Model Question Paper-1 with effect from 2021 (CBCS Scheme)

First Semester Engineering Degree Examination
Subject Title 21CHE12/22

TIME: 03 Hours **Max. Marks: 100**

Note: Answer any **FIVE** full questions, choosing at least **ONE** question from each **MODULE.**

		MODULE 1	Marks
Q.1	a	Define Single Electrode Potential. Derive Nernst equation for single electrode potential.	7
	b	Describe the construction and working of calomel electrode	6
	c	Explain the construction and working of Li-ion battery, mention its applications.	7
		OR	
Q.2	a	Distinguish between primary, secondary and reserve batteries.	6
	b	Explain construction and working of glass electrode.	7
	c	For the cell, Fe/Fe^{2+} (0.01M)//Ag^{+} (0.1M)/Ag write the cell reaction and calculate the emf of the cell at 298K, if standard electrode potentials of Fe and Ag electrodes are -0.44V and 0.8 V respectively.	7
		MODULE 2	
Q.3	a	Define metallic corrosion? Describe the electrochemical theory of corrosion taking iron as an example.	7
	b	Explain: (i) Differential metal corrosion & (ii) Water-line corrosion	6
	c	What is electroplating? Explain the electroplating of chromium	7
		OR	
Q.4	a	What is meant by metal finishing? Mention (any five) technological importance of metal finishing.	6
	b	What is electroless plating? Explain the electroless plating of copper.	7
	c	Explain the factors affecting the rate of corrosion (i) Nature of corrosion product, (ii) Ratio of anodic to cathodic areas & (iii) pH	7
		MODULE 3	
Q.5	a	Explain the synthesis and application of Polyurethane.	7
	b	Describe the mechanism of conduction in Polyaniline and factors influencing conduction in organic polymers.	7
	c	Explain any two size dependent properties of nanomaterials	6
		OR	
Q.6	a	What are nanomaterials? Explain the synthesis of nanomaterial by sol gel process.	7
	b	Write a note on Fullerenes. Mention its applications.	6
	c	Explain the synthesis, properties and application of Polylactic acid.	7

MODULE 4			
Q.7	a	With suitable example explain microwave synthesis and bio catalyzed reactions	7
	b	Explain the synthesis of Adipic acid by conventional route from Benzene and green route from Glucose.	7
	c	Describe the construction and working of Methanol –Oxygen fuel cell.	6
OR			
Q.8	a	Describe the hydrogen production by photo catalytic water splitting method.	7
	b	Explain the synthesis of Paracetamol by conventional and green route from phenol.	7
	c	Explain the construction and working of photovoltaic cells.	6
MODULE 5			
Q.9	a	Explain the theory, instrumentation and applications of flame photometry.	7
	b	Write the principles and requirement of titrimetric analysis.	7
	c	In a COD test, 30.5 cm^3 and 15.5 cm^3 of 0.05 N FAS solutions are required for blank & sample titration respectively. The volume of test sample used was 25 cm^3. Calculate the COD of the sample solution.	6
OR			
Q.10	a	Explain the determination of hardness of water by EDTA method.	7
	b	Define the following units of standard solution. i) Molarity ii) Normality iii) ppm	6
	c	Explain the theory and instrumentation of potentiometry.	7

Model Question Paper - I

First Semester Engineering Degree Examination

Q1

a : Define Single Electrode Potential. Derive Nernst equation for Single Electrode potential. (7 Marks)

Ans: Defination

Potential developed at the Interface (junction) of substance and its ionic solution due to the tendency of the substance ~~and its ionic solution due to the~~ tendency of the substance to undergo reduction or oxidation at specified activity of ionic species, temperature and gas pressure if it's gas electrode

Derivation

Nernst in 1889 derived a quantitative relationship amongst three quantities. Electrode potential, system temperature and active mass or molar concentration

of the ionic species. This known as Nernst equation.

Let the reversible reduction electrode potential reaction be

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

When the reaction is spontaneous decrease in the free energy of the system ($-\Delta G$) is equal to the maximum energy obtainable from the system (W_{max}).

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

$$= (nF) \times E$$

Where,

nF - is the coloumbs of charge that is transfered during the reaction.

n - is the number of moles of electrons transfered in the reaction.

F - is the faraday of electricity (96500 C mol^{-1})

E - is the electrode potential [Voltage V or J energy available per coloumb(J C^{-1})]

for reactants and products of the reaction at unit activity, standard changing in free energy

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

E° – standard electrode potential

Change in free energy is related to equilibrium constant of the reaction, Keq by Vant Hoff reaction isotherm

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

Q – Reaction Quatient

R – Molar gas constant

T – Temprature of the system expressed in Kelvin.

Also standard Free energy change

$$\Delta G^\circ = -RT \ln Keq.$$

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

By defination $[M] = 1$

Substitution of ΔG and ΔG° in equation (4)

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

$$\div -nF$$

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

OR

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

Substituting the Values.

$R = 8.314 \text{ J mol}^{-1} \text{K}^{-1}$

$F = 96500 \text{ Coulombs/mol}$.

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

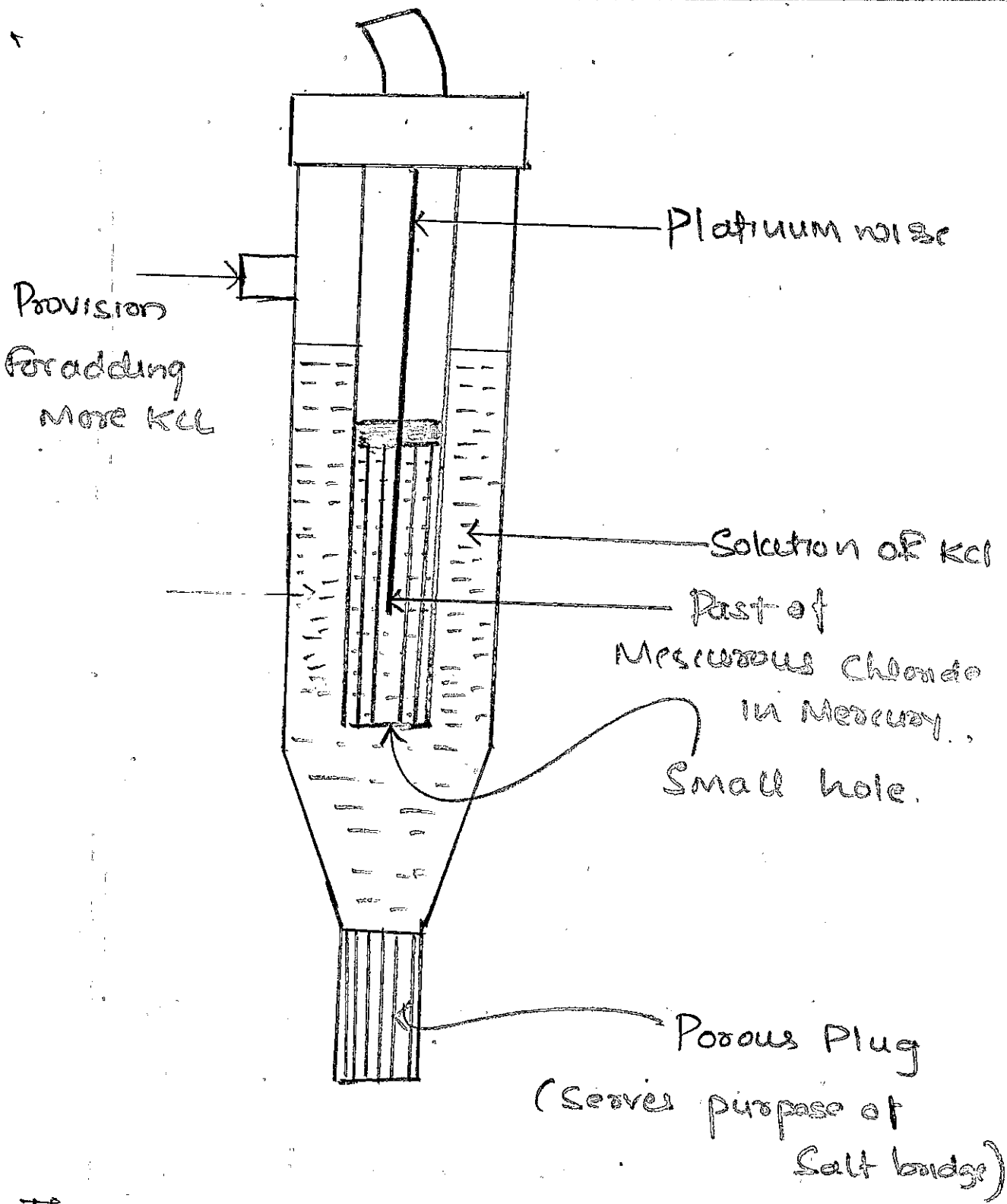
b. Describe the construction and working of calomel electrode (6 MARKS)

~~Ed~~ Ans:

Calomel Electrode

$Hg(l), Hg_2Cl_2(s) \mid KCl(aq)\ [KCl] = C$

1. The electrode consists of two concentric glass tubes.
2. The inner tubes contains a paste of mercurous chloride in mercury.



