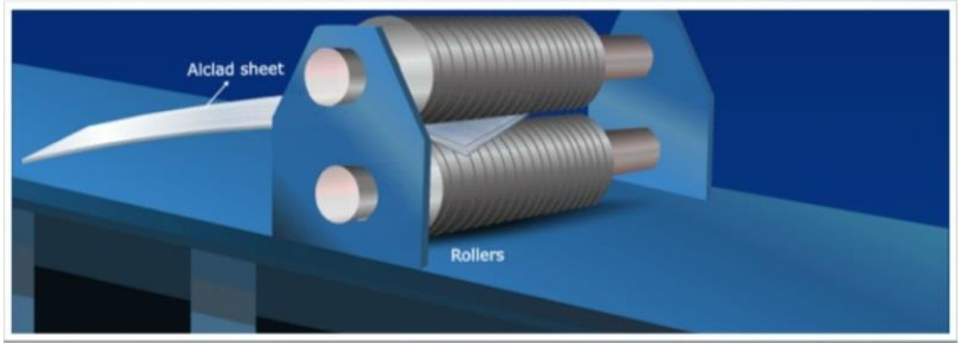


Tinning

- The process of coating of iron or steel with a thin coat of Tin.
- Base metal is cleaned by dipping in dil. H_2SO_4.
- Metal is passed through a bath of $ZnCl_2$ flux.
- Metal is passed through molten tin.
- Metal piece is pressed between two rollers from a layer of palm oil.



Metal Cladding



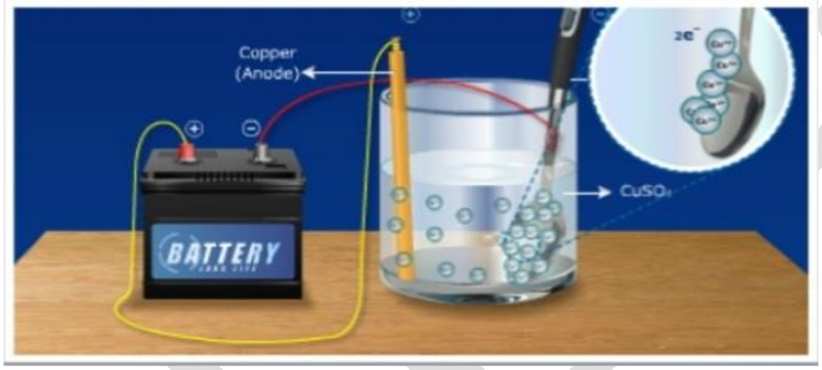
- The choice of cladding of material depends on the corrosion-resistance is required for any particular environments.
- Nearly all existing corrosion resisting metals (like Nickel, Cu, Pb, Ag, Pt etc.) and alloys like (stainless steel, Ni alloy, Cu alloys, Pb alloys etc.) can be used as cladding materials. Among the base a metal on which cladding is done are, mild steel, Aluminum, Cu, Ni and their alloys.

- Generally, cladding is accomplished by arranging thin sheets of the coating metal and the base metal sheet in the form of a sandwich, which are then passed through rollers, under the action of heat and pressure.

  Ex: Duralumin is sandwiched between two layers of 99.5% pure aluminum results in cladded sheet known as "alclad".
- It is used in aircraft industry.
- It is the process by which a dense, homogeneous layer of coating metal is bonded firmly and permanently to the base metal on one or both sides.

Electro Plating

It is the process by which the coating metal deposited on the base metal by passing a d.c. through an electrolytic solution containing the soluble salt of coating metal.



Electroless Platting

The driving force is autocatalytic redox reaction on pretreated catalytic surface. Various aspects of electroless plating are

Preparation of active surface of the object to be plated:

- This step is most important in this technique. This is achieved by using one of the following methods.
- Etching, i.e. by acid treatment.
- Electroplating a thin layer of the metal to be plated or any other suitable metal. This is usually followed by heat treatment.
- Treating with stannous chloride, followed by dipping in palladium chloride solution. This treatment yields thin layer of Pd on the treated surface. Usually, this is followed in case of plastics and printed circuit boards.

Plating bath is composed of

- Soluble salt of metal (like chloride or sulphate) to be plated.
- Reducing agent like formaldehyde, hypophosphite, etc.
- Complexing agent like tartarate, citrate succinate, etc. This improves the quality of deposit.
- Exaltant like succinate, flouride, glycinate, etc. This enhances the plating rate.
- Stabilizer like thiourea, cation of lead, calcium, thalium, etc. is added to prevent the decomposition of the plating bath solution.
- Buffer like sodium acetate, sodium hydroxide + Rochelle salt, etc. is added to control the pH of the bath. It may be pointed out that pH of the bath plays a critical role in getting a uniform, but thin deposit.

Advantages of electroless plating over electroplating

- No electrical energy is required.
- Better throwing power.
- Plating on articles made of insulators (like plastics) and semiconductors can be plated uniformly.
- Electroless plated coatings possess unique mechanical, chemical and magnetic features.

2. Organic Coatings

Organic coatings are inert organic barriers applied on metallic surfaces for protection against corrosion.

Ex: Paints

- Paint is a dispersion mixture of one or more pigments in a vehicle.
- Vehicle is a liquid consisting of non-volatile and film forming drying oil and a highly volatile solvent called thinner. Vehicle = Drying oil + Thinner

Constituents of paint

Pigment

- Pigment is a solid substance, which is an essential constituent of paint.
- Provides desired colour to paint
- Reflects harmful UV rays, there by prevents cracking of paint film.

Ex: White Colour - White lead, lithophone
Red Colour - Red lead, Ferric oxide
Black - Carbon black
Blue - Prussian blue
Green - Chromium oxide
Brown - Brown Umbre etc.

Functions of pigments are:

- Provide capacity to paint
- Provide strength to paint
- Provide desired colour to paint
- Give aesthetical appeal (i.e. Pleasing to look at) to the paint film.
- Give protection to the paint film by reflecting harmful ultraviolet light.
- Provide resistance to paint film against abrasion/wear.
- Improve the impermeability of paint film to moisture.
- Increase weather-resistance of the film.

