COURSE HANDOUT

CHEMISTRY

Course Overview:

The purpose of this course is to develop a strong foundation in the principles and methods to understand the current topics in society and industries such as water treatment, batteries, fuel cells, corrosion, pharmaceutical drugs, engineering materials (traditional polymers), conducting polymers and bio-degradable polymers. The knowledge of the above mentioned topics will make the engineering student to up grade the existing technologies and pursue further research for emerging new technologies.

Course Objectives:

- To bring adaptability to the concepts of chemistry and to acquire the required skills to become perfect engineer.

- To impart the basic knowledge of atomic, molecular and electronic modifications which make the students to understand the technology based on them.

- To acquire the knowledge of electrochemistry, corrosion, polymers and water treatment which are essential for the engineers and in industry.

- To impart the knowledge of stereochemistry and synthetic aspects useful for understanding reaction pathways.

Course Outcomes:

- Acquire knowledge of atomic, molecular and electronic changes related to conductivity.

- Apply the various processes of treatment of water for both domestic and industrial purpose.

- Apply the knowledge of electrode potentials for the protection of metals from corrosion.

- Analyze the major chemical reactions that are used in the synthesis of compounds.

- Apply the knowledge of polymers in every day's life.

Course Syllabus

UNIT I: Atomic and molecular structure

Introduction, Concept of atomic and molecular orbitals, Crystal field theory- Crystal field splitting patterns of transition metal ion d- orbital- tetrahedral & octahedral geometries. LCAO, Molecular orbitals of di-atomic molecules: Molecular orbital energy level diagrams of diatomic molecules (N_2, O_2 & F_2). Pi-molecular orbitals of butadiene and benzene.

UNIT II: Water Technology

Hardness of water, expression of hardness ($CaCO_3$ equivalent), units and types of hardness. Estimation of temporary and permanent hardness of water by EDTA method. Numerical problems based on hardness of water. Potable water: Characteristics, treatment of water for domestic supply. Desalination of brackish water: Reverse osmosis. Alkalinity of water and its determination. Boiler feed water and its treatment: Internal treatment (Colloidal, Phosphate Calgon conditioning of water). External treatment (Ion –exchange process).

UNIT III: Electrochemistry and corrosion

Electrode, electrode potential, galvanic cell, cell reactions and cell notation, cell EMF, types of electrodes (Calomel electrode and Quinhydrone electrode), Determination of P^H using quinhydrone electrode. Nernst equation, Numerical problems.

Batteries: Introduction to cell and battery, Primary (lithium cell) and secondary cells, (Lead-acid cell, and Lithium-ion cells). Fuel cells – Methanol – Oxygen fuel cell, advantages and engineering applications of fuel cells.

Corrosion: Introduction, types of corrosion: chemical and electrochemical corrosion, factors affecting the rate of corrosion: Nature of the metal - Position of metal in galvanic series, Purity of metal, Nature of corrosion product. Nature of environment - Effect of temperature, Effect of P^H, Humidity. Corrosion control methods: Cathodic protection: Sacrificial anode method and Impressed current cathode method. Protective coatings: Metallic coatings (anodic and cathodic), methods of application on metals- Electroless plating of Ni.

UNIT IV: Stereochemistry

Structural isomers and stereoisomers, configurations, symmetry and chirality, enantiomers, diastereomers, optical activity. Conformations of n-butane.

Organic reactions and synthesis of a drug molecule

Introduction to reactions involving substitution (SN1 & SN2), addition (addition of HBr to propene, Markownikoff and Anti Markownikoff addition), elimination, oxidation (oxidation of

alcohols using KMnO4 &CrO3), reduction (reduction of carbonyl compounds by LiAlH4 &NaBH4). Synthesis of a commonly used drug molecule- Paracetamol and Asprin.

UNIT V: Polymer Chemistry

Introduction, classification of polymers, types of polymerization (addition and condensation, mechanisms not included). Plastics- types of plastics -Thermoplastics and Thermosetting plastics. Preparation, properties and engineering applications of PVC, Teflon and Bakelite. Fibers: Nylon 6, 6 and Terelene (Dacron). Elastomers: Natural rubber-structure, vulcanization. Synthetic rubbers: Buna-S & Butyl rubber. Conducting polymers: Classification, polyacetylene and applications.

Biodegradable polymers: Types, examples: Polyhydroxy butyrate (PHB), Polyglycolic acid (PGA), Polylactic acid (PLA). Applications of biodegradable polymers.

Text Books:

Engineering Chemistry by P.C Jain & Monica Jain, Dhanpat Rai Publishing Company.

Engineering Chemistry by Shashi Chawla, Dhanpat Rai PublishingCompany.

Reference Books:

Physical Chemistry, by P. W. Atkins, W.H.Freeman&Company. Text book of Engineering Chemistry by Dr.M. Tirumala Chary & Dr. E.Laxminarayana. ScitechPublicaions (INDIA) Pvt Ltd., Engineering Chemistry (NPTEL Web-book), by B.L. Tembe, Kamaluddin and M.S.Krishnan

UNIT-I: Atomic and Molecular Structure

Definitions:

Atom:

- An atom is the smallest unit of matter and indivisible.
- They are made up of particles called protons, neutrons and electrons, which are responsible for the mass and charge of atoms.
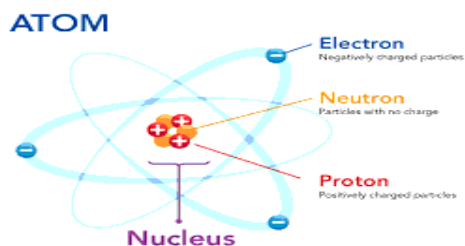
Molecule: Atoms combine to form molecules

Node: It is a space where the probability of finding an electron is zero.

Orbit: Orbit is a circular path around the nucleus in which an electron revolves

Orbital: Orbital is a 3D space where the probability of finding an electron is maximum.

Formula:

$$\text{Bond order (B.O)} = \frac{\text{no.of } e^- \text{ in BMO - no.of } e^- \text{ in ABMO}}{2}$$
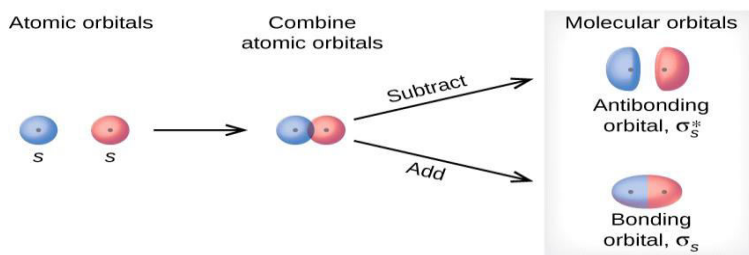
Molecular Orbital theory

Molecular orbital: Two or more atomic orbitals combine together to form molecular orbitals.

- According to this theory, molecular orbitals are formed by the Linear Combination (addition or subtraction) of Atomic Orbitals ((LCAO) of atoms.

- Consider two atoms A and B, which form a molecule AB.

- Let wave function of atom A = ψ_A and wave function of atom B = ψ_B.

- The wave function for the molecular orbitals can be obtained by a linear combination of atomic orbitals ψ_A and ψ_B. i.e addition or subtraction of wave functions of atomic orbitals.

$$\psi_{MO} = \psi_A + \psi_B$$

- The above equation forms two molecular orbitals.
     1) Bonding molecular orbital   2) Anti bonding molecular orbital

Atomic orbitals   Combine atomic orbitals   Molecular orbitals

Bonding molecular orbital:

Bonding molecular orbitals are formed by the constructive interference(addition) of wave functions of atomic orbitals.

$$\text{i.e } \psi_b = \psi_A + \psi_B$$

Probability density is given by ψ^2

$$\psi_b{}^2 = (\psi_A + \psi_B)^2$$

$$\psi_b{}^2 = \psi_A{}^2 + \psi_B{}^2 + 2\,\psi_A\,\psi_B$$

Probability of finding an e^- in bonding molecular orbital is greater than atomic orbitals.

$$\text{i.e } \psi_b{}^2 > \psi_A{}^2 + \psi_B{}^2$$

Antibonding molecular orbital:

Antibonding molecular orbitals are formed by the distructive interference (subtraction) of wave functions of atomic orbitals.

$$\text{i.e } \psi_a = \psi_A - \psi_B$$

Probability density is given by ψ^2

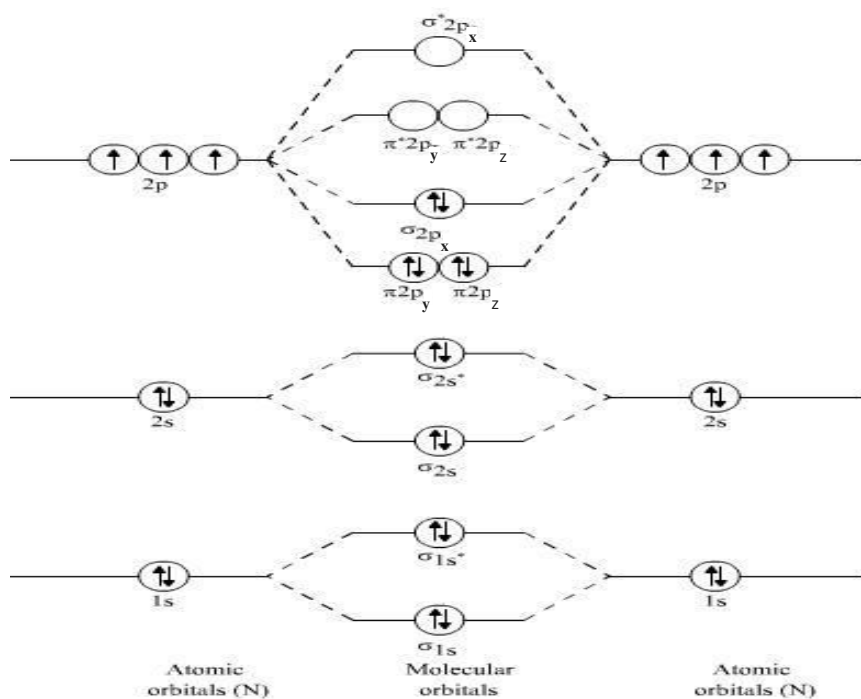$$\psi_a{}^2 = (\psi_A - \psi_B)^2$$

$$\psi_a{}^2 = \psi_A{}^2 + \psi_B{}^2 - 2\,\psi_A\,\psi_B$$

Probability of finding an e^- in anti bonding molecular orbital is less than atomic orbitals.