3. The Outer tube Contains a solution of KCl

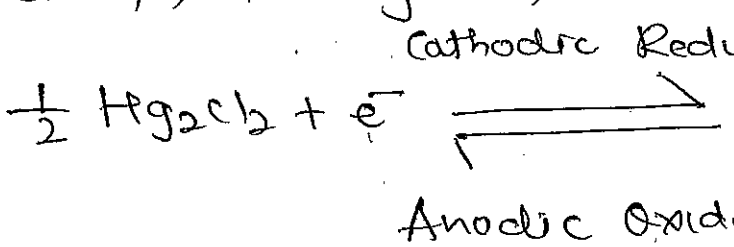
4. A little Mercury along with platinum wire in the inner tube helps the external Contacting of electrode.

* A hole at the bottom of outer tube with a porous plug attached helps in establishing contact with the external analyte.

* During potentiometric measurements KCl solution drains through porous plug at the bottom. It is refilled by addition from a small side tube.

Working

Depending on the potential of electrode with which the calomel electrode is connected, calomel electrode acts as cathode or anode. Reactions when the electrode acts as cathode (in the forward direction) or anode (in the backward direction) are given below.



Electrode potential equation

$$E = E^{\circ} - \frac{2.303\,RT}{F} \log[Cl^-]$$

Electrode is reversible to chloride ions potential changes with changing concentration of chloride. (decreases with increasing concentration of chloride ion).

Electrode potential values at 298 K. are

0.336 V for [KCl] = 0.1 N

0.279 V for [KCl] = 1.0 N

0.244V for [KCl] = Saturated KCl.

C. Explain the construction and working of Li-ion battery. Mention its applications.

Ans:

Construction

Li ion cell when in changed condition is schematically represented as

$Li(6) \mid Li$ - Salt (in mixed organic 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.

$Cu; C_6 \mid LiPF_6, LiBF_6, LrClO_4$ etc (mixed with organic solvent) $\mid LiCoO_2, Al$.

Anodic Material - highly crystallized specialty carbon

Cathodic Material - $LiCoO_2$ - Lithium Cobalt Oxide.

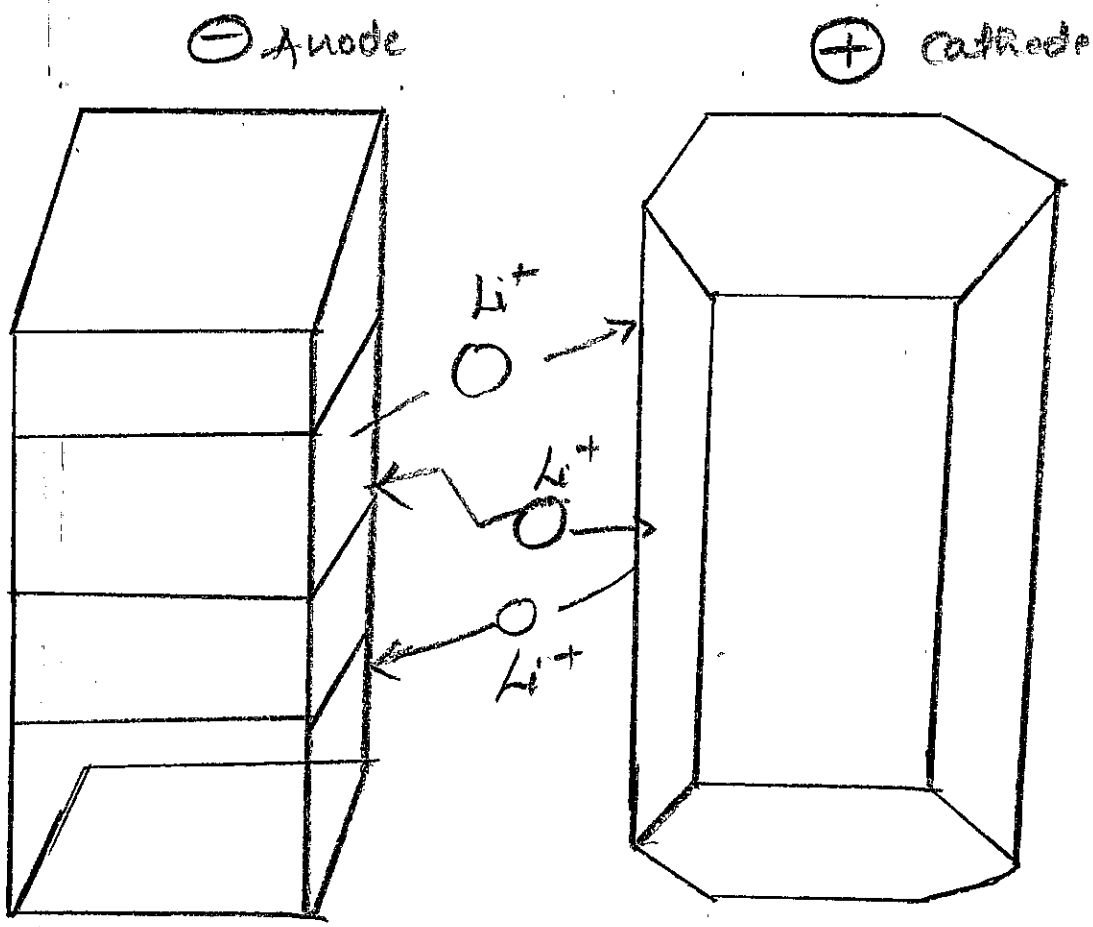
Electrolyte :- $LiPF_6$, $LiBF_4$, $LrClO_4$ in organic solvent such as ether or mixed organic solvents.

Seperator - Microporous polypropylene used.

Working

The principle behind the working is that during charge, lithium ion in the cathode (lithium cobalt oxide) moves from layer to layer in crystallized 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).



	At Anode	At 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

$$LiCoO_2 \rightleftharpoons Li^{+}_{(1-x)}Co^{3+}_{(1-x)}Co^{+4}_{x}O_2 + x Li^{+} + x e^{-}$$

At Cathode of electrolytic cell

$$C_6 + x Li^{+} + x e^{-} \rightleftharpoons C_6 Li_x^{*}$$

Discharge Reactions

At Anode

$$C_6 Li_x \rightleftharpoons C_6 + x Li^{+} + x e^{-}$$

At Cathode

$$Li^{+}_{(1-x)}Co^{+3}_{(1-x)}Co^{+4}_{x}O_2 + x Li^{+} + x e^{-} \rightleftharpoons LiCoO_2$$

Cell Reaction during charge & discharge

$$C_6 + LiCoO_2 \rightleftharpoons C_6 Li^{+} + Li^{+}_{(1-x)}Co^{+3}_{1-x}Co^{+4}_{x}O_2$$

Cell Potential 3.7 V.

Q2.

a Distinguish between primary, secondary and reserve batteries. (6 Marks).

Ans:

Primary Batteries :

Irreversible, to be discarded on discharge.

Function as galvanic cells during discharge

Eg: $Zn-MnO_2$ battery, $Li-MnO_2$ battery etc.

Primary batteries are designed for discharge alone. Attempt to recharge these cells/ batteries results in explosion or fire hazard.

Secondary Batteries :

Reversible are recharged after discharge from an external source of emf by reversal of polarity of these electrodes. thus, are re-dischargeable. the cells function as galvanic cells during discharge and as electrolytic cells during recharge.

Eg: $Pb-H_2SO_4$ battery, Ni-MH battery.

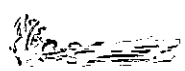
Nicad battery etc.

Reseove Batteries

Batteries with reserved activity with one of the essential battery component kept isolated. Batteries can be activated by insertion of the isolated component. during requirements of electrical energy

$Pb | H_2SO_4 | PbO_2$ battery

$Zn | KOH | Ag_2O$ battery.



