Code No: CH102BS R20

CMR ENGINEERING COLLEGE: HYDERABAD

UGC AUTONOMOUS

I- B.Tech-I Semester End Examination (Regular)-July-2021

ENGINEERING CHEMISTRY

(Common to CSM, ME and ECE)

[Time: 3 Hours] [Max Mark: 70]

1. Answer any FIVE Questions. Each Question carries 14 Marks
2. Illustrate your answer with NEAT sketches wherever necesary

5x14 = 70M

Q1. a. Discuss
i. Caustic Embrittlement
ii. Calgon and phosphate conditing.

b. A sample of water on analysis has been found to contain the following $Ca(HCO_3)_2$ = 10.5ppm, $Mg(HCO_3)_2$ = 12.5ppm, $CaSO_4$ = 7.5ppm, $CaCl_2$ = 8.2ppm, $MgSO_4$ = 2.6 ppm. Determine temporary, and permanent hardness in degree Clarke.

A1.(i) Caustic Embrittlement :- is a type of boiler corrosion caused by using highly alkaline water in the boiler. During softening process by lime-soda process, free Na_2CO_3 is usually present in small proportion in the softened water. In high pressure boilers, Na_2CO_3 decomposes to give sodium hydroxide and Carbon di oxide and this makes the boiler water "caustic".

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2$$

The NaOH containing water flows into the minute hair-cracks always present in the inner side of boiler, by capillary action. Here water evaporates and the dissolved caustic soda concentration increases progressively. This caustic soda attacks the surrounding area, there by dissolving iron of boiler as Sodium ferrate. This causes embrittlement of boiler parts particulary stressed parts (like bends, joints, rivets etc) causing even failure of the boiler. Caustic cracking can be explained by considering the following concentration cell

Iron at- rivets, bends joint, etc. (+)	Concentrated NaOH solution	Dilute NaOH solution	Iron at- plane surface. (−)

The iron surrounded by the dilute NaOH becomes the Cathodic side, while the iron in contact with rather Concentrated NaOH becomes anodic part which is consequently dissolved or corroded.

Caustic Embrittlement can be prevented by:

(1) By using sodium phosphate as softening reagent.

(2) By using tannin or lignin to boiler water,

(3) By using sodium sulphate to boiler water

(ii) Calgon and phosphate conditioning.

Calgon conditioning involves in adding calgon [sodium hexa meta phosphate] $(NaPO_3)_6$ to boiler water. It prevent the scale and sludge formation by forming soluble complex compound with $CaSO_4$

$$Na_2[Na_4(PO_3)_6] \rightleftharpoons 2Na^+ + [Na_4P_6O_{18}]^{2-}$$

$$2CaSO_4 + [Na_4P_6O_{18}]^{2-} \longrightarrow [Ca_2P_6O_{18}]^{2-} + 2Na_2SO_4$$

Soluble complex ion.

Phosphate Conditioning: In high-pressure boilers, scale formation can be avoided by adding sodium phosphate, which react with hardness of water forming non-adhering and easily removable soft sludge of calcium and magnesium phosphates which can be removed by blow-down Operation.

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

Main phosphates used are

[a] NaH_2PO_4, sodium di hydrogen phosphate. (alkaline)

[b] Na_2HPO_4 disodium hydrogen phosphate. (weakly alkaline)

[c] Na_3PO_4 trisodium phosphate (alkaline)

A 1 (b)

Hardness producing Salt	Amt of Hardness producing salt	Mol.wt of Hardness producing salt	$CaCO_3$ equivalent of Hardness producing salt
$Ca(HCO_3)_2$	10.5 ppm	162	$\frac{10.5 \times 100}{162} = 6.48$ ppm
$Mg(HCO_3)_2$	12.5 ppm	146	$\frac{12.5 \times 100}{146} = 8.56$ ppm
$CaSO_4$	7.5 ppm	136	$\frac{7.5 \times 100}{136} = 5.51$ ppm
$CaCl_2$	8.2 ppm	111	$\frac{8.2 \times 100}{111} = 7.38$ ppm
$MgSO_4$	2.6 ppm	120	$\frac{2.6 \times 100}{120} = 2.16$ ppm.

Determination of temporary and permanent hardness in [e.g.]

Temporary Hardness

$Ca(HCO_3)_2 = 6.48$ ppm

$Mg(HCO_3)_2 = 8.56$ ppm

15.04 ppm

Temporary Hardness = 15.04 ppm

1 ppm = 1 mg/l = 0.07°C = 0.1°Fr.

15.04 × 0.07 = 1.0528°C

Permanent Hardness

$CaSO_4$ = 5.51

$MgSO_4$ = 9.16

15.05

15.05 × 0.07 = 1.0535°C

Q2(a) Explain desalination of brackish water by reverse osmosis method.

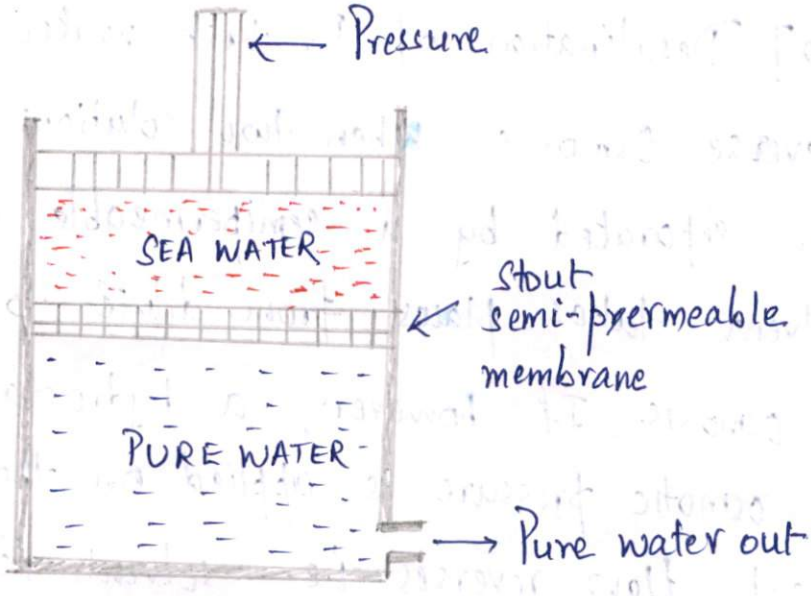
(b) Discuss softening of water by Ion Exchange process.

A2 [a] Desalination of Brackish water by reverse osmosis

Reverse Osmosis when two solutions of unequal concentrations are separated by a semipermeable membrane flow of solvent takes places from dilute to concentrated side, due to osmosis. If however, a hydrostatic pressure in excess of osmotic pressure is applied on the concentrated side, the solvent flow reverses i.e. solvent is forced to move from concentrated side to dilute side across the membrane.

This is the principle of reverse osmosis. Thus in Reverse osmosis method pure solvent (water) is separated from its contaminants, rather than removing contaminants from the water. This membrane filtration is also called "Super filtration".

Method: In this process pressure of the order 15 to 40 kg cm^{-2}) is applied to the sea water to force its pure water out through the semi-permeable membrane leaving behind the dissolved solids (both ionic as well as non ionic). The principle of reverse osmosis as applied for treating saline/sea water is illustrated in Fig. below. The membrane consist of very thin film of cellulose acetate, affixed to other side of perforated tube.



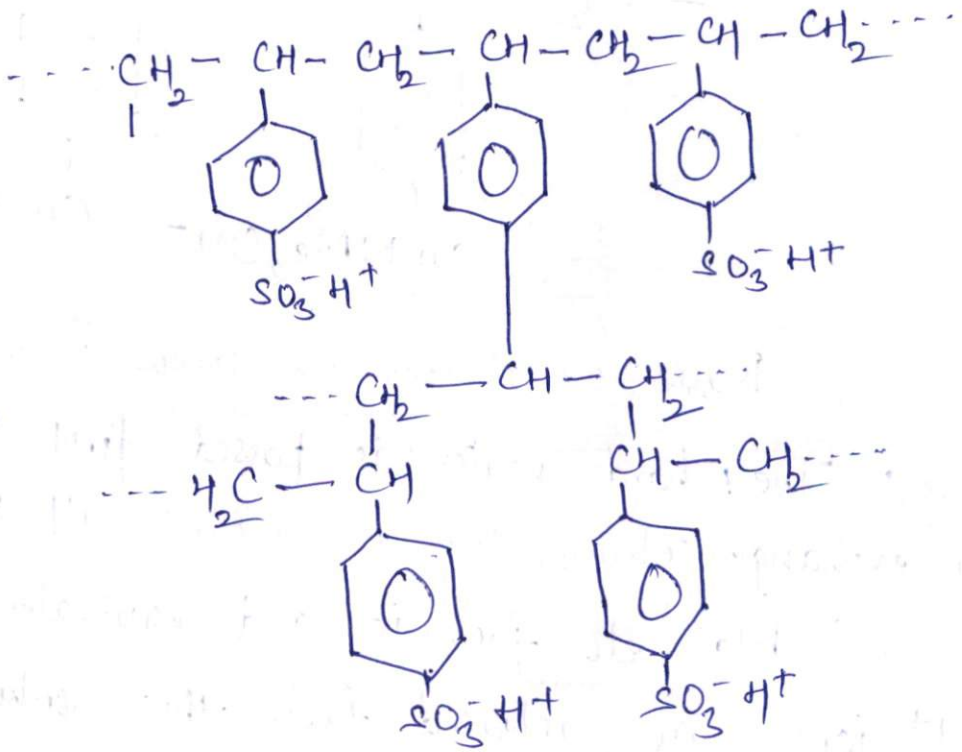
Reverse Osmosis Cell

A2(b) Ion exchange or Deionization or Demineralization process

Ion exchange resins are insoluble, crosslinked, long chain organic polymers with a microporous structure and the functional groups attached to the chain are responsible for the ion-exchange properties.