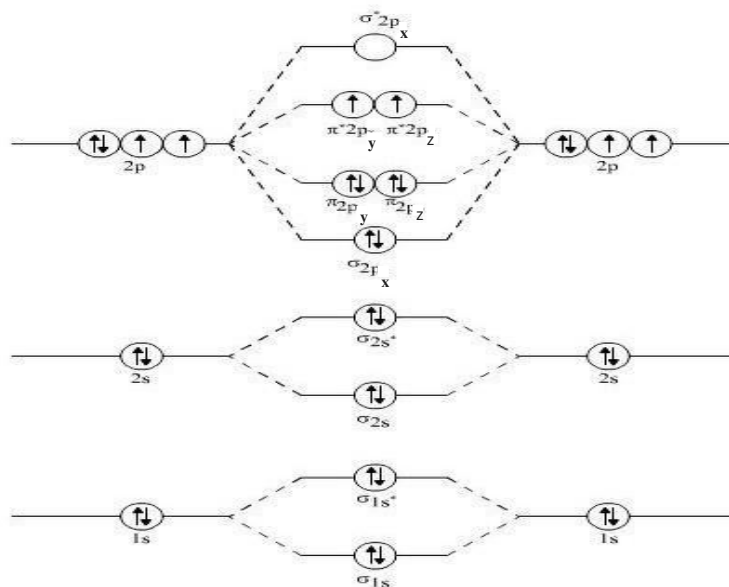$$\text{i.e } \psi_a{}^2 < \psi_A{}^2 + \psi_B{}^2$$

Energy level diagram of N_2 molecule:

Bond order is 3

Molecule is diamagnetic

Energy level diagram of O_2 molecule:

Bond order is 2

Molecule is paramagnetic

Energy level diagram of F₂ molecule:
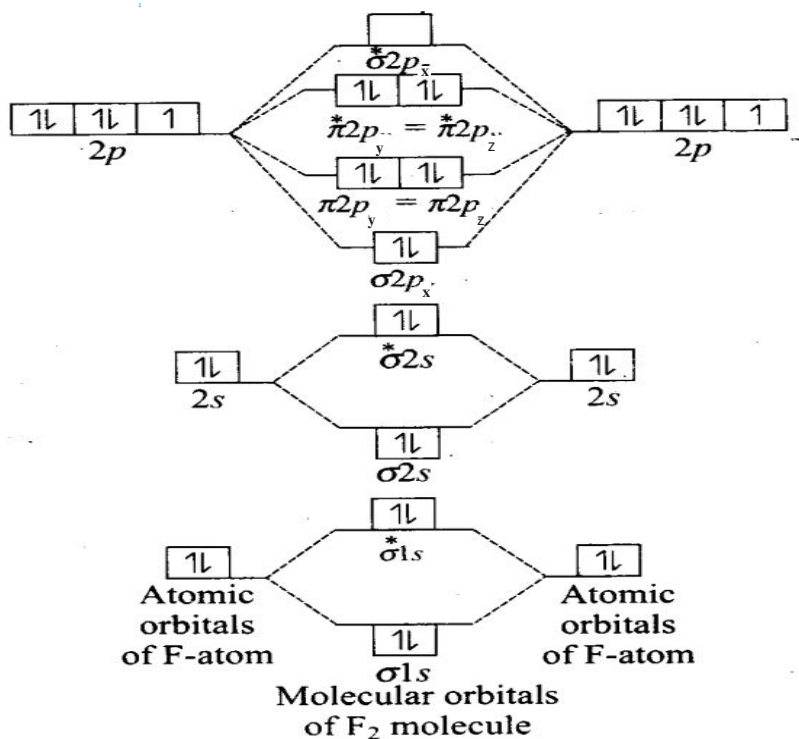
Bond order is 1

Molecule is diamagnetic

Molecular orbitals of F₂ molecule

Pi (π) molecular orbitals of 1,3-butadiene:

- The structure of 1, 3–butadiene is $CH_2=CH-CH=CH_2$

π molecular orbitals
1,3 butadiene
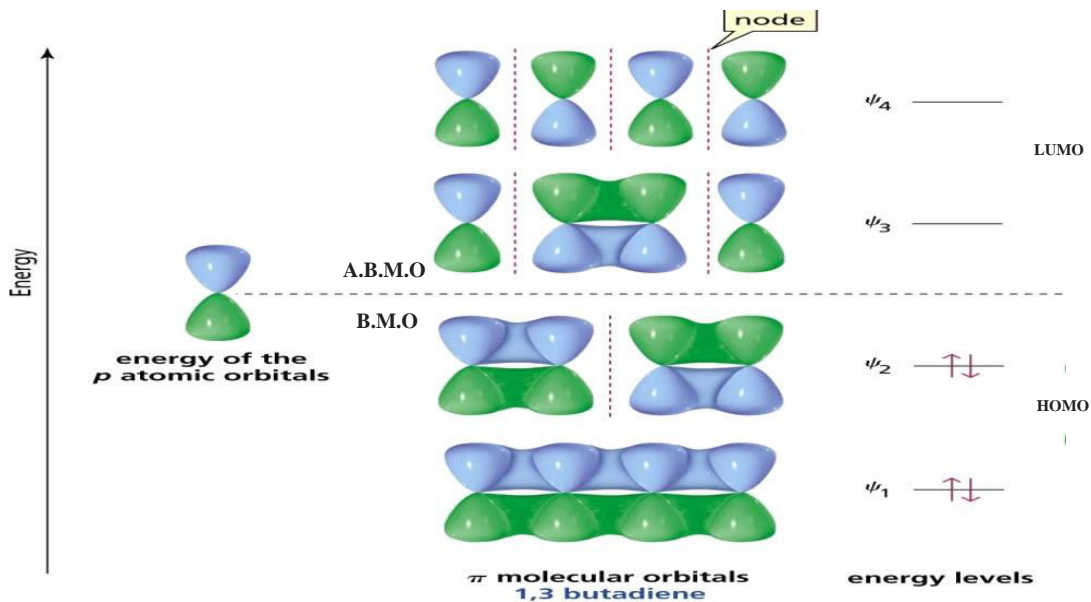
Pi (π) molecular orbital of benzene:

- Benzene is a planar cyclic compound with molecular formula C_6H_6.
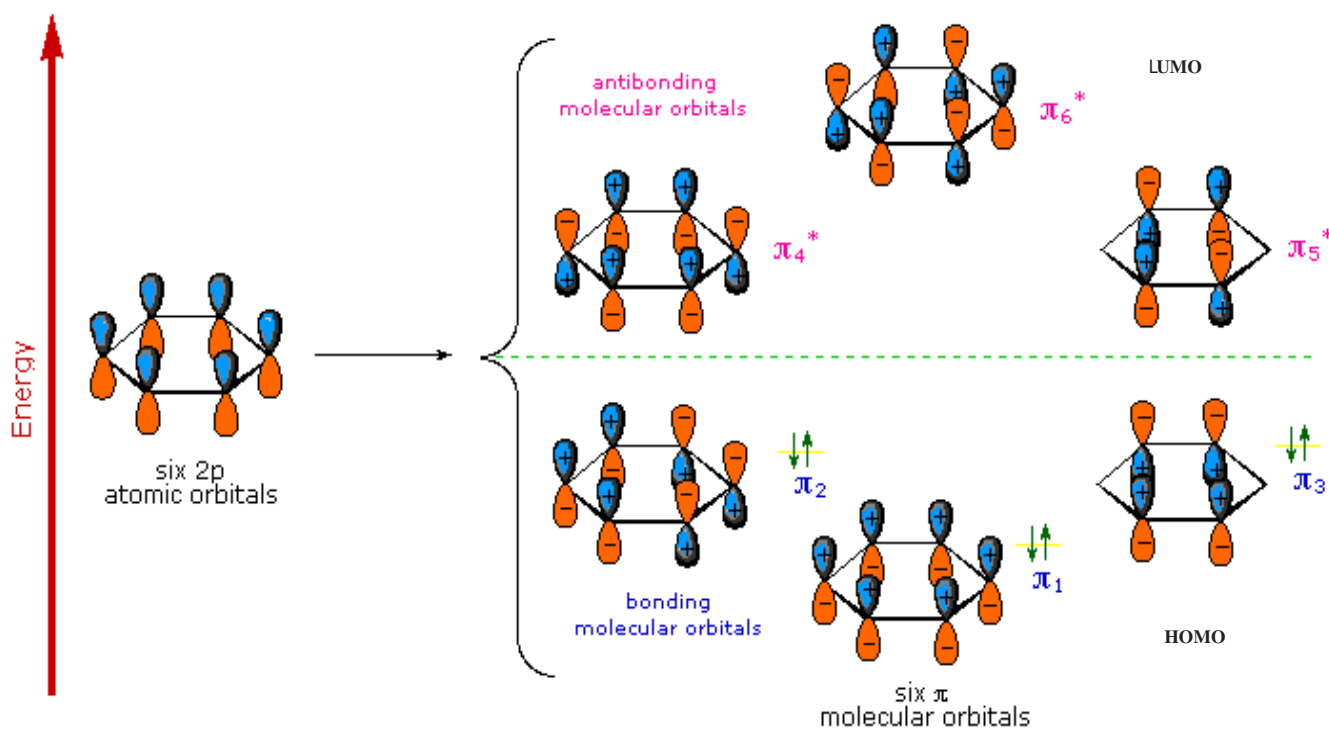
Crystal Field Theory

Postulates of CFT:

- Central metal cation is surrounded by ligands

- Ligands are point charges & negatively charged or dipoles.

- Bonding between metal & ligand is purely *electrostatic.*

- Degenerate orbitals – All the orbitals on the metal have *same energy.*

- Crystal field splitting: It is the difference in energy between d orbitals of ligands.
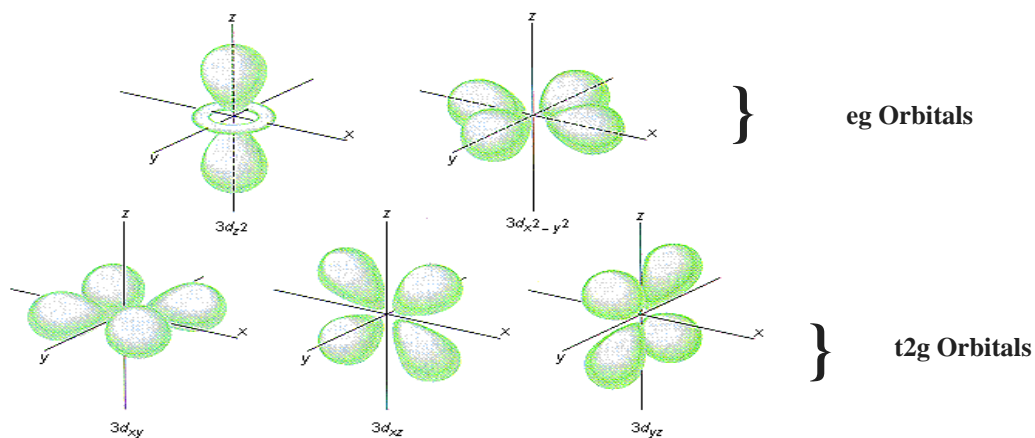
Crystal field splitting of d-orbitals in octahedral complexes:

- In an octahedral complex, the co-ordination number is 6.

- The metal ion placed at the center of the octahedron is surrounded by six lingands are placed at the 6 corners of a regular octahedron.

Eg : $[Co(NH_3)_4Cl_2]^+Cl^-$

Crystal field splitting of d-orbitals in tetrahedral complexes:

- In tetrahedral complexes, the co-ordination number is 4.

- The metal ion is at the center of the tetrahedron and four ligands surrounding it are placed at the 4 corners of the tetrahedron.

- **Eg : $[CoCl4]^{-2}$**
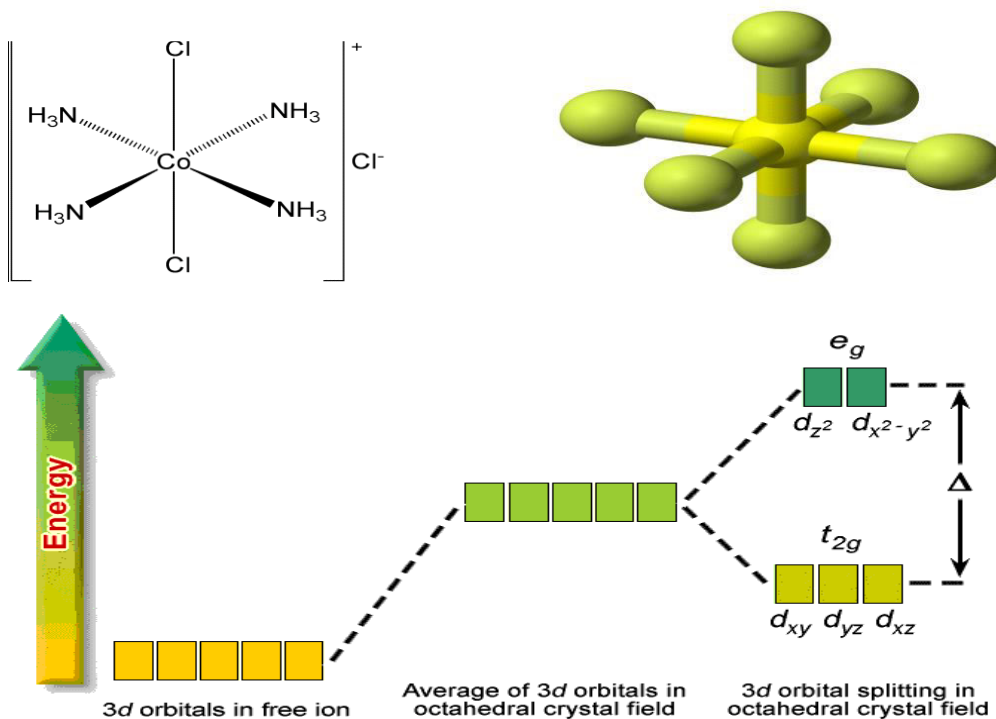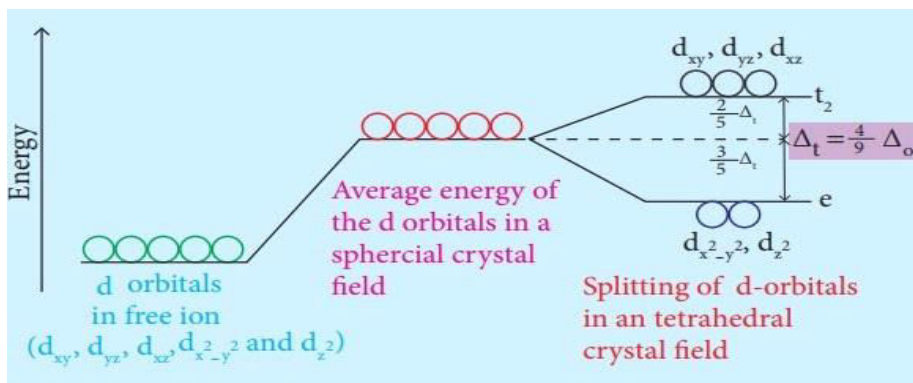
Splitting of d-orbitals in an tetrahedral crystal field