Reserve Batteries work (as reserved batteries) on the principle of isolation of essential component of the battery and making them inactive towards self destruction. Generally electrolyte is the component isolated. A battery with only electrode active components loaded and with no electrolyte, will ensure no reaction or decomposition or self destruction. In needs of requirement battery is activated by addition of the isolated electrolyte into the battery and the battery is made available for discharge.

Water activated

Mg | Seawater | AgCl Ag battery

Acid Activated

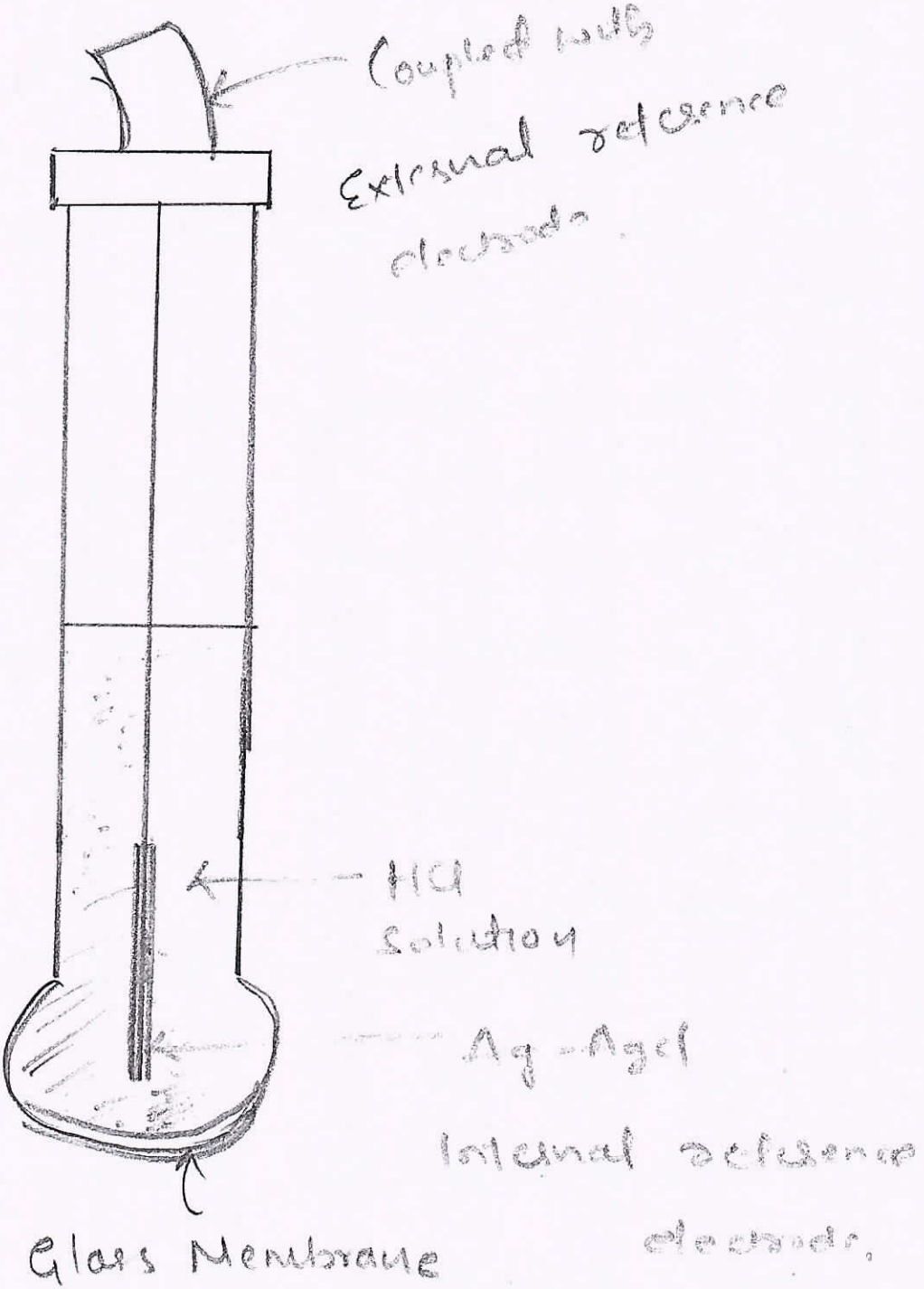
Pb | H_2SO_4 | PbO_2 battery

Alkali Activated

Zn | KOH | Ag_2O battery.

b. Explain construction and working of glass electrode. (7 marks).

Ans:



A glass Membrane electrode consists of a specially made glass membrane extending out as a bulb at the end of a-

plane glass tube containing Ag-AgCl electrode immersed in a solution of HCl.

* Composition of glass Membrane is

$6\% \cdot CaO$, $22\% \cdot Na_2O$, $72\% \cdot SiO_2$.

Glass electrode coupled with Calomel electrode or silver electrode and immersed into analyte, forming a cell.

Cell potential measured will assist the determination of pH of test solution.

By convention, membrane electrode made Cathode. Schematically written as,

$Hg(s), Hg_2Cl_2(s) | KCl(sat) ||$ Analyte $[H^+] = C_1$ Unknown | Glass Membrane | E_1 E_2 | $HCl[0.1\,M]$ $[H^+] = C_2$ Unknown

External Reference Electrode

$E_b = E_1 - E_2$

$| AgCl(s), Ag(s)$.

Very soon after the immersion of electrode into analyte (test solution) as equilibrium is reached.

$$Na^+Gl^- + H^+ \rightleftharpoons H^+Gl^- + Na^+$$

H^+Gl^-, further dissociates to different magnitudes on two sides and results in development of boundary potential

$$H^+Gl^- \rightleftharpoons H^+ + Gl^-.$$

Let E_1 and E_2 are the potentials developed at the Membrane surfaces on the external side (analyte side) and internal side (reference solution side) respectively. From thermodynamic considerations potential developed across the Membrane. boundary potential is given by

$$E_b = E_1 - E_2$$

$$= \frac{RT}{nF} \ln \frac{C_1}{C_2}$$

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

$$= 0.0591 \log C_2 + 0.0591 \log C_1$$

at 298 K for univalent ion H^+ ion $n=1$.

$E_b = \alpha - 0.0591 (-\log c_1)$

where $\alpha = 0.0591 \log c_2$

is constant, because c_2 is constant

$E_b = L - 0.0591 (-\log [H^+])$

Thus boundary potential

$E_b = \alpha - 0.0591\ pH.$

where pH is referred to the pH of test solution (Analyte).

Right side electrode potential or glass Membrane electrode potential.

$E_R = E_G = E_{REF-2} + E_b + E_{asy}$

where E_{assy} is the asymmetric Potential

and $E_{assy} = E_b$ where $c_1 = c_2$.

$= E_{REF-2} + (\alpha - 0.0591\ pH) + E_{assy}$

$= (E_{REF-2} + \alpha + E_{assy}) - 0.0591\ pH.$

$E_R = E_G = E_G^\circ - 0.0591\ pH.$

[where $E_G^\circ = E_{REF-2} - 0.0591 \log c_2 + E_{asy}$

= constant]

Glass Membrane electrode potential is thus a function of H^+ ion concentration or pH of analyte.

Left side electrode potential

$$E_L = E_{REF-1}$$

Cell potential is given by

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

$$= E_q - E_{REF-1}$$

$$= E^\circ_q - 0.0591\,pH - E_{REF-1}$$

$$\therefore pH = \frac{E^\circ_q - E_{REF-1} - E_{cell}}{0.0591}$$

$$pH = \frac{K' - E_{cell}}{0.0591} \quad \text{at } 298\,K.$$

c) For the cell, $Fe|Fe^{2+}(0.01N)||Ag^+(0.1N)|Ag$ Write the cell reaction and calculate the emf of the cell at 298K if standard potentials of Fe and Ag electrodes are $-0.44V$ and $0.8V$ respectively.

Ans:

$Fe|Fe^{2+}(0.01M)||Ag^+(0.1N)|Ag$.

cell scheme ↑.