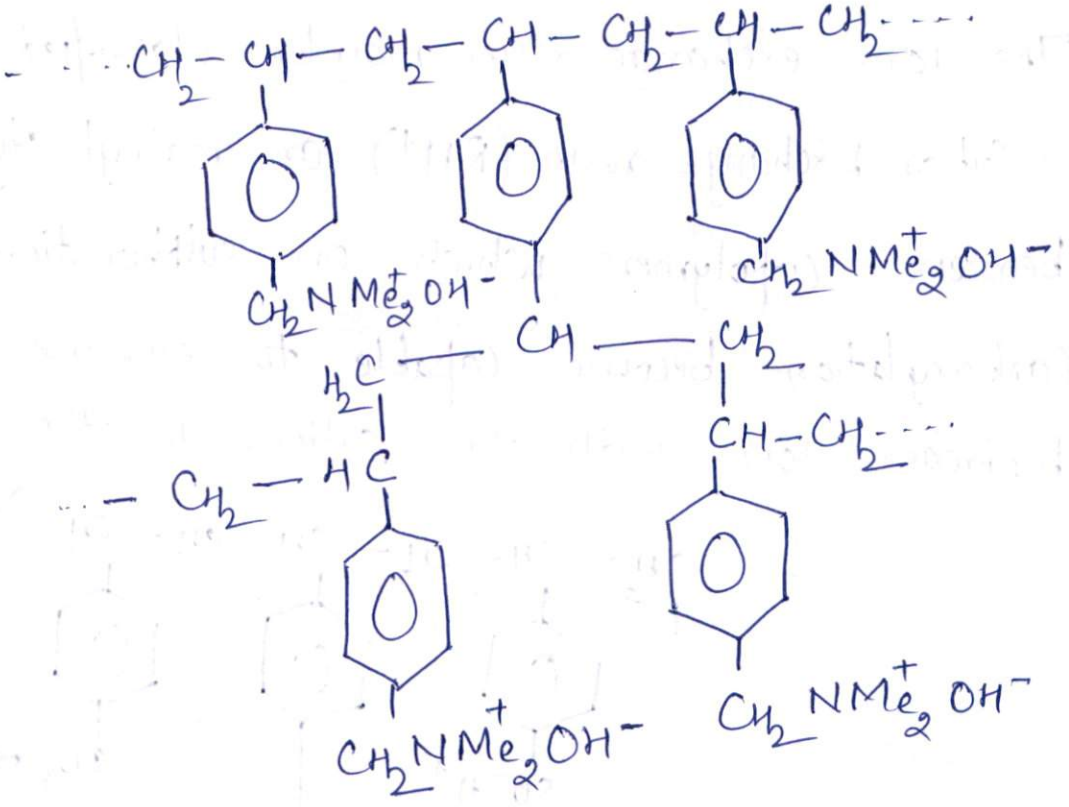
The ion-exchange resin may be classified as:-

(i) Cation Exchange resin (RH^+) are mainyl styrene divinyl benzene copolymers which on sulphonation or carboxylation become capable to exchange their hydrogen ion with the cations in the water.



Acidic or Cationic Exchange Resin

(ii) Anion exchange Resin ($R'OH^-$) are styrene-divinyl benzene or amine-formaldehyde copolymers which contain amino or quaternary ammonium or quaternary phosphonium group as an integral part of the resin matrix. These after treatment with dil. NaOH solution, becomes capable to exchange their OH^- anions with anions in water.



'Basic or Anion Exchange Resin'

Process: The hard water is passed first through cation exchange column, which removes all the cations like Ca^{2+}, Mg^{2+} etc from it and equivalent amount of H^+ ions are released from this column to water.

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

After Cation exchange column, the hard water is passed through anion exchange column which removes all the anions like SO_4^{2-}, Cl^- etc present in the water and equivalent amount of OH^- ions are released from this column to water. Thus

$$R'OH^- + Cl^- \longrightarrow R'Cl^- + OH^-$$

H^+ and OH^- ions released from cation exchange and anion exchange columns get combined to produce water molecule.

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

Thus the water coming out from exchanger is free from Cation as well as anion.

Regeneration :- When capacities of cation and anion exchanger to exchange H^+ and OH^- ions are lost, they are said to be exhausted.

The exhausted Cation exchange column is regenerated by passing a solution of dil. HCl.

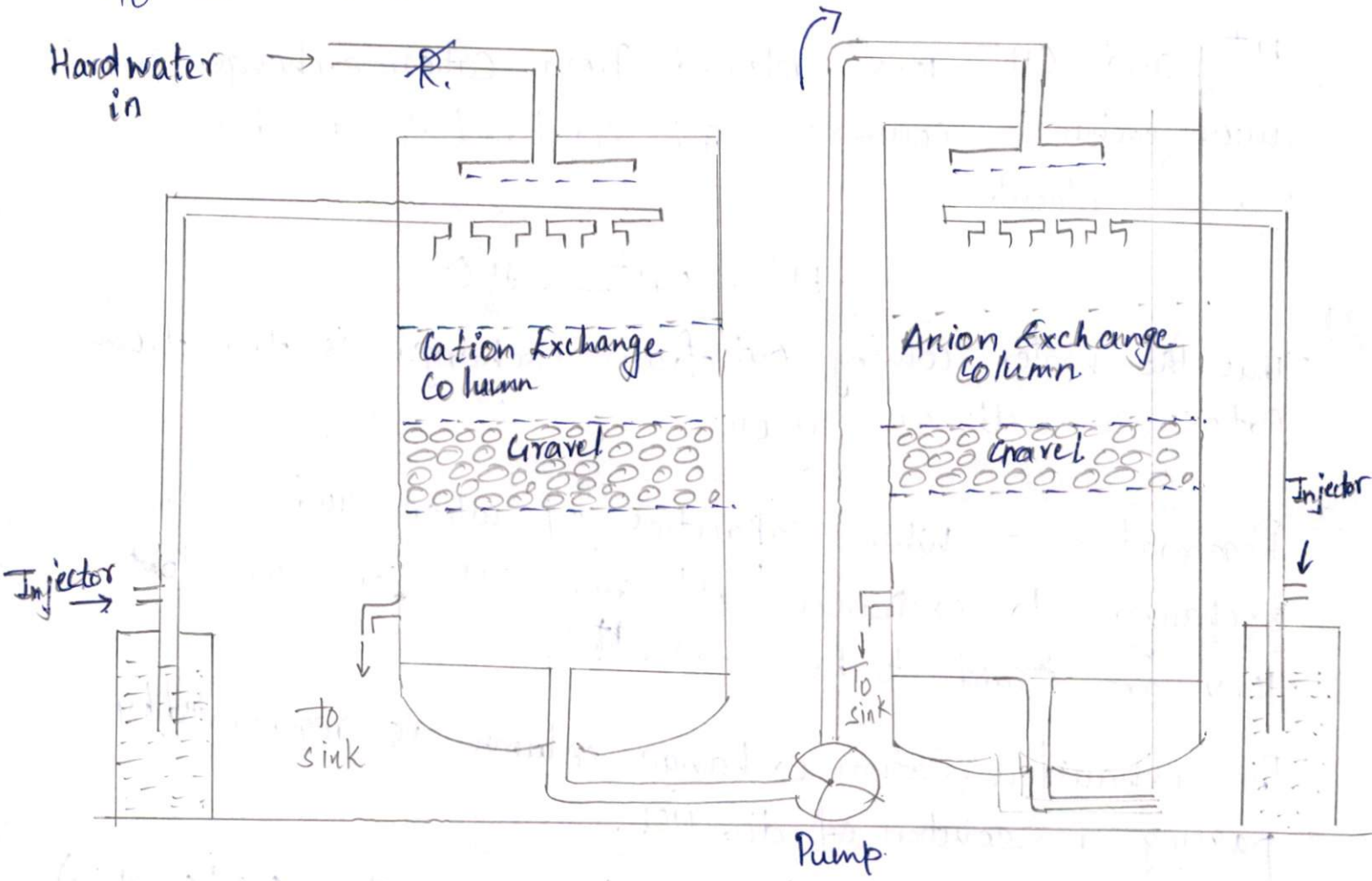
$$R_2Ca^{2+} + 2H^+ \longrightarrow 2RH^+ + Ca^{2+} \text{ (washing)}$$

The column is washed with deionized water and washing which contain Ca^{2+}, Mg^{2} is passed to sink or drain.

The exhausted anion exchange column is regenerated by passing a solution of dil. NaOH.

$$R_2SO_4^{2-} + 2OH^- \longrightarrow 2R'OH^- + SO_4^{2-} \text{ (washing)}$$

The column is washed with deionized water and washing which contain SO_4^{2-}, Cl^- ion ~~are~~ is passed to sink or drain.



Demineralization of water.

Q3(a) Explain LCAO method. Draw molecular orbital energy level diagram of N_2 molecule and comment on it magnetic behavior and bond Order.

A3. According to LCAO method, the linear combination of atomic orbitals can take by addition or (constructive), and substraction (Destructive) of wave function of atomic orbital involved.

Molecular Orbital obtained by addition of wave functions of atom involved is called Bonding Molecular Orbital

$$\boxed{\psi_{(MO)} = \psi_A + \psi_B} \text{ -(1) (Constructive Interference)}$$

The energy of bonding molecular orbital is less than that of the constitutent overlapping atomic Orbitals

The difference in energy between the combining atomic orbitals and the Bonding Molecular Orbital formed is called Stabilization Energy. Thus Bonding Molecular Orbital stabilizes the molecule.

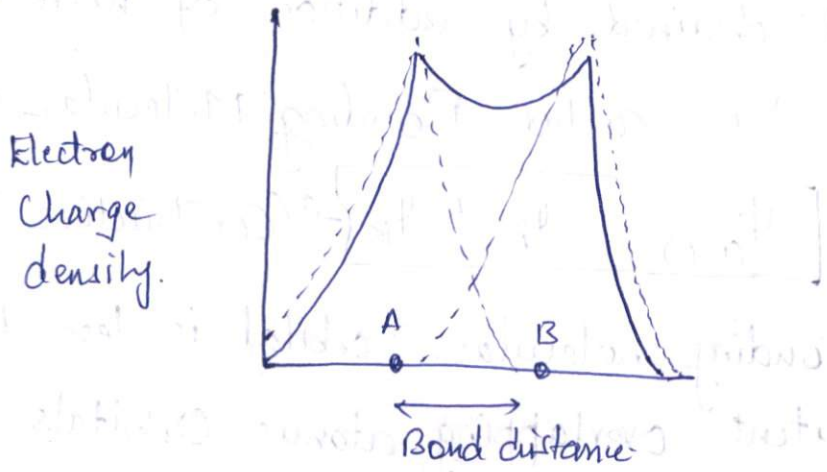
Probability of Bonding Molecular Orbital (ψ^2) is greater than that of antibonding molecular Orbital $(\psi^*)^2$ formation.

This because we know that probability is given by square of amplitude therefore on squaring above equation-(1)

$$(\psi^b)^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B \quad -(2)$$

The term ψ_A^2 and ψ_B^2 indicate electron charge densities of wave function ψ_A and ψ_B of the isolated atom A and B while the $(\psi_b)^2$ indicate electron charge density that of wave function ψ_b molecular Orbital.

It may be seen from above equation (2) that $(\psi_b)^2 > (\psi_A^2 + \psi_B^2)$ by a term $2\psi_A\psi_B$. This term result from the interaction or overlap of Atomic Orbitals.



$(\psi_b)^2$ shown by solid line.

ψ_A^2 and ψ_B^2 show by dotted line.

Fig. Plot of electron charge density.

Characteristics of Bonding Molecular Orbital.

a) It possess lower energy that that of combining atomic Orbital
b) It possess high electron density in the region between nuclei
c) It ~~possess~~ imparts stability to the molecule.
d) It is only formed when the lobes of combining atomic Orbital possess the same sign.

Molecular Orbital obtained by substraction of ware functions of atom involved is called Antibonding Molecular Orbital

$$\boxed{\psi^* = \psi_A - \psi_B} \quad \text{— (3)}$$

The energy of Antibonding molecular Orbital is more than that of the constituent overlapping atomic Orbitals.