Multiple Choice Questions

1. The constructive interference of atomic orbitals leads to

   a) Non bonding molecular orbitals   b) Bonding molecular orbitals
   c) Anti bonding molecular orbitals

2. The orbitals have maximum electron density directed between the x,y and z axes are called as

   a) eg orbitals   b) t2g orbitals   c) all 5 d-orbitals   d) p-orbital

3. Maximum number of nodal planes in benzene molecule

   a) 6   b) 5   c) 4   d) 3

4. Bonding and anti bonding molecular orbitals in 1,3 – butadiene respectively are

   a)1,3   b) 3,1   c) 2,2   d) 3,3

5. Which molecular orbitals have highest energy ?

    a) Non bonding molecular orbitals b) Bonding molecular orbitals

   c) Anti bonding molecular orbitals

6. Number of electrons in fluorine molecule are

   a) 9   b)14   c) 16   d)18

7. Bond Order of O_2, F_2, N_2 respectively are

    a) +1, +2, +3   b) +2, +3, +1   c) +2, +1, +3   d) +3, +2, +1

8. The region, where the probability of finding an electron is zero

   a) Orbital   b) Atomic orbital c) Node   d) Molecular Orbital

9. Magnetic nature of N2 molecule is

   a) Diamagnetic   b) Paramagnetic   c) Ferromagnetic d) Antiferromagnetic
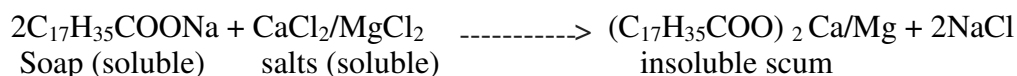
10. Degenerate orbitals have

a) Different energies   b) Same energies   c) Different energies & same shapes

d) Different energies & different shapes
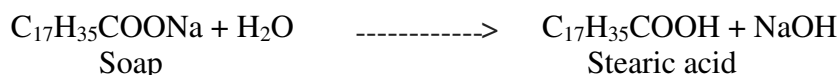
UNIT-II: Water technology

Definitions:

Hardness of water: The water that has certain salts like Ca^{+2}, Mg^{+2} and other heavy metals dissolved in it is caused hard water.

- Hard Water: The water which does not give lather with soap is called hard water.

$$2C_{17}H_{35}COONa + CaCl_2/MgCl_2 \quad \text{----------}> \quad (C_{17}H_{35}COO)_2 Ca/Mg + 2NaCl$$
$$\text{Soap (soluble)} \qquad \text{salts (soluble)} \qquad\qquad \text{insoluble scum}$$

- Soft Water: The water which gives more lather with soap is called soft water.

$$C_{17}H_{35}COONa + H_2O \quad \text{-----------}> \quad C_{17}H_{35}COOH + NaOH$$
$$\text{Soap} \qquad\qquad\qquad\qquad \text{Stearic acid}$$

Types of hardness:

Hardness of water is mainly two types:
1. Temporary Hardness 2. Permanent Hardness

1. Temporary Hardness: Bicarbonates of Calcium, Magnesium $Ca(HCO_3)_2$, $Mg(HCO_3)_2$.
Temporary Hardness can be largely removed by boiling of water.

$$Ca(HCO_3)_2 \quad \text{----------}> \quad CaCO_3\downarrow + H_2O + CO_2 \uparrow$$
$$\text{Calcium bicarbonate}$$

$$Mg(HCO_3)_2 \quad \text{----------}> \quad Mg(OH)_2\downarrow + 2CO_2 \uparrow$$
$$\text{Magnesium bicarbonate}$$
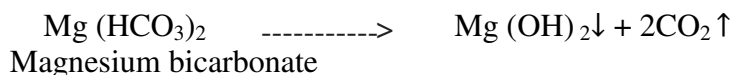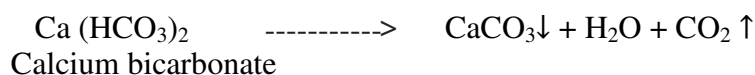
2. Permanent Hardness: Chlorides and Sulphates of Calcium & Magnesium salts ($CaCl_2$, $MgCl_2$, $CaSO_4$, and $MgSO_4$).
Permanent Hardness cannot be removed by boiling but it can be removed by the other methods.

Expression and Units of Hardness:

$$\text{Degree of Hardness} = \frac{\text{The amount of hardness causing salts}}{\text{Molecular weight of hardness causing salts}} \times 100 \text{ (Mol.wt of } CaCO_3)$$

Units of Hardness:

1. Parts per Million (ppm):
1ppm hardness = 1 part of equivalent $CaCO_3$ in 10^6 parts of water.

2. Milligrams per litre (mg/l): 1 mg/L hardness = 1 mg of equivalent $CaCO_3$ in 1 litre of water.

3. Degree Clark's (°Cl): The number of grains of equivalent $CaCO_3$ presents in one gallon of water.

4. Degree French (°Fr): The number of parts of equivalent $CaCO_3$ presents in 10^5 parts of water.

Relationship between various units of hardness:

$$1 \text{ ppm} = 1 \text{ mg/L} = 0.1° \text{ Fr} = 0.07° \text{ Cl}$$

Numerical Problems:

Problem-1: A sample of water is found to contains following analytical data in milligrams per litre
Mg $(HCO_3)_2$ = 14.6, $MgCl_2$ = 9.5, $MgSO_4$ = 6.0 and Ca$(HCO_3)_2$ = 16.2. Calculate temporary and permanent hardness
Of water in parts per million, Degree Clarke's and Degree French.

Solution:

Name of the hardness causing salts	Amount of the hardness causing salts(mg/Lit)	Molecular weight of hardness causing salts	Amounts equivalent to $CaCO_3$ (mg/Lit)
$Mg(HCO_3)_2$	14.6	146	14.6×100/146 = 10
$MgCl_2$	9.5	95	9.5×100/95 = 10
$MgSO_4$	6.0	120	6.0×100/120 = 5
$Ca(HCO_3)_2$	16.2	162	16.2×100/162 =10

Temporary hardness [Mg $(HCO_3)_2$ + Ca $(HCO_3)_2$] = 10 + 10 = 20mg/Lit
= 20ppm
= 20×0.07°Cl = 1.4°Cl
= 20×0.1°Fr = 2°Fr

Permanent hardness [$MgCl_2$ + $MgSO_4$] = 10 + 5 = 15mg/Lit
= 15ppm
= 15×0.07°Cl = 1.05°Cl
= 15×0.1°Fr = 1.5°Fr

Experiments:

I. Estimation of Hardness of water by Complexometric method or EDTA method:

Basic principle:

The determination of hardness is carried out by titrating water sample with Sodium salt of Ethylene Diamine Tetra Acetic Acid (EDTA) using Eriochrome Black-T as an indicator and keeping the pH of the water at 9.0 - 10.0. The end point is the change in colour from wine - red to blue, when the EDTA solution complexes the calcium and magnesium salt completely.

(Ca^{2+} / Mg^{2+}) + EBT $\xrightarrow{\text{pH (9-10)}}$ {Ca – EBT} / {Mg – EBT}

From hard water   indicator   unstable and Wine red coloured complex

{Ca – EBT} / {Mg – EBT} + EDTA -----------> {Ca – EDTA} / {Mg – EDTA} + EBT
    Unstable and   stable complex (colourless)   blue
    Wine red coloured complex
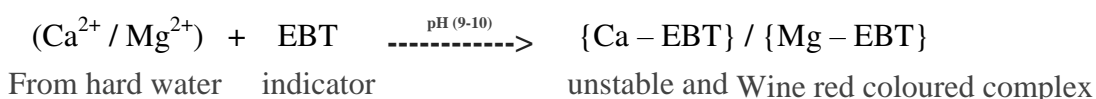
Procedure:

Step 1: Preparation of standard hard water

Step 2: Standardization of EDTA solution

Step 3: Determination of Total Hardness of water

Step 4: Determination of Permanent Hardness

Formulae:

$$N = \frac{Gram\ eq.of\ Solute}{Volume\ of\ sol.in\ litre}$$

$$= \frac{Weight}{Equivalent\ weight} \times \frac{1000}{V\ ml}$$

$$Equivalent\ Weight = \frac{Molar\ Mass}{n}$$

2. $N_1V_1 = N_2V_2$
3. Total hardness = Temporary hardness + Permanent hardness

II. Alkalinity of water and its determination:

Alkalinity is a measure of the water's ability to neutralize acidity.

The alkalinity of water is due to the presence of carbonates, bi carbonates and hydroxide ions.

The possible combinations of ions causing alkalinity of water are:

1) Only OH^-

2) Only CO_3^{-2}

3) Only HCO_3^-

4) OH^- and CO_3^{-2} together

5) CO_3^{-2} and HCO_3^- together

Alkalinity of water can be classified into two categories based upon the anion present

1. Caustic alkalinity –due to OH^- and CO_3^{-2} ions.

2. Bicarbonate alkalinity (or) temporary alkalinity – due to HCO_3^- ions.

$$M \begin{cases} OH^- + H^+ \quad \text{-------------->} \quad H_2O \\ CO_3^{-2} + H^+ \quad \text{----------->} \quad HCO_3^- \\ HCO_3^- + H^+ \quad \text{------------>} \quad H_2O + CO_2 \end{cases} \Bigg\} \text{Phenolphthalein}$$
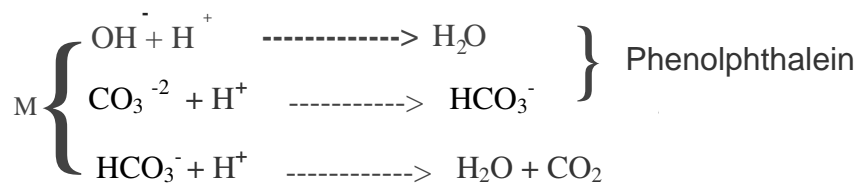
Procedure:

Take 100ml of water sample into a clean conical flask and add 2 or 3 drops of phenolphthalein indicator. The burette is filled with N/50 H_2SO_4. The end point is noted after titrating the acid against the water sample. The end point is the just disappearance of pink colour. Then continue the titration after adding 2 or 3 drops of methyl orange indicator. The end point is the color change from yellow to pink.

