Module - 1

1 a) Define standard reduction potential and derive Nernst equation for single electrode potential.(6M)

### Standard reduction potential

It is a measure of the electrode to undergo reduction when in contact with its Ionic solution at unit active mass of ions, at 298 K and at 1 atmospheric gas pressure if it is a gas electrode.

Derivation of Nernst equation

In 1889, Nernst derived an equation which tells the relationship amongst three quantities and they are —

1) Electrode potential
2) System temperature
3) Molar concentration of Ionic species.

Nernst considered the spontaneous reduction electrode reaction;

1M

$$M^{n+} + ne^- \longrightarrow M$$
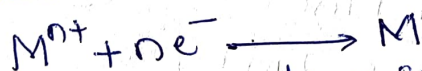
When this reaction is spontaneous, there must be decrease in free energy of the system $(-\Delta G)$. The decrease in free energy of the system is equal to maximum energy obtainable from the system (W_{max})

$$-\Delta G = W_{max}$$

W_{max} can be written as $(nF) \times E$

$$\therefore \quad -\Delta G = +nFE$$

$$\Delta G = -nFE \quad \underline{\hspace{2cm}} (1)$$

where, nF is the coulombs of charge that is transferred during the reaction

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'n' is the number of moles of electrons transferred in the reaction.

'F' is one Faraday of electricity ($96500 \, C \, mol^{-1}$)

'E' is the electrode potential

For reactants and products of the reaction at unit activity, standard change in free energy

$$\Delta G^\circ = -nFE^\circ \quad\text{—————}\quad (2)$$

where,

'E°' is standard electrode potential

change in free energy is related to equilibrium constant of the reaction, K_{eq}, by Van't Hoff reaction isotherm:

$$\Delta G = -RT \ln K_{eq} + RT \ln Q \quad\text{—————}\quad (3)$$

where, Q is the reaction quotient

R is molar gas constant

T is the temperature of the system expressed in kelvin

Also, standard change in free energy,

$$\Delta G^\circ = -RT \ln K_{eq}$$

$$\therefore \quad \Delta G = \Delta G^\circ + RT \ln Q$$

$$= \Delta G^\circ + RT \ln \frac{[M]}{[M^{n+}]} \quad\text{—————}\quad (4)$$

By definition, $[M] = 1$.

Substitution of ΔG and ΔG° in equation (4) gives

$$-nFE = -nFE^\circ + RT \ln \frac{1}{[M^{n+}]} \quad\text{—————}\quad (5)$$

or

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]} \quad\text{—————}\quad (6)$$

or

$$E = E^\circ + \frac{2.303 RT}{nF} \log [M^{n+}] \quad\text{—————}\quad (7)$$

Substituting the values of $R = 8.314 \, J \, mol^{-1} K^{-1}$

$F = 96500 \, C \, mol^{-1}$

$$E = E° + \frac{0.0591}{n} \log [M^{n+}] \text{ at } 298 K \text{—————(8)}$$

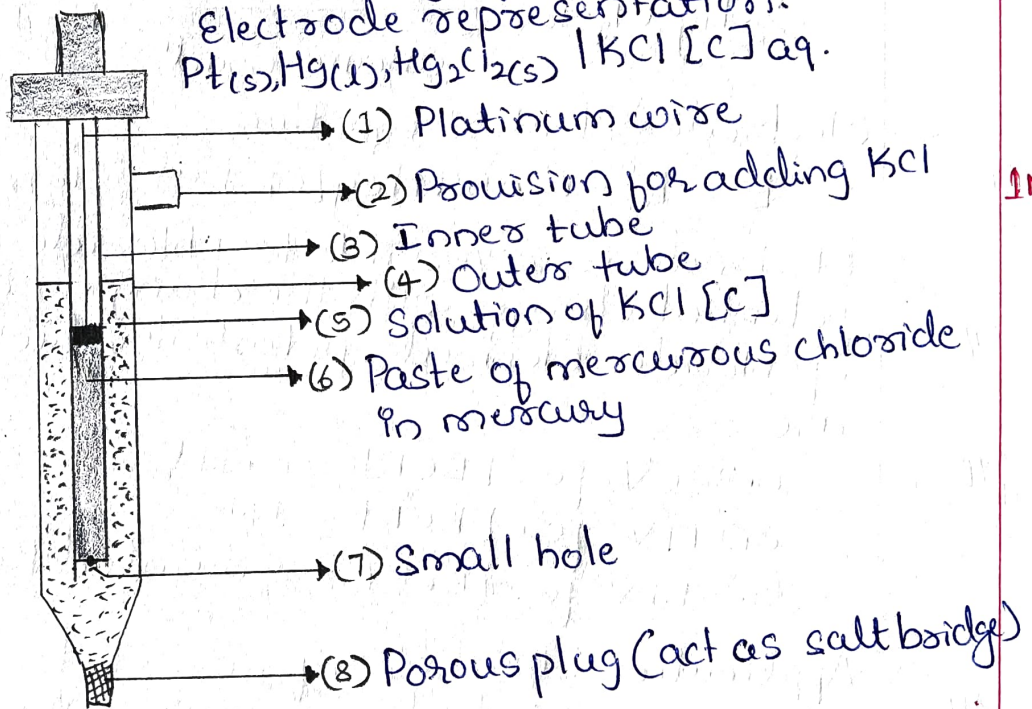Equation (7) & (8) is suggested to be Nernst equation for electrode potential.

1b. What is a Reference electrode? Explain construction and working of Calomel electrode. (7M)

Reference electrode:

An electrode of known potential, relative to which, the electrode potential of test electrode or unknown electrode is determined is reference electrode. Ex: SHE, Calomel, Ag-AgCl   1M

Construction and working of Calomel electrode

Electrode representation:
$Pt_{(s)}, Hg_{(l)}, Hg_2Cl_{2(s)} | KCl [c]$ aq.

→ (1) Platinum wire
→ (2) Provision for adding KCl   1M
→ (3) Inner tube
→ (4) Outer tube
→ (5) Solution of KCl [c]
→ (6) Paste of mercurous chloride in mercury

→ (7) Small hole

→ (8) Porous plug (act as salt bridge)

Construction
→ The electrode consists of two concentric glass tubes namely Inner and outer tube.
→ Inner tube contains platinum wire and a paste   1M of mercurous chloride in mercury
→ The outer tube contains solution of KCl
→ A little of mercury along with platinum wire in the inner tube helps the external contacting of electrode

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→ A small hole at the bottom of the outer tube with a porous plug establish the contact with external analyte.

→ Small hole at the bottom of inner tube establishes contact with KCl in the outer tube

→ There is provision for adding more KCl.

Working

Depending on the potential of the electrode with which the calomel electrode is connected, calomel electrode acts as cathode or anode. Reactions when the electrode acts as cathode or anode are given below

$$\frac{1}{2} Hg_2Cl_2 + e^- \xrightarrow[\text{anodic Oxid}^n]{\text{Cathodic red}^n} Hg + Cl^-$$ 1M
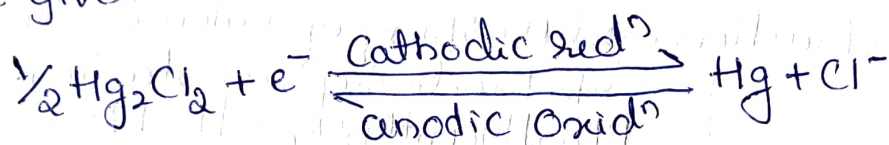
→ Electrode potential equation   1M

$$E = E^\circ - 0.0591 \log[Cl^-] \text{ at } 298K$$

→ Electrode is reversible to chloride ions; potential changes with the changing concentration of chloride. Electrode potential values at 298 K are —

  0.336 V for [KCl] = 0.1N   1M
  0.279 V for [KCl] = 1N
  0.244 V for [KCl] = saturated KCl

→ Application: Used as reference electrode in potentiometric estimations

→ Advantages: Construction is simple, it is portable obeys Nernst equation   1M

→ Limitations:
 * Calomel electrode cannot be used beyond a temperature of 60°C
 * Mercury employed in the construction, poses pollution problem

1c. Define cell potential. Give the cell representation, cell reactions and calculate the cell potential of the cell consists of Li and Cu electrodes dipped in 0.1M LiCl and 0.5M $CuSO_4$ solutions at 25°C. Given $\varepsilon^0_{Li} = -3.05V$ and $\varepsilon^0_{Cu} = 0.34V$ (7M)

Soln:

Cell potential

It is the measure of the potential difference between two half cells in an electrochemical cell. It is mathematically expressed as — 1M

$$E_{cell} = \varepsilon_R - \varepsilon_L$$

where ε_R = reduction electrode side (cathode)

ε_L = Oxid^n electrode side (anode)

Given: $\varepsilon^0_{Li} = -305V$ LiCl = 0.1M

$\varepsilon^0_{Cu} = 0.34V$ $CuSO_4 = 0.5M$ 1M

$T = 25°C + 273 = 298K$

$\varepsilon^0_{Li} < \varepsilon^0_{Cu}$

∴ Li act as anode and Copper act as cathode

Cell representation

$$Li_{(s)} | LiCl (0.1M) || CuSO_4 (0.5M) | Cu$$ 2M

Anodic oxidation $Li \longrightarrow Li^+ + e^- \times 2$

Cathodic reduction $Cu^{2+} + 2e^- \longrightarrow Cu \times 1$

Cell reaction $2Li + Cu^{2+} \rightleftharpoons 2Li^+ + Cu$ 1M

$$\boxed{n = 2}$$
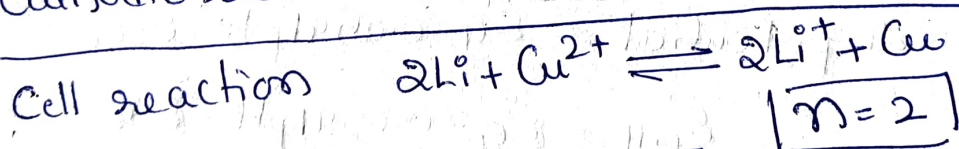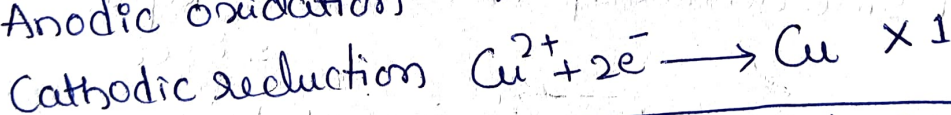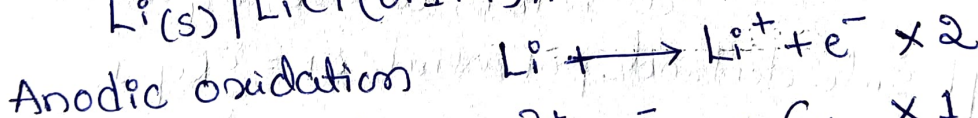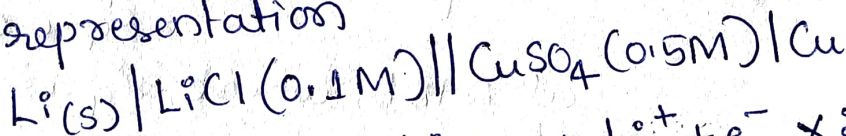
$$\varepsilon = \varepsilon^0 + \frac{2.303RT}{nF} \log \frac{[Cu^{2+}]}{[Li^+]^2}$$ 1M

$$= \{\varepsilon_R - \varepsilon_L\} + \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log \frac{[0.5]}{[0.1]^2}$$

$$= \{0.34 + 3.05\} + \frac{0.0591}{2} \log \frac{[0.5]}{[0.01]}$$

$$= \{3.39\} + 0.02955 \log 50$$

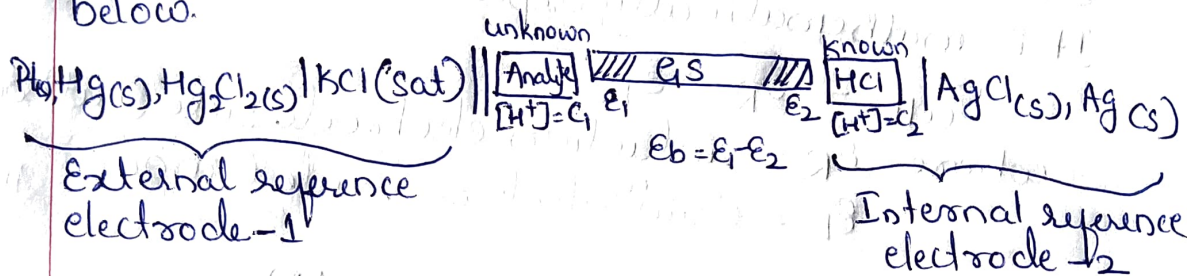$$= 3.39 + 0.05 \implies 3.44V \quad \boxed{\varepsilon = 3.44V}$$

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2a. Define ion selective electrode. Explain the determination of pH using glass electrode (6M)

→ **Ion selective electrode:**
Electrode, which responds selectively to the presence of specific ion ignoring all other ions, is ion selective electrode.

→ **Determination of pH using glass electrode**
A cell is constructed by coupling glass electrode or silver chloride electrode as shown below.

$$Pb, Hg_{(s)}, Hg_2Cl_{2(s)} | KCl(sat) \| \underset{[H^+]=C_1}{\underset{\text{Analyte}}{\text{Analyte}}} \overset{\text{unknown}}{\varepsilon_1} \quad \overset{\varepsilon_b=\varepsilon_1-\varepsilon_2}{GS} \quad \underset{[H^+]=C_2}{\underset{\varepsilon_2}{HCl}} \overset{\text{known}}{|AgCl_{(s)}, Ag_{(s)}}$$

External reference electrode - 1

Internal reference electrode - 2

glass membrane electrode or pH electrode.