The difference in energy between the Anti bonding Molecular orbital and the combining atomic orbital is called destabilization Energy.

In case of Antibonding Molecular Orbital in terms of wave function it is necessary to know the electric charge distribution of Anti molecular orbital. therefore on squaring equation-3

$$\boxed{(\psi^*)^2 = \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B}$$

It may be seen from this equation $(\psi^*)^2 < (\psi_A^2 + \psi_B^2)$ by a term $2\psi_A\psi_B$. This means that in antibonding molecular orbital there is less electron density between the interacting atoms.

Thus the energy of Antibonding molecular is greater than the sum of the energies of two interacting atom A and B and the resulting bond is less stable.

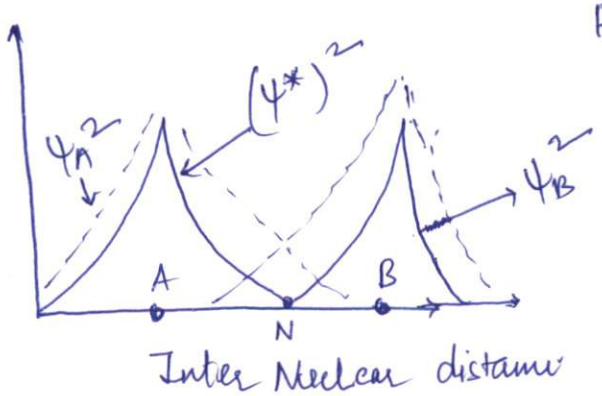


Fig. Plot for Electron density Vs Internuclear distance

· Molecular Orbital Energy level of N_2 molecule.

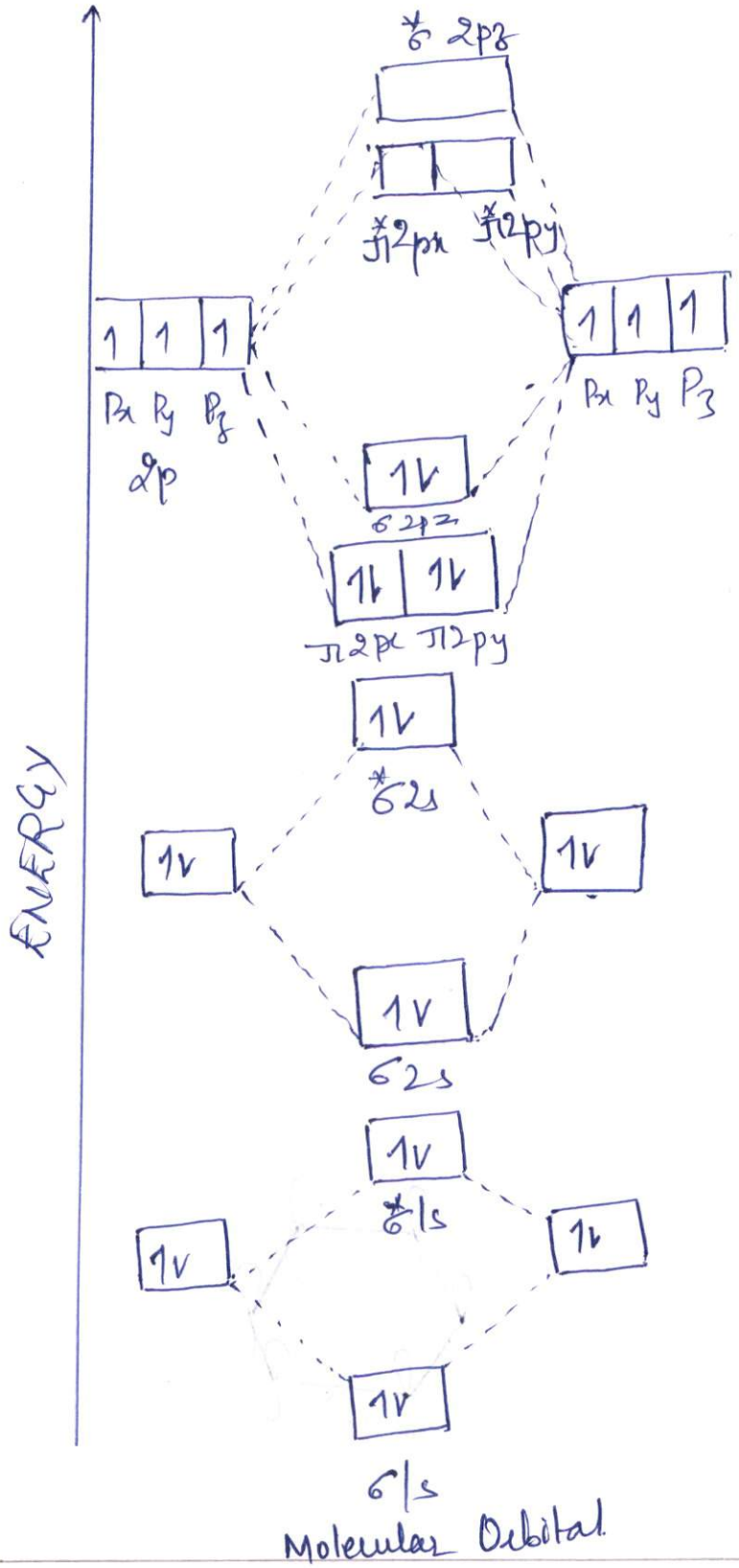
Atomic number of Nitrogen is 7

Electronic configuration is $1s^2\ 2s^2\ 2p^3$

N_2 molecule has a total of 14 ele$^-$

Electronic Configuration of N_2 molecule

$\sigma 1s^2,\ \sigma^* 1s^2,\ \sigma 2s,\ \sigma^* 2s^2,\ \pi 2px^2 = \pi 2py^2$



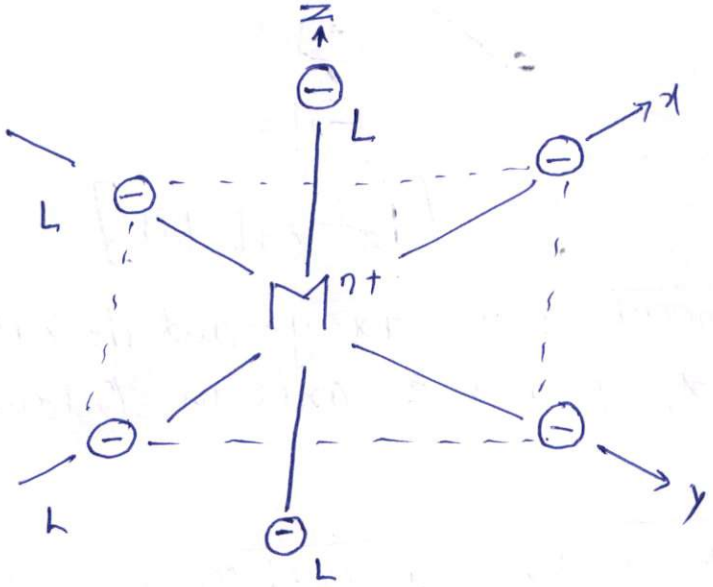
Bond Order :

$$= \frac{N_b - N_a}{2} = \frac{8-2}{2} = 3$$

Nitrogen molecule contain triple bond.

N_2 is having pair of electron therefore it shows Diamagnetic in nature.

A3(b) An octahedral complex $[ML_6]^{n+}$ in which the central metal cation, M^{n+} is placed at the center of Octahedron and is surrounded by six ligands which resides at the six-corners of the Octahedron shown in Fig. 1



[Fig. 1] Position of the central metal ion M^{n+} and six ligands L's in a Octahedral complex $[ML_6]^{n+}$

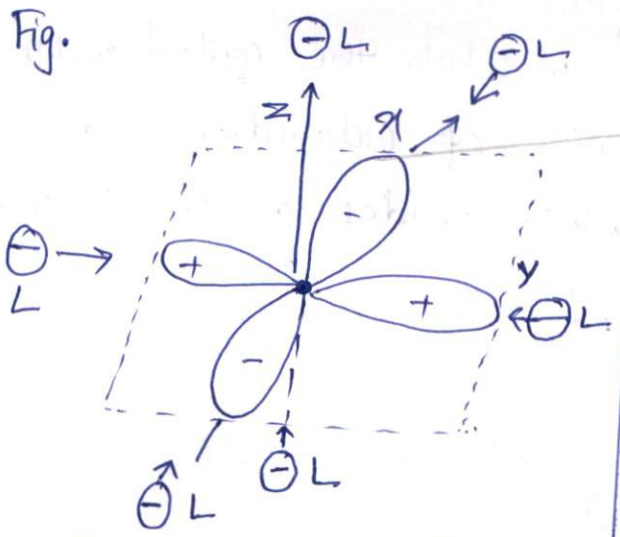
In the above Fig the ligand on each of three axes are allowed to approach towards the metal cation $[M^{n+}]$ from both the end of the axes.

→ In this process the electron in d-electrons of the metal cation are repelled by negative point charge or by the negative end of the dipole of the ligands. This repulsion will raise the energy of all five d-orbitals.

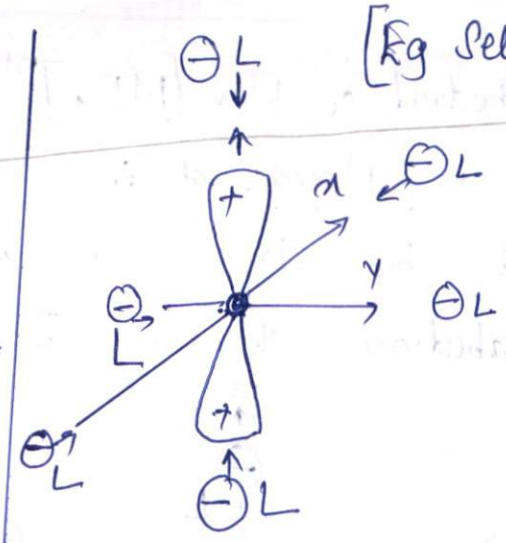
→ Since the lobes of the two eg-orbitals (i.e dz^2 and dx^2-y^2) lie directly in the path of approaching ligands, the electrons in these orbitals experience greater force of repulsion than those in t_{2g} orbitals (i.e. dxy, dyz and dzx orbitals) whose lobes are directed in space between the path of the approaching ligand. i.e the energy of eg orbital is

[Fig. 2]

Fig.



[dx^2-y^2 orbital]



[dz^2 orbital]

Fig 2: Six ligand approaching the dx^2-y^2 and dz^2 orbitals [eg set] along x, y and z axes in Octahedral Complexes

increased while that of t_{2g} is decreased (Greater is the repulsion, greater the increase in energy. Therefore Under the influence of approaching ligand the five-d orbital which were originally degenerate in the free metallic cation are now split into two level.