Phenolphthalein alkalinity in terms of $CaCO_3$ = 10 V_1 ppm

Methyl orange alkalinity in terms of $CaCO_3$ = $(V_1 + V_2)$10ppm

Potable Water treatment:

Steps involved in the treatment of Potable water:

Source of water ----- Screening ------ Aeration ---- coagulation and sedimentation

Disinfection ----- Filtration -------⌐

Desalination of water by Reverse Osmosis:

When two solutions of unequal concentration are separated by a semi permeable membrane which does not permit the passage of dissolved solute particles. If high pressure is applied on the concentrated side of solvent molecules forced to move from higher concentration side to lower concentration side. Thus the solvent flow is reversed, hence this method is called reverse osmosis.

Reverse Osmosis
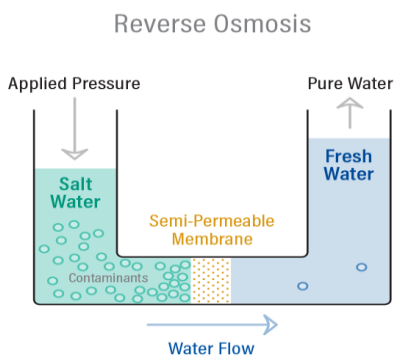
Internal treatment of boiler feed water:

The softening of water carried out inside the boiler is called internal treatment of water.

• **Colloidal conditioning:**

• **Phosphate conditioning:**

The main phosphates are

NaH_2PO_4 (Sodium dihydrogen phosphate)
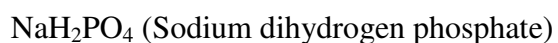
Na_2HPO_4 (disodium hydrogen phosphate)

Na_3PO_4 (trisodium phosphate)

• **Calgon conditioning:**

'Sodium hexa meta phosphate' is also called as Calgon.

External treatment of boiler feed water:

Softening of water by ion-exchange process:

Ion exchange process includes the exchange of cations and anions of the dissolved salts with H^+ and OH^- ions respectively.

Two types of ion exchanges are used

- Cation exchange resin (RH)

$$2RH + Ca^{+2} \quad \text{-------->} \quad R_2Ca + 2H^+$$

$$2RH + Mg^{+2} \quad \text{-------->} \quad R_2Mg + 2H^+$$

- Anion exchange resin (R^1OH)

$$R^1OH + Cl^- \quad \text{-------->} \quad R^1Cl + OH^-$$

$$R^1OH + HCO^-_3 \quad \text{-------->} \quad R^1HCO_3 + OH^-$$

$$2R^1OH + SO^{-2}_4 \quad \text{-------->} \quad R^1_2SO_4 + 2OH^-$$

Fig. **Demineralization of Water**

UNIT- III: Electrochemistry & Corrosion

Definitions :

Electrical conductors: Substances which allow electrical current to pass through them are known as electrical conductors.

Conductance: It is the tendency of a material to allow the flow of current.
It depends on mobility of the ions and number of ions present in the electrolytic solution.

Electrode: It is a material or a metallic rod / bar / strip which conduct electrons.

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

Electrode potential:

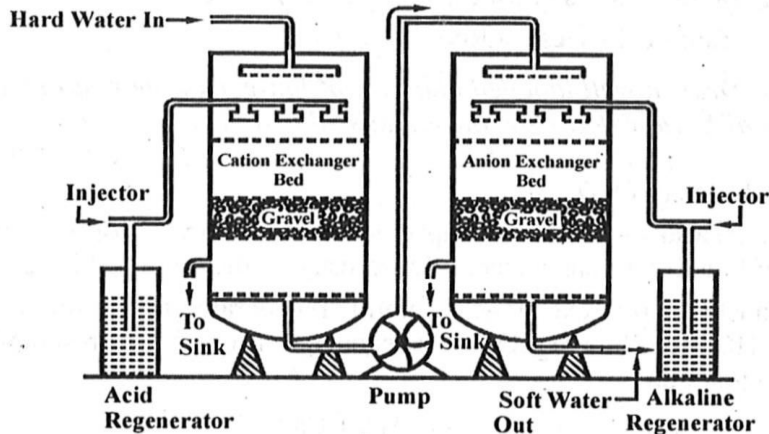•   When a metal rod is dipped in its salt solution (electrolyte), the metal atom tends to lose electrons (oxidation) or to accept electrons (reduction).the process of oxidation or reduction depends on the nature of metal.
•   In this process there develops a potential between the metal atom and its corresponding ion called the electrode potential.'

$$\text{Oxidation: } M \text{ --------> } M^{n+} + ne^-$$

$$\text{Reduction: } M^{n+} + ne^- \text{ ----------->. } M$$
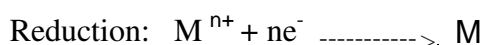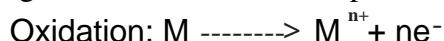
Standard electrode potential:

The potential of electrode at 25^oC with 1M concentration of electrolyte is called Standard electrode potential (E^o).

Electromotive force (EMF): The force which causes the flow of electrons from one electrode to another electrode and thus results in the flow of current from electrode at higher potential to electrode at lower potential is called electromotive force.

Calculation of EMF of the cell:

$$E^o_{cell} = E^o_{cathode} - E^o_{anode}$$

Electro chemical cell:

•   It is a device used for converting chemical energy into electrical energy.

Types of electrodes:
i. Saturated Calomel Electrode: (SCE)

ii. Quinhydrone electrode:

Determination of pH of a solution:

To determine pH of a solution, quinhydrone electrode is connected to reference electrode like calomel electrode whose electrode potential is known. Quinhydrone electrode is known as indicator (or) working electrode. These two electrodes are connected through potentiometer and emf is determined.

Cell notation: $Pt/Hg_{(l)}, Hg_2Cl_{2(s)}, KCl_{(sat)}//H^+, Q, QH_2/Pt$

Cell reaction: $2 Hg_{(l)} + 2Cl^- + Q + 2H^+$ ------------> $Hg_2Cl_{2(s)} + QH_2$

$$\therefore E_{cell} = E_R - E_L$$

$$= E_Q - E_{SCE}$$

$$= (0.6994 - 0.0591 P^H) - 0.2422$$

Nernst equation:

$$E = E^0 + \frac{2.303RT}{nF} \log [M^{n+}]$$

If $R = 8.303 J$, $T = 298 K$ at $25^o C$ and $F = 96500 C$ then,

$$E = E^0 + \frac{0.0591}{n} \log [M^{n+}]$$

This equation is known as "Nernst Equation" for electrode potential.

Applications of Nernst Equation:

- One of the major applications of Nernst equation is in determining ion concentration.
- It is used in oxygen and the aquatic environment.
- It is also used in solubility products and potentio-metric titrations.
- It is also used in pH measurements.

Battery
- A battery is a device in which number of electrochemical cell are connected in a series. It transformed chemical energy into electrical energy.

Classification of Batteries

- Primary battery
- Secondary battery
- Fuel cell

Primary batteries:

In which the cell reaction is irreversible. Once the reactants are converted into products no more electricity is produced and the battery becomes dead so it can't be used after that, it can't be recharged.
For example: lithium cell, dry cell, mercury cell

Lithium cells: Lithium cells belong to primary cells. The cells having lithium anodes are called lithium cells, irrespective of cathodes used.

Lithium cells are two types

- Lithium cells with solid cathodes

- Lithium cells with liquid cathodes

Secondary batteries:

Secondary batteries are those which recharge when electric current pass through the cell. These are rechargeable and cell reactions are reversible, therefore they can be use again and again.

For example: lead storage battery (lead acid battery), Li-ion battery.

Lead-acid cell: Construction:

- The lead acid storage cell contains of lead anode and lead dioxide cathode.
- A number of lead plates (- ve plates) are connected in parallel and a number of lead dioxide plates (+ve plates) are also connected in parallel.
- The lead plates are fit in between the lead dioxide plates.
- The plates are separated from adjacent plates by insulators like wood strips, rubber or glass fibre.
- The entire combination is immersed in 20 – 21 % dil. H_2SO_4.

Cell reaction:

At anode: $Pb + SO_4^{-2}$ $\underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftarrows}}$ $PbSO_4 + 2e^-$

At Cathode: $PbO_2 + 4 H^+ + SO_4^{-2} + 2e^-$ $\underset{\text{charging}}{\overset{\text{Discharging}}{\rightleftarrows}}$ $PbSO_4 + 2H_2O$

Net Reaction: $Pb + PbO_2 + 4 H^+ + 2SO_4^{-2}$ $\underset{\text{charging}}{\overset{\text{Discharging}}{\rightleftarrows}}$ $2 PbSO_4 + 2H_2O + E$
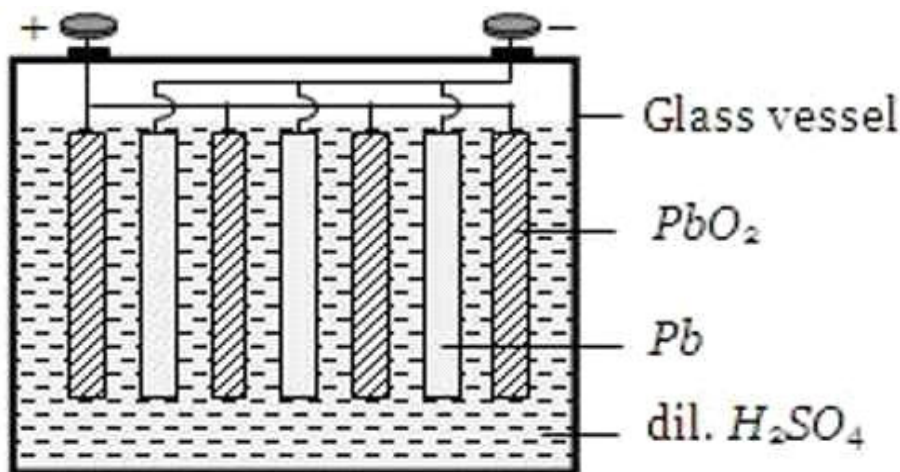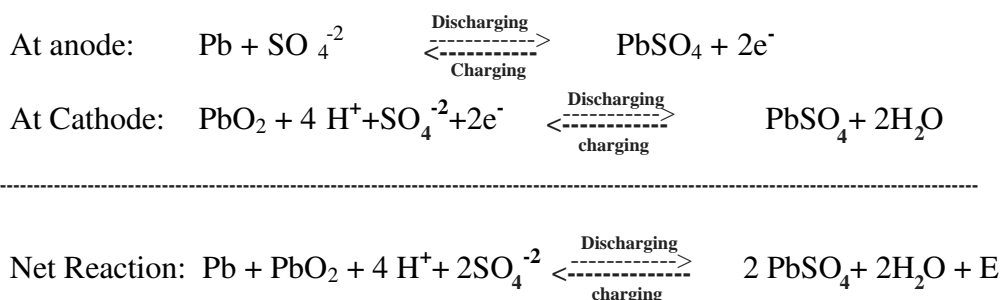
Lithium ion battery:

- A lithium ion battery is a rechargeable portable battery in which lithium ions move from negativeelectrode to positive electrode.

- The primary components of lithium ion battery are the negative electrode made from carbon (graphite), positive electrode made from a metal oxide like lithium cobalt oxide or lithium manganese oxide and the electrolyte is either non aqueous lithium hexafluro phosphate ($LiPF_6$) or lithium perchlorate ($LiClO_4$).