Cell potential is calculated as
$$E_{cell} = E_R - E_L$$
Right side electrode potential $E_R = E_{e_1}$
$$= E_{e_1}^\circ - 0.0591 \, pH$$
at 298 K, where, $E_{e_1}^\circ$ is constant
Left side electrode potential, $E_L = E_{Ref-1}$
$$= E_{SCE}$$

Cell potential $= E_{e_1}^\circ - 0.0591 pH - E_{SCE}$

$$E_{cell} = E_{e_1}^\circ - 0.0591 pH - E_{SCE}$$

$$0.0591 pH = E_{e_1}^\circ - E_{SCE} - E_{cell}$$

$$pH = \frac{E_{e_1}^\circ - E_{SCE} - E_{cell}}{0.0591}$$

$$= \frac{K' - E_{cell}}{0.0591}$$

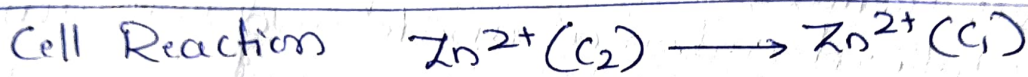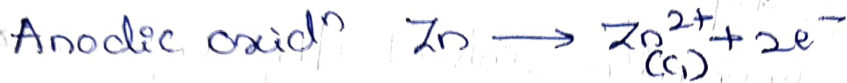where, K' is glass membrane electrode assembly constant. Thus pH is measured using glass electrode.

2b. Derive an equation for potential of concentration cell. and calculate the potential of following cell at 25°C $Ag|AgNO_3 (0.005M) || AgNO_3 (0.5M)|Ag (TM)$

Derivation

Electrolytic cell concentration is formed when electrodes made of same chemical substance are coupled but immersed in electrolytic solutions of different concentrations. $\qquad$ ·1M

Ex: $Zn|ZnSO_4 (C_1) || ZnSO_4 (C_2)| Zn$ provided $C_2 > C_1$

Anodic oxid^n $Zn \longrightarrow Zn^{2+}_{(C_1)} + 2e^-$ $\qquad$ 1M

Cathodic red^n $Zn^{2+}_{(C_2)} + 2e^- \longrightarrow Zn$

Cell Reaction $\quad Zn^{2+}(C_2) \longrightarrow Zn^{2+}(C_1)$

Cell potential is calculated as

$\mathcal{E}_{cell} = \mathcal{E}_R - \mathcal{E}_L$ $\qquad$ 1M

$= \left\{ \mathcal{E}_R^\circ + \dfrac{2.303RT}{nF} \log C_2 \right\} - \left\{ \mathcal{E}_L^\circ + \dfrac{2.303RT}{nF} \log C_1 \right\}$

$= \left\{ \mathcal{E}_R^\circ - \mathcal{E}_L^\circ \right\} + \dfrac{2.303RT}{nF} \log \dfrac{C_2}{C_1}$

$= \dfrac{2.303RT}{nF} \log \dfrac{C_2}{C_1}$

Given:

$T = 25°C \Rightarrow 25 + 273 \Rightarrow 298K$ $\qquad$ 2M

$Ag|AgNO_3 (0.005M) || AgNO_3 (0.5M)|Ag$
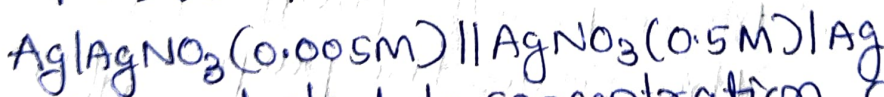
This is an electrolyte concentration cell because $C_2 > C_1$ $\qquad$ 2M

$\therefore \mathcal{E}_{cell} = \dfrac{2.303RT}{nF} \log \dfrac{C_2}{C_1}$

$= \dfrac{2.303 \times 8.314 \times 298}{1 \times 96500} \log \dfrac{[0.5]}{[0.005]}$

$= 0.0591 \times \log 100$

$= 0.0591 \times 2$

$= 0.1182 V$

Anodic oxid^n
$Ag \longrightarrow Ag^+_{(0.005M)} + e^-$

Cathodic red^n
$Ag^+_{(0.5M)} + e^- \longrightarrow Ag$

Cell Rxn
$Ag^+_{(0.5M)} \longrightarrow Ag^+_{(0.05M)}$

$\boxed{n = 1}$
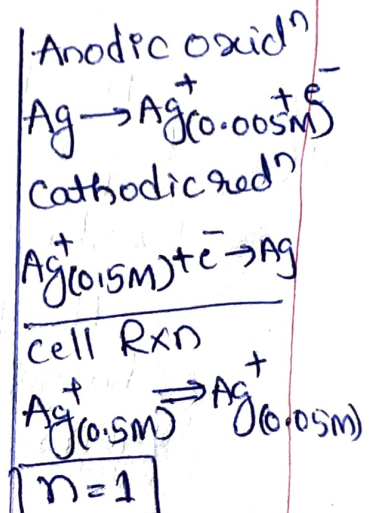
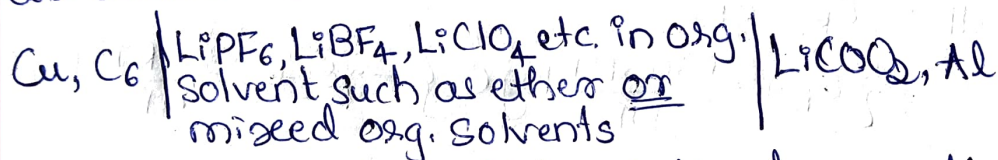**2c.** Explain construction and working of Li-ion cells. Mention its applications (7M)

Li-ion battery

These are available with loading of $LiCoO_2$, $LiMnO_2$, $LiNiO_2$ etc. as cathodic material. More common cell with $LiCoO_2$ loading is described.

1M

→ ### Construction

Li-ion cell when in charged condition is schematically represented as

$$Li_x C_6 \mid Li\text{-salt (in mixed org. solvents)} \mid Li_{1-x} Co^{(+3)}_{1-x} Co^{(+4)}_x O_2$$
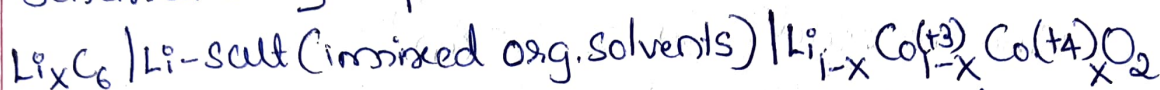
However, actual construction refers to loading of crystallised carbon at anode and lithium cobalt oxide at cathode. Copper and aluminium are used as current collectors.

M

$$Cu, C_6 \left| \begin{array}{c} LiPF_6, LiBF_4, LiClO_4 \text{ etc. in org.} \\ \text{solvent such as ether } \underline{or} \\ \text{mixed org. solvents} \end{array} \right| LiCoO_2, Al$$

2M

Anodic material: highly crystallised specialty carbon (graphite with layer structure)

Cathodic material: $LiCoO_2$ - Li Cobalt oxide

Electrolyte: $LiPF_6, LiBF_4, LiClO_4$ etc. in organic solvent such as ether $\underline{or}$ mixed organic solvents.

Separator: Micro-porous polypropylene is used This serves the purpose of an insulated separator between the electrodes and as electrolyte absorbent

The battery needs to be taken for charging before it is made available for discharge.

Working:

The principle behind the working is that, during charge, lithium ion in the cathode ($LiCoO_2$) moves from layer to layer in crystallised carbon anode.

charge balancing in cathode is ensured by oxidation of $Co(+3)$ to $Co(+4)$. Electrons released by such oxidation are transferred to anode through external circuit. During discharge, lithium ions from anode move to the cathode and $Co(+4)$ is reduced to $Co(+3)$.

Working of the Li-ion cell is schematically shown below
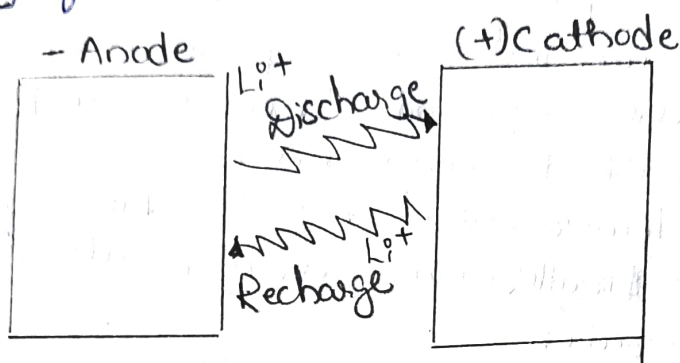
    – Anode   (+) Cathode

Before charging C_6 $LiCoO_2$

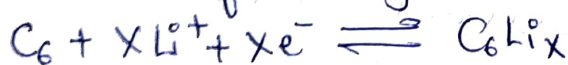After charging C_6Li_x $Li^+_{1-x} Co(+3)_{1-x} Co(+4)_x O_2$.

Charging Reactions:

At anode of electrolytic cell (cathode of galvanic cell)
$$LiCoO_2 \rightleftharpoons Li^+_{1-x} Co^{3+}_{1-x} Co^{+4}_x O_2 + xLi^+ + xe^-$$
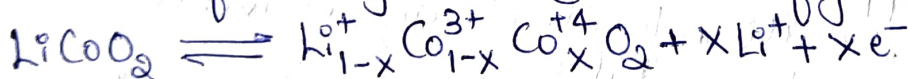
At cathode of electrolytic cell (anode of galvanic cell)
$$C_6 + xLi^+ + xe^- \rightleftharpoons C_6Li_x$$

Discharge reactions:

At anode: $C_6Li_x \rightleftharpoons C_6 + xLi^+ + xe^-$

At cathode: $Li^+_{1-x} Co^{3+}_{1-x} Co^{+4}_x O_2 + xLi^+ + xe^- \rightleftharpoons LiCoO_2$

Cell Rxn $\quad C_6LiCoO_2 \rightleftharpoons C_6Li_x + Li^+_{1-x} Co^{3+}_{1-x} Co^{+4}_x O_2$
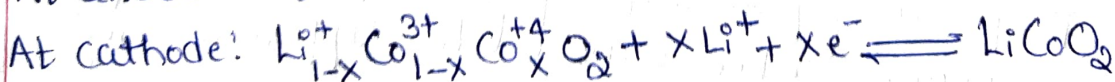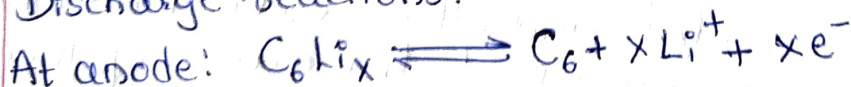
Cell potential : 3.7V

Applications: Used in calculators, cameras, camcorders cellular phones, medical instruments portable radios, television sets Laptop computers etc.

Module 2

3a. Briefly explain the effect of following factors on rate of corrosion
i) The ratio of Anodic and cathodic areas
ii) Nature of corrosion product
iii) pH of the medium (6M)

→ The ratio of Anodic and cathodic areas

Corrosion rates are dependent on the relative surface areas of anode and cathode. Relatively smaller cathodic area and larger anodic area result in lower corrosion rates. Larger cathodic area and smaller anodic area result in higher corrosion rates.   1M

   Ex: Steel water tank with a small brass tap anodic steel tank will hardly exhibit corrosion effects.   1M

   However, when the relative surface area of cathode is larger, larger cathodic current developped is countered by small anodic area; which, result in localised, aggressive corrosion of the anodic metal.

   Ex: Brass water tank with steel tap; steel tap exhibits severe corrosion

→ Nature of corrosion product

   Some metals and alloys exhibit an inherent property of forming a protective coating of their compounds when exposed to different media.   1M
when the corrosion product film over the object metal surface is
i) Inert to metal and medium
ii) Continuous (non porous)
iii) Adherent to metal surface, it starts acting as barrier between metal and medium. Further corrosion of the metal is prevented   1M

Some metal and medium combinations are known to give protective coatings:
i) mild steel – conc; H_2SO_4
ii) Aluminium – fuming HNO_3
iii) lead – dil H_2SO_4

→ **PH of the medium**

Lower pH suggests the acidic medium and many of the metals undergo severe corrosion except those with higher reduction potentials. Higher pH represents alkalinity and many metals exhibit resistance. However, too alkalinity may lead to corrosion of the metal. [1M]

Iron exhibits lower rate of corrosion in a medium of pH = 5.0 in the absence of O_2. At the same time pH, with dissolved O_2, it exhibits relatively higher corrosion rate.

At pH value below 4.5, it exhibits aggressive corrosions irrespective of the presence of or absence of O_2. Metals are known to show minimized corrosion rates at certain pH values specific of the metal. Any higher or lower pH leads to increased rates of corrosion of the metals. [1M]

3b. Define corrosion of metals. Describe the electrochemical theory of rusting of iron. (7M)

Corrosion of metals

Destruction or disintegration of metals when exposed to the surrounding corrosive starting at their surface by either chemical or electrochemical means is metallic corrosion. [1M]

Electrochemical theory of corrosion

→ This corrosion is characterised by the formation of small galvanic cells due to heterogeneities
→ Part of metal acts as anode and another part cathode

Anodic part of the metal undergoes destruction by oxidation.
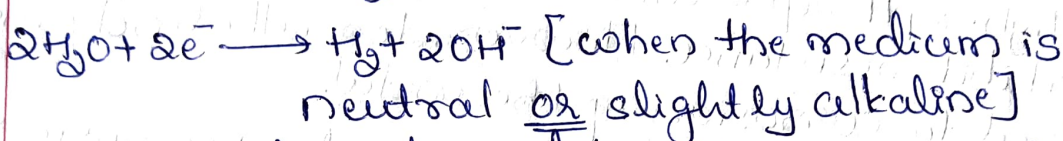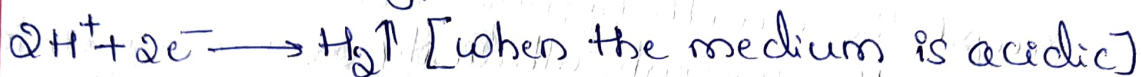
Steel undergoes corrosion by following reaction

Anodic oxidation reaction

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

1M

Reduction depends on the contents in the medium

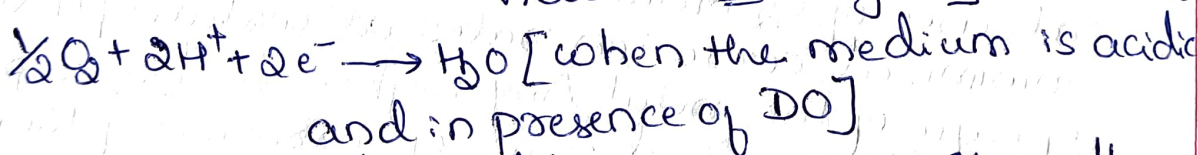Some important reactions are

→ H_2 evolution type

$$2H^+ + 2e^- \longrightarrow H_2\uparrow \quad [when \; the \; medium \; is \; acidic]$$

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^- \quad [when \; the \; medium \; is \; neutral \; or \; slightly \; alkaline]$$
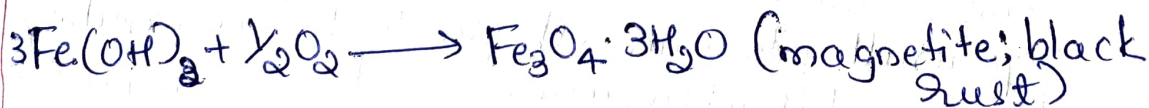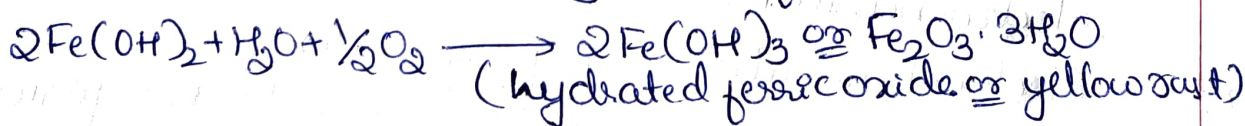
2M

It is characterised by the presence of large anodic area and small cathodic area. Corrosion is uniform and less aggressive. Higher the acidity of the medium, higher is the corrosion rate.