(i) t_{2g} level which is triply degenerate and is of lower energy

(ii) e_g level which is doubly degenerate and is of higher energy

In other words the degeneracy of the five-d orbitals is removed under the influence of ligands. The separation of five-d orbitals of the metal ion into two set having different energies is called CRYSTAL FIELD SPLITTING OR ENERGY LEVEL SPLITTING.

The energy gap between t_{2g} and e_g set is denoted by Δ_o or $10Dq$ where 'O' in Δ_o indicates an Octahedral arrangement of the ligand around the central metal ion.

This energy difference in electrostatic field exerted by ligand on 't2g' and 'eg' set of orbitals of the central metal cation Δ_o or $10Dq$ is called CRYSTAL FIELD SPLITTING ENERGY

T_{2g} set loses an energy equal to $0.4\Delta_o$ $(= 4Dq)$ while eg set gain an energy equal to $0.6\Delta_o$ $[= 6Dq]$

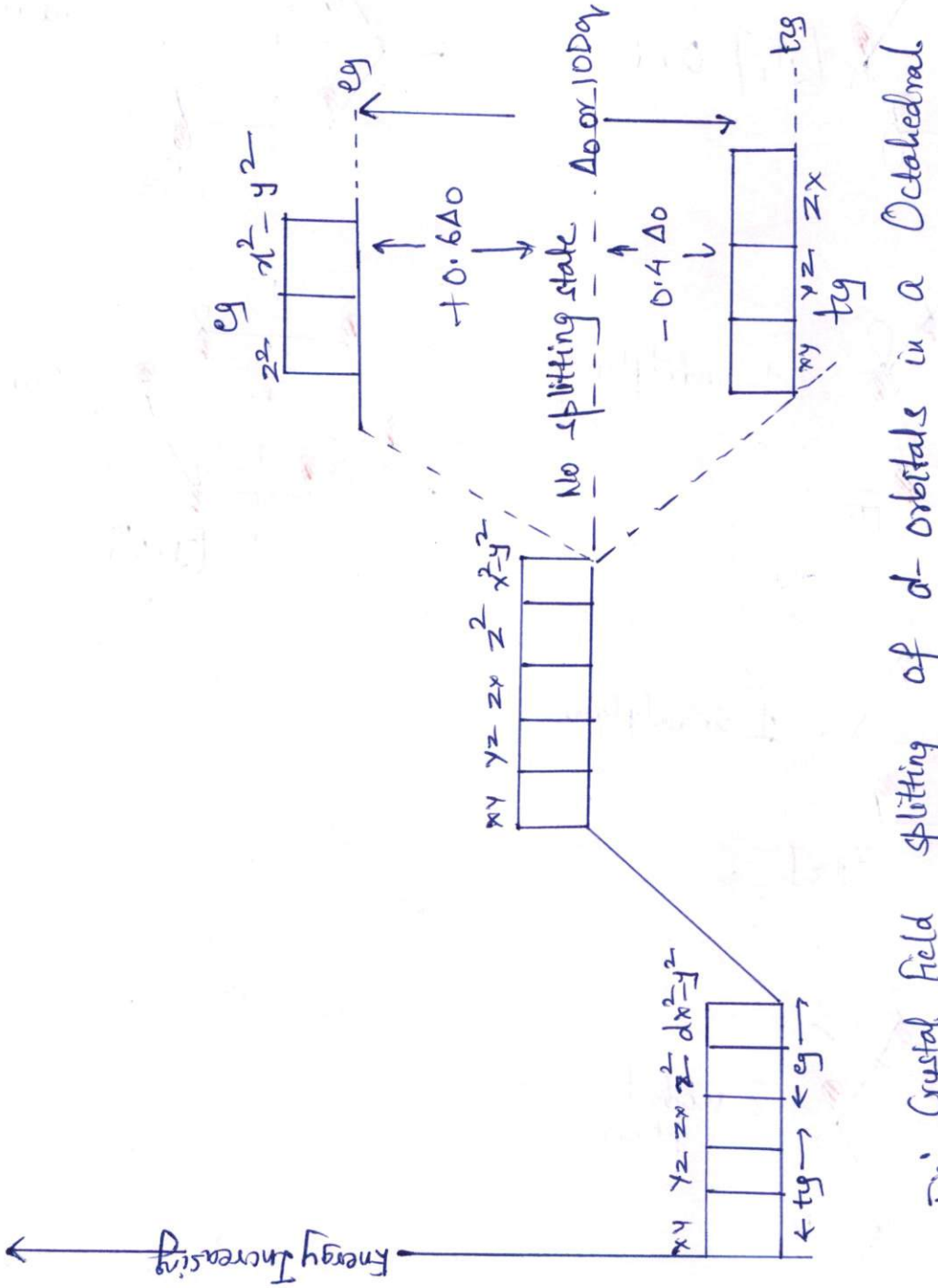
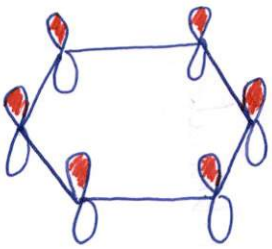


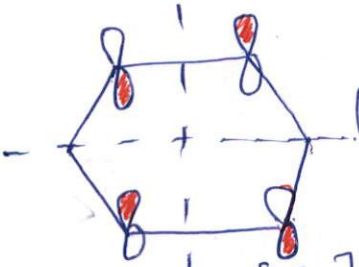
Fig: Crystal field splitting of d orbitals in a Octahedral Complex.

A 4[a] π Molecular Orbital of Benzene

Benzene is a planar cyclic compound with molecular formula C_6H_6 is a combination of six component p_z - orbitals. All the six p_z - orbitals are atomic orbitals containing a valence electron. Hence six molecular orbitals. The six combination of Benzene are shown as follows:-

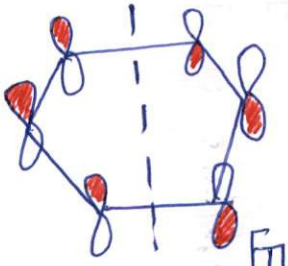


$[\pi_1]$ Anodes



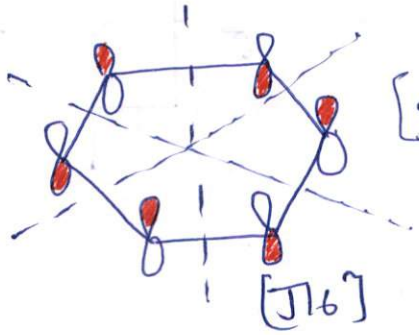
(2 nodal plane)

$[\pi_5]$



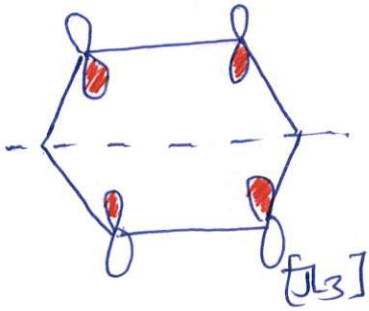
1 nodal plane

$[\pi_2]$



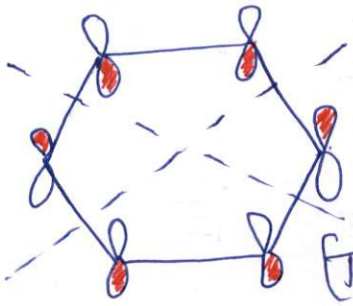
[3 nodal plane]

$[\pi_6]$



1 nodal plane.

$[\pi_3]$



2 nodal plane

$[\pi_4]$

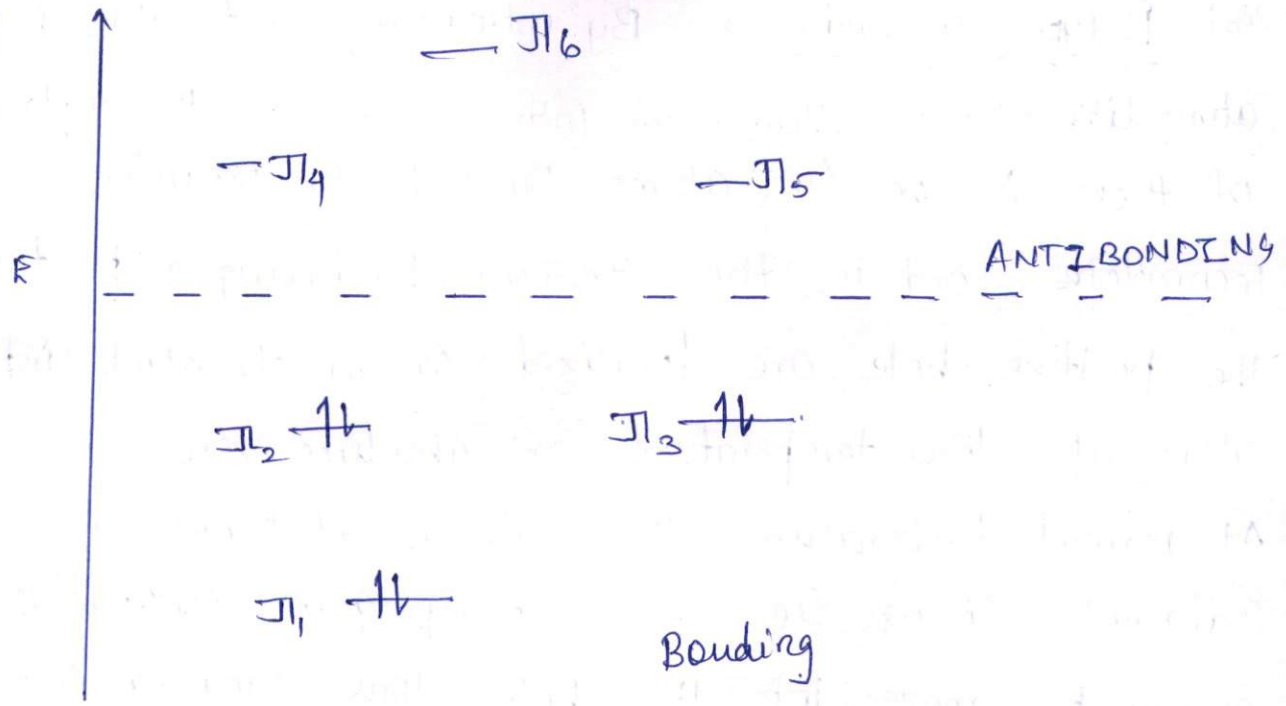


Fig: Pi molecular Orbitals of Benzene.

Aromaticity:- An aromatic molecule is flat with cyclic clouds of delocalised electron above and below the plane of molecule. The molecular orbital present in Benzene permit delocalisation of electron which gives stability to the compounds. The number of π electrons must conform to Huckel's $(4n+2\pi)$ electron rule.

1) According to Huckel Rule for a compound to become aromatic should have $(4n+2)\pi$ electrons where 'n' is an integer $(n = 0, 1, 2, 3)$
2) All these compound are flat, cyclic molecule with very good stability.
3) These molecule contain cyclic clouds of delocalised electrons above and below the plane of the molecule
4) These molecule undergo electrophilic substitution.