Lithium-ion Battery: Powering a device

Cell reaction:

At anode: $Li_xC_6 \xrightleftharpoons[\text{charging}]{\text{Discharging}} xLi^+ + xe^- + 6C$

At cathode: $Li_{(1-x)}CoO_2 + xLi^+ + xe^- \xrightleftharpoons[\text{Charging}]{\text{Discharging}} LiCoO_2$

Net reaction: $Li_xC_6 + Li_{(1-x)}CoO_2 \xrightleftharpoons[\text{charging}]{\text{Discharging}} LiCoO_2 + 6C + E$
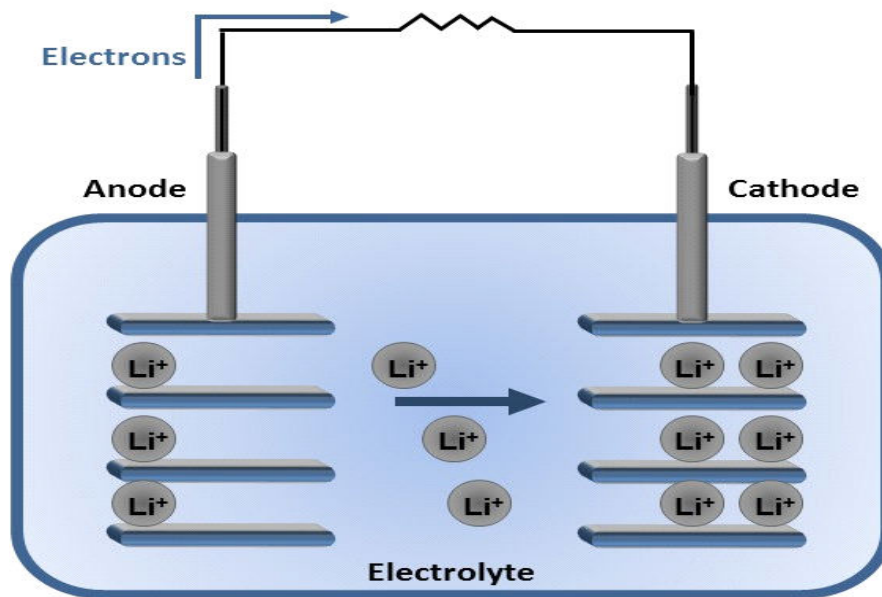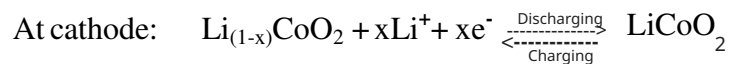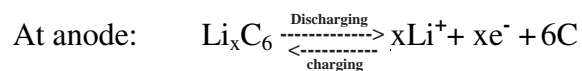
Fuel cell:

In a fuel cell electrical energy is obtained from oxygen and a fuel that can be oxidized.

Fuel + Oxygen   -------------------->   Oxidation product +Electricity
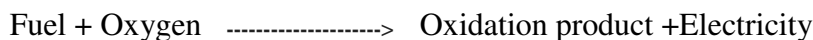
Methanol- oxygen fuel cell:

- It consists of two electrodes made up of platinum in between the electrodes H_2SO_4 is placed as a electrolyte

- Methanol and H_2O is supplied at the anode and pure oxygen gas is supplied at the cathode.
- In this H^+ ions moved from anode to cathode
- The Methanol is oxidized to CO_2 & H_2O with the liberation of electrical energy.

$$CH_3OH + 3/2\ O_2 \text{ ----------> } CO_2 + 2H_2O$$

Uses:
- Used in Military applications.
- Used for large scale power production station

Electrical current

Carbon dioxide

Water

CO_2

H^+

CH_3OH

H_2O

Methanol

H_2O

H^+

O_2

Air

Water

Anode

Electrolyte

Cathode

H_2O
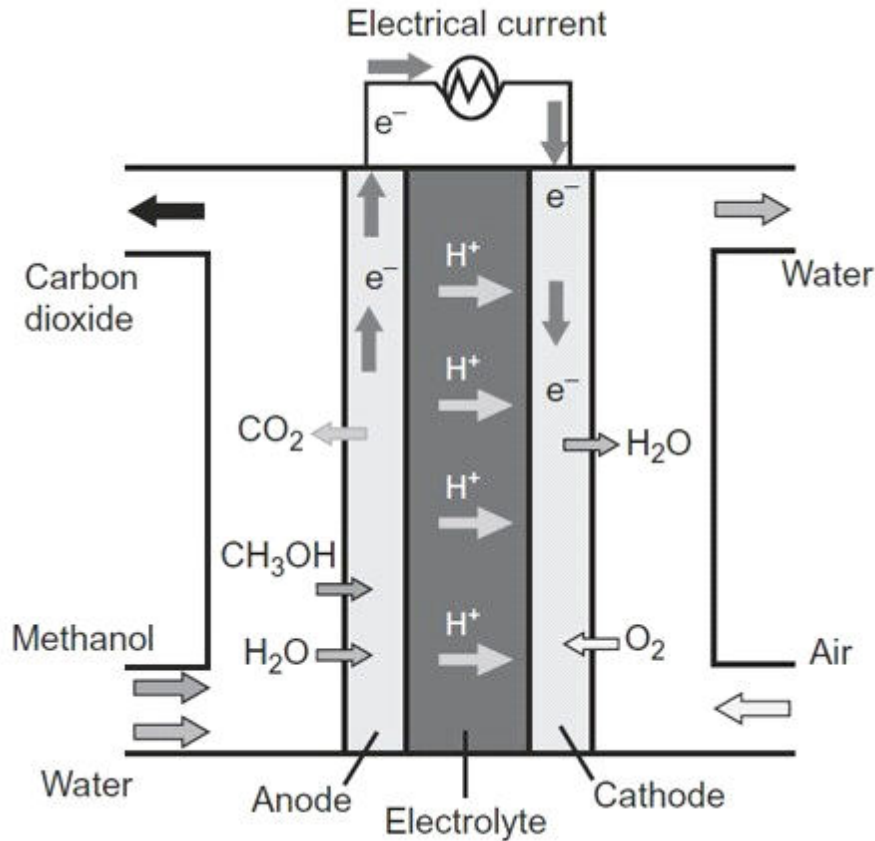
Corrosion

Definition: It's a gradual disintegration of metal by chemical or electrochemical attack by environment. It is an oxidation process which means loss of electrons takes place.

Eg: Rusting of iron – Hydrated ferric oxide $Fe_2O_3.H_2O$ - Brown in colour

Green film of copper – Copper Carbonate $CuCO_3+Cu(OH)_2$

Causes of corrosion:

Ore (thermodynamically + Energy stable) $\xrightarrow{\text{Metallurgy}}$ Metal (thermodynamically unstable) $\xrightarrow{\text{Corrosion}}$ Corrosion product (thermodynamically stable)

Effects of corrosion

- Due to corrosion the major properties of metal like malleability, ductility & conductivity are lost.

- Loss of mechanical strength of a metal takes place.

- Efficiency of machine is reduced.

- Buildings and historic monuments are damaged due to corrosion (e.g., Taj Mahal).

Theories (or) Mechanism of Corrosion: There are two theories to explain the mechanism of corrosion. They are

- Dry or Chemical(or) Direct Chemical Corrosion

- (ii) Galvanic (or) Electrochemical (or) Wet Corrosion.

Dry or Chemical Theory of Corrosion:

It occurs mainly through the direct chemical action of environment or atmospheric gases such as O2, H2S, SO2, N2, halogen or anhydrous liquid with metal surfaces.

Chemical corrosion
- Oxidation corrosion
- Corrosion by other gases
- Liquid metal corrosion
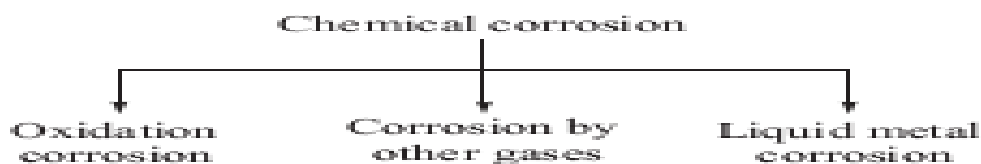
Oxidation corrosion (Reaction with oxygen):

Direct action of oxygen at low or high temperature on metal surface in the absence of moisture is known as oxidation corrosion.

At ordinary temperature – most of the metals are slightly attacked by oxygen

Low temperature – alkali & alkaline earth metals are rapidly oxidised

High temperature – all metals except noble metals are oxidized

Formation of metal oxide on the surface of metal:

During oxidation of a metal, metal oxide is formed as a thin film on the metallic surface which protects the metal from further corrosion. The magnitude of corrosion by oxygen depends upon the nature of metal oxide film. It may be

Stable oxide layer:

Oxide layer- tightly adhering & acts as a barrier to prevent the entry of oxygen.

Eg.   Copper (Cu), Aluminum (Al), Tin (Sn), Lead (Pb)

Unstable: Oxide layer formed decomposes back into the metal & oxygen.
Eg. Oxides of Ag, Au & Pt.

Volatile: MO evoparates soon after its formation, thereby exposing the fresh metal surface to the environment. It leads to rapid & continuous corrosion.
Eg: MoO_3

Porous: Continuous corrosion
Eg. Alkali & Alkaline earth metals

Pilling-Bedworth rule:

Volume of metal oxide $\geq$ volume of metal - Protective & non-porous

Volume of metal oxide $\leq$ volume of metal   - Non protective & p*orou*s

Wet (or) Electrochemical (or) Immersed Corrosion:

According to this theory, there is a formation of *galvanic cell* on the surface of metal.

This type of corrosion occurs a) when two dissimilar metals or alloys are either immersed in a solution b) when a conducting liquid is in contact with metal.

At anode – Oxidation takes place &

 at cathode – Reduction - consumption of electrons takes place either by

a) Evolution of hydrogen

b) Absorption of oxygen

Anodic (oxidation) reaction: Fe+ corrosive $\xrightarrow{\text{environment}}$ $Fe^{2+} + 2\ e^{-}$

Cathodic reaction:

A) Evolution of hydrogen: This corrosion usually occurs in acidic environment. Anodic areas are large and cathodic areas are small. All metals above hydrogen in electrochemical series show this type of corrosion. Oxygen is absent

Anodic (oxidation) reaction Fe -------------> $Fe^{2+} + 2e^-$

Cathode (Reduction) $2H^+ + 2e^-$ -------------> H_2

Net reaction $Fe + 2H^+$ ------------> $Fe^{2+} + H_2$

Mechanism of wet corrosion by hydrogen evolution
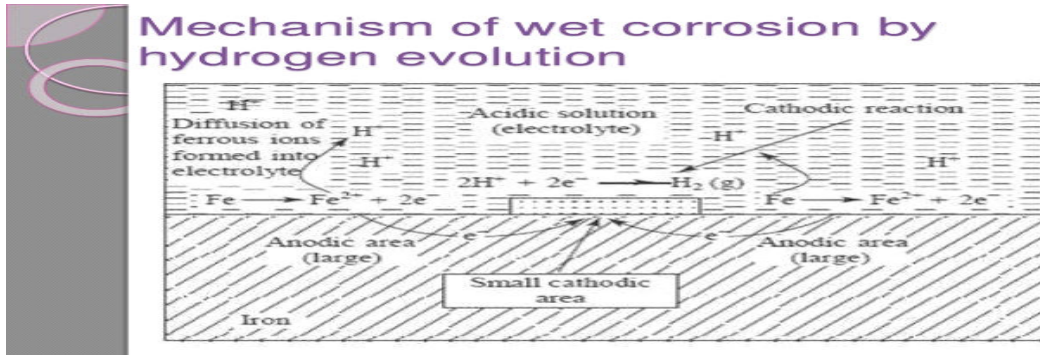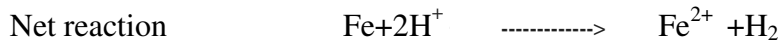
B) **Absorption of oxygen:** This corrosion occurs when anodic areas are large & cathodic areas are small. Environment neutral (or) alkaline

Anodic (oxidation) reaction Fe -------------> $Fe^{2+} + 2e^-$

Cathode (Reduction) $\frac{1}{2}O_2 + 2H_2O + 2e^-$ ----------> $2OH^-$

Net reaction: $Fe + 1/2\ O_2 + H_2O$ -------------> $Fe^{+2} + 2O\dot{H}$ (or) $Fe(OH)_2$