→ O_2 absorption type

$$\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^- \quad [when \; the \; medium \; is \; neutral \; or \; slightly \; alkaline]$$

$$\frac{1}{2}O_2 + 2H^+ + 2e^- \longrightarrow H_2O \quad [when \; the \; medium \; is \; acidic \; and \; in \; presence \; of \; DO]$$

1M
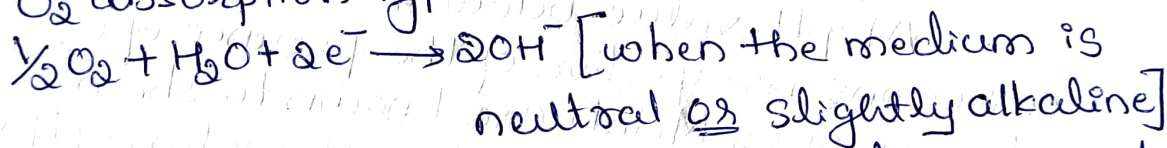
It is characterised by the presence of small anodic area and a large cathodic area. Corrosion is localised and very aggressive. Higher is the oxygen content in the medium, higher is corrosion rate. Ferrous hydroxide is formed as corrosion product. Excess of O_2 can oxidize it further to yellow rust or black rust.

2M

$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2 \; or \; FeO \cdot H_2O \\ (hydrated \; ferrous \; oxide)$$

$$2Fe(OH)_2 + H_2O + \frac{1}{2}O_2 \longrightarrow 2Fe(OH)_3 \; or \; Fe_2O_3 \cdot 3H_2O \\ (hydrated \; ferric \; oxide \; or \; yellow \; rust)$$

$$3Fe(OH)_2 + \frac{1}{2}O_2 \longrightarrow Fe_3O_4 \cdot 3H_2O \; (magnetite; \; black \; rust)$$
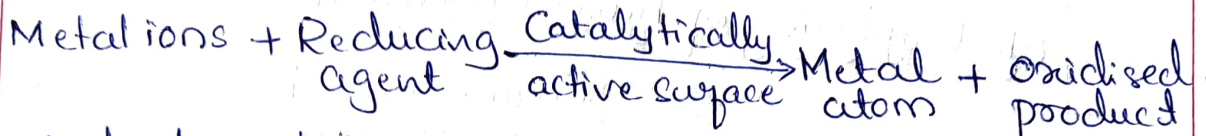
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3C. Define electroless plating and explain electroless plating of copper (7M)

Electroless plating

Deposition of metal or alloy over a conducting or non conducting substrate surface by chemical reduction of the metal ions by use of reducing agent and without the use of electrical energy is called electroless plating.

1M

$$Metal\ ions + Reducing\ agent \xrightarrow[\text{active surface}]{\text{Catalytically}} Metal\ atom + Oxidised\ product$$

Electroless plating of copper

Substrate surface needs to be cleaned by suitable cleaning methods (solvent degreasing, acid pickling, alkali pickling etc). However, when the object is non conducting or insulator material such as, plastics, PCBs, glass etc. it needs to be activated by treatment with acidified $SnCl_2$ and then with acidified $PdCl_2$.
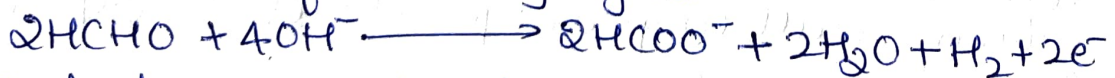
Following bath compositions are used for plating

4M

Constituents	Amount	Purpose
$CuSO_4$	12 g/L	Provides metal ions
H-CHO	8 g/L	Reducing reagent
Rochelle salt	14 g/L	Complexing agent
NaOH	15 g/L	Provides alkaline medium
EDTA	20 g/L	Exaltant & complexing agent
pH	11.0	
Temperature	25°C	

Control of metal concentration and pH are important

Reactions
Oxidation of Reducing agent
$$2HCHO + 4OH^- \longrightarrow 2HCOO^- + 2H_2O + H_2 + 2e^-$$

2M

Reduction over object surface
$$Cu^{2+} + 2e^- \longrightarrow Cu$$

Overall Reaction:
$$Cu^{2+} + 2HCHO + 4OH^- \longrightarrow Cu + 2HCOO^- + 2H_2O + H_2 \uparrow$$

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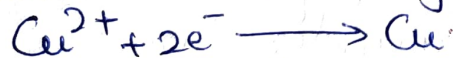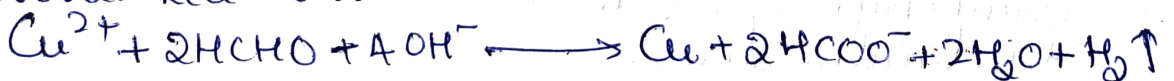
Applications
→ Establishing through-hole connections on double sided PCBs
→ For plating on non-conductors or as a base before electroplating

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4a. Explain electroplating of hard chromium & mention its applications (6M)

Electroplating of hard chromium

	Engineering hard Coating
Thickness	$2.5 - 300 \mu m$
Hardness	$835 - 925$ VPN
Bath composition	250 g/L chromic acid + 2.5 g/L H_2SO_4 (in $100:1$ ratio) + 1 g/L Cr^{3+}
Temperature	$50 - 65°C$
Current density	$290 - 580$ A/ft^2
Current efficiency	$17 - 21\%$
Anodic material	Insoluble lead-Pb alloy or Pb-Sn alloy
Cathodic material	Surface cleaned object metal
Reaction at anode	$H_2O \longrightarrow \frac{1}{2}O_2\uparrow + 2H^+ + 2e^-$
Reaction at cathode	$Cr^{3+} + 3e^- \longrightarrow Cr.$

4M

Active chromium anode is not used because, the anode efficiency is nearly 100% and that of cathode is only around 20% at the best. There will be increase in concentration of Cr^{3+} ions which result in poor quality electrodeposits.

Applications.
Used in industries in the making of gauzes, dies cutting tools, piston rings, cylinder liners, crankshafts of marine and aero engines, hydraulic rams.

2M

14

4b. Discuss the following i) Differential metal corrosion
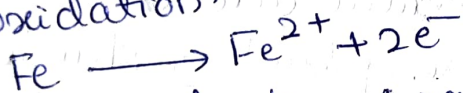ii) Anodizing of aluminium. (7M)

→ Differential metal corrosion (Galvanic corrosion)
      Corrosion arising out of formation of
galvanic cell is galvanic corrosion. Two or
more metals in contact and exposed together
to the corrosive form a galvanic cell. Anodic   1M
metal undergoes corrosion.
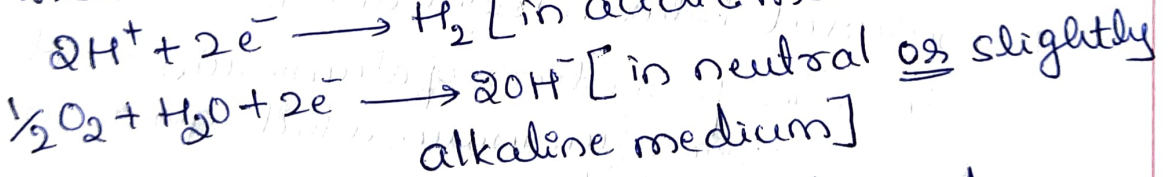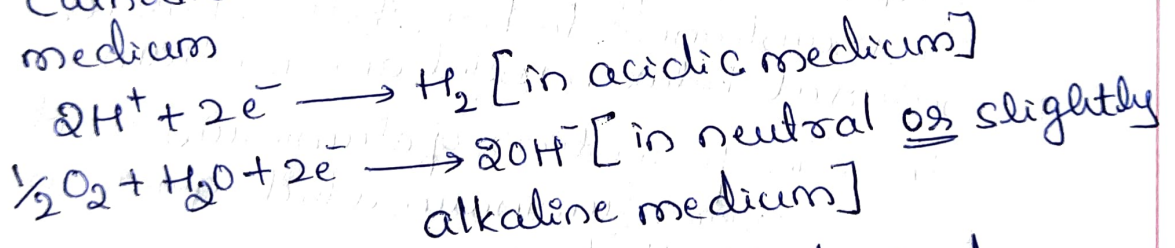Driving force: Difference in electrode potentials   1M
          of two metals.

Ex:
i) Steel vessel with brass tap
ii) Brass vessel with steel tap
Steel act as anode and undergoes corrosion   1M
by oxidation:
       Fe $\longrightarrow$ Fe^{2+} + 2e$^-$

Cathodic reduction reaction depends on the   1M
medium
    $2H^+ + 2e^- \longrightarrow H_2$ [in acidic medium]
    $\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$ [in neutral or slightly
                              alkaline medium]

    Smaller surface area of cathode and
larger surface area of anode ensure little
corrosion [Example (i) above]
Larger the difference in anodic & cathodic
metal electrode potentials leads to aggressive
corrosion
Higher concentration of corrosives and higher
temperatures also can result in higher
corrosion rates.
Ex: Brass hinges, latches etc with steel screws
      Steel tank with brass taps (or vice versa)

15.

→ **Anodizing of aluminium**

1) It is also called as inorganic coating.

2) Metals on corrosion will form corrosion products. A careful choice of the oxidising medium will help the deposition of protective corrosion product. Surface metal atoms of the object are chemically converted into a protective, barrier material. Therefore, the method is referred to as chemical conversion coating. **1M**

3) Anodizing of aluminium
→ It refers to chemical conversion coating over metal surfaces and control of corrosion. The method is applicable to non-ferrous metals
→ Aluminium article is made as anode in an electrolytic bath containing oxidizing agent such as chromic acid, sulphuric acid, phosphoric acid, boric acid, oxalic acid etc.
→ Cathode is made of lead or stainless steel
→ Moderate temperature and current densities are maintained to have better barrier material between metal and medium **1M**

→ There is formation of aluminium oxide coating over aluminium, which grows in thickness with time

$$2Al + 3[O] \longrightarrow Al_2O_3 \downarrow$$
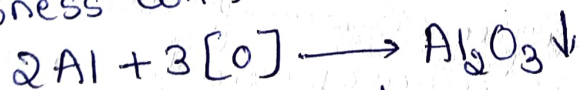
→ Outer, porous oxide film is sealed by immersion into boiling water or metal salt solution. There is hydration of Al_2O_3 into $Al_2O_3 \cdot H_2O$ which will have expanded size and thus, seal the pores. **1M**
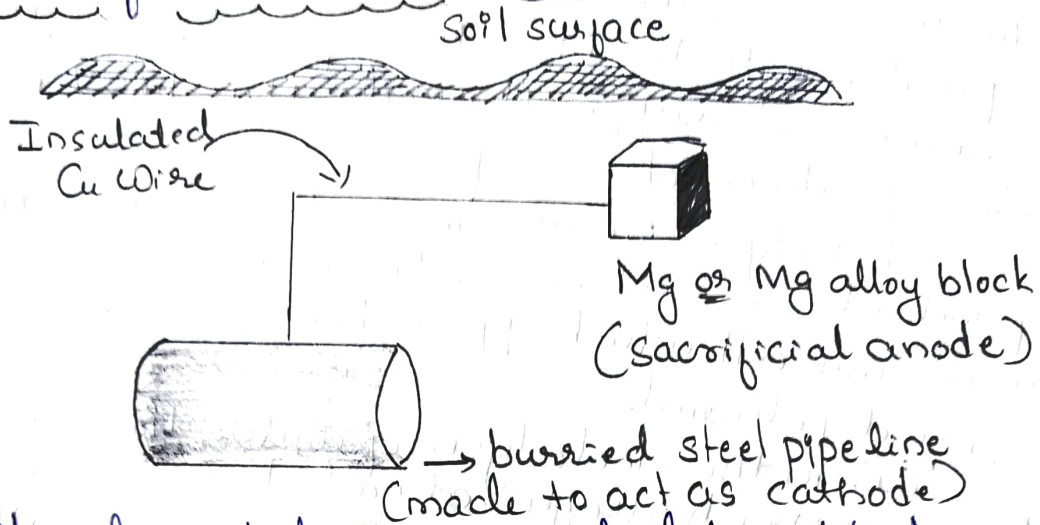
Applications:
Used for many designs or architectural purposes

the making of window frames, soap boxes

4c Explain in brief i) Sacrificial anode method
ii) Decomposition potential. (7M)

→ Sacrificial anode method

Soil surface

Insulated
Cu Wire

Mg or Mg alloy block
(sacrificial anode)

→ burried steel pipe line
(made to act as cathode)

1M

Object metal is connected to a block of an
anodic metal such as Zn, Al, Mg or their alloys, 2·5M
whenever there is a demand of electrons by
the corrosives in the medium, anodic metal
will sacrificially undergo oxidation and
release the electrons. Thus the object metal is
protected.