Pigment Volume Concentration:

The most important concept for a modern paint formulator is pigment volume concentration (PVC), which is the concentration by volume of the pigments expressed as a percentage of the total volume of non-volatile constituents of the paint. As non-volatile volume in paint is the sum of the volumes of the pigment and non-volatile vehicle. PVC can be expressed as

$$\text{PVC} = \frac{\text{Volume of pigment in paint}}{\text{Total volume of non} - \text{volatile constituents of the paint}}$$

$$\text{PVC} = \frac{\text{Volume of pigment in paint}}{\text{Volume of [pigment + non volatile constituents of the paint]}}$$

Drying oil

- A film forming constituent of the paint.
- These are glyceryl esters of high molecular weight fatty acids obtained from animal and vegetable sources.
- The most widely used drying oils are linseed oil, soyabeen oil, and dehydrated castrol oil.

Functions of drying oil:

Drying oil supplies to paint-film:

(i) Main film-forming constituent (ii) Vehicle or medium (iii) Toughness (iv) adhesion (v) Durability (vi) Water-proffness

Thinners

- Reduce the viscosity of the paints, so it can be easily handled and applied on metals
- Dissolve dry oil and other constituents.
- Suspend the pigments in them
- Help in the drying of the paint film, when they evaporate.
- Common thinners used are turpentine, mineral spirits (from petroleum), benzene, dipentene, naptha, xylol, kerosene, methylated napthalene etc.

Driers:

- Driers are oxygen carrier catalysts.
- They accelerate the drying of the oil film through oxidation, polymerization and condensation.
- Thus, their main function is to improve the drying quality of the oil-film.
- The most effective dries are resonates, linoleates, tungstates and napthenates of Co, Mn, Pb and Zn.
- Cobalt substances are the most efficient of all and are surface-driers.

- Lead substances are bottom-driers.
- Manganese substances ate through-dries. Too much of a drier tends to produce hard and brittle films. **Ex:** Resinates, Linoleate, tunstates etc.

Fillers

- Extenders or fillers are low refractive indices materials, generally of white colour, which are added to:
- Reduce the cost.
- Increase the durability of the paint.
- Help reduce the cracking of dry paint film and sometimes help keep the pigments in suspension.
- Servers to foil voids in the film.
- Increase random arrangement of pigment particles, and
- Acts as carrier for the pigment colour.
- **Ex:** Important extenders used are barites (Ba), talc, asbestos, ground silica, gypsum, ground mica, china clay, whiting (Ca), magnesium silicate, diatomite clay, calcium sulphate, etc.

Plasticizers

Sometimes, plasticizers are incorporated in paint

- To avoid elasticity to the film.
- To minimize its cracking.

  Ex: Common plasticizers used are tricresyl phosphate, triphenyl phosphate, tributyl phthale, diamyl phthalate and dibutyl tartarate.

Anti Skinning Agents

Anti skinning agents are used to prevent gelling, cracking of paint films.

Ex: Polyhydroxy phenols.

UNIT-IV

ELECTROCHEMISTRY AND CORROSION

IMPORTANT QUESTIONS

1. What is reference electrode? Explain the construction of Hydrogen & Calomel electrode.
2. What is primary cell? Explain the mechanism of dry cell.
3. Explain the construction and discharging, charging reactions of Lead-acid and Ni-Cd battery.
4. Explain the construction and working of Fuel cells.
5. Describe the chemical and electrochemical theories of corrosion.
6. Explain how nature of metal and nature of environment influences the rate of corrosion?
7. Describe the cathodic protection.
8. What are the different constituents present in paints? Discuss the functions of each constituent.
9. Explain the following

   a) Hot-dipping b) Electroplating

   c) Electro less plating d) Metal Cladding

UNIT-V

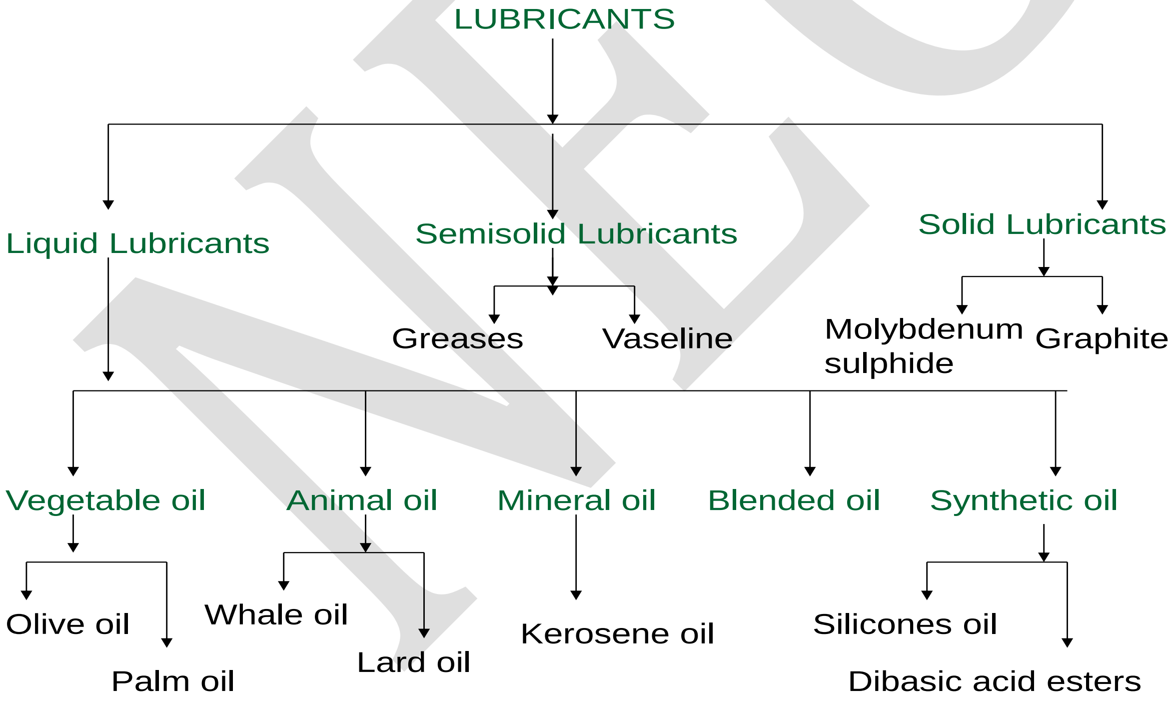
CHEMISTRY OF ENGINEERING MATERIALS

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.