$E^\circ_{Fe^{2+}/Fe} = 0.44V$ $\quad E^\circ_{Ag^+/Ag} = 0.8V$

Electrode Reaction

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

$$Ag^+ + e^- \longrightarrow Ag$$

Multiply by 1 and 2.

$$Fe \longrightarrow Fe^{2+} + 2e^- \quad \times 1$$

$$2Ag^+ + 2e^- \longrightarrow 2Ag \quad \times 2$$

$$Fe + 2Ag^+ \longrightarrow Fe^{2+} + 2Ag$$

Reactant Product

$$E_{cell} = E_R - E_L + \frac{2.303\,RT}{nF} \log \frac{[\text{Reactant}]}{[\text{Product}]}$$

$$= 0.8 - (-0.44) + \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log \frac{0.1}{0.01}$$

$$= 1.24 + \frac{0.0591}{2} \log \frac{0.1}{0.01}$$

$$= 1.24 + 0.02955 \times \log(10)$$

$$= 1.24 + 0.02955 \times 1$$

$$= 1.24 + 0.02955$$

$$= 1.24\ V$$

Q3

a. Define metallic Corrosion? Describe the electrochemical theory of corrosion taking iron as an example. (07 Marks)

Ans: * The Corrosion is characterised by the formation of Small galvanic cells due to heterogeneities.

* Part of the metal acts as anode another part of the metal acts as cathode.

Anodic part of the metal undergoes destruction by Oxidation

Steel (Iron) undergoes Corrosion by following reaction

Anodic (Oxidation or corrosion)

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

Reduction depends on the content in the medium. some important reactions are

H_2 - evolution type:

$2H^+ + 2e^- \longrightarrow H_2$ (Medium is acidic)

$2H_2O + 2e^- \longrightarrow H_2 + 2\overline{O}H$

[When the medium is neutral or slightly alkaline]

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

O_2-absorption type

$\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2\overline{O}H$

[When medium is neutral or slightly alkaline]

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

[When the medium in acidic & presence of dissolved oxygen Do

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

$$Fe^{2+} + 2\bar{O}H \longrightarrow Fe(OH)_2 \cdot FeO \cdot H_2O$$

$$2Fe(OH)_2 + H_2O + \frac{1}{2}O_2 \longrightarrow 2Fe(OH)_3$$

$$Fe_2O \cdot 3H_2O$$

$$3Fe(OH)_2 + \frac{1}{2}O_2 \longrightarrow Fe_3O_4 \cdot 3H_2O.$$

Q3

b) Explain i) Differential metal corrosion

ii) Water line corrosion.

Ans: Corrosion arising out of formation of galvanic cell is galvanic corrosion. Two or more metal is contact and exposed together to the corrosive form a galvanic cell.

Anodic metal undergoes corrosion. Doving force for the corrosion is the difference in electrode potentials of the two metals.

Examples: i) Steel vessels with brass tap.

ii) Brass Vessels with steel tap

Steel acts as anode and undergoes corrosion by oxidation

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

Brass acts as cathode and facilitates reduction reaction over its surface

$$2H^+ + 2e^- \longrightarrow H_2\uparrow \quad \text{(Acidic Medium)}$$

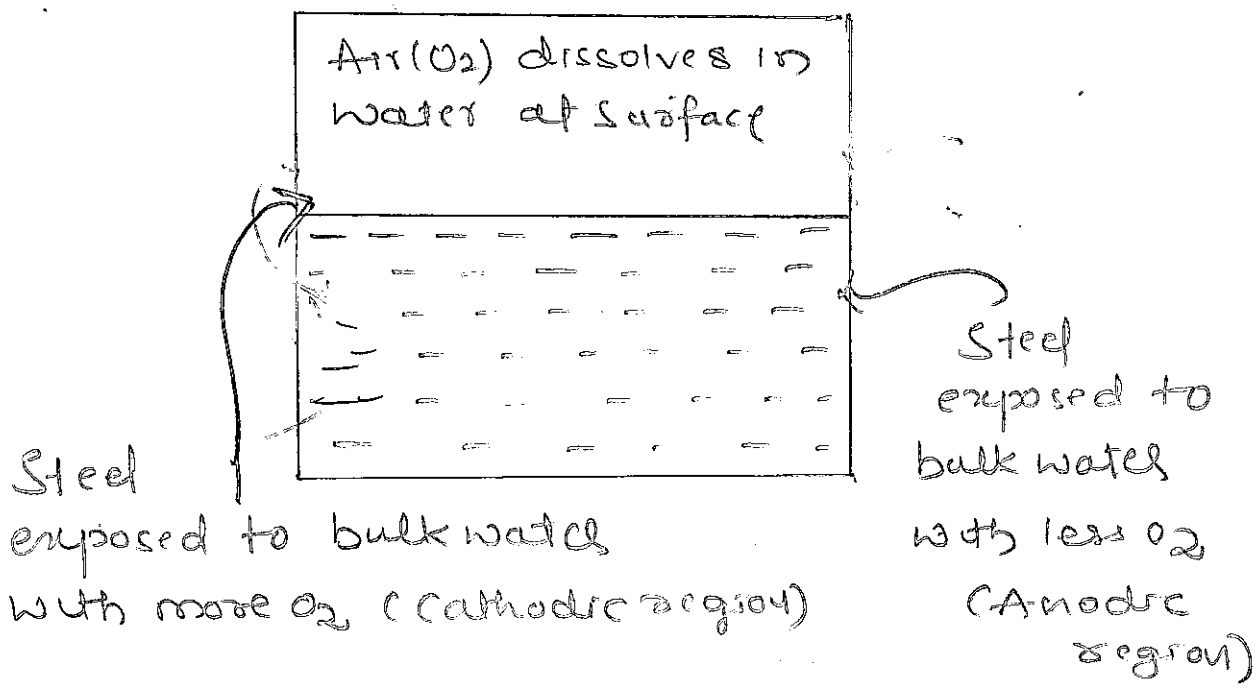
$$\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^-$$

(Neutral or Slightly alkaline medium.

Water line Corrosion

Metal corrosion that occurs along the water line is called water line corrosion.

For example, when steel tank is used for storing water, there is formation of O_2 concentration cell. Steel metal exposed to more oxygenated surface water acts as cathode. Steel parts exposed to less oxygenated bulk water acts as anode.



Suppose a steel tank partially filled with water. Following reaction occur.

Anodic corrosion reaction beneath the water surface level.

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

Cathodic reduction reaction at water surface level.

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

Fe^{2+} ions and OH^- ions reacts to form $Fe(OH)_2$ precipitate.

Q2c What is electroplating? Explain the electroplating of chromium. (7 marks)

Ans: The process of deposition of thin and uniform layer of metal or metal alloy on to the electrically conducting object surface by electrolysis is known as electroplating.

Electroplating of Chromium

Chromium is employed for either decorative purposes (as a thinner coat) or engineering purposes (as a thicker hard coat). Mentioned below are coating specifications.

	Decorative Coating	hard Coating
Thickness Hardness	0.25 – 0.75 μm	2.5 – 300 μm 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}	250 g/L chromic acid + 2.5 g/L H_2SO_4 (in 100:1 ratio) + 1 g/L Cr^{+3}
Temperature	35 to 45 °C	50 to 65 °C
Current density	245 – 430 A/ft²	290 – 580 A/ft²

Current efficiency	10 to 15 %.	17 to 21 %.
Anode Material	Insoluble lead-Pb-Sb alloy or Pb-Sn alloy	Insoluble lead-Pb Sb alloy
Cathodic Material	Surface cleaned object Metal	Surface cleaned Object Metal
Reaction at anode	$H_2O \longrightarrow \frac{1}{2}O_2\uparrow + 2H^+ + 2e$	$H_2O \longrightarrow \frac{1}{2}O_2\uparrow + 2H^+ + 2e^-$
Reaction at Cathode	$Cr^{+3} + 3e^- \longrightarrow Cr$	$Cr^{+3} + 3e^- \longrightarrow Cr$

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

Fe^{2+} ions and OH^- ions reacts to form $Fe(OH)_2$ precipitate.

Q4.

a. What is meant by Metal finishing? Mention (any five) technological importance of Metal Finishing. (6 marks).

Defn: Process of Surface Modification by way of deposition of another metal or alloy or polymer or ceramic or oxide layer to bring about intended surface characteristics is known as metal Finishing.

Technological Importance of Metal Finishing.

1) Better corrosion resistance
2) Better hardness, strength, Impact resistance
3) Better thermal conductance or resistance.
4) Better Optical reflectance
5) Better electrical conductance or insulation.

b) What is electroless plating? explain the electroless plating of copper. (7 Marks)

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

Electroless plating of copper.