Mechanism of wet corrosion by oxygen absorption
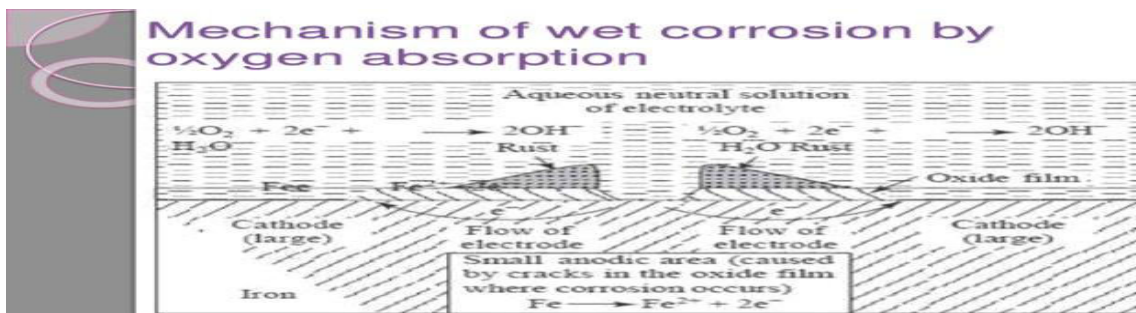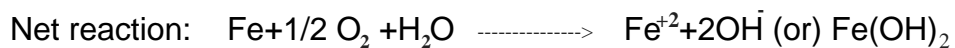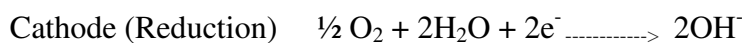
Enough oxygen

- $4\ Fe(OH)_2 + O_2 + 2H_2O$ -----------> $4Fe(OH)_3$

- $4Fe(OH)_3$ ------------> $2\ Fe_2O_3 . 3H_2O$ (yellow)

Limited oxygen

- $Fe(OH)_2$ -----------> $Fe_3O_4 . 6H_2O$ Brown black magnetite

Factors affecting rate of corrosion

- Nature of metal :

  a) Relative position of metal in the galvanic series

  b) Purity of metal

c) Nature of corrosion product

- Nature of environment:

  a) Temperature   b) Humidity   c) pH

  Nature of environment:

  $$\text{Corrosion} \infty \text{ Temperature}$$

  $$\text{Corrosion} \infty \text{ Humidity}$$

  $$\text{Corrosion} \infty \text{ 1/PH}$$

Corrosion control methods:

1. Cathodic protection   a) Sacrificial anodic protection-SAP

   b) Impressed current cathodic protection-ICCP

Principle of cathodic protection: Metal is *forced* to behave like *cathode.*

Sacrificial anodic protection-SAP: The metal structure to be protected is connected by a wire to a more active metal. So that the corrosion is concentrated at more active metal and saving the parent metal from corrosion. Sacrificial anodes are Mg, Zn, Al and their alloys.
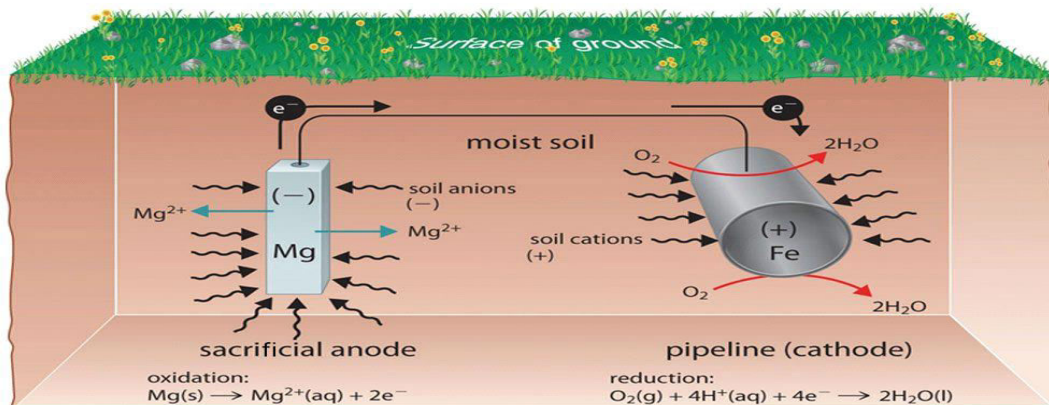
Impressed current cathodic protection:

Impressed current – DC – battery, rectifier ; Impressed current – applied in opposite direction to the corrosion current. Anode – placed in back fill – gypsum
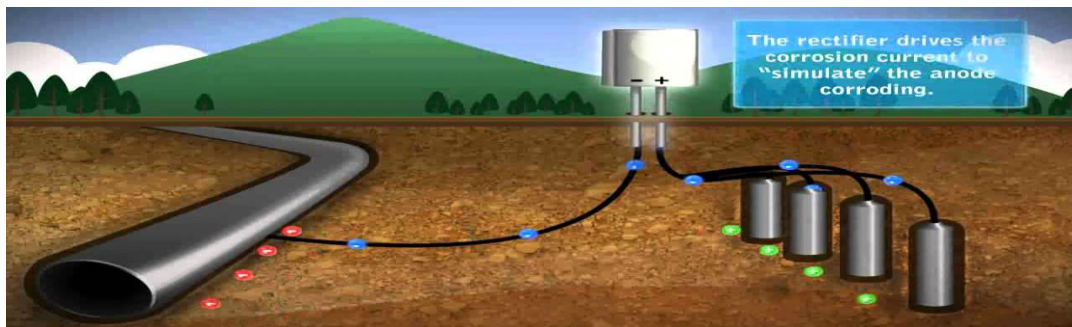
- Metallic coatings Coating of a metal on the surface of another metal.

a). Anodic coating – Galvanisation

More active metal on the base metal

Eg. Coating of Mg/Al on Fe/steel.

b) Cathodic coating – Tinning

Noble metal on the base metal

Eg: Coating of Ni/Cr/Cu/Ag on Fe/steel.

Electroless/Displacement/Immersion/Chemical/Autocatalytic Plating:

Principle: It is a technique of depositing a noble metal from its salt solution on a catalytically active surface of a less noble metal by using a suitable reducing agent without using electrical current.

- **Metal ions + Reducing agent   -------------> Metal + Oxidised product**

Electroless plating- Nickel coating on insulators:

- Coating solution – $NiCl_2$

- Reducing agent - Sodium hypophosphite NaH_2PO_2

- Buffer - Sodium acetate – CH3COONa

- PH - 4.5

- Temperature - 93 degree centigrade

ELECTROLESS PLATING OF NICKEL

→ component to be coated
← electrolyte $NiCl_2$ (soluble salt of coating metal)

metal ions (M^{n+}) + reducing agent → metal (M) + oxidised product
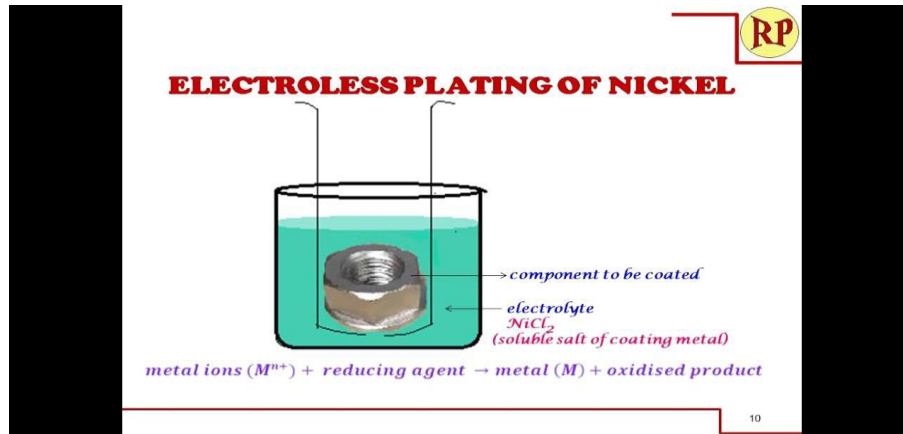
Multiple Choice Questions:

- Salt bridge maintains the ----------- neutrality of the solution.

  a)Ionic   b) Positive ionic   c) Negative ionic   d)Electrical

- Nernst equation is the relationship between

  a) Gibbs free energy & electrode potential b) workdone & concentration of the electrolyte   c) electrode potential & concentration of the electrolyte

- In qui-hydrone electrode, quinine and hydroquinone are in

  a) 75 :25   b) equimolar proportion   c) 65 : 35   d) 90 :10

- Secondary batteries are

  a) Rechargeable b) reversible c) electrochemical & electrolytic cells d) all of the above

- Calomel electrode is an example of

  a) Gas electrode b) metal ion electrode c) metal-metal insoluble salt ion electrode

 d) inert electrode

- In Pb-acid battery, acid is

  a) HCl   b) H_2SO_4 c) HNO_3 d) H_3PO_4

- Fuel cell is

  a)energy storage cell b) energy exchange cell c) energy conversion cell

   d) energy limiting device

- Corrosion is an ------------ process

  a) oxidation   b) reduction   c) redox   d) none

- Sacrificial anodes are

  a) Sn,Pb   b) Au, Ag   c)Hg, Na   d) Mg, Zn

- Volatile metal oxide layer is observed in

  a) Cu, Al   b) Pt, Au   C) MoO_3 d) Na, Fe

UNIT- IV

Stereochemistry, Organic reactions and synthesis of drug molecules

Definitions:

Isomerism

The phenomenon by which two or more compounds possess same molecular formula but different physical and chemical properties is known as isomerism.

There are two types of isomerism: structural isomerism and stereoisomerism
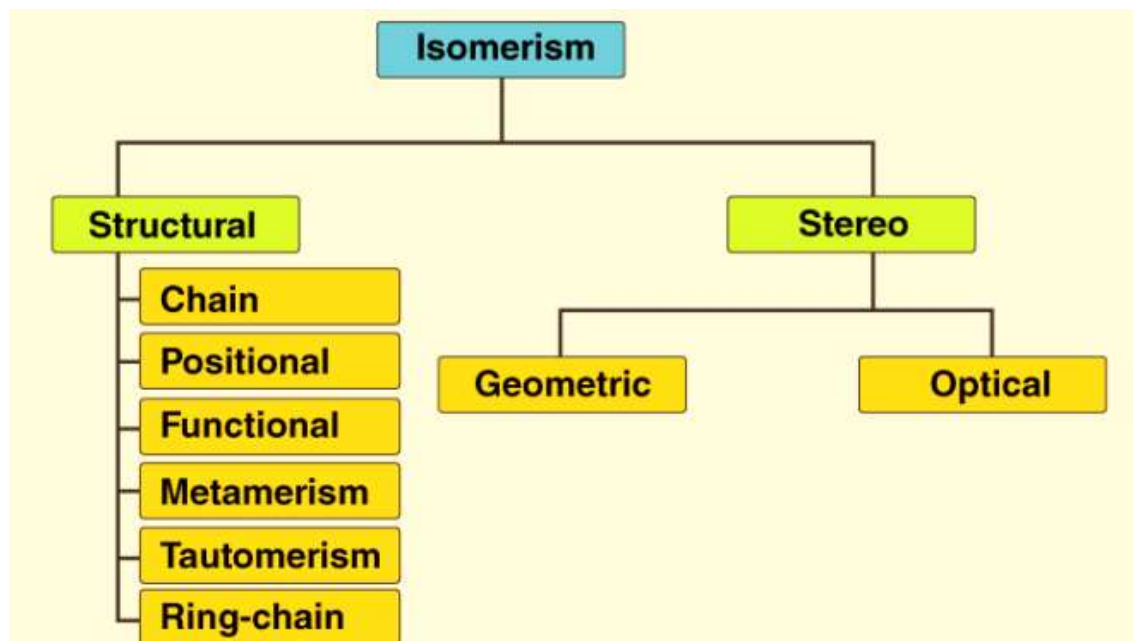
Structural isomerism

The compounds which have the same molecular formula but differ in connectivity of atoms in molecules is known as constitutional isomers and phenomenon is called constitutional (structural) isomerism.

Structural isomerism is divided to Chain Isomerism, Positional Isomerism, Functional Isomerism, Metamerism Isomerism, Tautomerism Isomerism, and Ring Chain Isomerism.