CLASSIFICATION OF LUBRICANTS



Functions of lubricants:

- 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.

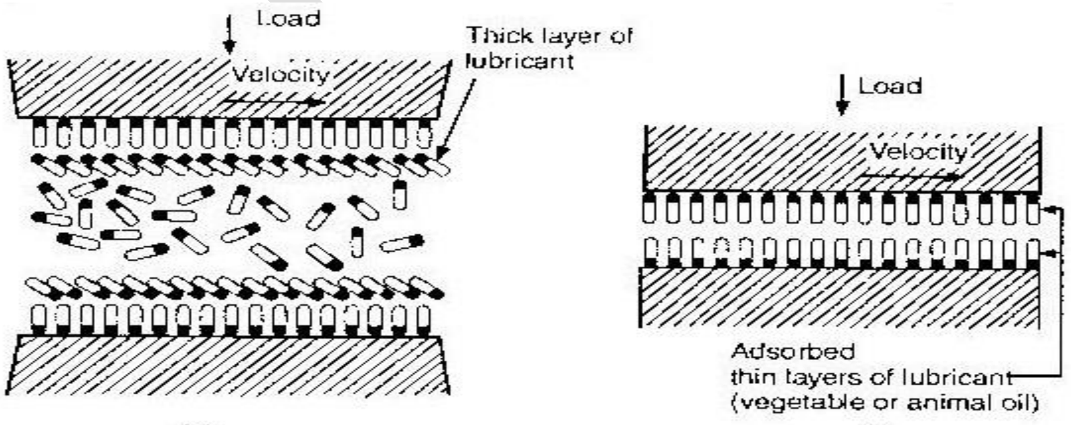
- It reduces expansion of metal by local frictional heat.
- It avoids seizure of moving surfaces.
- It reduces the maintenance and running cost of the machine.
- It also, sometimes, acts as a seal. For example, lubricant used between piston and the cylinder wall of an internal combustion engine acts 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

1. Fluid-film or thick-film or hydrodynamic lubrication:

- In this, the moving/sliding surfaces are separated from each other by a thick-film of fluid (at least 1,000 Å thick), so that direct surface-to surface contact and welding of junctions rarely occurs.
- The lubricant film covers of the sliding/moving surfaces and forms a thick layer in-between them, so that there is no direct contact between the material surfaces.
- The resistance to movement of sliding/moving part is only due to the internal resistance between the particles of the lubricant moving over each other.
- So, the lubricant chosen should have the minimum viscosity and should remain in place and separate the surfaces.
- Delicate instruments, light machines like watches, clocks, guns, sewing machines, scientific instruments provided with this type of lubrication.
- Hydrocarbon oils are considered to be satisfactory lubricants for fluid-film lubrication.



(a) (b)

Fig. 3. (*a*) Fluid-film lubrication ; (*b*) boundary lubrication.

2. 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 the lubricant 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

3. **Extreme-pressure lubrication:**

- When the moving/sliding surfaces are under very high pressure and speed, a high local temperature is attained and under such conditions, liquid lubricants fail to stick and may decompose and even vaporize.
- To meet these extreme-pressure conditions, special additives are added to mineral oils. These are called "extreme-pressure additives". These additives form on metal surfaces more strong films, capable of withstanding very high loads and high temperatures.
- Important additives are organic compounds having active radicals or groups such as chlorine (as in chlorinated esters), sulphur (as in sulphurized oils) or phosphorus (as in tricresyl phosphate).
- These compounds react with metallic surfaces, at prevailing high temperatures, to form metallic chlorides, sulphide or phosphides. These metallic compounds possess high melting points and serve as good lubricant under extreme-pressure and extreme-temperature conditions.

Properties of Lubricants

Lubricants have several properties. Some important properties are

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.

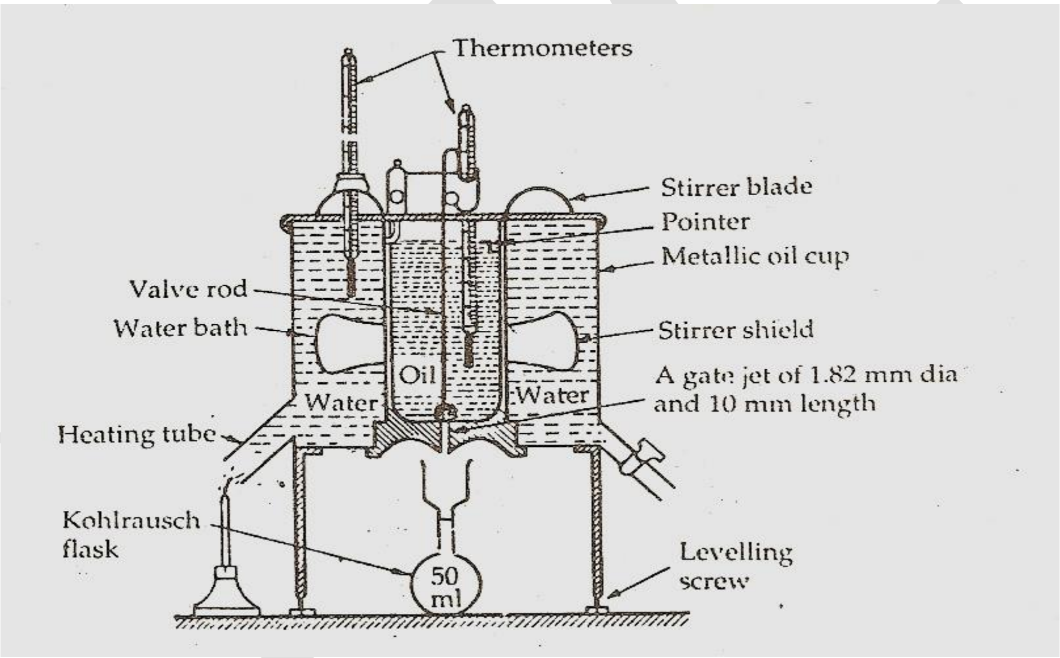
Effect of temperature on viscosity:

- Viscosity of liquids decreases with increasing temperature. Viscosity of good lubricating oil should not change much with temperature, so that can be used continuously, under varying conditions of temperature.