Substrate surface needs to be cleaned by suitable cleaning Methods (Solvent degreasing acid pickling, alkali pickling, Mechanical Polishing etc). However, when the object is non-conducting or insulator material such as plastics, PCB's, glass etc. it needs to be activated by treatment with acidified $SnCl_2$ and then with acidified $PdCl_2$

$$SnCl_2 + PdCl_2 \longrightarrow Pd\downarrow + SnCl_4$$

Constituents.	Amount	Purpose
$CuSO_4$	12g/L	Provides Metal ions
HCHO	8g/L	Reducing reagent
Rochelle Salt	14g/L	Complexing Agent
NaOH	15g/L	Provides alkaline Medium
EDTA	20 g/L	Complexing Agent & exaltant
pH	11.0	
Temperature	25°C	

Reactions :

Oxidation of reducing reagent

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

Reduction over object surface

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

Overall reaction

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

Applications :

1) Establishing through-hole connections on double sided PCB's
2) For plating on non-conductors or as a base before electroplating.

c. Explain the factors affecting the rate of corrosion (i) Nature of corrosion product (ii). Ratio of anodic to cathodic areas (iii) pH.

Ans:

1> Nature of corrosion product

Some metals and alloys exhibit an inherrent property of forming a protective coating of their compounds when exposed to different medid. When corrosion product film over the objed metal surface is i> Inert to the metal and medium, further corrosion of the metal is prevented. This is known as passivation of metal. Some of the 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 etc.

2) Ratio of Anodic and cathodic area

Corrosion Rates are dependent on the relative areas of anode and cathode corrosion rates.

for example: steel water tanks with a with a small brass tap; anodic steel tank will hardly exhibit corrosion effects. However, when the relative surface area of cathode is larger, larger cathodic current developed is countered by small anodic area which, result in localized aggressive corrosion of the anodic metal. For example, a brass water tank with a steel tap, steel tap exhibits severe corrosion.

pH

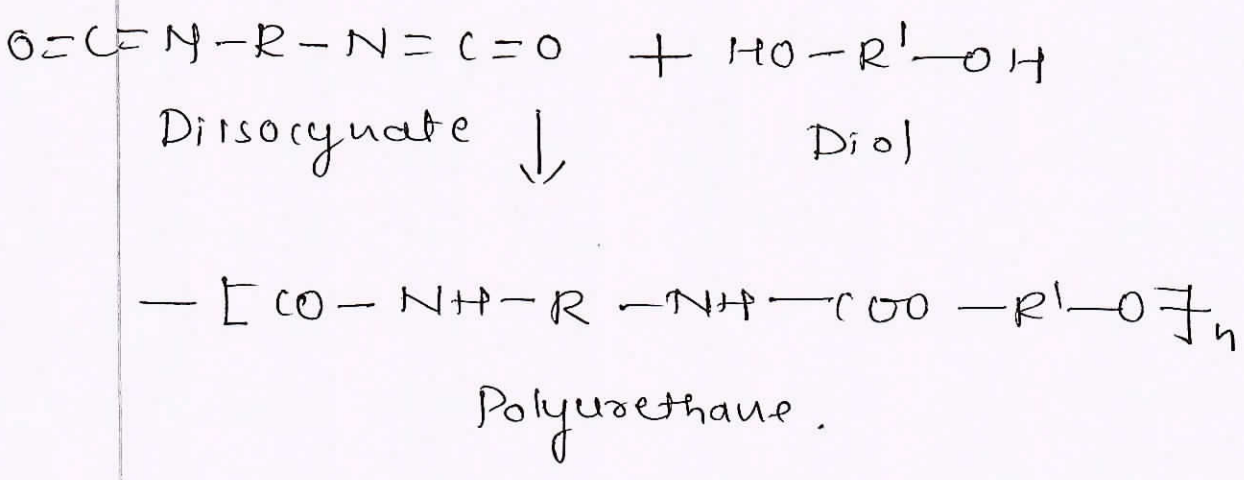
Lower pH suggests the acidic medium and many of the metals undergo severe corrosion except those with higher reduction potential. Higher pH represents alkalinity and many metals exhibit resistance. However too high alkalinity may lead to the corrosion of metals. Iron exhibit lower rate of corrosion in a medium of pH 5.0 in the absence of O_2. At the same pH, with dissolved O_2 it exhibits relatively higher corrosion rate.

At pH values below 4.5, it exhibits aggressive corrosions irrespective of the presence or absence of O_2. Metals are known to show minimised corrosion rates at certain pH values specific of the metal. At highes or lower pH leades to increased rates of corrosion of the Metals.

Q.5.

a) Explain the Synthesis and applications of Polyurethane. (4 Marks).

Ans: Polyurethanes are synthesized by reaction between diisocynate and a diol or a triol. During addition, H-atom of OH group migrates and adds to nitrogen atom as shown below.



Properties and applications

1) As an elastomer, because of its resistance to oil, grease and corrosive chemicals. it's used for tyre treads and industrial wheels. with air (or inert gas) bubble trapped inside the solid bulk

2) It is also used in tubeless tyres.

3) Because of cushioning effect of the PU foams, PU foams, PU foams are widely used in the making of automobile furniture.

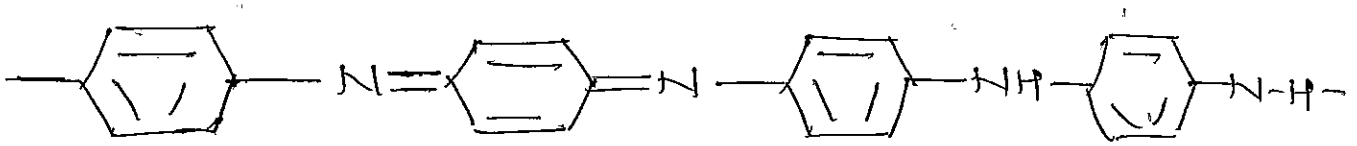
4) As a flexible fibre, because of its stretching property. It is used in lightweight garments and swimsuits.

b) Describe the Mechanism of Conduction in Polyaniline and factors influencing Conduction is organic polymers. (7 Marks)

Mechanism:

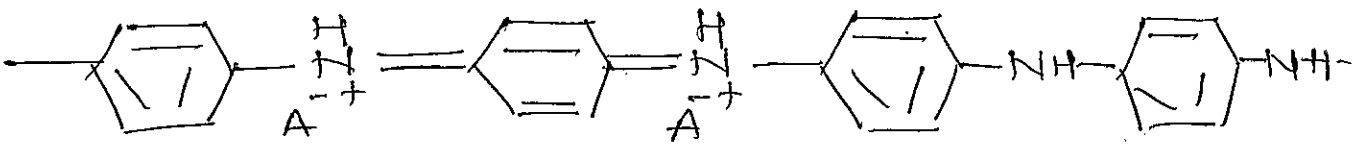
It has been demonstrated that the polyaniline chain can be formed by various combinations of two repeating units.

owing to this · PANI has many unique properties and electronic ~~condition~~ conduction mechanisms that distinguish it from the rest of the conducting polymer.



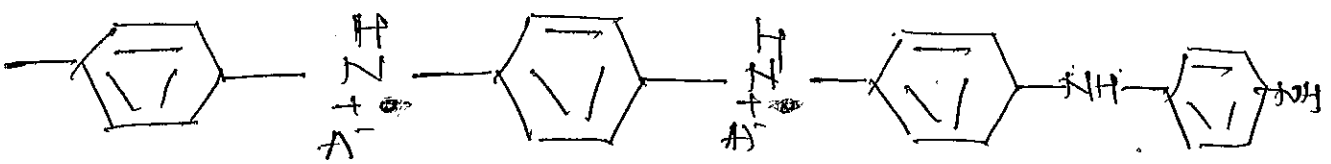
Polyemeraldine

H^+A^- Protonation



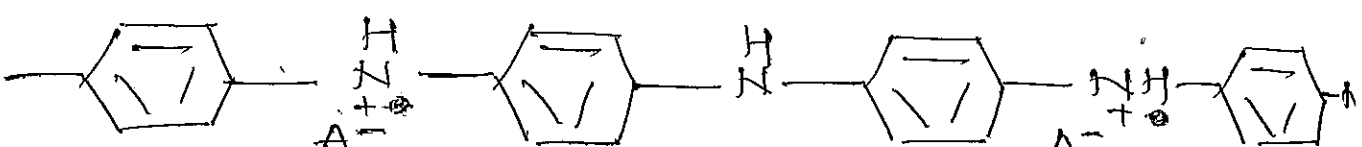
Bipolaron form

Dissociation of bipolaron to form two polaron.