As long as anodic metal block is existent,
protection is achieved. When it disappears, fresh
block is replaced.

Applications:
Employed for buried pipe lines used for water
or oil, water tanks, ocean going ships, piers etc.

→ Decomposition potential:
i) It is the experimentally determined minimum
external potential that needs to be applied in
order to have continuous decomposition of the
electrolyte.

1M

Ex: In the decomposition of water, a dilute
solution of either an acid or alkali is electrolysed
using smooth platinum electrodes.

P.T.O

17

For the applied potential of less than 1.68V, there is initial surge of current which will drop to zero in a while. When the applied potential is 1.68V or more, there is continuous decomposition of water with the liberation of hydrogen at cathode and oxygen at anode. Thus, 1.68V is the decomposition potential of water.

2)   Electrolysis results in discharge of some products at electrodes. These products form a galvanic cell, which oppose the externally applied potential.

    Ex: in the electrolysis of water, there is liberation of hydrogen at cathode & oxygen at anode. A H_2-O_2 galvanic cell is formed with H_2 electrode acting as anode & O_2 electrode acting as cathode. This galvanic cell potential opposes the externally applied pressure (potential) Thus back emf is produced.

3) A knowledge of discharge potentials of different electrodes helps in

→ knowing the potential to be externally applied for electrolysis of any electrolyte.
    Ex: In the electrolysis of zinc iodide solution, a potential of 1.30V needs to be applied

→ Predicting the order in the different substances discharge or deposit at respective electrodes.
    Ex: By the electrolysis of a solution containing Cu^{2+} ions, Zn^{2+} ions and Cd^{2+} ions, the discharge or deposition of metals happens to be in the order of Cu then Cd & later Zn. If on the other hand, when Zn, Cd, and Cu are made active anodes, their dissolution happens to be in the sequence Zn, Cd & Cu.

2M

1M

0.5M

18

Module 3

5a. Define Calorific value of a fuel and calculate the gross & net calorific value of a coal from the following data

i) Mass of coal burnt = 0.85 gm
ii) water equivalent of calorimeter = 0.65 kg
iii) Mass of water taken in copper calorimeter = 2.2 kg
iv) Rise in temperature of water = 3.0°c
v) Percentage of H_2 in the coal = 3.2
vi) Latent heat of steam = 2457.76 kJ/kg. (6M)

Given:

Calorific value of a fuel:

It is the amount of heat energy released when unit quantity of fuel burnt completely in air or oxygen. The energy released by the fuel is measured interms of calorific value. **[1M]**

Specific heat of water = 4.187 kJ/kg/K
Mass of coal burnt = 0.85 gm = 0.00085 kg [m]
water eq. of calorimeter = 0.65 kg [w_2]
Mass of water taken in Copper calorimeter (w_1) = 2.2 kg
Rise in temperature of water (ΔT) = 3.0°C
= 3.0 K **[2M]**

Percentage of H_2 in the coal = 3.2
Latent heat of steam = 2457.76 kJ/kg

$$\text{Gross Calorific value} = \frac{(w_1 + w_2)\Delta T \, S}{m} \, \ldots \text{kJ/kg}$$ **[1M]**

$$= \frac{(0.65 + 2.2) \, 3 \times 4.187}{0.00085}$$

$$= 42,116.29 \text{ kJ/kg}$$ **[2M]**

Net calorific value = GCV − 0.09 H × LV

$$= 42116.29 − (0.09 \times 3.2) \times 2457.76$$

$$= 42116.29 − 707.83$$

$$= 41408.46 \text{ kJ/kg}$$

5b | Define fuel cell and explain the construction and working CH_3OH-O_2 fuel cell. (7M)
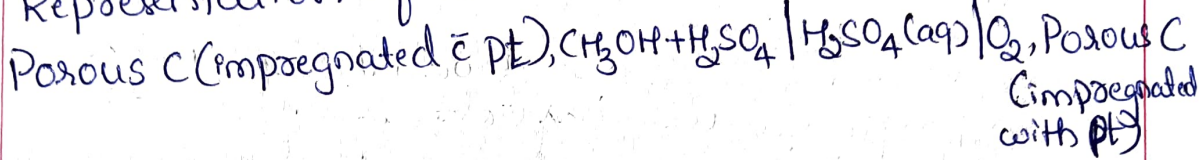
→ **Fuel Cells**

These are galvanic cells that convert the chemical energy of fuel oxidant system directly into electrical energy by oxidation of fuel at anode and reduction of oxidant at cathode. | 2M

Methanol-oxygen (CH_3OH-O_2) fuel cell

Construction

Representation of Cell

Porous C (impregnated c̅ Pt), $CH_3OH+H_2SO_4$ | $H_2SO_4 (aq)$ | O_2, Porous C (impregnated with Pt)

The cell consists of

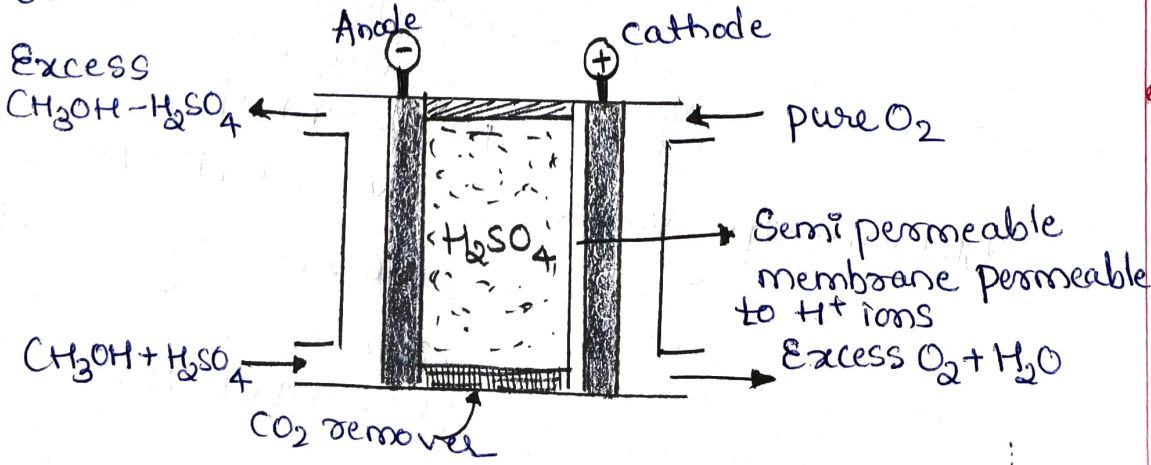Anode: Porous Carbon with dispersed platinum
Cathode: Porous Carbon with dispersed platinum
Electrolyte: Aqueous H_2SO_4 | 2M

Active components:
  1) Fuel: Methanol mixed with H_2SO_4 supplied at anode.

  2) Oxidant: Pure oxygen, supplied at cathode

Adjucent to cathode, towards the electrolyte side, a semi-permeable membrane is inserted to allow the diffusion of H^+ ions but disallow the diffusion of methanol to avoid methanol-oxidation directly at cathode.

Anode ⊖   Cathode ⊕

Excess
$CH_3OH-H_2SO_4$ ←   ← pure O_2 | 2M

H_2SO_4 → Semi permeable
                            membrane permeable
                            to H^+ ions

$CH_3OH+H_2SO_4$ →   → Excess O_2+H_2O

CO_2 removed

20

Working

Following reactions occur during power generation

Anodic oxid^n $CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$

Cathodic red^n $1\frac{1}{2}O_2 + 6H^+ + 6e^- \longrightarrow 3H_2O$

Cell Reaction $CH_3OH + 1\frac{1}{2}O_2 \longrightarrow CO_2 + 2H_2O$ 2M
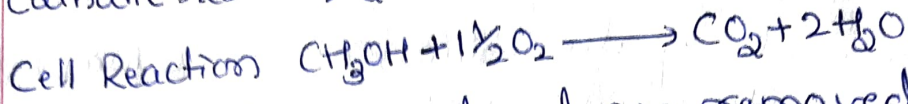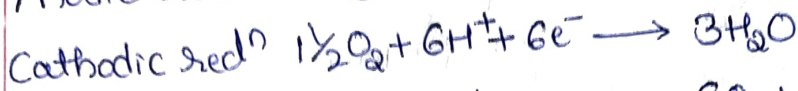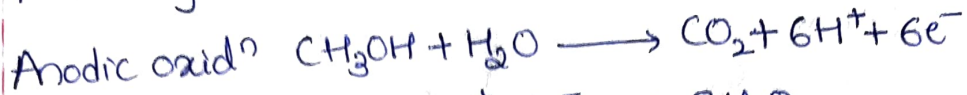
Water and CO_2 produced are removed as and when they formed and do not harm the cell functioning. Water is removed using wicks, However part of it comes out at cathode compartment along with excess of O_2

Cell potential: $1.2V$

Applications:
Used in military applications and large scale   1M
power production.

___

5c. Describe the preparation of solar grade silicon by union carbide process. (7m)

Preparation of silicon for use in photovoltaic cells by union carbide process involves three steps.

1st step:

Preparation of Metallurgical grade silicon from naturally occuring quartz.

→ A mixture of quartz (SiO_2) and carbon (metallu-gical coal or coke) is struck by an electric arc in an arc furnace. (carbothermic reduction) using   2M
carbon electrodes.

$$SiO_2 + 2C \xrightarrow{\;>1500°C\;} Si + 2CO$$
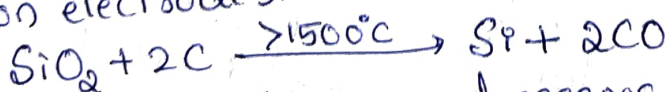
CO oxidizes to CO_2 and escapes into the atmosphere

→ Silicon is obtained in molten form & is contaminated with Al, Ca & Mg

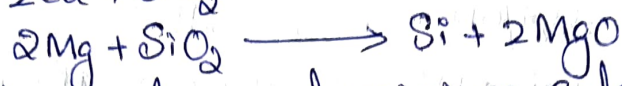The impurities are removed by the addition of silica. Following reactions take place

$$4Al + 3SiO_2 \longrightarrow 3Si + 2Al_2O_3$$
$$2Ca + SiO_2 \longrightarrow Si + 2CaO$$
$$2Mg + SiO_2 \longrightarrow Si + 2MgO$$

→ The oxides of aluminium, calcium & Magnesium combine with silica to form corresponding silicates and are removed as slag. The silicon left behind is called metallurgical grade silicon (98.5%)

2nd step :

Synthesis of silane from silicon

→ Metallurgical grade silicon is heated to 300-350°C and dry hydrogen chloride gas is passed. Trichlorosilane & a small amount of tetrachloro-silane are formed as given below

$$Si + 3HCl \xrightarrow{300-350°C} HSiCl_3 + H_2$$
$$(A) \qquad Trichlorosilane.$$
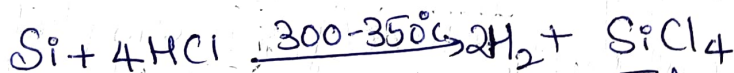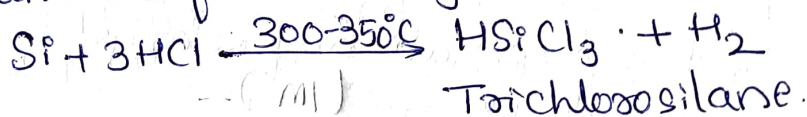
$$Si + 4HCl \xrightarrow{300-350°C} 2H_2 + SiCl_4$$
$$\qquad\qquad\qquad\qquad Tetrachlorosilane$$

Trichlorosilane is passed through a column bed filled with ion exchange resin containing quaternary ammonium salts as catalyst to give dichlorosilane and tetrachlorosilane. Dichlorosilane subsequently forms silane & trichlorosilane

$$2HSiCl_3 \xrightarrow[\substack{Containing\ quaternary \\ ammonium\ salt\ as \\ Catalyst}]{Ion\ exchange\ resin} H_2SiCl_2 + SiCl_4$$

$$3H_2SiCl_2 \xrightarrow{Ion\ exchange\ resin} SiH_4 + 2HSiCl_3$$
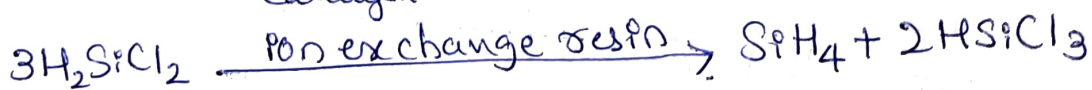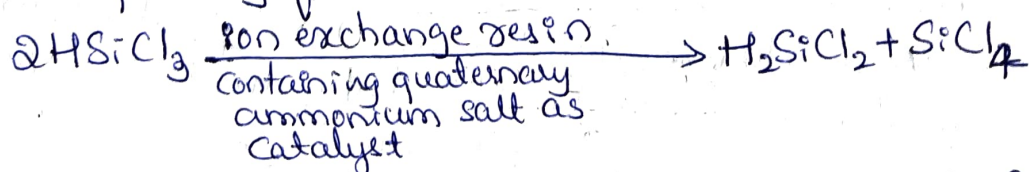
Tetrachlorosilane is converted into trichlorosilane by treating with hydrogen at 1000°C

$$SiCl_4 + H_2 \xrightarrow{1000°C} HSiCl_3 + HCl$$
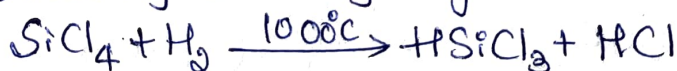
The process is continued to get silane

3rd step:

Purification of silicon hydride & Deposition of Si

→ Silicon hydride or silane obtained above is further purified by distillation. Silane is passed into a reactor containing hot silicon seed rods. This method is called Union carbide process. Silane gets pyrolysed at higher temperature to form polycrystalline silicon

$$SiH_4 \xrightarrow{800-1000°C} Si + 2H_2$$

1M

6a **Explain the experimental determination of calorific value of fuel using bomb calorimeter.**

Calorific value of solid or liquid fuels is determined by using Bomb calorimeter. (7M)

Principle:

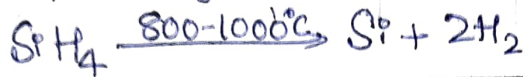Heat generated by combustion of fuel is equal to the heat absorbed by surrounding water and calorimeter.