- The rate at which the viscosity of oil changes with temperature is measured by an arbitrary scale, known as the "Viscosity-Index" (V.I.).
- If the viscosity of an oil falls rapidly as the temperature is raised, it has a low viscosity-index. On the other hand, if viscosity of oil is slightly affected on raising the temperature, its viscosity-index is high.

Determination of viscosity of lubricating oil by Redwood viscometer

Redwood viscometer is of two types. Redwood viscometer No-1 is commonly used for determining viscosities of thin lubricating oils and it has a jet of bore diameter 1.62mm and length of 10mm. On the other hand Redwood viscometer No-2 is used for measuring viscosities of highly viscous oils like fuel oil. It has jet of diameter 3.8mm and length of 15mm. Redwood viscometer No-1 consists of the following essential parts.



1. **Oil cup:** It is a brass cylinder, open at the upper end. The bottom of the cylinder is fitted with agate jet with a bore of 1.62 mm. For thin film lubricates a jet of a bore of 1.60 mm and 10 mm length and for thick lubricants a jet of 3.8 mm and length 15 mm. is used. There is a valve rod to open and close the jet. A pointer in the oil cup indicates the level of oil in the cup. A thermometer is fitted in the lid of the cup for measuring the temperature of oil.

2. **Heating bath:** Oil cup is surrounded by a cylindrical copper bath filled with water. A thermometer is inserted in to the bath to measure the temperature of water. Heating bath is also provided with a stirrer to maintain uniform temperature of bath and oil cup.
3. **Leveling screws:** There are three leveling screws to level the apparatus.
4. **Kohlrausch's flask:** A flask of 50 ml capacity is placed below the jet to receive the oil from the jet out let.

Working:

- The apparatus is leveled with leveling screws. Water bath is filled with water and a thermometer is inserted into it. Oil cup is thoroughly cleaned and the jet is closed with ball valve.
- The oil is filled in the cup up to the point, and a thermometer is inserted into the cup to note the temperature of oil. Water bath is heated to a certain temperature with constant stirring to maintain uniform temperature of water.
- When the oil acquires desired temperature, heating is stopped and the ball valve in lifted. The time taken to fill the Kohlrausch flask of 50 ml capacity is noted. The valve is immediately closed to prevent the overflow of oil.
- The experiment is repeated and the mean value of time of flow for 50 ml oil sample is reported and the result is expressed in "Redwood No 1 seconds" at a particular temperature.
- Viscosity of liquids decreases with increases in temperature. Good lubricating oil should not undergo change in viscosity with temperature.

Significance of viscosity measurements:

Viscosity is the property of lubricating oil that determines its ability to lubricate and its film strength, viscosity values are used in evaluating load carrying capacity, in denoting the temperature changes.

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.

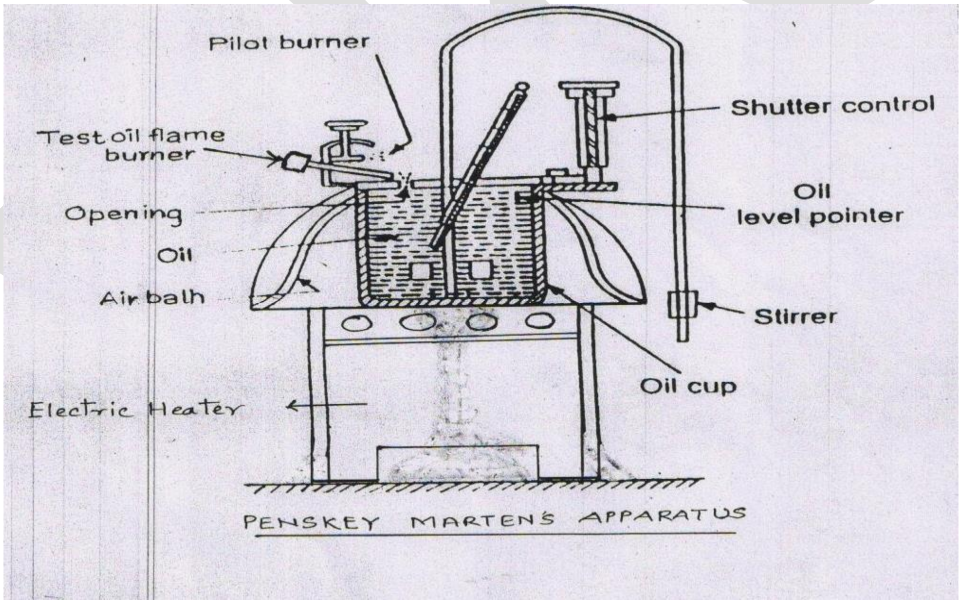
- A good lubricant should have flash point at least above the temperature at which it is to be used. In most of cases the fire point is 5 to 40^{o}C higher than flash point.

The Flash point & Fire point are usually determined by

- Pensky-Marten's Apparatus
- Abel's Apparatus
- Cleavland open cup Apparatus

Determination of flash and fire point by Pensky-Marten's Apparatus:

- The flash and fire points of a lubricating oil are determined experimentally by Pensky - Marten's apparatus. The apparatus consists of a small cup of 5 cm diameter and 5.5 cm. height.
- The cup is closed at the top with a lid containing three openings for inserting a thermometer, stirrer and for introducing test flame.
- A shutter which can be moved on the top of the container by lever mechanism is used to open the lid for introducing the test flame.



PENSKEY MARTEN'S APPARATUS

Working:

- The container is filled up to the standard mark with the lubricating oil. The cup is gradually heated using a burner.
- Stirrer is worked and oil is exposed to the flame for every 1^{o}C rise in temperature of lubricating oil.

- The temperature at which the introduced test flame produces a flash is noted as the flash point. Similarly the temperature at which the oil ignites and continues to burn for at least 5 seconds is noted as the fire point of the oil.

Significance of Flash point & Fire point:

The Flash point & Fire points are used to indicate the fire hazards of petroleum product and evaporation losses under high temperature operations. Knowledge of flash & fire points in lubricating oil aids in precautionary measures against fire hazards.