Stereo isomerism

The substances having the same molecular formula and same structural formula but differ in the spatial arrangement of atoms or groups are called stereo isomers and the phenomenon is called stereo isomerism. This isomerism divided to two types namely Configurational and Conformational isomerism.

Types of Organic Reactions:

Organic reactions are of following types:

1. Addition   2. Elimination   3. Substitution   4. Oxidation   5. Reduction

Addition reactions

An addition reaction occurs when two or more reactants combine to form a single product. This product will contain all the atoms that were present in the reactants. Addition reactions occur with unsaturated compounds.

$$H_3C-CH=CH_2 \ + \ HCl \longrightarrow H_3C-CH-CH_3$$
$$| $$
$$Cl$$
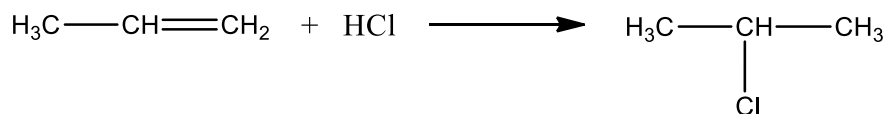
Elimination reactions

The reactions in which two atoms (or) two groups eliminated from either same carbon atom

Of the substrate or adjacent carbon atom of the substrate is known as elimination reaction. In this form an unsaturated compound.

$$H_3C-CH-CH_3 \xrightarrow{\ OH^-\ } H_3C-CH=CH_2 + Br^- + H_2O$$
$$| $$
$$Br$$
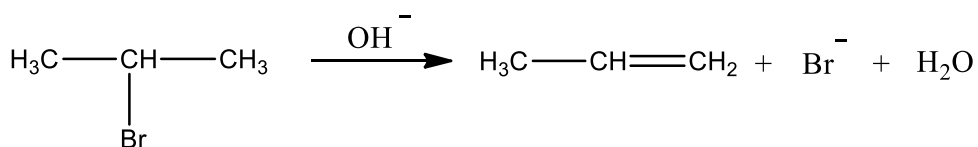
These elimination reactions may follow E_1 or E_2 mechanism.

Substitution reactions

Replacement of an atom or group of the substrate by any other atom or group is known as substitution reaction.

$$R-X + Y \longrightarrow R-Y + X$$
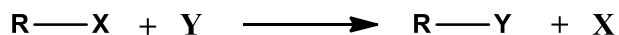
The mechanism of the nucleophile substitution reactions proceed through either S_N^1 or S_N^2 mechanism.

Reduction of carbonyl compounds by LiAlH$_4$ and NaBH$_4$

Aldehydes undergo reduction either NaBH$_4$ or LiAlH$_4$ and produces primary alcohols.

$$R-CHO \xrightarrow[H_3O^+]{LiAlH_4/THF} R-CH_2-OH$$

Ketones undergo reduction either NaBH$_4$ or LiAlH$_4$ and produces secondary alcohols.

$$\underset{R-\overset{\overset{\displaystyle O}{\|}}{C}-R}{} \xrightarrow[H_3O^+]{LiAlH_4/THF} \underset{R-\overset{\overset{\displaystyle OH}{|}}{CH}-R}{}$$
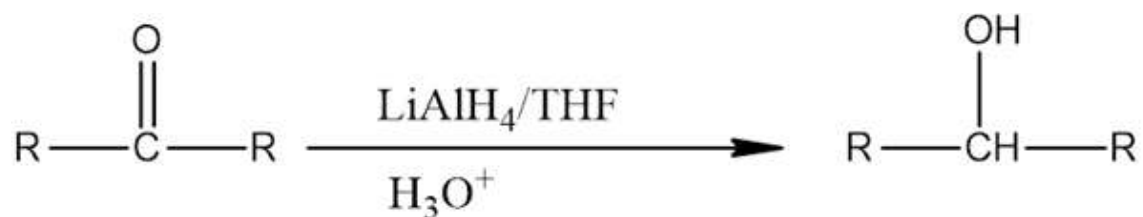
Oxidation of alcohols using KMnO$_4$ and H CrO$_4$

Primary alcohols on oxidation with KMnO$_4$ give the corresponding aldehyde, which are oxidised to carboxylic acid.

$$R-CH_2-OH \xrightarrow{KMnO_4/OH^-} R-COOH$$
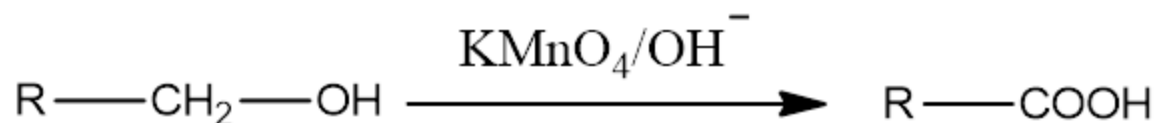
Secondary alcohols can be oxidized by KMnO$_4$ in alkaline condition to give the ketone.

$$\xrightarrow{KMnO_4/OH^-}$$
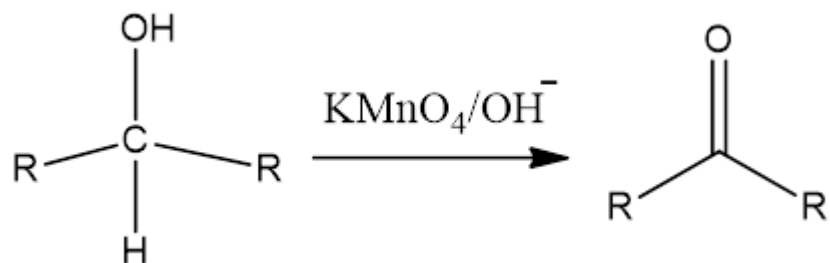
Tertiary alcohols do not reacts with KMnO$_4$.

In this unit we will study synthesis of a commonly used drug molecule namely Aspirin (Acetylsalicylic acid) Paracetamol (N-acetyl-para-aminophenol).

Aspirin

An excess of anhydride is added to salicylic acid in presence of H_2SO_4. The mixture is heated to form the aspirin and acetic acid. After the reaction takes place water is added to destroy the excess acetic anhydride.

| Salicylic acid | Acetic anhydride | Acetyl salicylic acid | Acetic acid |
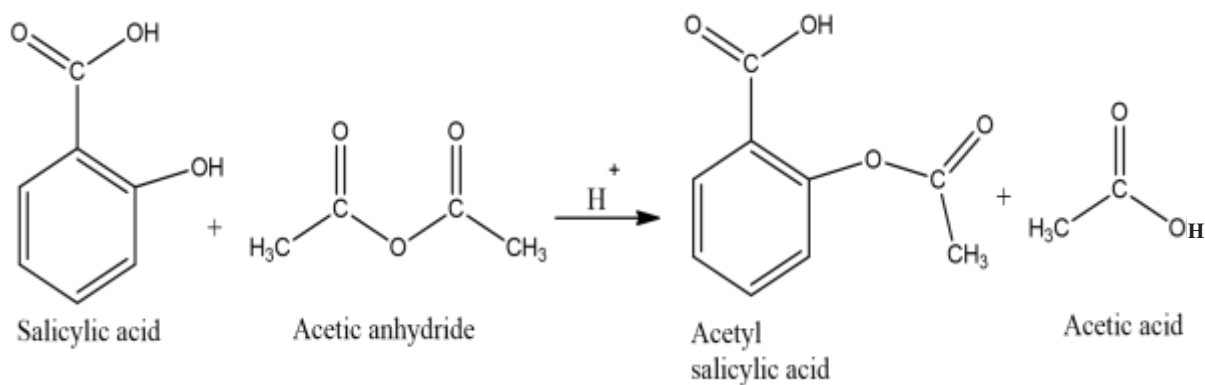
Paracetamol

Paracetamol is prepared by reacting 4-aminophenol with acetic anhydride in the presence of conc H_2SO_4 solution

4-Amino phenol   Acetic anhydride   N-Acetyl-para-amino phenol   Acetic acid

Objective questions

1. Hexane and 3-methylpentane are examples of: [ ]

    A) Enantiomers.   B) Stereoisomers.

    C) Diastereomers   D) Constitutional isomers.

2. Enantiomers are: [ ]

    A) Molecules that have a mirror image.

    B) non-superimposable molecules.

    C) non-superimposable constitutional isomers.

    D) non-superimposable molecules that are mirror images of each other.

3. Which of the following is the definition of chirality? [ ]

    A) A molecule that has a carbon atom with four different substituents

    B) The non-superimposability an object on its mirror image

    C) A molecule with a mirror image

    D) The superimposability of an object on its mirror image

4. For assigning configuration to optical isomers the order of priority to isotope is [ ]

    A) H>D>T   B) H>T>D

    C) D>H>T   D) T>D>H

5. The most stable conformation of n-butane is [ ]

    A) Anti   B) eclipsed

    C) Staggered   D) Gouche

6. Hydrogenation and hydrohalogination reactions are examples for [ ]

    A) Elimination   B) Addition

    C) Substitution   D) none of the above

7. The chemical name of Aspirin is _____

    A) N-acetyl-para-aminophenol   B) Acetic acid

    C) Acetylsalicylic acid   D) none of the above

8. In the SN1 reaction the intermediate is _____

    A) Free radical   B) Carbocation

    C) Carbanion   D) Alkyl

9. The isomer with non-superimposable mirror images is called

_____

    A) Enantiomer   B) Diastereomer

    C) Conformational isomer   D) Cis-trans

UNIT-V: Polymer Chemistry

Definitions:

Polymers: These are high molecular weight organic compounds in which a large number of simple units repeat themselves in a regular fashion. The simple units are called as monomers.

Degree of polymerization: The number of repeat units in the polymer is known as degree of polymerization.

$$H_2C{=}CH_2 \xrightarrow{\text{Polymerization}} {-}[H_2C{-}CH_2]_n$$

Monomer (ethylene) Polymer (polyethylene)

Degree of polymerization = n

Classification of Polymers:

1. Classification based on source of origin
    a. Natural polymers: Natural Rubber, Starch, Cellulose, Nucleic acids, Protein and etc.
    b. Synthetic polymers: Polyvinyl chloride (PVC), Bakelite, Teflon, Polyethylene terephthalate (PET), Nylons and etc.
2. Classification based on structure
    a. Linear Polymers: PVC, polystyrene and polypropylene.
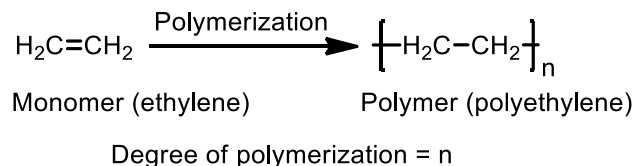   b. Branched Chain Polymers: Low-density polyethythlene
    c. Cross-linked Polymers/Network Polymers: Bakelite and melamine formaldehyde resin.
3. Classification based on variety of monomers
    a. Homo-polymer: Polyvinyl Chloride, Polyethylene and Teflon
    b. Co-polymer: Styrene-butadiene copolymer, Nylon 6, 6 and Terelene
4. Classification based on molecular forces
    a. Thermoplastics: Polystyrene, polyethylene, polypropylene.
    b. Thermosets: Bakelite and melamine.
    c. Elastomers: Natural rubber, vulcanized rubber
    d. Fibers: Silk, Nylon and etc.
5. Classification based on mode of polymerization
    a. **Addition polymers:** These are formed by the repeated addition of monomer molecules. In this type of polymers, the monomers are unsaturated hydrocarbons. There is no elimination product in the reactions.

Eg: Polyvinyl chloride and Teflon

$$n \; H_2C=CH{\scriptstyle\diagdown}_{Cl} \xrightarrow{\text{Polymerization}} \left[H_2C-\underset{Cl}{CH} \right]_n$$

Vinyl chloride   **Polyvinyl chloride**
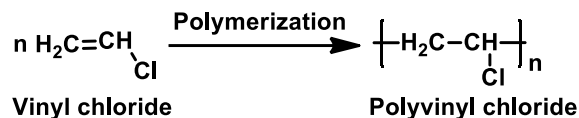
b. **Condensation polymers:** These are formed by repeated Condensation between two different bi-functional or tri-functional monomeric units, along with the formation of elimination product like water, NH_3, HCl etc.