1M

Labels: Battery, electrodes, oxygen inlet, Stirrer, Water jacket, Air jacket, Stainless steel bomb, Ebonite cover, Sensitive thermometer, Mg fuse wire with fuel attached, Stainless Steel crucible

1M
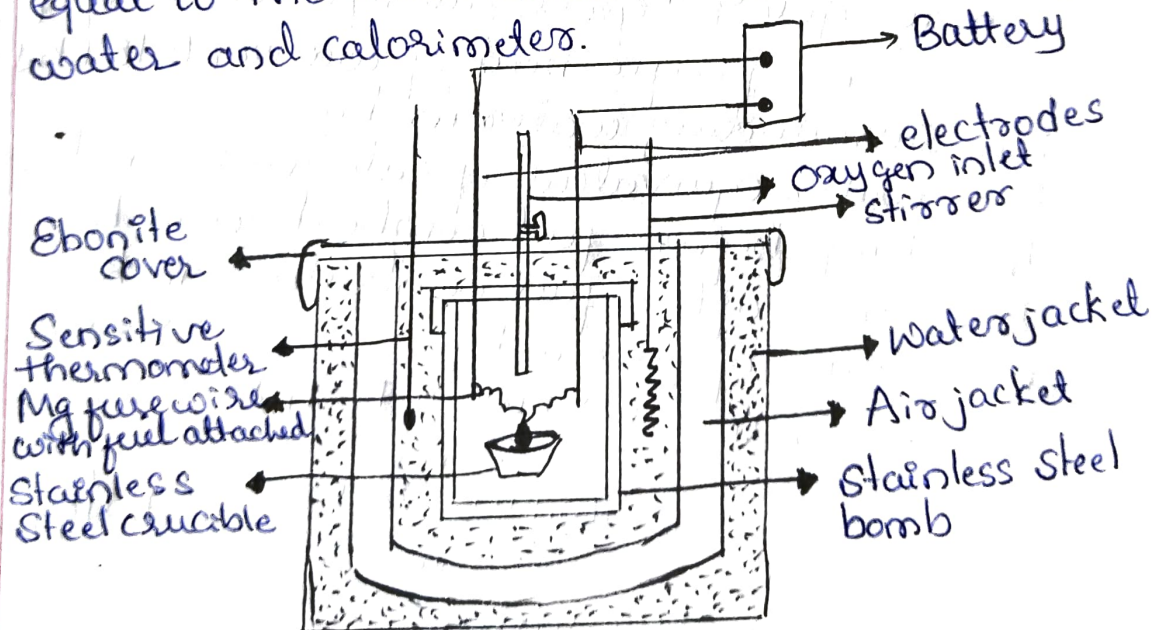
Construction:

The calorimeter consists of a stainless steel bomb in which, known (m kg) of fuel is taken, excess of oxygen is filled (to 25 atm. pressure) & immersed in known mass of water (w, kg) contained in the copper calorimeter.

2M

↓ 23

Fuel is ignited by passage of electricity through a fuse wire tied to the fuel

→ Heat liberated by fuel combustion, is absorbed by surrounding water and copper calorimeter

→ Temperature of water before fuel combustion $(=T_1 K)$ and maximum temperature it attains after fuel combustion $(=T_2 K)$ in the calorimeter, help in the calculation of GCV & NCV. Temperatures are measured by use of sensitive Bechman's thermometer.

Working:

Heat generated by burning m kg of fuel = Heat gained by (surrounding water + Calorimeter)

$$m \times GCV = (W_1 + W_2)(T_2 - T_1) S$$

where GCV is gross calorific value of fuel and S is specific heat of water (4.187 KJ/kg/k)
W_1 = Surrounding water in kg
W_2 = water equivalent of calorimeter in kg
T_1 = Temp before fuel combustion in K
T_2 = Temp after fuel combustion in K
m = mass of fuel in kg

$$\therefore GCV = \frac{(W_1 + W_2)(T_2 - T_1) S}{m}$$

$$= \frac{(W_1 + W_2) \Delta T S}{m} \quad \cdots \text{KJ/kg}$$

The net calorific value,
$$NCV = GCV - 0.09 H \times L_V \cdots \text{KJ/kg}$$
where, H is the percentage amount of hydrogen in the fuel and $L_V = 587 \times 4.187$ KJ/kg is the latent heat of condensation of steam.
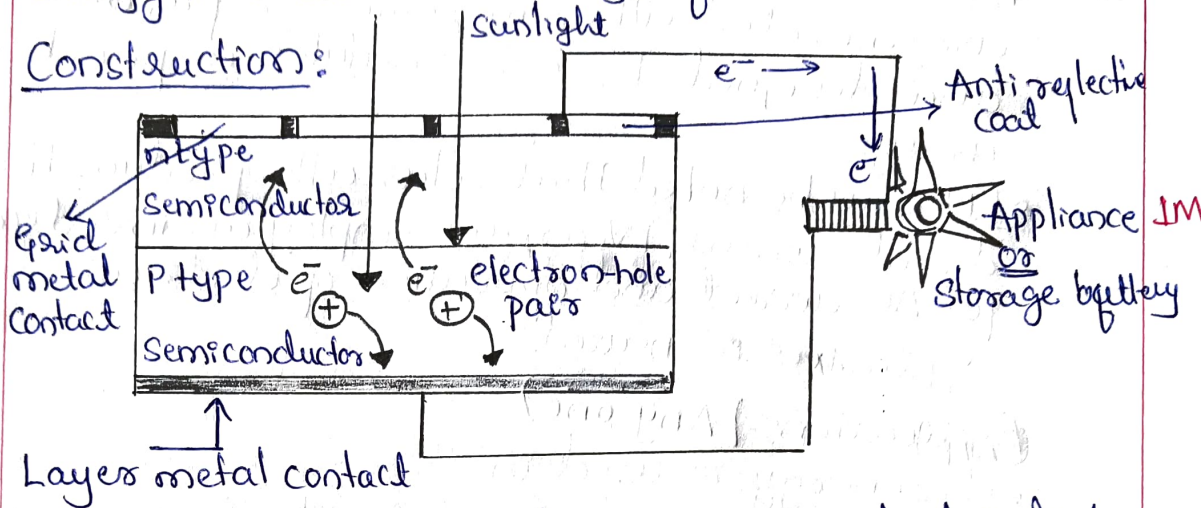
6b) What are solar cells? Explain construction and working of a photovoltaic cell. (6M)

Photovoltaic cells

These are devices that converts solar energy into electrical energy. from semiconductors. 1M

Construction:

Layer metal contact

1] Photovoltaic cell is made of a semiconductor diode
2] The diode has two electrical contacts; A grid metal contact is used on top side and a layer metal contact on the bottom side. Grid metal or layer metal contact is generally made by silver. 1M
3] The metal grid permits the light to fall on the diode between the grid lines.
4] An antireflective coat (Si_3N_4 - silicon trinitride) or (titanium dioxide (TiO_2) is used between the grid lines to increase the efficiency of light absorbance or energy conversion.

Working:

1] When a electromagnetic radiation having energy sufficient to overcome the barrier potential falls normal to the surface of the p-n junction, electron -hole pairs are formed. 2M
2] The electrons move towards the n-region (as it is positively charged) and holes move towards p-region (as it is negatively charged)
3] When an appliance or battery is connected between the two contacts, circuit is completed

and electrons are driven into external circuit enabling the functioning of the appliance or charging of battery. Charged battery is used for applications such as lighting, telecommunication etc.

4] Depending on the energy requirement, PV cells are connected either in series or parallel and designed to make modules or panels or arrays.

5] It may be noted that solar cells produce the direct current. PV arrays employ an inverter for AC current and operation of electrical appliances is ensured.

Applications [Any one]
Solar energy is used in

i] Domestic requirement, for lighting or running home appliances   1M

2] Community services, social religious and cultural gatherings, health centres, communication systems, sattelite linking, transport sector etc.

6C. Disuss i) knocking of petrol engine ii) power alcohol

Knocking (7M)

It is defined as the characteristic rattling metallic sound produced due to thermall shock waves hitting the cylender walls and pistons during explosive combustion of gasoline in an internal combustion (IC) engine.   1M

Following are the reasons for knocking to occur:
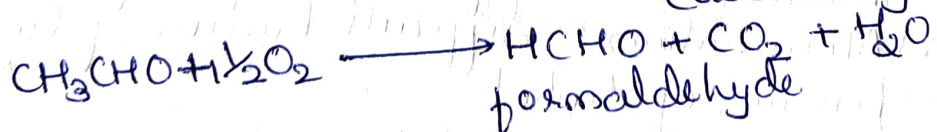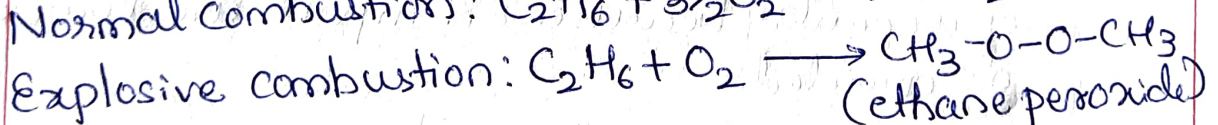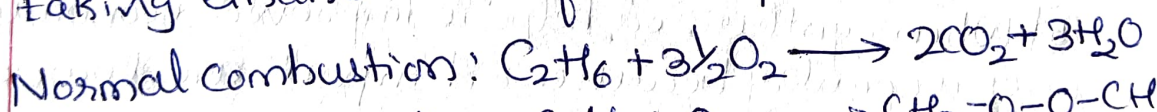
1] Higher compression ratio beyond optimum level

2] Lower octane petrol or gasoline   2M

3] Slow or fast movement of flame front in the IC engine.

4] Formation of highly reactive intermediates during combustion which lead to explosive reactions.

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Process:

Gasoline is burnt in IC engines to produce energy. Fuel-air mixture is drawn into the combustion chamber and is ignited using a spark plug at the end of suction stroke. When the flame front moves at optimum speed, fuel is burnt smoothly and completely. When the flame front moves slowly, products of initially burnt fuel, exert pressure on un-burnt fuel-air mixture. Due to build-up of pressure, temperature will also increase. All of the un-burnt fuel is ignited ahead of flame front. This produces thermal shock waves which hit the cylinder walls & piston; resulting in a characteristic metallic sound called knocking or pinging. When the flame front moves very fast beyond the optimum speed, once again, there is explosive burning resulting in knocking.

The probable reactions during normal combustion and knocking are presented below taking ethane as the fuel component.

Normal combustion: $C_2H_6 + 3\frac{1}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$

Explosive combustion: $C_2H_6 + O_2 \longrightarrow CH_3-O-O-CH_3$ (ethane peroxide)

$CH_3-O-O-CH_3 \longrightarrow CH_3CHO + H_2O$ (acetaldehyde)   1.5M

$CH_3CHO + \frac{1}{2}O_2 \longrightarrow HCHO + CO_2 + H_2O$ formaldehyde

$HCHO + O_2 \longrightarrow H_2O + CO_2$

Ill effects

1] Undesirable rattling noise/noise & air pollution
2] Mechanical damage, lowered power output, Increased fuel consumption
3] Air pollution by emission of unburnt hydrocarbons

Prevention of knocking
1] Improved engine design
2] Optimized compression ratio
3] Use of higher octane gasoline
4] Use of antiknocking agents

Power alcohol

A blend containing 10-85% of ethanol and 15-90% of gasoline, used as motor fuel is known as power alcohol.

Advantages: [Any three]

1] Increases octane number and reduces knocking
2] Because of increased ON, higher CR with better power output is achieved
3] Because, alcohol contains oxygen, it is referred as oxygenate which assist better combustion efficiency. Also VOC emissions are reduced or pollution is lessened.
4] Alcohols can be synthesized from plants. Thus especially, with higher proportion of alcohol one has a sustainable fuel.
5] When synthesized, helps in improved economy of a country because oil imports are lowered or avoided.

Disadvantages: [Any three]

1] lowers the calorific value of the fuel
2] Atomization is difficult because of higher surface tension of alcohol
3] Alcohol gets oxidized to acids and may corrode the engine equipment.
4] Modification of CR engine is required
5) Alcohols as such has good affinity for water possible phase separation of alcohol and gasoline due to absorbed water needs to be avoided by using benzene or ether as blending agents.

Module-4

7a Discuss the sources, effects and control measures of oxides of nitrogen. (6M)

Nitrogen oxides (NO_x) refer to the presence of N_2O, NO and NO_2 in the air.

Sources of Nitrogen oxides

Natural

i) Most of the nitrous oxide (N_2O) is formed due to bacterial decomposition of nitrogenous compounds

ii) Nitric oxide (NO) is formed by bacterial decomposition of nitrogen and oxygen in internal combustion engines or during lightening

iii) Nitrogen dioxide (NO_2) is formed by the oxidation of nitric oxide (NO)

[2M]

Anthropogenic

1) IC engines in automobiles

$$N_2 + O_2 \xrightarrow{1200°C - 1750°C} 2NO; 2NO + O_2 \longrightarrow 2NO_2$$
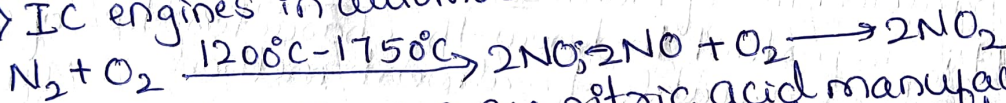
2) Some other sources are nitric acid manufacturing/utilization plants, explosives production plants, fertilizer plants etc.

Ill effects of nitrogen oxides:

1) Exposure to 150-250 ppm of NO_x causes infection of the bronchi and may prove fatal

2) Oxides of nitrogen lead to acid-rain.

3) Leads to formation of secondary pollutant, PAN in photochemical smog, a potential irritant, which also attacks plants, dyes, textiles etc.