A 4[b] P-type semiconductor By introducing a trivalent impurity atom like Boron, Aluminium into Si or Ge, the replacement of these Si or Ge atoms by impurity produces an incomplete bond in the structure producing a positive hole. The positive hole are localized around trivalent impurity atom at low temperature or absolute zero.

At normal temperature the valence electrons on the adjacent Si or Ge atom may gain sufficient energy to move into the hole, thus creating a new hole in the Si or Ge. The positive hole can migrate across the crystal thus current is carried out by the migration of positive centers

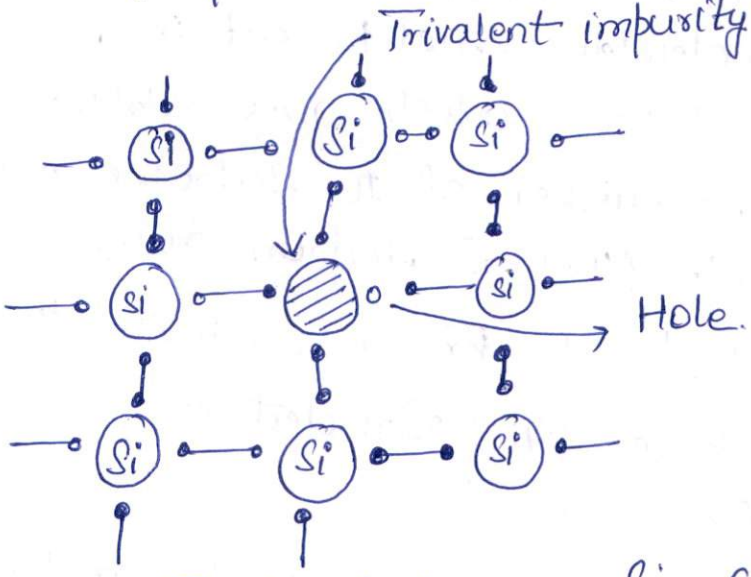


Figure :- Positive hole on Si- Crystal Lattice.

N-type semiconductor.- n-type semiconductors were produced by doping Si or Ge with pentavalent impurity atoms like P, As etc. A minute amount of Si or Ge atoms are replaced by P with five electrons in its outer shell. Only four election form covalent bond.

with Si or Ge and fifth electron remains loosely bound around pentavalent impurity. At the normal temperature some of the fifth election of impurity are promoted to conduction band, causing conduction. Since, the conductivity of such semiconductors are due to negative electrons they are called as n-type semiconductors.

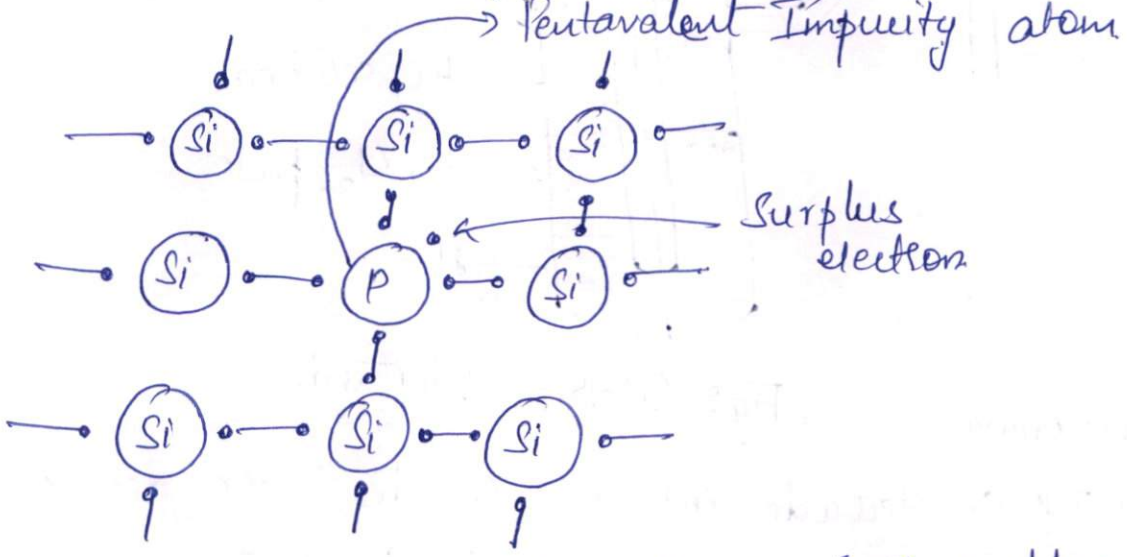


Fig: Doping of Impurity Crede [a] surplus election

Q5 a. Explain construction and functioning of Calomel Electrode.

b. What are secondary batteries. Discuss in detail about Li-ion battery and give its application.

A5 a. Calomel electrode consist of a glass tube containing mercury at the bottom over which mercurous chloride is placed The remaining portion of the tube is filled with a saturated solution of KCl. The bottom of the tube is sealed with a platinum wire (Fig) The side tube is used for making electrical contact with a salt Bridge. The electrode potential of the

the Saturated Calomel electrode is +0.2422 V

Calomel electrode is represented as

Hg, Hg_2Cl_2, KCl (sat, solution); $E^\circ = 0.2422\ V$

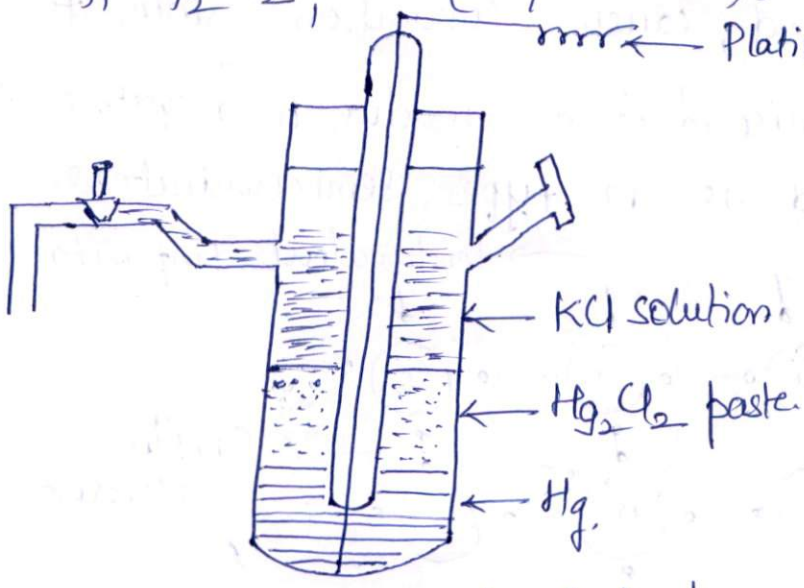


Fig: Calomel Electrode

Functioning

(i) If the electrode act as anode the reaction is

$$2Hg_{(l)} \longrightarrow Hg_2^{2+} + 2e^-$$

$$Hg_2^{2+} + 2Cl^- \longrightarrow Hg_2Cl_{2\,(s)}$$

$$2Hg_{(l)} + 2Cl^- \rightleftharpoons Hg_2Cl_{2\,(s)} + 2e^-$$

Hg undergoes oxidation to give Hg_2^{2+} ions which then combine with Cl^- ions to form Hg_2Cl_2. Here the concentration of Cl^- ion get decreased.

(ii) If the electrode act as cathode the reaction is

$$Hg_2Cl_{2\,(s)} \longrightarrow Hg_2^{2+} + 2Cl^-$$

$$Hg_2^{2+} + 2e^- \longrightarrow 2Hg_{(l)}$$

$$Hg_2Cl_2 + 2e^- \rightleftharpoons 2Hg_{(l)} + 2Cl^-$$

The Hg_2^{2+} ion furnished by Hg_2Cl_2 get reduced at the electrode. Here the concentration of Cl^- ion get increased.

The electrode potential is given by

$$E_{(calomel)} = E^{\circ}_{(calomel)} - \frac{RT}{2F} \ln a_{Cl^-}$$

The electrode potential depends on the activity of the Chloride ions. and it decreases as the activity of the chloride ion increases.

The single electrode potential of the three calomel electrodes on hydrogen scale at 298 k are given as

Concentration of KCl	0.1 N	1.0 N	Saturated.
Electrode potential (V)	+0.3338	+0.2800	

A5[b] Secondary battery (or secondary cells) in which the cell reaction can be reversed by passing direct electric current in Opposite direction. Thus a secondary battery may be used through a large number of cycles of discharging and charging.

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

Lithium-ion battery is a secondary battery. The movement of lithium ions are responsible for charging and discharging.

Lithium ion cell has the following three components:

→ A positive electrode (Layers of Lithium-metal oxide) (Cathode)

→ A negative electrode (Layers of porous Carbon) (Anode)

→ An electrolyte (Polymer gel) (Separator)

Construction

The positive electrode is typically made from a layers of chemical compound called Lithium Cobalt oxide ($LiCoO_2$).

The negative electrode is made from layers of Porous carbon (C) (graphite)$_x$. Both the electrodes are dipped in a polymer gel electrolyte and separated by a separator which is perforated plastic and allow the Li^+ ion to pass through

Working

Charging

During charging Li^+ ions flows from the positive electrode ($LiCoO_2$) to the negative electrode (graphite) through the electrolyte. Electrons also flow from the positive electrode to the negative electrode. The electrons and Li^+ ions combine at the negative electrode and deposit there as Li.