3. Oiliness

Oiliness of a lubricant is a measure of its capacity to stick on to the surfaces of machine parts, under conditions of heavy pressure or load. When a lubricating oil of poor oiliness is subjected to high pressure, it has a tendency to be squeezed out of the lubricated machine parts; thereby its lubrication action stops. On the other hand, lubricants, which have good oiliness, stay in between the lubricated surfaces, when they are subjected to high pressure.

Significance of Oiliness:

Oiliness is very important property of lubricants, particularly for extreme pressure lubrication. Mineral oils have got very poor oiliness; while vegetable oils have good oiliness. So, in order to improve the oiliness of mineral oils, additives like vegetable oils and higher fatty acids (such as oleic and stearic acids) are added to them.

4. 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.

Determination of cloud and pour points:

- The cloud and pour points are determined experimentally using cloud and pour point apparatus. The apparatus consists of flat bottomed glass tube filled with lubricating oil of standard height enclosed in an air jacket.
- The jacket is surrounded by freezing mixture (ice + $CaCl_2$). A thermometer is introduced in the oil. As the cooling proceeds slowly, the temperature falls continuously.
- For every 1°C fall of temperature, the tube is withdrawn from air jacket for a moment and observed for cloudiness.
- The temperature at which cloudiness is noticed is recorded as cloud point. Similarly after sometime the temperature at which the lubricating oil solidifies and resists to flow is recorded as the pour point.

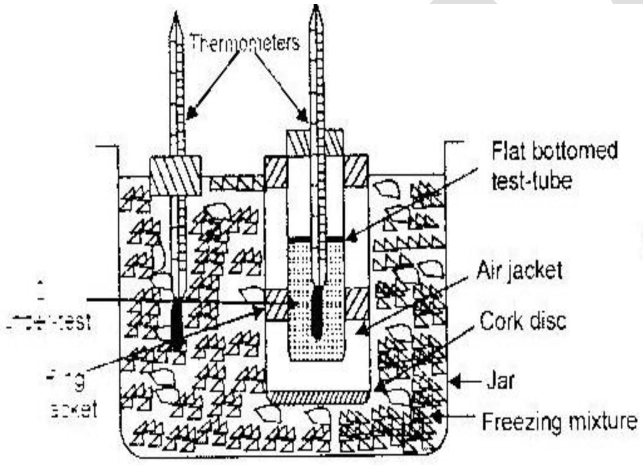


Fig. 8. Cloud and pour-point apparatus.

Significance of Cloud and pour-points:

Cloud and pour-points indicate the suitability of lubricants in cold conditions. Lubricant used in a machine working at low temperatures should possess low pour-point; otherwise solidification of lubricant will cause jamming of the machine. It has been found that presence of waxes in the lubricating oil raise the pour-point.

5. Emulsification

- Emulsification is the property of oils to get intimately mixed with water, forming a mixture, called emulsion. Certain oils form emulsions with water easily.
- Emulsions have a tendency to collect dirt, grit, foreign matter, etc., hereby causing abrasion and wearing out of the lubricated parts of the machinery.
- So, good lubricating oil should form an emulsion with water, which breaks off quickly.

- In this, 20 mL of oil is taken in a test tube and steam at 100°C is bubbled through it till the temperature is raised to 90°C.
- The tube is then placed in a bath maintained at 90°C and the time in seconds is noted, when the oil and water separate out in distinct layers.
- The time in second in which oil and water emulsion separates out in distinct layers, is called "**Steam Emulsion Number**" (S.E.N.). A good lubricant should possess a low steam emulsion number.

Significance of Emulsification:

To avoid corrosion of polished steel surfaces like roll necks and to insure proper lubrication.

6. Carbon residue

- Lubricating oils contain high percentage of carbon in combined form. On heating, they decompose depositing a certain amount of carbon.
- The deposition of such carbon in machine particularly in internal combustion engines and air-compressors.
- A good lubricant should deposit least amount of the carbon of the carbon in use. The estimation of carbon residue is generally carried out by Conradson's Method.

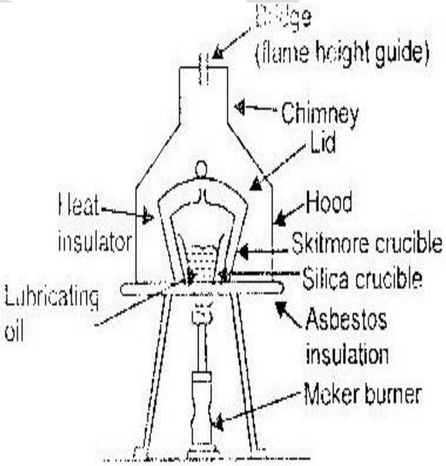


Fig. 9. Conradson's apparatus f[illegible]
residue estimation.

Determination of Carbon residue:

- A weighed quantity of oil is taken in silica crucible. Skitmore crucible is provided with a lid, having a small tube type opening for the escape of volatile matter.
- The combination is then placed in wrought iron crucible covered with chimney shape iron hood. The wrought iron crucible is heated slowly for 10 minutes, till flame appears.

- Slow heating is continued for 5 minutes more. Finally, a strong heating is done for about 15 minutes, till vapours of all volatile matter are burnt completely.
- Apparatus is then allowed to cool and weight of residue left is determined. The result is expressed as percentage of the original weight of oil taken.

Significance of Carbon Residue:

Certain lubricating oils tent to deposit carbon in the internal combustion engines. Excessive built-up of carbon deposits in the combustion chamber result in decreased volume of charge at the end of compression stroke.

7. Aniline point

- Aniline point of oil is defined as "the minimum equilibrium solution temperature for equal volumes of aniline and oil sample".
- Aniline point is determined by mixing mechanically equal volumes of the oil sample and aniline in a test-tube.
- The mixture is heated, till homogenous solution is obtained. Then, the tube is allowed to cool at a controlled rate.
- The temperature at which the two phases (oil and aniline) separate out is recorded at the aniline point.

Significance of Aniline point:

Aniline point gives an indication of the possible deterioration of oil in contact with rubber sealing's, packings etc.