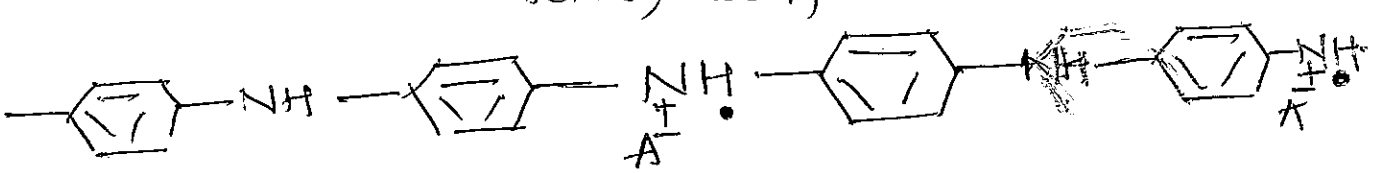


Polaron form.

delocalization of Polaron



↕ Resonance forms of delocalized Polaron form



Q5
c Explain any two size dependent properties of nanomaterials.

1> Surface Area

When a bulk material is divided into smaller fragments, its total volume remains same but the total surface increases. if a cubic meter is progressively cut into smaller and smaller cubes, until it forms cubic nanometers, the surface area is continuously increased as is shown below. Thrs increases surface to volume or surface area to mass ratio results in very interesting physical and chemical properties of the nanomaterials. one such property increase the catalytic activity of the substances per unit volume or mass of the nano-scale. Also the reactivity of substances will increase at nano scale dimensions.

2> Electrical Properties.

Substances can be classified as good conductors.

Semiconductors, and insulators depending on their electrical conductivity or resistivity. The energy gap (forbiddon gap) between the valence band (VB) and conduction band and the presence and number of electrons in the conductoy band decides the conductivity of the materials. In good conductor like metal there is overlaping of VB and CB, in semiconductor it is of the order of 1-2eV and in an insulator, the band gap is larger. Large number of atoms (billions or billions) in a bulk metal and overlaping of VB with CB and energy levels are continous and the metals are very good conductors.

Q6
a: What are nanomaterials? Explain the synthesis of nano-materials by sol-gel Process.

Ans: Nano-Materials are the materials having nano-scale dimension in at least one direction. Material containing particles in nan

unbound state or as an aggregate or as an agglomerate and where for 50% or more of the particles in the number size distribution one of the external distribution. one or more external dimensions is in the size range 1nm to 100nm.

Aim: The sol-gel route offers a degree of control of composition and structure at the molecular level. The process involves the generation of a colloidal suspension (sol). which is subsequently converted to viscous gel. and solid material.

1) The sol-gel process is a wet-chemical technique that uses either a chemical solution or colloidal particles to produce an integrated network.

2) The Metal alkoxides. and Metal chlorides are typical precursors. They undergo hydrolysis condensation and polycondensation reaction to form a gel.

* After a drying process, the liquid phase is removed from the gel. Thermal treatment (calcination) favours further polycondensation and formation of nanomaterials.

Different steps in sol-gel Methods are briefly below.

1. Formation of different stable solutions of the alkoxides or solvated metal salt precursor.

2. Gelation resulting from the formation of an oxide or alcohol bridged net (the gel) by a polycondensation reaction which result in increased viscosity of the solution.

3. Aging of the gel (Syneresis) during which polycondensation reactions continue until the gel transforms into a solid mass accompanied by contraction of the gel network and expulsion of solvent from gel pores.

4) Drying of gel, when water and other volatile liquids are removed from the network.

5) Dehydration

6) Densification and decomposition of the gels at high temperature (T > 800°C) The pores of the gel network are collapsed and remaining organic species are volalized.

b) Write a note on Fullerenes. Mention its applications.

Fullerenes are zero dimensional solids Fullerene is an allotrope of Carbon C_{60}. It's hallow spherical molecule found in Carbon soot. The molecule is called fullerene because it is resembled the geodesic dome designed by the American Architect Buckminister fuller. Fullerene Molecule with 60 carbon atoms contain interlocked.

Pentagons and hexagons similar to a soccer ball. They are also called bucky ball and have truncated isohedron structure. May other bucky ball with 70 76, 78, 84 carbon atoms are discovered.

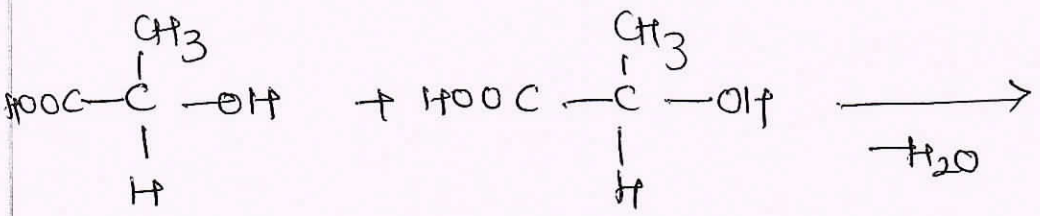
Fullerenes are discored Kroto, Smalley and Curl in 1995.

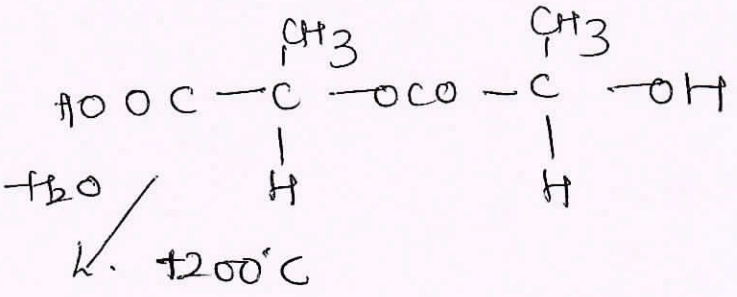
Applications :

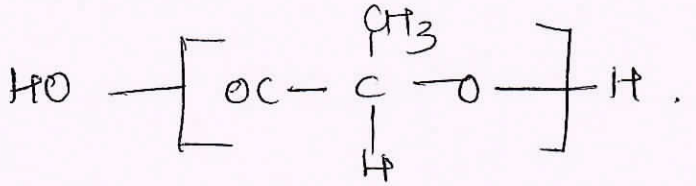
1) Fullerenes are used as lubricants due to their spherical shape and slippery nature.
2) Fullerenes are used for reinfroing different structures where lightness and strength of materials is required.
3) C60 can theoretically take up 60 atoms of hydrogen and can be used as hydrogen storage material for fuel cells and same secondary batteries
4) Fullerene acts as electrophile.

Qc Explain the Synthesis, properties and application of Polylactic acid (7 Marks).

Ans: Lactic acid has a Carboxylic acid group and a hydroxyl group attached to the same Carbon atoms. The acid group of one molecule and the hydroxyl group of another react (esterefication reaction) and result in Condensation of water molecule. The reaction is irreversible and forword reaction is favoured by removal of water.







Polylactic acid.

Properties

1) It is amorphous or crystalline thermoplastic Polymer

2) Glass transition temperature T_g = 60-65°C

3) Melting Point = 130 - 180°C

4) Soluble in Ethyl acetate, propylene Carbonate, pyridine, hot benzene

5) High Surface energy.

Applications:

1) Micro and nanoparticles are important catagory of delivery systems used in Medicine

2) Poros PLA Scaffolds have been found to be potential reconstruction matrices for damaged tissues and Organs

3) High Surface energy results in good printability, making it widely used in 3D printing.

Q7

a. With suitable example explain Microwave synthesis and bio catalyzed Reactions. (7 Marks).