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

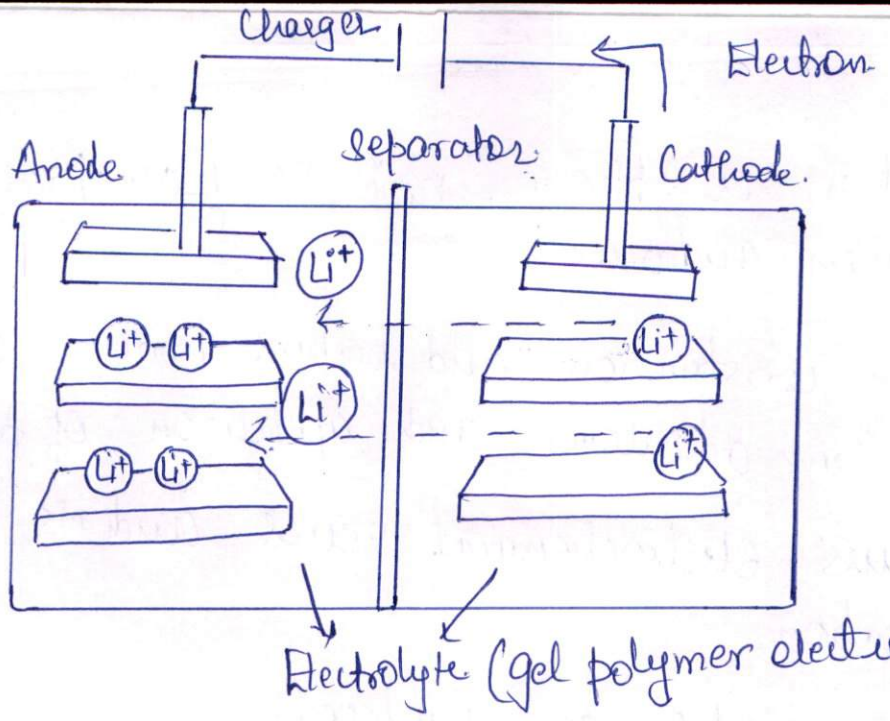
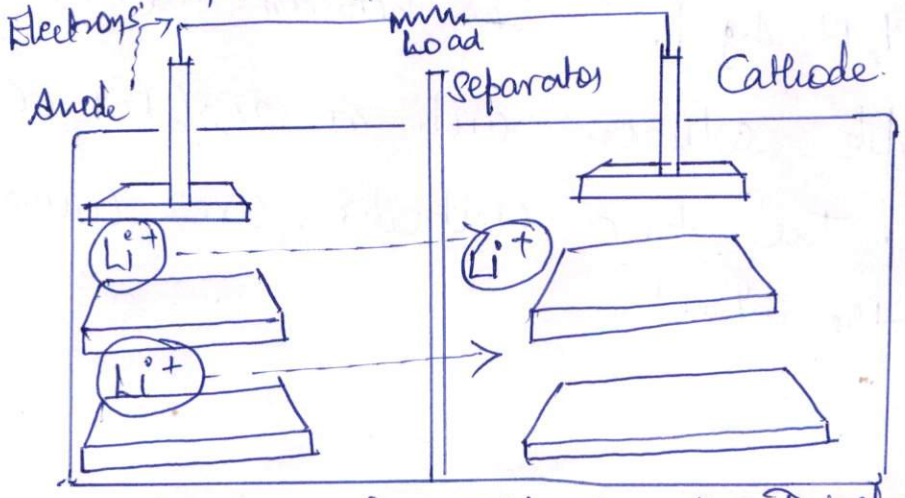


Fig:- Lithium ion during charging

Discharging

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

$$Li_{1-x}CoO_2 + C_{Li} \longrightarrow LiCoO_2 + C$$



Lithium ion cell during Discharging

Uses.
It is used in cell phone, note PC, LCV, TV semiconduc-tor driven, audio etc.

Q 6(a) Explain construction and working principle of H_2-O_2 fuel cell. Leive advantages and application of fuelcells

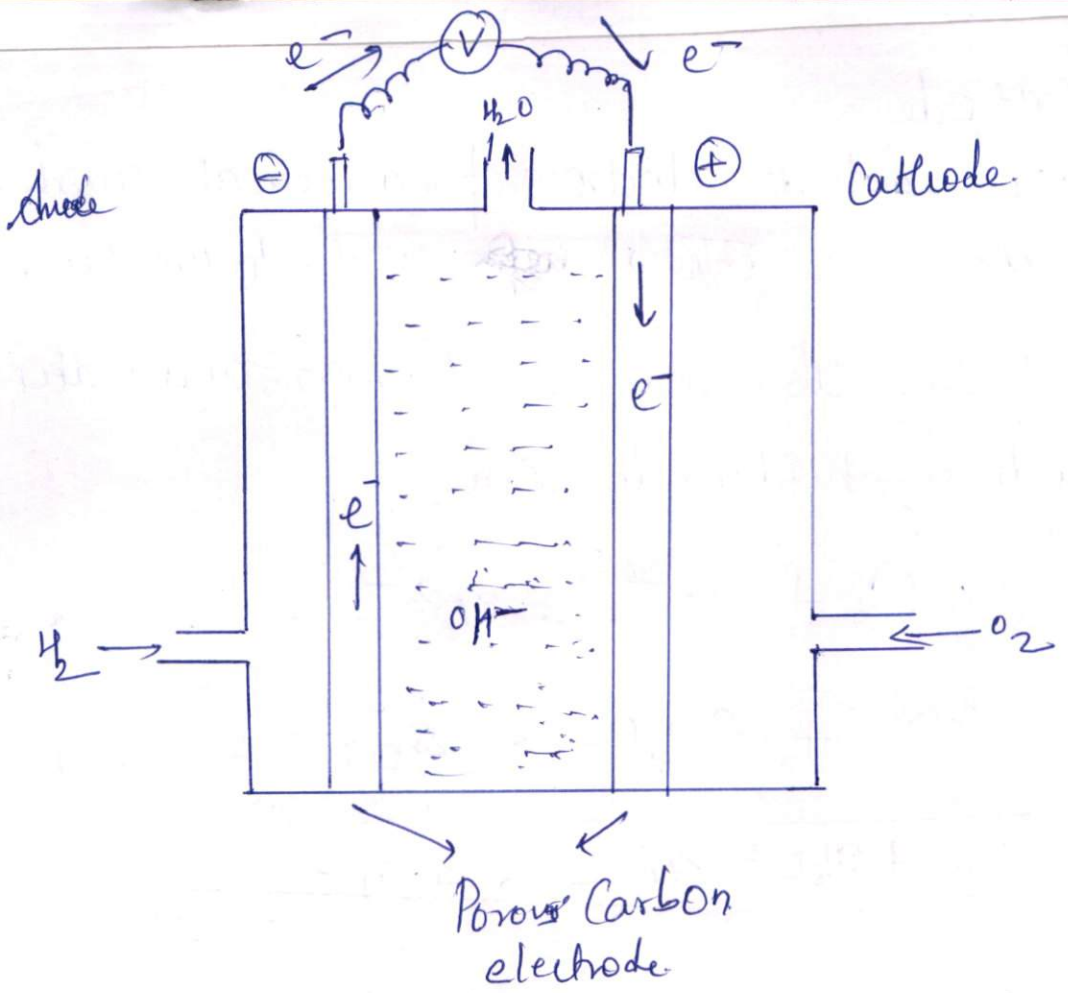
(b) Discuss electrochemical series and its important application.

A6(a) Hydrogen and Oxygen fuel cell

Hydrogen - oxygen fuel cell is the simplest and most successful fuel cell in which the fuel - hydrogen and the oxidiser oxygen and the liquid electrolyte are continuously passed through the cell.

Description

It consist of two porous electrodes anode and cathode. These porous electrode are made of Compressed carbon containing a small amount of Catalyst [Pt, Pd, Ag]. In between the two electrode an electrolyte solution such as 25% KOH or NaOH is filled. The two electrodes are connected through the voltmeter.



Working: Hydrogen the fuel is bubbled through the anode compartment where it is oxidised. the Oxygen (oxidiser) is bubbled through the cathode where it is reduced.

At anode

Hydrogen gas passed through the anode is Oxidised with the liberation electrons which then combine with hydroxide ion to form water

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

$$2H^+ + H_2O \longrightarrow$$

$$2H^+ + 2OH^- \longrightarrow 2H_2O$$

Multiply by 2 $\quad H_2 + 2OH^- \longrightarrow 2H_2O + 2e^-$

$$2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$$

At Cathode.

The ~~electrode~~ electrons produced at anode passthrough the external wire to the cathode where it is absorbed by Oxygen and water to produce hydroxide ions

$$O_2 + 4e^- \longrightarrow 2O^{2-}$$

$$2O^{2-} + 2H_2O \longrightarrow 4OH^-$$

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

Over all Cell reaction:-

At anode: $2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$

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

$$2H_2 + O_2 \longrightarrow 2H_2O$$

Applications:- H_2-O_2 fuel cell are used as auxillary energy source in space vehicles, Submarines or other military vehicles

* Incase of H_2-O_2 fuel cell the product of water is proved to be a valuable source of fresh water by the astronauts.

A 6(b) Electrochemical Series

When the various electrode (metal) are arranged in the order of their increasing values of standard reduction potential on the hydrogen scale, then the arrangement is called Electrochemical series.

Eg.

Electrode	E^0 volts
$Li^+/Li \rightarrow$	-3.01
$Mg^{2+}/Mg \rightarrow$	-2.37
$Zn^{2+}/Zn \rightarrow$	$+0.76$
$H^+/H_2 \rightarrow$	$0.00\ V$
$Cu^{2+}/Cu \rightarrow$	$+0.34\ V$

Application of electrochemical series

1. Calculation of Standard EMF of cell.

The standard emf of a cell (E^0) can be calculated if the standard electrode potential value are known using the following relation

$$E^0_{cell} = E^0_{RHE} - E^0_{LHE}$$

2. Relative ease of Oxidation or reduction

Higher the value of standard reduction potential greater is tendency to get reduced.

Fluorine has higher positive value of Standard reduction potential (+2.87V) and shows higher tendency towards reduction.

(ii) The lithium has highest negative value (−3.01 V) and shows higher tendency towards oxidation.

Displacement of one element by the other

Metal which lie higher in the emf series can displace those elements which lie below them in the series

For eg. We may known whether Cu will displace Zn from the solution or vice-versa.

Standard Red potential of Cu & Zn

$= -0.76V$

$E^\circ_{Cu^{2+}/Cu}$ $+0.34$ $E^\circ_{Zn^{2+}/Zn}$

So Cu^{2+} has a great tendency to acquire Cu form, than Zn^{2+} has for acquiring Zn form.

Determination of Standard free energy change

ΔG & equilibrium ~~reac~~ equilibrium constant for the reaction.

Standard electrode potential can also be used to determine the Standard free energy change (ΔG) and equilibrium constant (K) for the reaction

$$-\Delta G^\circ = RT \ln K = 2.303\, RT \log K$$

$$\log K = \frac{-\Delta G^\circ}{2.303RT}$$

$$= \frac{nFE^\circ}{2.303RT} \qquad [-\Delta G = nFE)$$

From the value of E° the equilibrium constant for the cell reaction can be calculated.

Predicting Spontaneity (or) feasibility of Redox Reactions

Q7. [a] What is cracking? Explain Fixed bed Catalytic Cracking with a neat sketch?

[b.] Explain proximate analysis of coal and give its significance

[c] Define HCV and LCV

A7 [a] Cracking is defined as "the decomposition of bigger hydrocarbon molecules into simple low boiling hydrocarbons of lower molecular weight e.g.

$$C_{10}H_{22} \xrightarrow{\text{Cracking}} C_5H_{12} + C_5H_{10}$$

(Decane) (n-pentane) (Pentene)

B.p = 174°C B.p = 36°C

Fixed bed Catalytic Cracking: The oil vapours are heated in a pre-heater to cracking temperature (420-450°C) and then forced through a catalytic chamber (containing Artificial Clay mixed with Zirconium oxide) maintained at 425-450°C and 1.5 kg/cm^2 pressure. During their passage through the tower about 40% of the charge is converted into gasoline and about 2-4% Carbon is formed. The latter gets adsorbed on the catalyst bed. The vapours produced are then passed through a fractionating column, where heavy oil fraction condense. The vapours are often then led through a cooler, where some of gases are condensed along with gasoline and uncondensed gases moves on. The gasoline containing some dissolved gases is sent to stabilizer where the dissolved gases are removed and pure gasoline is obtained.