[2M]

Control of nitrogen Oxides:

1) NO_x pollution is controlled by use of catalytic converters in exhaust lines

$$2NO_x \xrightarrow[Catalyst]{Pt/Rh} xN_2 + xO_2$$

[2M]
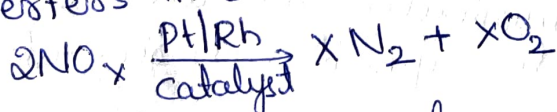
2) Emission of NO_x from flue gases can be controlled by catalytic reduction or by sorption

$$4NO + 4NH_3 + O_2 \xrightarrow[\substack{\text{Catalyst} \\ 300-400°C}]{V_2O_5 \text{ or } WO_3} 4N_2 + 6H_2O$$
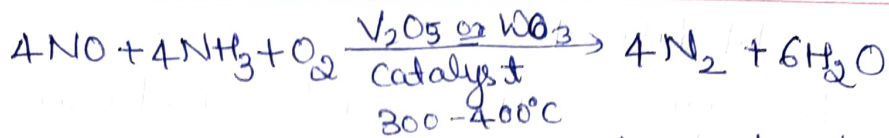
3) Treatment of flue gases by sorbents such as ammonia, limestone, alumina, activated charcoal etc.

7b | Explain the causes, effects and disposal methods of biomedical wastes. (7M)

It is solid waste generated during diagnosis, testing, treatment, research or production of biological products for humans or animals; sometimes, known as infectious waste or medical waste.

Sources of biomedical wastes
1) Hospitals, nursing homes, clinics, testing labs etc
2) Research centres and animal research centres.
3) Blood banks

Characteristics of biomedical waste.
It is important to know the characteristics of waste to adopt suitable treatment method.

characteristics suitable for incineration
i) Heating value or Calorific value - should be higher
ii) Combustible matter - should be higher
iii) Moisture content - should be lesser
iv) Should not really end up in hazardous emissions or otherwise, there should be treatment method before discharge of gases or ash.

characteristics suitable for appropriate disposal
1) Infectious waste - waste may contain virus, bacteria, parasites, lab cultures, tissues, body parts, body fluids, swabs, excretia, needles, knives etc.
2) Radioactive waste - Radiotherapy solutions, lab solutions, contaminated glassware etc.
3) Chemical waste: Expired lab reagents, disinfectants, cleansers etc.

4m

P.T.O

iii) Chemical pharmaceutical waste:
Expired and contaminated medicines etc.

v) No risk waste - office paper, wrapper, kitchen waste, general sweeping etc.

Disposal of biomedical waste: [Any 3 methods]

Disposal methods are to chosen carefully to eliminate the risks by exposure to hazardous emission or other consequences. Generally incineration, chemical disinfection, microwave irradiation or sanitary landfilling are employed.

3M

i) Incineration

This method is selected for waste that can not be reused, recycled or disposed of in a landfill It results in emission of toxic substances, acids, particulate matter apart from water and carbon dioxide. The ash and waste water produced also may contain toxic compounds which are to be treated to avoid adverse effects on health and the environment. Modern incinerators are designed to recover energy.

ii) Chemical disinfection:

This method kills or inactivates the pathogens which otherwise would spread the diseases. It is suited for blood, urine, stools or hospitals, sewage healthcare waste including microbiological cultures sharps etc. Formaldehyde (H-CHO), glutaraldehyde, sodium hypochlorite and chlorine oxide are the generally employed chemical disinfectants. The kind of disinfectant and conditions of treatment depend on the kind of substrate.

iii) Microwave irradiation

microorganisms can be destroyed completely by this technique, with a frequency of 2450 MHz and 12.24 cm wavelength, rapid and higher heat generated can kill all the microorganisms in the waste.

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iv) Sanitary landfills
    Dumping the medical waste into open spaces can lead to acute pollution problems transmitting the diseases by leaching and harmful emissions. This is the last option adopted and with plenty of care by geological isolation, appropriate engineering preparations and skilled staff.

7C Explain scale and sludge formation in boilers.(7m)

Sludge:
    It is soft, loose and slimy precipitate formed in the boiler water during, the generation of steam. It is formed by $MgCO_3$, $MgCl_2$, $MgSO_4$, $CaCl_2$ etc.   2m

Steel metal

water

sludge   Scale.

1m
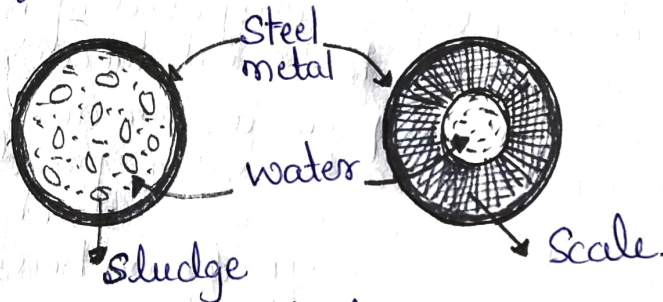
Disadvantages of sludge:
→ sludge is poor conductor of heat, so it tends to waste the portion of heat generated
→ If formed in excess, decreases the efficiency of boiler.   2m

Prevention of sludge: 1m
→ Boiler feed water should be well softened.
→ Blow down operation should be carried out frequently to avoid the problems.

Scale:
    This is hard and adherent coating formed on the inner walls of boilers, during steam generation. It is formed due to precipitation of following in the boilers.   1m
→ Low pressure boilers: $Ca(HCO_3)_2$, $MgCl_2$ etc.
→ High pressure boilers: $CaSO_4$, silica etc.

Disadvantages of scales.   1m
1) It is poor conductor of heat and reduces the rate of heat transfer.

→ Boiler tubes may clog due to scale formation

→ Due to scale formation on heating surfaces, overheating occurs and metal becomes soft & weak, and this makes the boiler unsafe.

→ Scale formation leads to uneven expansion of boiler metal. Thicker scale tends to crack, & when water comes suddenly in contact with overheated steel surface, it results in the formation of large amount of steam, which in turn develops a sudden high pressure that lead to explosion of boiler.

Prevention of scales:

Internal treatment: Conditioning methods

External treatment: Lime soda, zeolite or ion exchange process.

1M

8a. Define BOD and COD. Calculate the COD of a wastewater if 25mL of which consumes 10.5mL of 0.02N $K_2Cr_2O_7$ for complete oxidation. (6M)

BOD - biological oxygen demand

It is a measure of biodegradable pollutants in water. It is defined as the number of miligrams of dissolved oxygen (DO) consumed by micro-organisms for the oxidation of pollutants in one litre of water under aerobic conditions at 20°C over a period of 5days.

1M

COD - Chemical oxygen demand

COD is used to measure the total oxidisable impurities present in the sewage. This includes both biodegradable and nonbiodegradable matter. It is defined as the number of miligrams of oxygen required to oxidise the pollutants in one litre of waste water by a strong chemical oxidant such as, acidified $K_2Cr_2O_7$ in the presence of Ag^+ ion as the catalyst."

1M

33

Given:
$Z = 25\,mL$
$(Q-P) = 10.5\,mL$
$Y = 0.02\,N\ K_2Cr_2O_7$ 1M.

$COA = \dfrac{8}{1000} \times (Q-P) \times \dfrac{Y}{Z} \times 10^6$ 1M.

$= \dfrac{8}{1000} \times (10.5) \times \dfrac{0.02}{25} \times 10^6$ 1M

$= 6.72 \times 10^{-5} \times 10^6$ 1M.

$= 67.2\,ppm.$

8b) Explain the softening of water by Ion exchange method (7M)

Softening of water by Ion-exchange process
        Removal of hardness causing constituents from water is called softening of water. Partial or complete removal of dissolved salts by reversible ions exchange resin is an efficient method of softening the water. Resins used are generally insoluble, cross linked organic polymers with micro-porous structure. The functional groups attached to the chains enable reversible exchange H^+ ions and OH^- ions for cations and anions in the feed water. strongly acidic functional group like, sulphonic acid $[R-SO_3H]$ will contain replaceable H^+ ions and exchange the cations in feed water strongly basic functional groups like trimethylammonium hydroxide $[R-N^+(CH_3)_3OH^-]$ will contain replaceable OH^- ions and will exchange the anions in the feed water.   2m
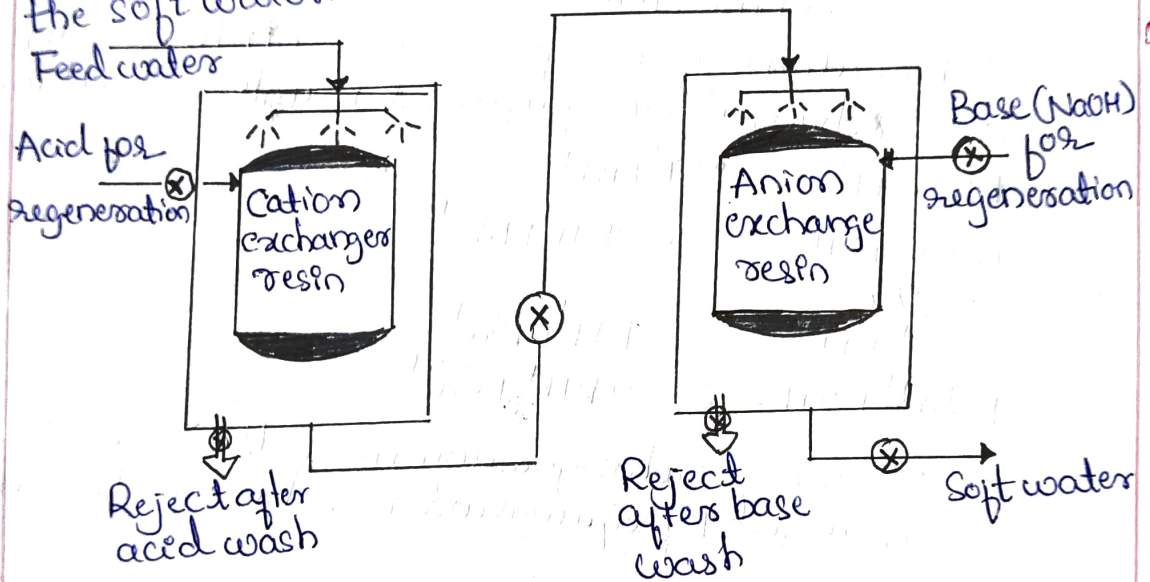
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Cation exchange resins are generally, styrene
-divinyl benzene co-polymers with sulfonic acid
[R-SO₃H] groups and anion exchange resins are
generally, styrene-divinyl benzene co-polymers
with quaternary ammonium hydroxide groups

Process

Feed water is passed through cation
exchanger and then anion exchanger to get
the soft water.

Following reactions occur
i) In cation exchanger, cations are exchanged
   by equivalent number of H^+ ions
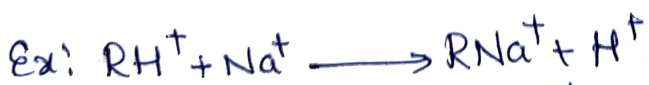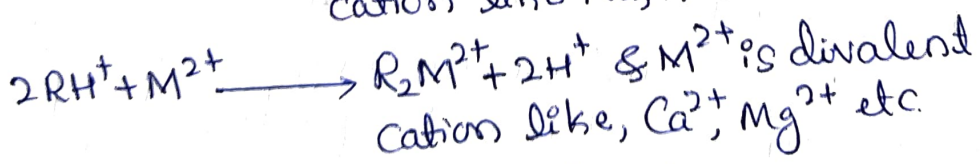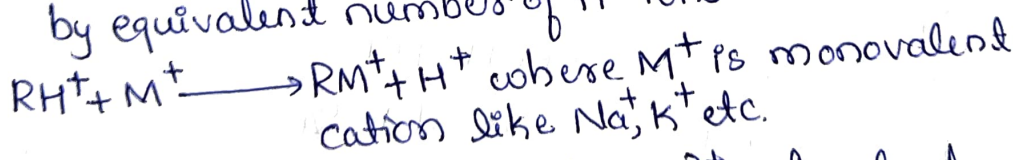
$$RH^+ + M^+ \longrightarrow RM^+ + H^+ \text{ where } M^+ \text{ is monovalent}$$
   cation like Na^+, K^+ etc.

$$2RH^+ + M^{2+} \longrightarrow R_2M^{2+} + 2H^+ \text{ & } M^{2+} \text{ is divalent}$$
   cation like, Ca^{2+}, Mg^{2+} etc.

Ex: $RH^+ + Na^+ \longrightarrow RNa^+ + H^+$

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

ii) In anion exchanger, anions are exchanged
   by equivalent number of OH^- ions

$$R-OH^- + X^- \longrightarrow RX^- + OH^- \text{ where, } X^- \text{ is}$$
   monovalent anion like
   Cl^-, F^-, NO_3^- etc

Ex:

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

$$2ROH^- + SO_4^{2-} \longrightarrow R_2SO_4^{2-} + 2OH^-$$
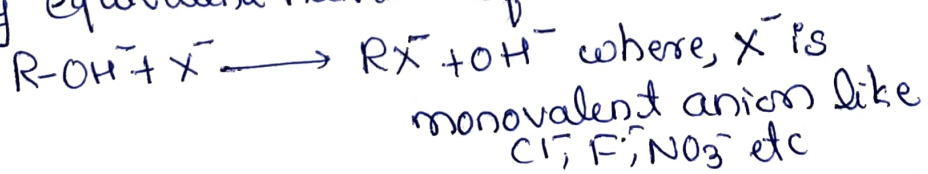
With the continuous inflow of feed water into cation exchanger and anion exchanger, the corresponding resins get inactive or lose their ability exchange the cations or anions. The cation exchange resin and anion exchange resin are regenerated by washing with acid (HCl) and base (NaOH) respectively.

i) In cation exchanger, cations on the resin are exchanged by equivalent number of H^+ ions.
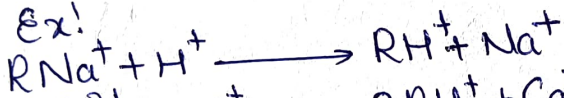
$$RM^+ + H^+ \longrightarrow RH^+ + M^+$$

$$R_2M^{2+} + 2H^+ \longrightarrow 2RH^+ + M^{2+}$$

2M

Ex:

$$RNa^+ + H^+ \longrightarrow RH^+ + Na^+$$

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

ii) In anion exchanger, anions on the resin are exchanged by equivalent number of OH^- ions.
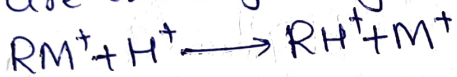
$$Rx^- + OH^- \longrightarrow ROH^- + X^-$$

$$R_2x^{2-} + 2OH^- \longrightarrow 2ROH^- + X^{2-}$$

1M

Ex:

$$RCl^- + OH^- \longrightarrow ROH^- + Cl^-$$

$$R_2SO_4^{2-} + 2OH^- \longrightarrow 2ROH^- + SO_4^{2-}$$
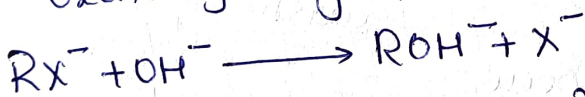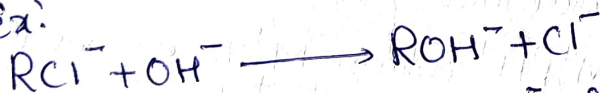
Regenerated ion exchange resins will thus be ready for softening the fresh feed of hard water onceagain.