8. Neutralization number (Acid value):

Lubricating oil acidity and alkalinity is determined in the term of neutralization number.

- **TAN (Total Acid Number):** "The number of milligrams of potassium hydroxide (KOH) required neutralizing any acid in 1 g of the oil.
- **TBN (Total Basic Number): "**The number of milligram of hydrochloric acid (HCl) required neutralizing any base in 1 g of the oil."

Significance of Neutralization number:

This test shows relative changes in oil due to oxidation. Comparing the TAN of TBN with the values of new oil will indicate the development of harmful products or effect of additive depletion. This will consequently lead to corrosion.

9. Saponification number

- Saponification number is the number of milligrams of KOH required to saponify 1 g of oil. Mineral oils do not saponify at all, but vegetable and animal oils do.
- Consequently, this test helps us to ascertain whether the oil under reference is animal and vegetable oil or a compounded oil containing mineral and vegetable oils.

Significance of Saponification number:

Mineral oils do not undergo saponification but animal & vegetable oil undergo saponification hence it indicates the amount of animal and vegetable oils added to improve oiliness.

10. Iodine value

Iodine value of oil is the number of milligrams of iodine that can be taken by 1 g of oil. Iodine is absorbed by the oil, due to unsaturation.

Significance of Iodine value:

Iodine value provides an idea of the extent of unsaturation in the oil. Consequently, it is an indicative of its drying quality. Iodine value thus can serve as basic for the classification of vegetable oils as “drying” or “semi-drying” or “non-drying” oils.

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°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%

Preparation of Portland cement

Raw Materials:

- **Calcareous Materials:** Materials which supply lime.

Ex: Limestone, Cement rock, Chalk, and Waste $CaCO_3$ from industrial process.

- **Argillaceous Materials:** Materials which supply silica, alumina and iron oxide.

  Ex: Clay, Blast furnace, Slag, Ashes, Shale and Cement rock.

Gypsum: It is added during the final grinding and it controls the ration of setting and hardening.

Mixing of raw materials

A mixture of finely ground limestone and clay (3:1) is made for any one of the following.

- Dry Process
- Wet Process

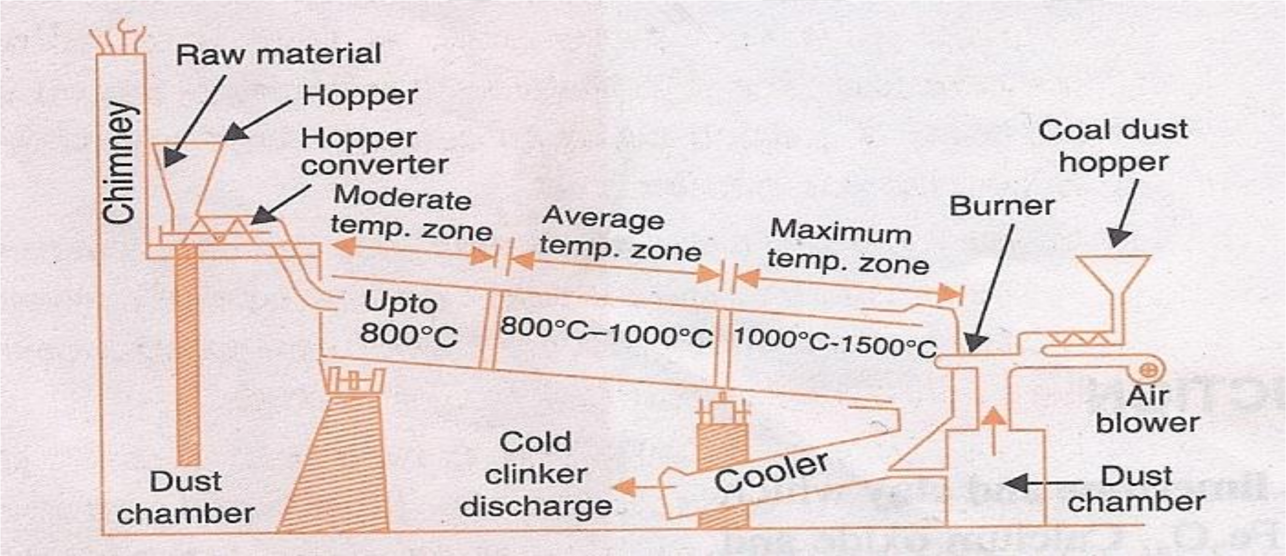
- **Dry Process:**
  - Dry process produces a fine ground powder.
  - This process is employed if lime and clay are hard.
  - In this process, initially limestone is crushed into pieces and then it is mixed with clay in the proportion of 3:1.
  - This mixture is crushed to a fine powder and is stored in storage bins and later on, it is introduced into the upper end of the rotary kiln.

- **Wet Process:**
  - The wet process takes place in the presence of water and usually results in a slurry formation.
  - This process is preferred if limestone and clay are soft.
  - In this process, initially limestone is crushed into pieces and then it is mixed with clay in the proportion of 3:1.
  - Powdered limestone is then mixed with the clay paste in a proper proportion (3:1).
  - The mixture is then finely ground and homogenized to form slurry containing about 40% of water.

Burning the mixture in a Rotary Kiln

- The rotary kiln is an inclined steel cylinder 150-200ft long, 10ft in diameter and it is lined inside with fire bricks.
- The kiln can be rotated at a desired speed of 1 r.p.m.
- As the kiln rotates, the mixture of raw materials stored from the above two process, passes slowly from the upper to the lower end.

- Burning fuel and air are introduced from the lower end of the kiln.
- As the mixture or slurry gradually descends the temperature rises and in fact this creates different zones in the rotary kiln, with increasing temperature.
- The clinkers are cooled and then ground to requisite fines.
- The finely ground clinkers set quite rapidly by absorption of moisture from the atmosphere.
- In order to reduce the rate of setting it is mixed with 2 to 3% gypsum ($CaSO_4.2H_2O$).
- After the initial setting, Al_2O_3 which is a fast setting constituent of clinkers react with gypsum to form the crystals of tricalcium sulphoaluminate, which is insoluble.
- The formation of insoluble tricalcium sulphoaluminate presents too early reactions of setting and hardening.
- This mixture of clinkers and gypsum powder is known as Portland cement.