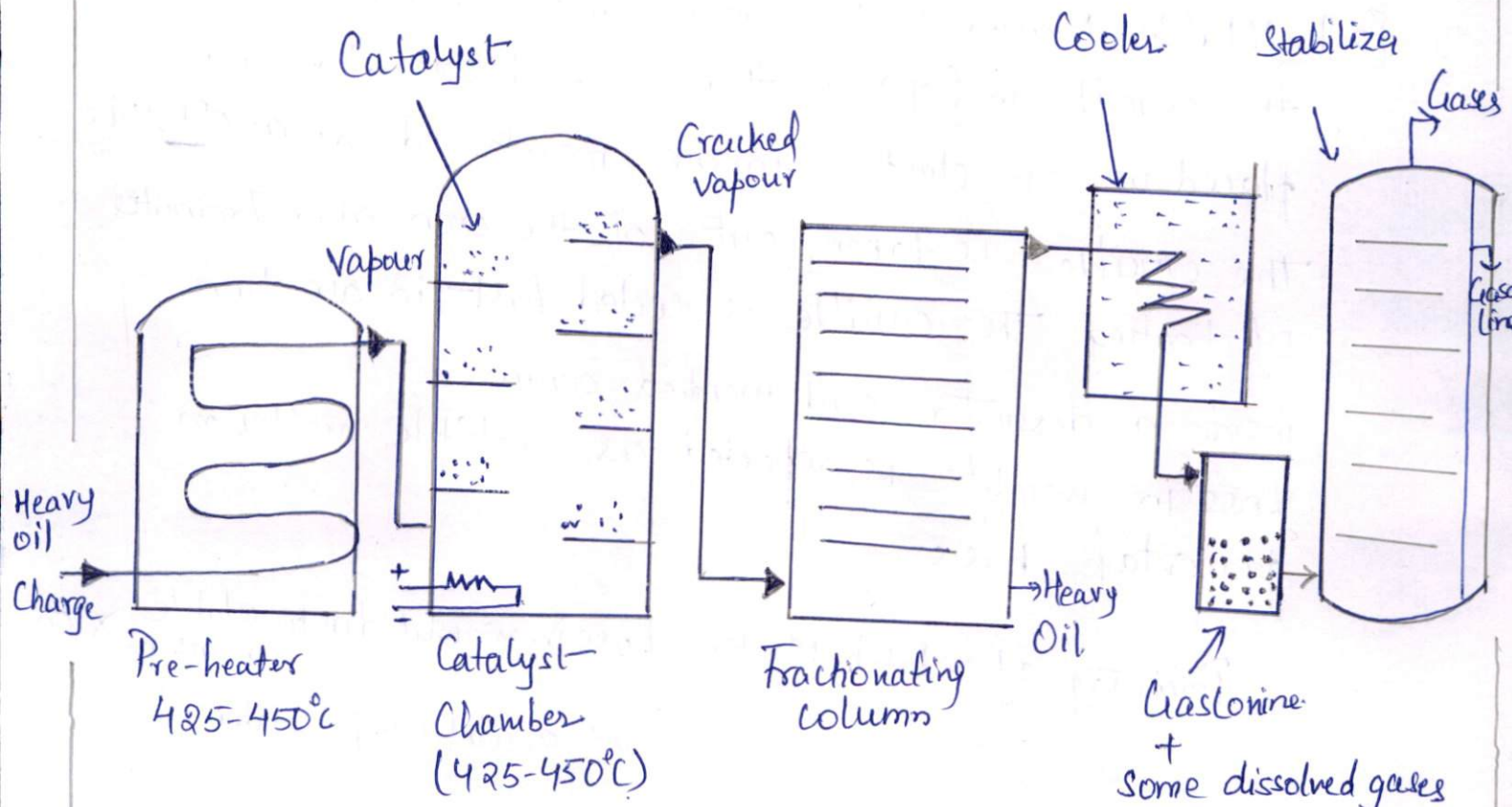


Fig: Fixed bed Catalytic Cracking

A7[b] Proximate analysis of coal.

Proximate analysis involve in the following determination

[1] Moisture: About 1g of fine powdered air-dried coal sample is weighed in crucible. The crucible is placed inside an electric hot air-oven, maintained at 105°-110°C. The crucible is allowed to remain in oven for 1 hour and then taken out cooled in dessicator and weighed.

Loss in weight is reported as moisture

$$\text{Percentage of Moisture} = \frac{\text{Loss in weight}}{\text{Wt. of coal taken}} \times 100$$

[2] Volatile Matter:- The dried sample of coal left in the crucible in (1) is then covered with lid and placed in an electric furnace maintained at 925° ± 20°C. The crucible is taken out of the oven after 7 minutes of heating. The crucible is cooled first in air, then inside a dessicator and weighed again. Loss in weight is reported as volatile matter on percentage basis

$$\text{Percentage of Volatile Matter} = \frac{\text{Loss in weight due to volatile matter}}{\text{Wt. of coal sample taken.}} \times 100$$

[3] Ash: The residual coal in the crucible in (2) is the heated without lid in a muffle furnace at 700 ± 50°C for ½ hour. The crucible is then taken out, cooled first in air then in dessicator and weighed. Heating, cooling and weighing is repeated till a constant weight is obtained. The residue is reported as ash on a percentage basis.

Thus percentage of Ash

$$= \frac{\text{Wt. of ash left}}{\text{Wt of coal taken}} \times 100$$

[4] Fixed Carbon: Percentage of Fixed Carbon

$$= 100 - \% \text{ of (Moisture + Volatile matter + ash)}$$

A7 [c] High Calorific Value:- "The total amount of heat produced, when unit mass/volume of the fuel has been burnt completely and the products of combustion has have been cooled to room temperature" (i.e. 15°C or 60°F)

Lower or net Calorific Value:- The net heat produced, when unit mass/ volume of fuel is burnt completely and the products are permitted to escape.

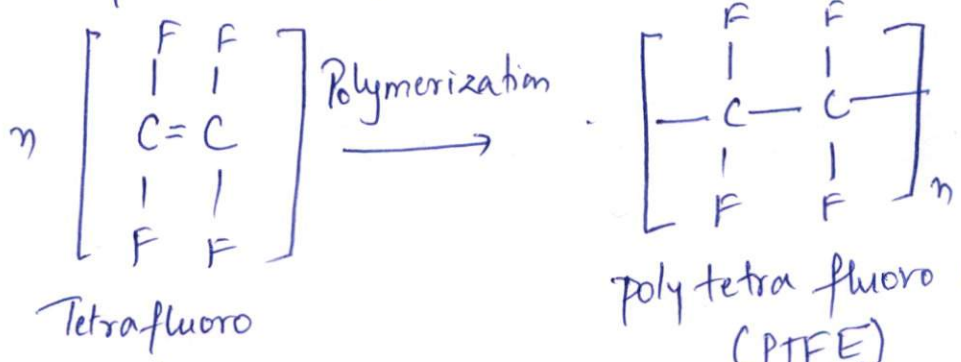
LCV = HCV - Latent heat of water vapour formed

= HCV - Mass of Hydrogen × 9 × Latent heat of steam.

Q8.(a) Explain preparation, properties and engineering application of Teflon, Bakelite and Dacron.

[b]. What is Cathodic protection. How metals are protected by Sacrificial Anodic and Impressed current Cathodic method.

A8 [a] Preparation of Teflon. PTFE or TEFLON is obtained by polymerization of water-emulsion of tetrafluoro ethylene under pressure in presence of benzoyl peroxide as catalyst.



Tetrafluoro ethene

poly tetra fluoro ethene (PTFE)

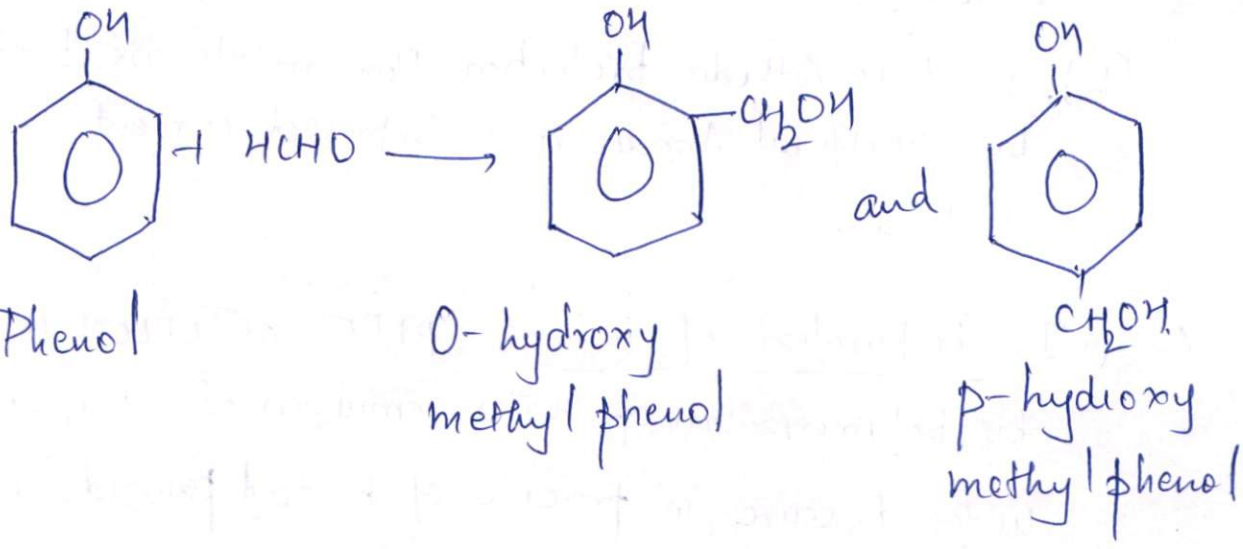
Properties: Teflon extreme toughness, high softening point is due to strong attractive forces.

2) High chemical resistance towards all chemicals
3) High density, waxy touch.
4) Very low coefficient of friction
5) Good Electrical and Mechanical properties

Bakelite :-

Bakelite is prepared by condensing phenol with formaldehyde in presence of acidic / alkaline catalyst.