Eg: Nylon-6,6, PET, Bakelite and etc.

$$n \; H_2N-(CH_2)_6-NH_2 \; + \; n \; HOOC-(CH_2)_4-COOH \xrightarrow{\quad\quad\quad}$$

Hexamethylene   **Adipic acid**   (2n-1) H_2O
diamine

$$\left[\underset{\displaystyle\underset{(CH_2)_6}{\overset{H}{|}}}{N}-(CH_2)_6-\underset{\overset{H}{|}}{N}-\overset{\overset{O}{||}}{C}-(CH_2)_4-\overset{\overset{O}{||}}{C} \right]_n$$

Nylon-6,6
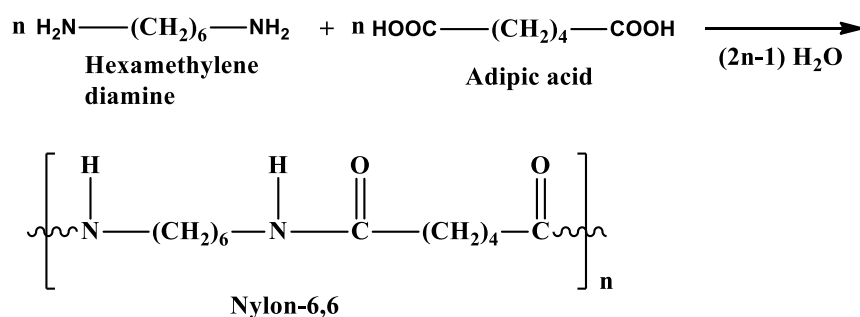
Plastics: These are high molecular weight organic materials, which can be moulded into any desired form by the application of heat and pressure.

Eg: Polyethylene, Polystyrene, Polyvinyl chloride and etc.

Thermoplastic polymers (Thermo plastics): Thermo plastics are the polymers that become soft on heating and hard on cooling and the process can be repeated for a number of times.

Eg: Polyethylene, polystyrene, PVC and Polypropylene

Thermosetting polymers (Thermosets): Thermosets are the polymers that undergo chemical changes and crosslinking on heating and become permanently hard, rigid and infusible.

Eg: Phenol formaldehyde resin (Bakelite), urea formaldehyde resin and melamine formaldehyde resin.

Fibers: Fibers belong to a class of polymers which are thread-like materials and can be woven into fabrics.

Fibres possess high tensile strength because the chains possess strong intermolecular forces such as hydrogen bonding. Eg: polyamides, polyester and etc.
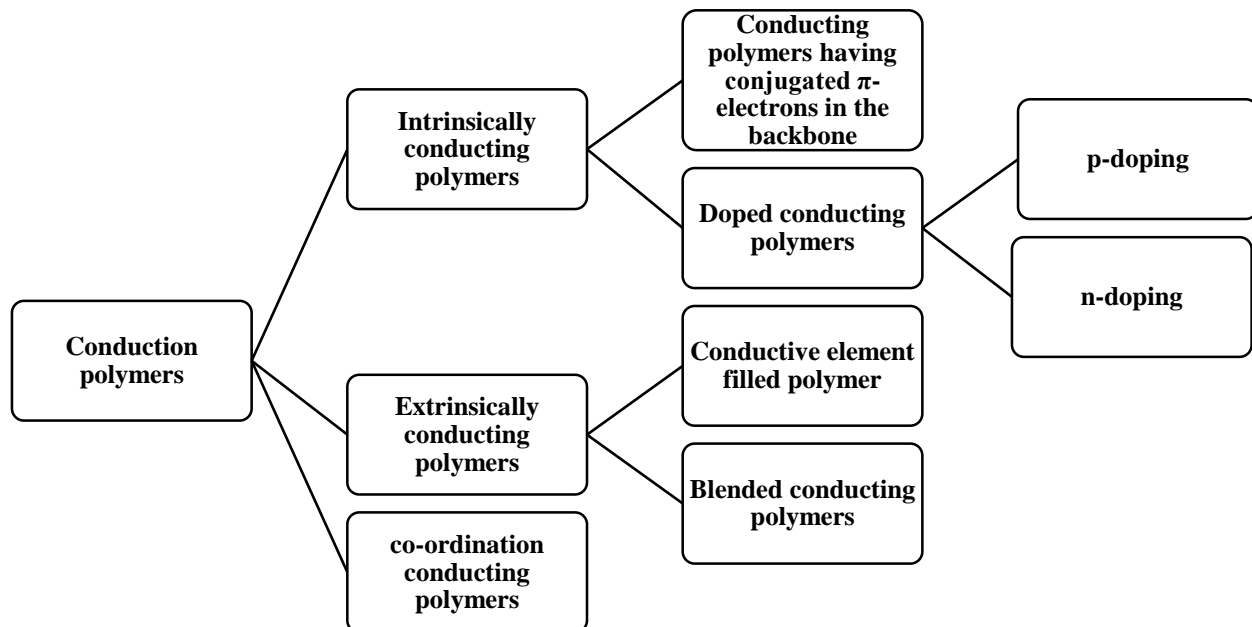
Rubber (Elastomers): These are high polymers, which have elastic properties in excess of 300 percent. Thus, a rubber-band can be stretched to 4 to 10 times its original length and as soon as the stretching force is released, it returns to its original length.

Natural rubber is a high polymer of isoprene (2-methyl-1,3-butadiene). The vulcanization process is used to improve the physical properties of natural rubber.

Vulcanization: It is a process of heating the raw rubber with sulphur at 100-140°C. The sulphur combines chemically at the double bonds of different rubber molecules and provides cross-linking between the chains.

Conducting polymers: A polymer that can conduct electricity is known as *conducting polymer*.

These can be classified as follows.

```
                                    ┌──────────────────┐
                                    │   Conducting     │
                                    │ polymers having  │
                                    │  conjugated π-   │
                  ┌──────────────┐  │ electrons in the │
                  │ Intrinsically│──│    backbone      │
                  │  conducting  │  └──────────────────┘           ┌──────────┐
                  │   polymers   │  ┌──────────────────┐           │ p-doping │
                  └──────────────┘──│ Doped conducting │───────────└──────────┘
  ┌────────────┐                    │    polymers      │───────────┌──────────┐
  │ Conduction │                    └──────────────────┘           │ n-doping │
  │  polymers  │                                                   └──────────┘
  └────────────┘  ┌──────────────┐  ┌──────────────────┐
                  │ Extrinsically│──│Conductive element│
                  │  conducting  │  │  filled polymer  │
                  │   polymers   │  └──────────────────┘
                  └──────────────┘  ┌──────────────────┐
                  ┌──────────────┐  │Blended conducting│
                  │co-ordination │  │    polymers      │
                  │  conducting  │  └──────────────────┘
                  │   polymers   │
                  └──────────────┘
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Applications of Conducting Polymers:

1. In rechargeable light weight batteries
2. In wiring in aircrafts and aerospace components.
3. In telecommunication systems.
4. In electromagnetic screening materials.
5. In electronic devices such as transistors and diodes.

6. In solar cells, drug delivery system for human body etc.,

7. In photovoltaic devices.

8. In electrochromic displays and optical filters

9. These are also used for making sensors.

Biodegradable polymers: These are defined as the degradable polymers in which degradation is caused by the action of naturally occurring microorganisms such as algae, fungi and bacteria.

Eg: Polylactic acid (PLA), Polyglycolic acid (PGA) and Polyhydroxy butyrate (PHB).

Preparation:

Lactic acid → Polylactic acid

Glycolic acid → Polyglycolic acid

3-hydroxybutyric acid → Polyhydroxybutyrate (PHB)
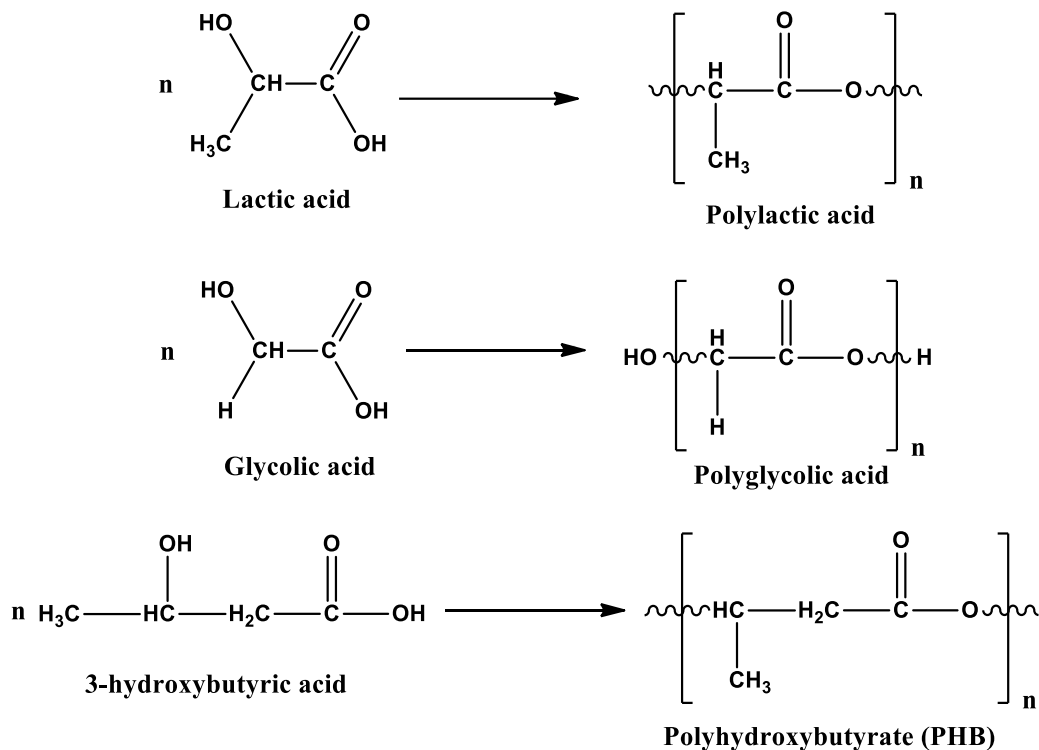
Applications of biodegradable polymers

1. These are used in a number of biomedical applications such as sutures, stents, drug delivery devices and dialysis media.
2. These are used as medical implants in the form of anchors, screws, plates, pins, rods, and mesh.
3. These can be in the form of fibers and nonwoven textiles.
4. These are used in the preparation of bio-plastics for packing food and disposable tableware.

Multiple Choice Questions:

1. Which polymers occur naturally?

    A. Starch and Nylon   B. Starch and Cellulose

    C. Proteins and Nylon   D. Proteins and PVC

2. Which one of the following is not a condensation polymer?

    A. Bakelite   B. Nylon 6,6   C. PET   D. PVC

3. Which of the following is a branched polymer?

    A. Polyvinyl chloride   B. Polystyrene   C. Polypropylene

    D. Low-density polyethythlene

4. Which of the following is a thermosetting polymer?

    A. Bakelite   B. Nylon 6,6   C. PET   D. PVC

5. Which one of the following is not a biodegradable polymers?

    A. Polylactic acid (PLA)   B. Polyglycolic acid (PGA)

    C. Polyhydroxy butyrate (PHB)   D. Polyvinyl chloride (PVC)

6. A polymer that can conduct electricity is known as a ....

    A. Insulator   B. Conducting polymer C. Biodegradable polymers D. None of the above

7. PET is obtained by the condensation polymerization of

    A. terephthalic acid and ethylene glycol   B. isoprene and butadiene

    C. starch and nylon   D. proteins and PVC

8. Which one of the following polymer is prepared by condensation polymerization?

    A. Teflon   B. PVC   C. Nylon 6,6   D. None of the above

9. The polymer containing strong inter molecular forces e.g. hydrogen bonding is

    A. Nylon 6,6   B. Teflon   C. PVC   D. None of the above

10. F C = CF is a monomer of

    A. Nylon 6,6   B. Teflon   C. PVC   D. None of the above