Zones in Rotary Kiln

- Drying Zone
- De-carbonating Zone
- Burning Zone

- **Drying Zone**
  - This is present in the upper part of the kiln where the temperature is around 400°C.
  - In this zone most of the water in the slurry gets evaporated because of the hot gases.
  - The clay is broken as Al_2O_3, $2SiO_2$, Fe_2O_3 i.e.

$$Al_2O_3.\ 2SiO_2.Fe_2O_3.2H_2O \rightarrow Al_2O_3 + 2SiO_2 + Fe_2O_3 + 2H_2O$$

- **De-carbonating Zone**
  - This zone is located in the middle portion of the kiln where the temperature is of the order 1000°C.
  - In this zone the limestone is completely decomposed into CaO which exists in the form of small lumps, called as noduls.

$$CaCO_3 \rightarrow CaO + CO_2$$

- **Burning Zone**
  - This zone is at the bottom and is considered to be the hottest portion of the kiln.
  - The temperature over here ranges around 1400-1500°C.
  - In this zone the mixture melts and forms little rounded pasty masses of about the size of peas, which are called as clinkers.

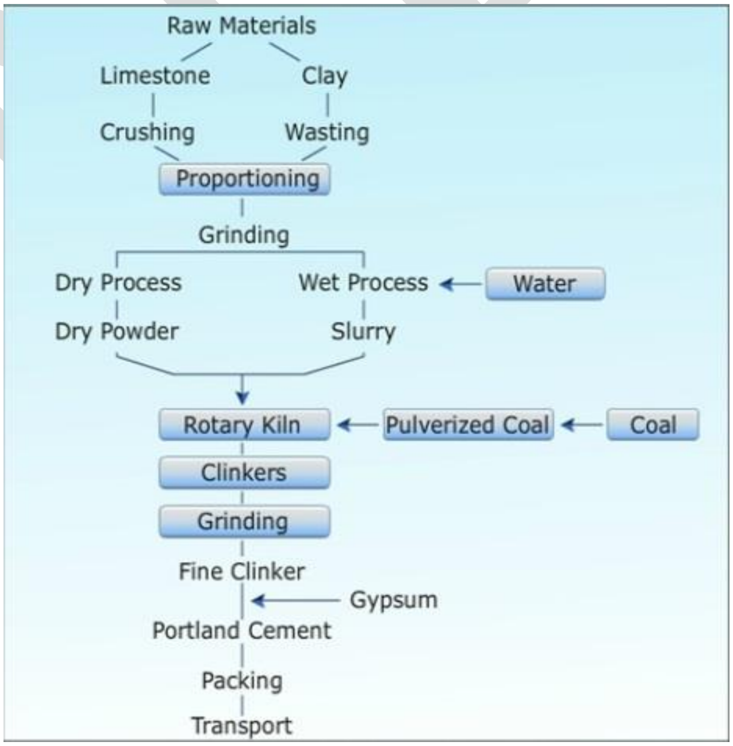
$CaO + SiO_2 \rightarrow 2CaO.\ SiO_2$ (C_2S) (dicalcium silicon)

$3CaO + SiO_2 \rightarrow 3CaO.\ SiO_3$ (C_3s) (tricalcium silicate)

$3CaO + Al_2O_3 \rightarrow 3CaO.\ Al_2O_3$ (C_3A) (tricalcium aluminate)

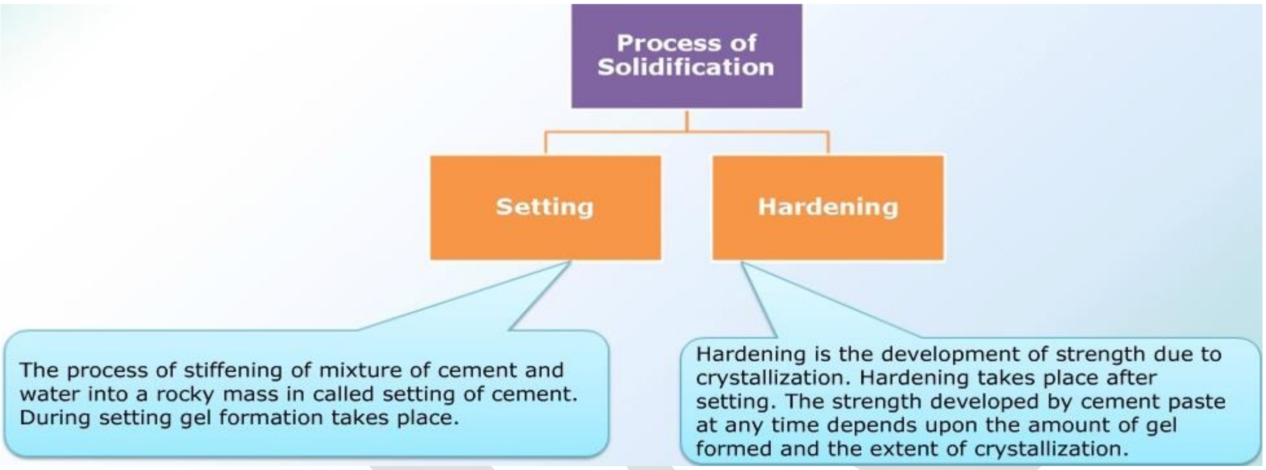
$4CaO + Al_2O_3 \rightarrow 4CaO.\ Al_2O_3$ (C_4 AF) (tetracalcium alumina ferrite)

Flow Chart of Cement Manufacturing



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 process of stiffening of mixture of cement and water into a rocky mass in called setting of cement. During setting gel formation takes place.

Hardening is the development of strength due to crystallization. Hardening takes place after setting. The strength developed by cement paste at any time depends upon the amount of gel formed and the extent of crystallization.

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.