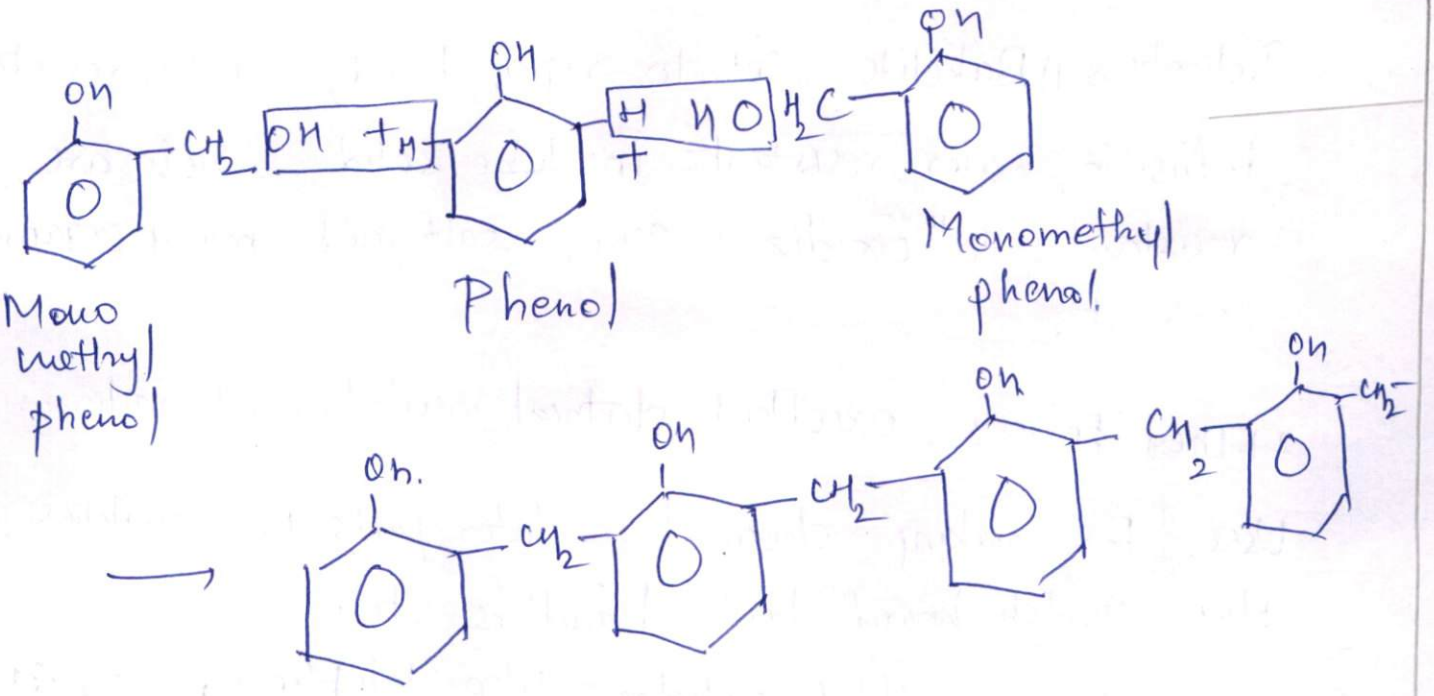
The initial reaction result in formation of o and p-hydroxy methyl phenol which react to form linear polymer Novolac.



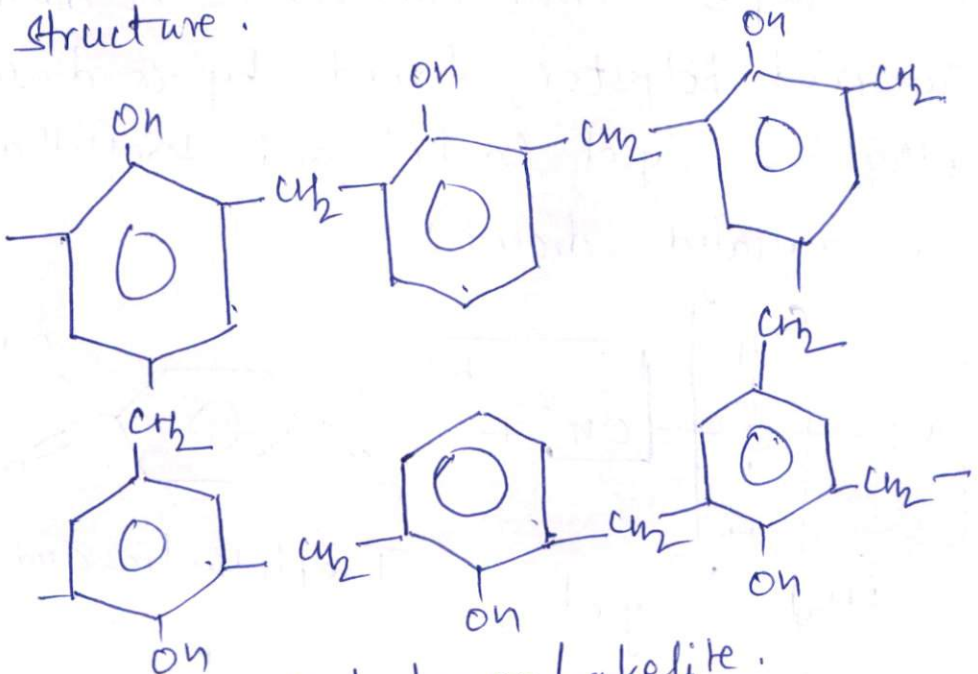
Phenol

O-hydroxy methyl phenol

p-hydroxy methyl phenol



During moulding hexamethylene tetramine $[(CH_2)_6N_4]$ are added. The addition of hexamethyle tetramine provide formaldehyde which convert soluble and fusible novolac into hard, infusible and insoluble solid of cross link structure.



Cross linked polymer bakelite.

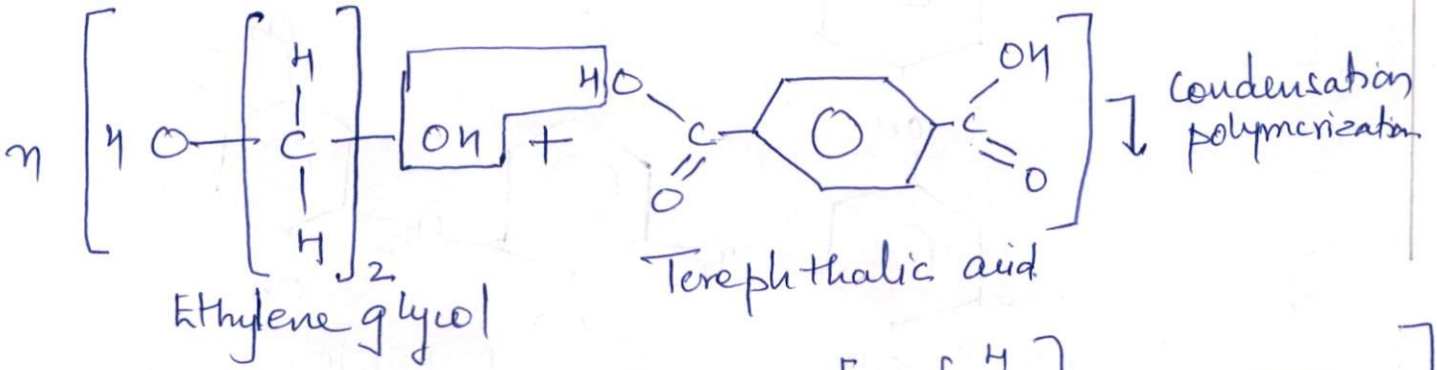
Properties. 1) Bakelite set to rigid, hard, scratch resistant, infusible, water resistant insolube solid which are resistant to non-oxidizing acid, salt and many organic solvent.

2) They posses excellent electrical insulating character.

Uses: For making electrical insulator parts like switches plug, switch board heat-handlers etc.

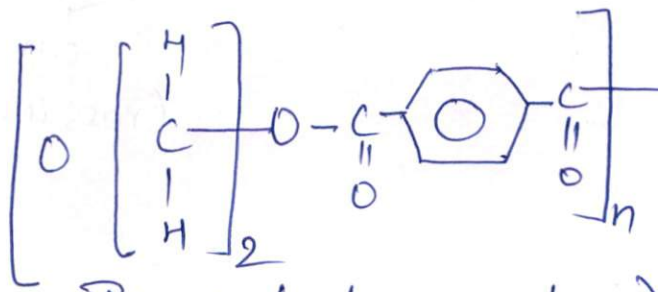
2) For making moulded articles like telephone parts, cabinet for radio and television.

Dacron: A polyester resin are the condensation products of dicarboxylic acid with dihydroxy alcohols. For example terene (or terylene or dacron) is a saturated polyester, formed by condensation of ethylene glycol (a diol) and terephthalic acid (a saturated diacid)



Ethylene glycol

Terephthalic acid



Polyester (or terene or dacron)

Properties: 1) Good fibre forming material
2) High stretch resistance, high crease
3) PET is highly resistant to mineral and organic acids.

Uses: 1) It is mostly used for making synthetic fibres like terylene, dacron etc.
2) For blending with wool to provide better crease and wrinkle resistance
3) As glass reinforcing material in safety helmet, aircraft battery etc.
4) Blending with wool

A8[b]. Cathodic Protection: — The principle involved in this method is to force the metal to be protected to behave like a cathode, there by corrosion does not occur.

There are two types of Cathodic protection:

(i) Sacrifical anodic protection method: — In this protection method the metallic structure to be protected is connected by a wire to a more anodic metal, so that all the corrosion is concentrated at this more active metal. The more active metal itself get corroded slowly while the parent structure (cathodic) is protected. The more active metal so employed is called "SACRIFICAL ANODE".

The corroded sacrifical anode block is replaced by fresh one when consumed completely

Commonly employed sacrifical anodes are Magnessium, zinc aluminium and their alloys.

Important Application of Sacrific Anodic method include protection of Buried pipelines, underground cables, marine structures, water tank etc.

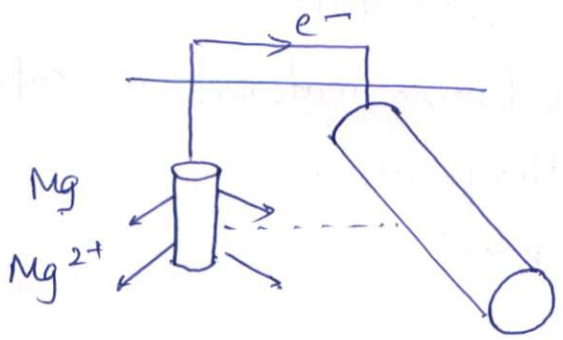
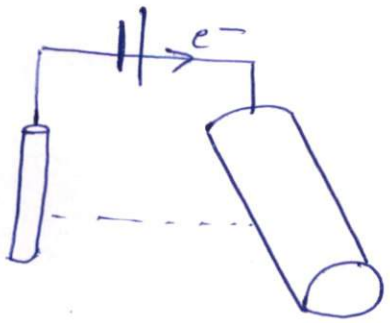


Fig: Sacrificial Anodic protection.

(ii) Impressed current Cathodic protection:- In this method an impressed current is applied in Opposite direction to nullify the corrosion current and convert the corroding metal from anode to cathode. Usually, the impressed current is derived from a direct current (like battery or rectifier on a.c. line with an insoluble anode. A sufficient d.c. current is applied to an insoluble anode buried in the soil and connected to the metallic structure to be protected. This type of cathodic protection has been applied to open water box coolers, water tanks buried oil or water pipes, condensers transmission line towers, marine piers, laid up ship etc.



In impressed current Cathodic protection electrons are supplied from an external cell so that the object itself become cathodic and is not oxidized