Ans: Microwave chemistry is based on the efficient heating of materials (in most cases solvents) by dielectric heating effects Dielectric heating works by two Major Mechanisms -

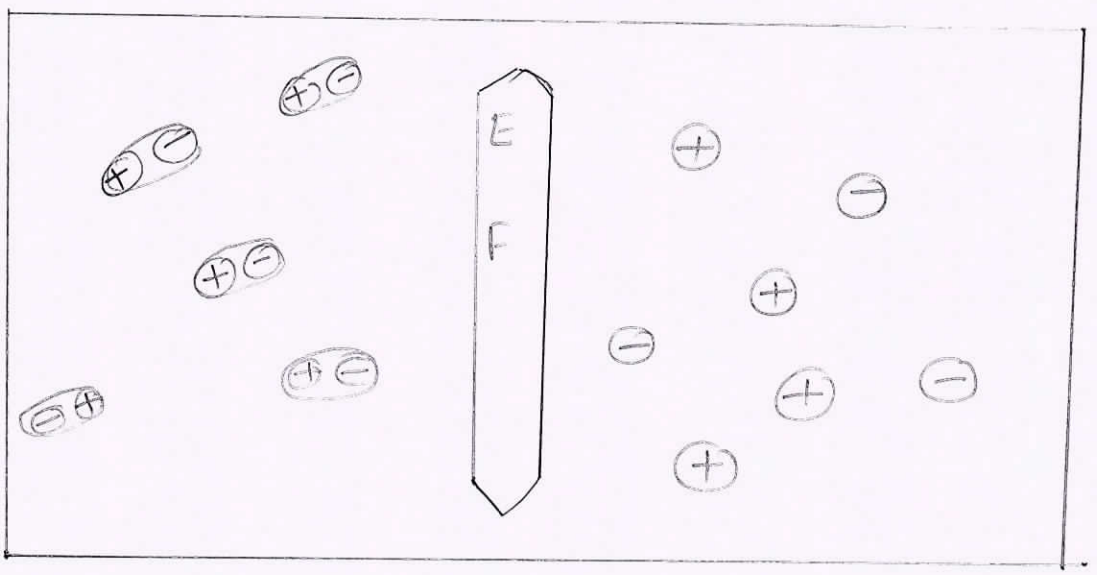
Dipolar Polarization.

For substance to be able to generate heat when irradiated with microwaves it must be a dipole. Since, the microwave field is oscillating, the dipoles in the field align due to the oscillating field This align-ment causes rotation - which results in friction and ultimately in heat energy.

Ionic conduction

During the conduction, dissolved (completely) charged particles (usually ions) oscillate back.

and fourth under the influence of microwave irradiation. This oscillation causes collisions of the charged particles with neighbouring molecule or atoms which are ultimately responsible for creating heat energy.



Dipolar Polarization

Ionic Polarization.

Q6 Explain the Synthesis of Adipic acid by conventional route from Benzene and green route from Glucouse (7Marks).

Ans:

Biocatalyst for Green chemistry.

Biocatalyst is an enzyme which alters the rate of Chemical or biochemical reactions.

Biocatalyzed reaction:

Enzymes are biocatalyst. These biocatalyst (enzymes) are used in the industrial preparation of ethanol.

Ethanol is prepared by the fermentation of molasses a dark brown coloured syrup left after crystallization of sugar which still contains about 40% of sugar. The process of fermentation actually involves breaking down of large molecules into simples ones in the presence of enzymes. The source of these enzymes is yeast. The various reaction taking place during fermentation of carbohydrates are

Invertase

$$C_{12}H_{22}O_{11} \longrightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

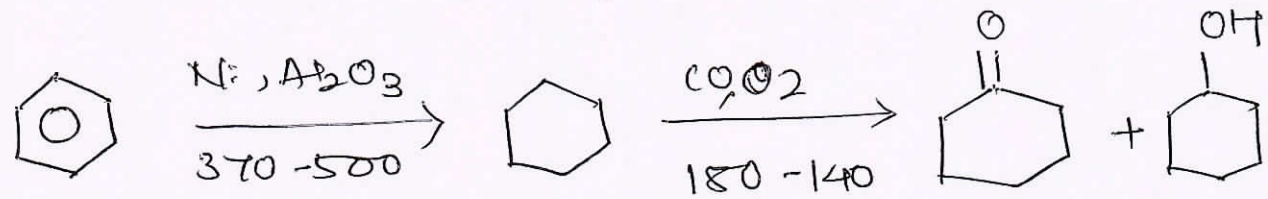
Zymase

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH + 2CO_2$$

b) Explain the Synthesis of Adipic acid by conventional route from Benzene and green route from glucose.

Ans:

Conventional Route.



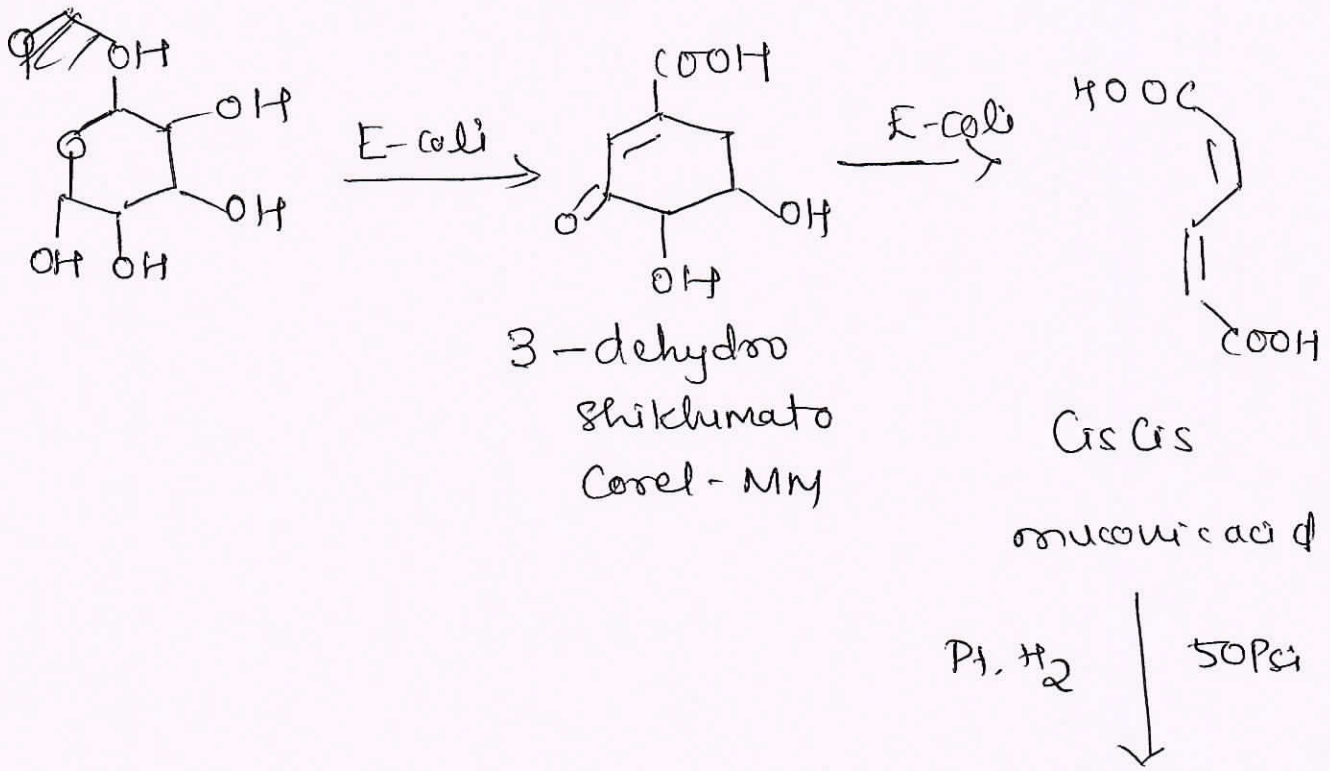
Benzene → Cyclo hexane → Cyclo hexanone + Cyclo hexanol

Cyclo hexanone / Cyclo hexanol → ($Cu\,NH_4\,VO_3$, HNO_3)

$$HOOC-(CH_2)_4-COOH$$

Adipic Acid.

Greenes Pathway



$HOOC-(CH_2)_4-COOH$

Adipic Acid.

c) Describe construction and working of Methanol – Oxygen fuel cell (6 marks).

Ans: This fuel cell is represented as,

Porous (Impregnated with Pt) $(CH_3OH + H_2SO_4)$ | H_2SO_4 (aq) | O_2 Porous (Impregnated with Pt.