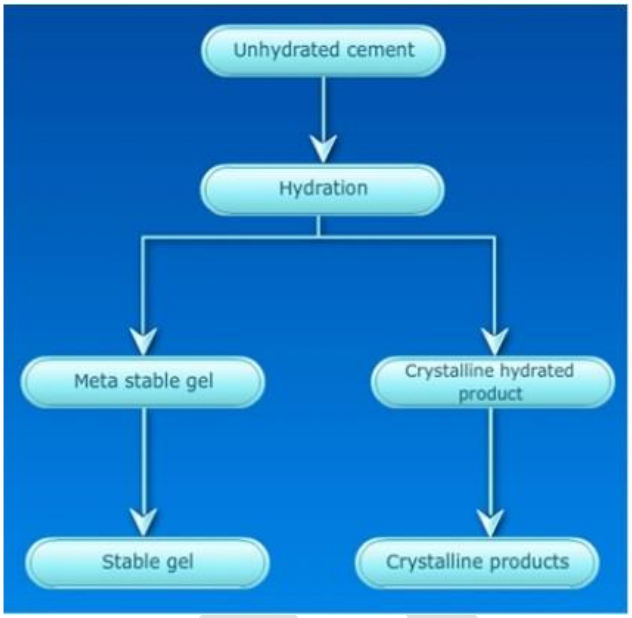
$$2[2CaO.SiO_2] + 4H_2O \longrightarrow 3CaO.2SiO_2.6H_2O + Ca(OH)_2 + 250\ KJ/Kg$$

- 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.

$$2[2CaO.SiO_2] + 6H_2O \longrightarrow 3CaO.2SiO_2.3H_2O + Ca(OH)_2 + 500\ KJ/Kg$$

Tobermonite gel

The setting and hardening of cement can be shown as



Failures of cement

Effect of CO_2:

The cement contains excess lime. In acidic water the lime reacts with CO_2 and it leads to decay of cement. The normal water has pH 7.5-8.5(slightly basic), this pH does not effects the decay of cement. The decay of cement increases with decrease in pH.

$$\mathbf{Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O}$$

Effect of Chloride:

- The chloride ions present in salts & sea water cause corrosion of steel present in cement concrete. Chlorides dissolved in water can diffuse through gaps or cracks present in cement and finally reach the steel.
- The risk of corrosion increases as the content of concrete increases when the chloride content at the surface of the steel exceeds a certain limit called threshold value corrosion will occurs, if water & oxygen are also available.
- The corrosion is prevented by controlling the availability of oxygen & humidity on the concrete.

REFRACTORIES

Introduction

Refractories are materials that can withstand high temperature without softening or suffering a deformation in shape.

Classification

1. **Acidic Refractory:** A refractory that is composed principally of silica and reacts at high temperatures with bases such as lime, alkalies, and basic oxides. These are used in areas where slag and atmosphere are acidic. The steel industries are the largest consumer of acidic refractories. Ex: silica, fire clay for lining of blast furnaces, open hearths and line kilns.
2. **Basic refractory:** These are used on areas where slags and atmosphere are basic, stable to alkaline Materials but reacts with acids. The main raw materialare calcium oxide and magnesia (MgO) is a very common example. Other example includes dolomite and magnesite.
3. **Neutral refractory:** These are used in areas where slags and atmosphere are either acidic or basic and are chemically stable to both acids and bases. The common examples of these materials are alumina (Al_2O_3), chrome (Cr_2O_3) and carbon. Normally we have to use acidic and basic refractories combined but we use neutral bricks to avoid the reaction. The neutral bricks are made of graphite and chromite's.

Properties of refractories

1. **Refractoriness:**

It is the ability of a refractory material to withstand the heat without appreciable softening or deformation under given service condition. Ability to withstand heat without getting deformed under operating conditions**.** It is measured as Softening Temperature. The softening temperature is measured by Seger Cone test. The test is also called Pyrometric Cone test.

Pyrometric/Seger Cone Test:

- Refractoriness is usually determined by comparing the behavior of heat on cone of material to be tested with series of seger cone of standard dimension.

- The refractoriness is expressed in terms of Pyrometric Cone (PCE). Standard Cones are Pyramidal shaped have triangular base 38 mm high and 19 mm long side**.**
- The standard seger cones are assigned numbers. The test cone is heated uniformly at 20°C/hr or 100°C/hr or 150°C/hr or 600°C/hr.
- When the test cone softens one of the standard cone also softens. The serial number of the standard cone is noted. This number is Pyrometric Cone Equivalent (PCE)

2. Strength (or) Refractoriness Under Load (RUL):

- Refractories are used in industrial furnaces have invariably to withstand varying load of products. A good refractory should have high temperature resistance as well as load bearing capacity that is strength.
- Strength is calculated by Refractoriness Under Load (RUL) test. The test is performed by applying a constant load of 3.5 or 1.75 kg/cm^2 to the specimen of size 5 cm and75 cm high and heating at the rate of 10°C/min in a furnace. RUL is expressed as temperature at which 10% deformation takes place.

3. Chemical inertness:

A refractory should be selected that is chemically inactive in use and does not easily form. Fusible products with slags, fuel ashes, furnace gases, etc. usually the environment in most furnaces is either acidic or basic. It is inadvisable to employ an acid refractory in contact with an alkaline product or vice-versa.

4. Porosity:

All refractories contain pores (may opened/closed) due to the manufacturing methods/defects. The porosity of a refractory material is the ratio of its pores volume to the bulk volume.

$$P= (W-D/W-A) \times 100$$

Where, W = Weight of saturated specimen in air, D = Weight of dry specimen in air &

A = Weight of saturated specimen in water.

Advantages of high porosity:

- It reduces thermal spalling.
- It is used for lining in ovens, furnaces, etc.

UNIT-V

CHEMISTRY OF ENGINEERING MATERIALS

IMPORTANT QUESTIONS

1. Define lubricant. And describe functions and various types of lubricants.

2. Explain theories for the mechanism of lubricants.

3. Explain the following the properties of lubricants

   a) Viscosity
   b) Flash and Fire point
   c) Oiliness
   d) Cloud and pour point
   e) Emulsification
   f) Carbon residue
   g) Aniline point
   h) Acid value
   i) Saponification value
   j) Iodine value

4. Describe the manufacturing of Portland cement with neat diagram.

5. Explain the following

   a) Setting and hardening of cement.
   b) failures of cement

6. What are refectories? Explain porosity and chemical inertness of refractories.

7. Explain the significance of the following properties in the evaluation of refractory material.

   a) Refractoriness
   b) Strength or RUL test