8c Explain the following i) ozone depletions
ii) Reverse osmosis (7M)

P.T.O

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→ Ozone, Ozone depletion

Ozone is available in relatively larger amounts at stratospheric levels and protects the life system over earth from the dangerous UV rays.

Ozone formation

It is formed in air by following reactions

$$O_2 \xrightarrow[\text{radiation}]{UV} 2O$$
$$<240nm$$

$$O_2 + O \longrightarrow O_3$$
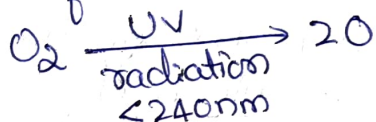
Also ozone is destroyed by

$$O_3 \xrightarrow[200-320nm]{UV \text{ radiation}} O_2 + O$$
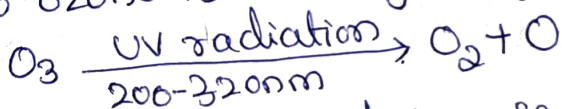
A dynamic equilibrium is established between the formation and dissociation of ozone in the stratosphere, maintaining a constant concentration of ozone with absorbance of UV radiations.

Ozone depletion:

Chlorofluorocarbons (CFCs); which are used as refrigerants, propellants and fire extinguishers are the cause for depletion. They are very stable, inert and non harmful. Because of their chemical stability and absence of natural sinks, they slowly drift towards the stratosphere. Here, they are dissociated by the action of UV-radiation, releasing reactive chlorine free radical which catalyses the dissociation of ozone.

$$CF_2Cl_2 \xrightarrow{UV-radiation} CF_2Cl + Cl$$

$$Cl + O_2 \longrightarrow ClO + O_2$$

$$ClO + O_2 \longrightarrow Cl + O_2$$
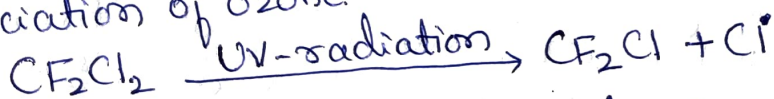
overall reaction is ___

$$O_3 + O \xrightarrow{Cl} 2O_2$$

[radical mentioning is imp]

1M

1M

1.5M

Ill effects of ozone depletion

i) UV radiations cause skin cancers and affect the immune system

ii) Absorption and cataracts. UV radiations kill microorganisms and thereby affect the dynamic biological balance on the earth.

Control of ozone depletion:

Use of hydrocarbons and hydrofluoro alkanes in place of CFCs. These compounds with one or more hydrogen atoms are susceptible to degradation. In HFAs, there no chlorine atoms and are not ozone destroyers. But these chemicals are green house gases. Use of propane and butane as freezers is more useful.

Desalination of sea water by Reverse Osmosis

When an aqueous solution of higher concentration is separated from another with lower concentration by semipermeable membrane, water will move from the region of lower concentration to the one at higher concentration. [1M] This process of movement of water molecules is called osmosis. The movement of solvent molecules through the semipermeable membrane from higher concentrated region to lower concentrated region by the application of external pressure higher than the osmotic pressure is called as reverse osmosis.

Principle and working

When a pressure (P) greater than the osmotic pressure (π) is applied on the solution side, the direction of movement of water molecules through the semipermeable membrane is reversed. This is termed as reverse osmosis. This method when applied to brakish water or sea water, water molecules move through

the semi permeable membrane from the salt solution towards fresh water side, leaving behind the concentrated salt solution.
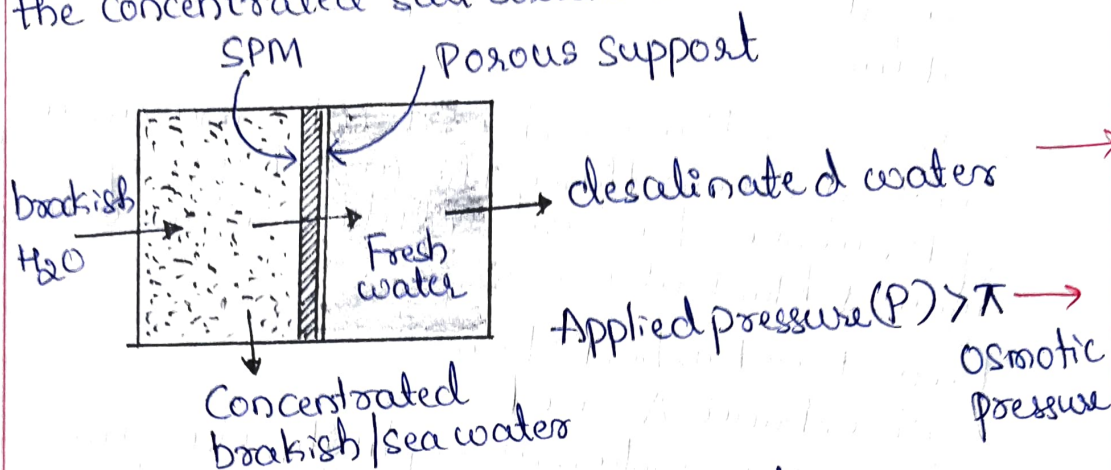
Semi permeable membranes used are
→ Cellulose acetate
→ Polymethacrylate
→ Polyimide
→ 100-150 μm in thickness
→ With 0.0001 – 0.01 μm pore size

Pressures of the order of 250-1000 psi are used on the feed side depending on the feed water.

Reverse osmosis can be affected for brakish water by the use of pressures up to 250-400 psi (17-27 bar) and for sea water, by use of pressure: 600-1000 psi (40-70 bar).

Important components of the reverse osmosis unit are semi permeable membrane and a high pressure pump. Reverse osmosis has the advantage of removal of all pollutants including micro-organisms. However, there is a disadvantage that desalinated water will not have even the required minerals (Ca^{2+}, Mg^{2+} etc) for good health.

9a. Explain theory and instrumentation of colorimetry

Theory: (7M)

A series of standard solutions of cuprammonium complexes is prepared by mixing cupric solution

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with excess ammonia.

$$Cu^{2+} + 4NH_3 \longrightarrow Cu[NH_3]_4^{2+}$$

light
blue

Deep blue

This deep blue complex absorbs maximum light at 620nm. Hence, the absorbance of each of the above standard solutions is measured against blank at 620nm.

From Beer Lambert's law,

Absorbance, $A = \epsilon c t$

where, ϵ is molar absorptivity, 'c' is the concentration of Cu and t is the solution thickness through which the light passes. ϵ is a constant for a given substance at a given wavelength. When same glass-cuvette is used for all the solutions during measurements, t will remain constant.

Therefore, in the equation above,

$$A = constant \times C$$

$$A \propto C$$

Hence, as the concentration increases, absorbance will also increase proportionally.

Procedure:

1] Known volumes (2, 4, 6, 8, 10 mL etc) of stock solution of copper sulfate are taken in separate 50mL standard flasks.

2] 2mL of ammonia is added to each of these flasks and diluted upto the mark with distilled water, shaken well to get homogeneous solutions.

3] Test solution is treated with 2mL ammonia and diluted upto the mark with distilled water in 50mL flask and made homogeneous

4] Absorbance of each standard solutions and analyte is measured against blank (2mL ammonia diluted with distilled water in a

50 mL std. flask) at 620 nm using colorimeter. Calibration curve is drawn by plotting absorbance against concentration of copper.

5] Absorbance of analyte is located on the calibration curve and concentration of copper is determined.

6] Colorimetry can be applied to estimate copper in brass, mangnese in steel, glucose in fluids, iron in haematite etc.

Advantages: [any one]
→ Accurate results are possible even when concentrations of analytes are low.
→ Analysis of biological samples is possible.

0.5M

Limitation: [any one]
Analysis is possible only when the analyte is colored. Otherwise, colourless species under investigation should be treated with suitable reagent to get the color. Poorly coloured solutions may not give reliable results.

0.5M

9b | Discuss the theory of conductometric titrations and explain the nature of graph for the following titrations.
i) Strong acid with strong base ii) Weak acid with strong base
i) Strong acid with strong base [2M]

vol. of NaOH

$(H^+ + Cl^-) + (Na^+ + OH^-) \longrightarrow (Na^+ + Cl^-) + H_2O$

0.5M

1M

1M
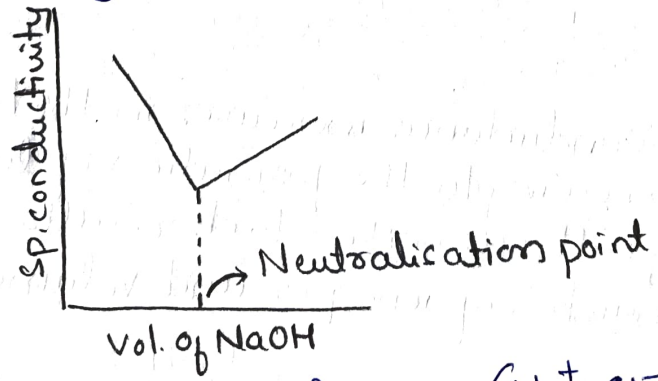
→ Specific conductance decreases in the beginning of titration owing to the replacement of highly mobile H^+ ions by less mobile cations (Na^+) for the base.

→ Conductivity continues to decrease until the neutralisation of the acid.
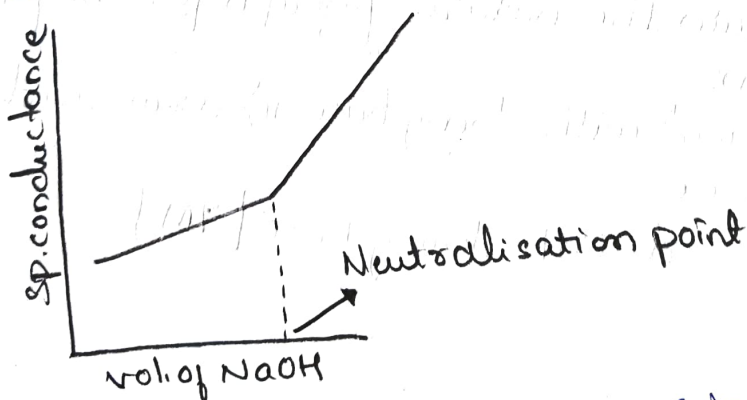
→ After the neutralisation of acid, the specific conductance rises rapidly with further addition of strong base because of increased concentration of relatively more mobile OH^- ions. **1M**

→ A pbt of conductance against volume of base added gives, two straight lines.

→ The point of intersection of two lines gives the neutralisation point.

→ Thus, on titration of known volume of HCl against NaOH, neutralisation point helps in calculating the quantity of HCl in the test solution

→ Weak acid against a strong base (CH_3COOH v/s $NaOH$) **1M**

$$CH_3COOH + (Na^+ OH^-) \longrightarrow (CH_3COO^- + Na^+) + H_2O$$

Neutralisation point

vol. of NaOH

(y-axis: sp. conductance)

0.5 M

1M

→ Specific conductance increases in the beginning of titration owing to the formation of highly dissociating salt, CH_3COONa which results in increased number of ions per unit volume of the analyte. **1M**

→ However, the rise in conductivity is not sharp because, the salt releases less mobile

Na^+ ions and CH_3COO^- ions.

→ Conductivity continues to increase slowly until the neutralisation of the acid.

→ After the neutralisation of acid, the specific conductance rises rapidly with further addition of strong base because of increased concentration of relatively more mobile OH^- ions.

→ A plot of conductance against volume of base added gives two straight lines. The point of intersection of two lines gives the neutralisation point.

→ Thus, on the titration of known volume of CH_3COOH against NaOH, neutralisation point helps in calculating the quantity of CH_3COOH in the test solution.

9c | Explain the synthesis of nanomaterials by chemical vapour deposition method [6M]

Chemical vapour deposition method

Chemical vapour deposition (CVD)

→ In 1993, chemical vapour deposition technique was first reported to produce MWNTs by Endo and his research group. Three years later, Dai in Smalley's group successfully adapted CO-based CVD to produce SWNTs   **1M**
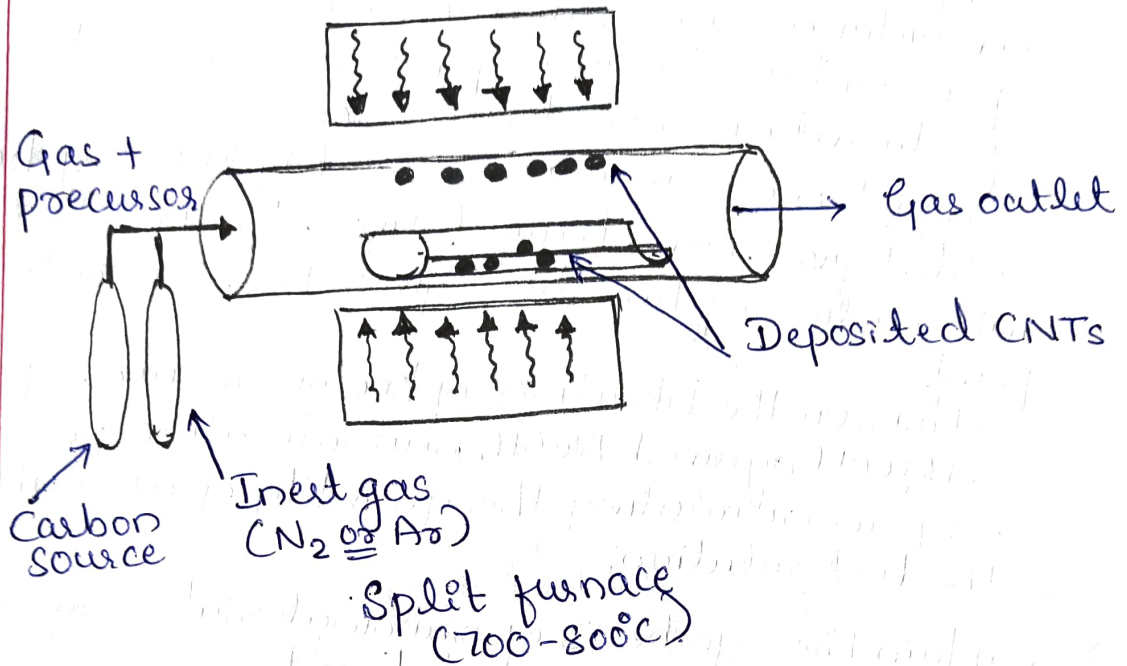
→ CVD technique can be achieved by taking a carbon source in the gas phase and using an energy source, such as plasma or a resistively heated coil, to transfer energy to a gaseous carbon molecule. The CVD process uses hydrocarbons as the carbon sources including methane, CO_2 and acetylene.   **2M**

→ The hydrocarbons flow through the quartz tube being in an oven at a high temp (~720°C)

→ At high temperature, the hydrocarbons are broken to be the hydrogen carbon bond, producing pure carbon molecules.

Ex: $C_2H_2 \longrightarrow 2C + H_2$

→ Then, the carbon will diffuse toward the substrate, which is heated and coated with a catalyst where it will bind.

Gas + precursor

Gas outlet

Deposited CNTs

Carbon source

Inert gas $(N_2 \text{ or } Ar)$

Split furnace $(700-800°C)$

Advantages [any 4 applications]

→ Uniform distribution over large areas
→ No compositional gradients across the substrate
→ No need to break vacuum for source changes
→ More selective area deposition because of higher activation energy for reaction with foreign substances
→ They are conformal to the substrate

Disadvantages:

→ Mostly involve safety and contamination
→ Hydrides and carbonyls are poisnous
→ They are not suitable for mixture of materials
→ High cost for compounds with sufficient purity.

10a) Explain sol-gel method of synthesis of nanomaterials. [6M]

→ It is a bottom up approach of synthesis of nano materials.

→ Sol-gel process:

A change from a liquid state to a gel state through poly-condensation reactions. A sol is a stable dispersion of colloidal particles or polymers in a solvent. The particles may be amorphous or crystalline. Typical size few nm. A gel consists of a three dimensional continuous network of the sol particles, which encloses a liquid phase.

In a colloidal gel, the network is built from agglomeration of colloidal particles. In a polymer gel the particles have a polymeric sub-structure made by aggregates of sub-colloidal particles. The sol-gel method involves the following steps:

1M

1M
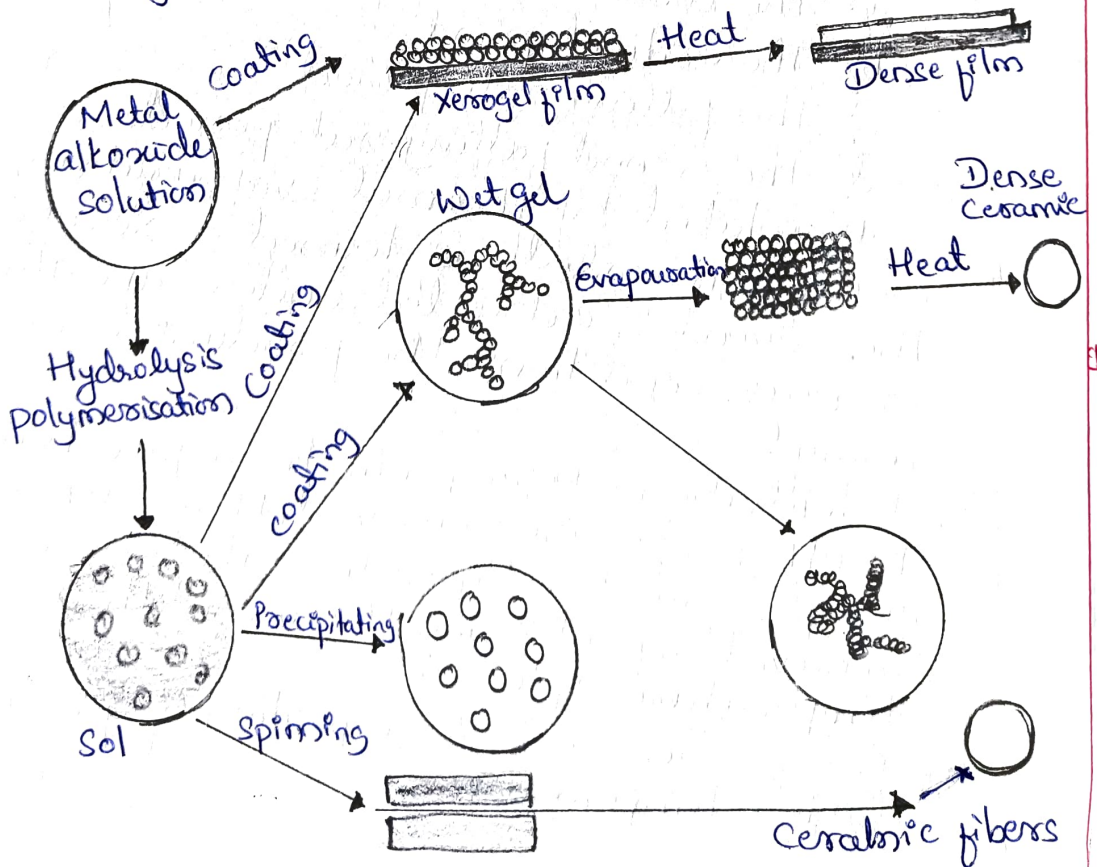
1. Formation of different stable solutions of alkoxide or solvated metal precursors

$$MOR + H_2O \longrightarrow MOH + ROH \text{ (hydrolysis)}$$
$$MOH + ROM \longrightarrow MOM + ROH \text{ (condensation)}$$
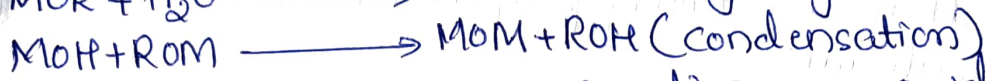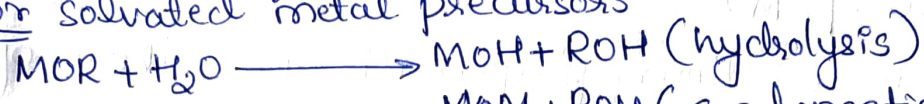
2. Gelation resulting from formation of an oxide or alcohol bridged networks by polycondensation reaction that results in dramatic increase in the viscosity of the solution.

3. Aging of gel: The polycondensation reactions continue until the gel transforms into a solid mass, accompained by contraction of gel and expulsion of solvent from gel pores. The aging process of gel can exceed 7 days and is critical to the prevention of cracks in gels that have been cast.

2M

u Drying of gel: Water and other volatile liquids are removed from gel network. The drying process has itself broken into four dinstinct steps

2M

a) The constant rate period
b) The critical point
c) The falling rate period
d) The second falling rate period
   If isolated by thermal evapouration, the resulting monolith is termed as xerogel. If the solvent is extracted under superitical or near conditions, the product is an aerogel.

5. Dehydration: During which surface bound M-OH groups are removed, there by stabilizing the gel against rehydration. This is normally achieved by calcining the monolith at temperature upto 800°C.

6. Densification and decomposition of gels at higher temperature.

<u>Advantages:</u> [Any one application]
→ It is very useful for synthesis of glasses, glass ceramics

→ Monosized nano particles are produced by this method.

→ Extended composition ranges; it allows the fabrication of any oxide composition, but also some non oxides, as well as the production of new hybrid organic-inorganic materials, which do not exist naturally.

Disadvantages
→ Cost of precursors
→ Difficult to avoid residual porosity and OH groups.

1m

10b. Write a note on synthesis, properties and uses of fullerenes. [7M] Note: Synthesis is not there for syllabus

<u>Fullerenes</u>
→ An allotrope of carbon
→ The most famous form of fullerene is C60.
→ Discovered by H.W. Kroto and R S Smalley at Rice University, USA (1985)
→ Popularly known as Buckminister fullerene in honor of American architect buck minister Fuller.
→ The shape of C60 resembles the dome structure based on hexagons and pentagons designed by Fuller.
→ C60 is also known as bucky ball as it is spherical cluster of carbon atoms arranged in series of five and six membered rings to form soccer Ball shape. Other relatively common clusters are C70, C72, C74, C76, C80, C84.

1m

<u>Properties</u>
→ No other element has such wonderful properties as carbon

2m

→ Buckyballs are relatively cheap

→ In fullerenes, 12 pentagonal rings are necessary and sufficient to effect the cage closure.

→ The most stable containing 60 atoms.

→ The diameter of the molecules C_{60} is 1nm.

→ It has 20 hexagonal faces, 12 pentagonal faces and 60 vertices.

→ Highest tensile strength of any known 2D structure or element

→ It is a black powdery material

→ Very tough and thermally stable.

→ Forms deep magenta solution in benzene

→ The mean diameter of molecule is measured to be 7-10°A.

→ The average carbon-carbon bond length for C_{60} is 1.44°A; which lies between that of graphite (1.42°A) and diamond (1.54°A).

Applications [6 applications]

→ It is used in electrographic imaging, solar cells, monolinear optical thin films, magnato optical recording.

→ It is used in making carbon films, tunnel diodes, photolithography, double layer capacitor & storage devices

→ It is widely used for the conversion of diamond

→ In the separation of chromatography materials, absorbent for gases etc

→ It is used as gas sensor, temperature sensor, particle sensor and in detection of organic vapours.

→ Used as lubricants, adhesives, charge transfer complexes, cosmetics etc.

→ Used in secondary batteries, fuel cell electrodes.

10c. Explain 'Atomic Absorption spectroscopy' [7M]

1M

3M

"Atomic Absorption Spectroscopy"

Atomic absorption spectroscopy is a technique which studies absorption of electromagnetic radiations in relationship to molecular structure, It is a technique for measuring the concentration of various elements in the sample through their absorption of light. It is a relatively simple and reliable technique which uses absorption of optical radiation by free atoms for determining the contents of different elements.

Theory

Atomic absorption spectroscopy is based on the principle that when a beam of electromagnetic radiation is passed through a substance, the radiation may either be absorbed or transmitted depending upon the wavelength of the radiation.

The absorption of radiation would bring about an increase in the energy of the molecule. The energy gained by the molecule is directly proportional to the wavelength of radiation.

The increase in energy of molecule leads to the electronic excitations where electrons jump to higher energy levels. A particular wavelength that a given molecule can absorb depends upon the changes in vibrational or rotational or electronic states.

When a monochromatic radiation of frequency ν is incident on a molecule, the molecule in the gaseous state ε_1 absorbs a photon of energy $h\nu$, it undergoes a transition from lower energy level to higher energy level. A detector is placed to collect the radiation after interaction with the molecule which shows that intensity has reduced.
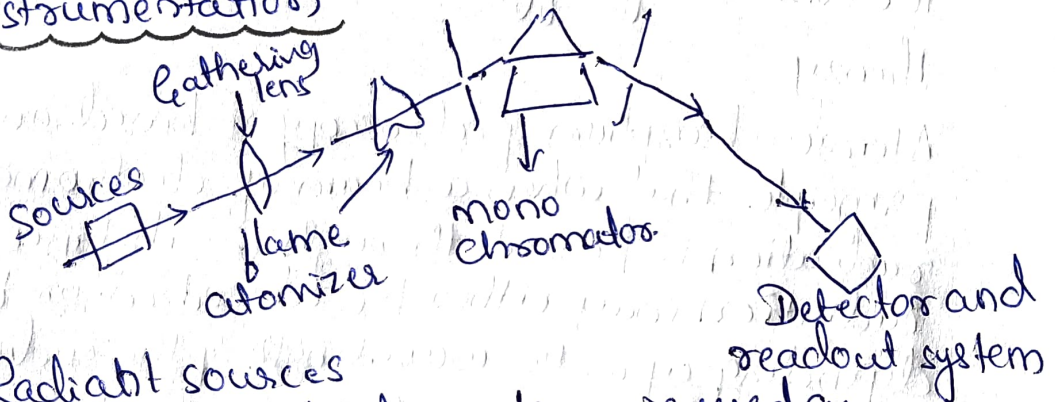
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with wide range of frequencies, the detector shows the energy has been absorbed only from the frequency.

$$\nu = \frac{\Delta E}{h}$$

∴ we obtain an absorption spectrum which is defined as a record of the radiation absorbed by the given sample as function of wavelength of radiation

$$\Delta E = e_2 - E_1 = h\nu = \frac{hc}{\lambda}$$

Instrumentation

- Sources
- Gathering lens
- flame atomizer
- monochromator
- Detector and readout system

1) Radiant sources
Generally a hydrogen lamp is used as continuous source of radiation.

2) Hollow cathode lamp
For atomic absorption spectroscopy the radiation source is hollow cathode lamp

3) Monochromator
Generally the monochromators are gratings and prisms.

4) Filters or slits
These are used for isolation of required spectral line if element has a simple line spectrum.

5) Detectors:
Generally photomultipliers are used as detectors

Application: [any two applications]
→ Atomic absorption spectroscopy can be used to analyze water for its metal quantity if present.
→ Atomic absorption spectroscopy can be used in biological tissues such as blood, liver, brain fluids for analyzing metals.

2M

1M

50