The cell consist of

Anode : Porous Carbon with dispersed Platinum

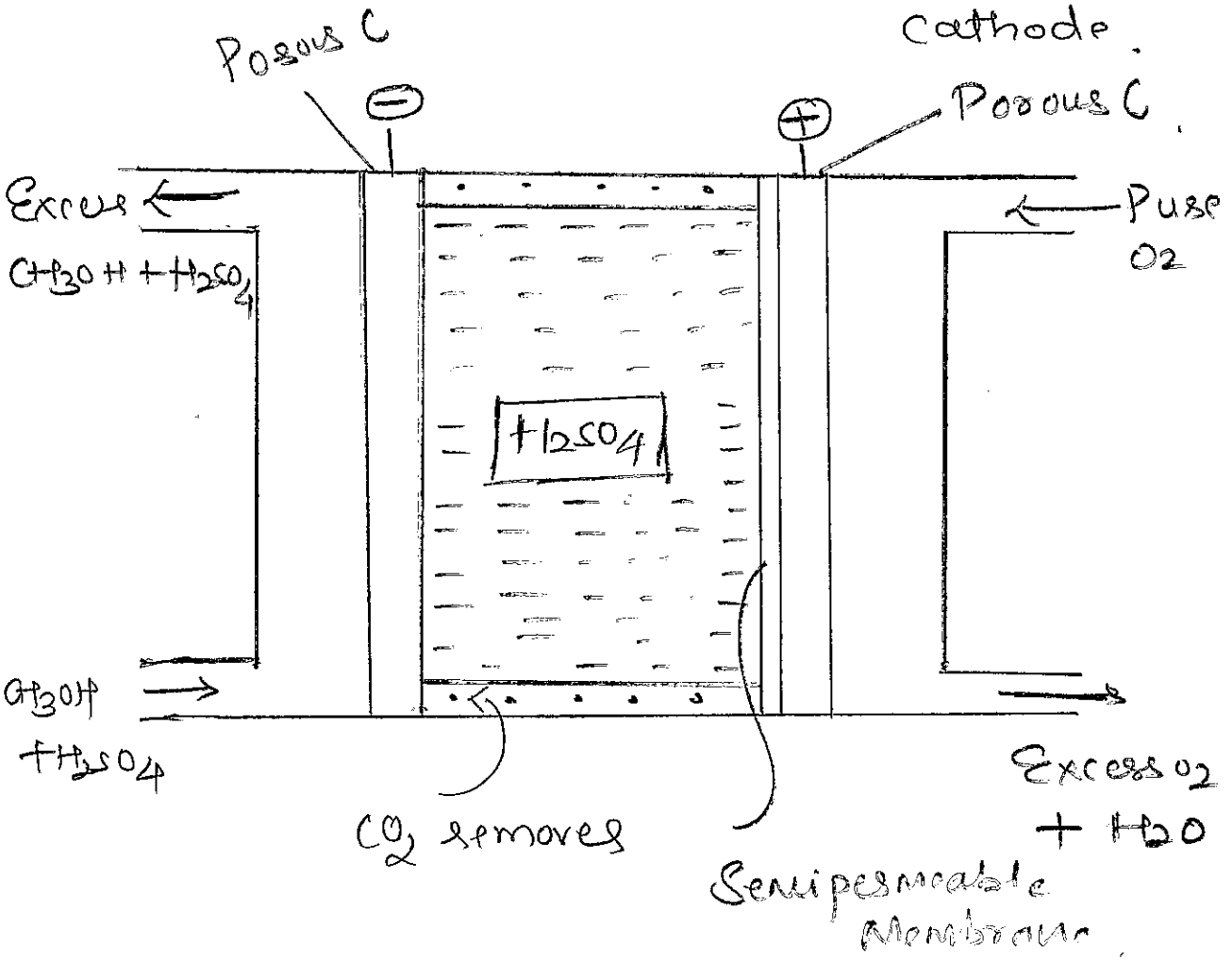
Cathode : Porous Carbon with dispersed Platinum

Electrolyte : Aqueous H_2SO_4.

Active Components :

Fuel : Methanol mixed with Sulphuric acid supplied at anode.

Oxidant : Pure oxygen supplied at cathode.



Adjacent 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 – Oxygen directly at cathode.

Working :

Following Reactions occur during power generation.

Anodic Oxidation

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

Cathodic Reduction

$$1\tfrac{1}{2}O_2 + 6H^+ + 6e^- \longrightarrow 3H_2O .$$

Cell Reaction

$$CH_3OH + 1\tfrac{1}{2}O_2 \longrightarrow CO_2 + 2H_2O$$

Cell Potential 1.2 V.

Applications : Used in Military applications and large Scale Power generations.

Q8 a Describe the hydrogen production by photo catalytic water splitting Method. (7 Marks).

Ans: Production of hydrogen - Hydrogen is the future green fuel and doesnot cause environmental pollution.

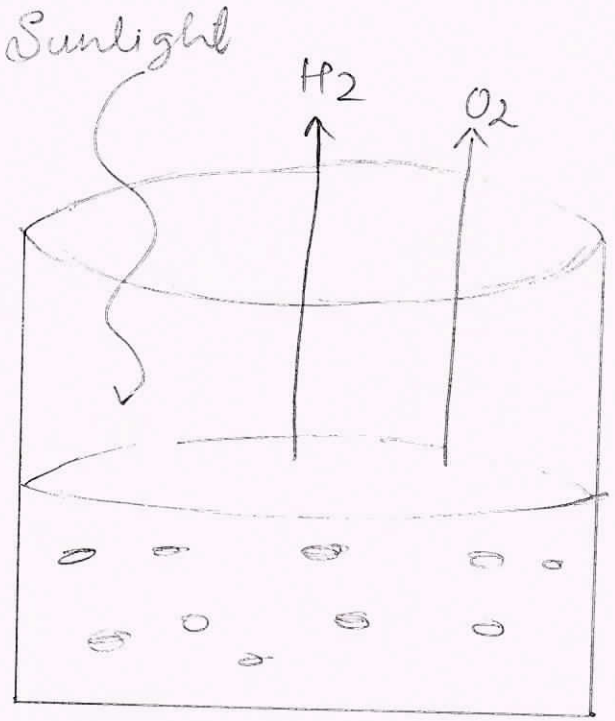
Photocatalytic reaction

Input : Photo catalyst particles, Sunlight and water

Output : oxygen and hydrogen

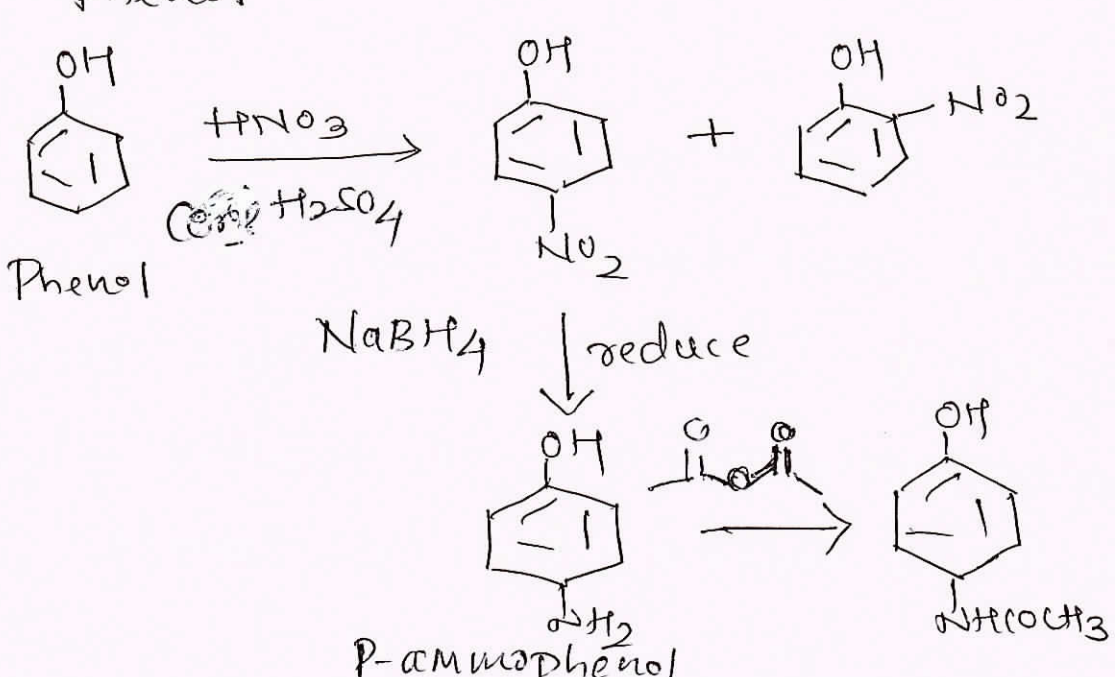
Photo catalyst in the from of particles is immersed in water based electrolyte and it produces charge carriers holes and electrons after absorbing sunlight. Charges are moved to surface of the photocatalyst to start the chemical reaction. Holes are oxidizing the water and electrons reduces hydrogen ions to hydrogen gas.

$$H_2O \xrightarrow{\text{Photocatalyst}} H_2 + O_2.$$

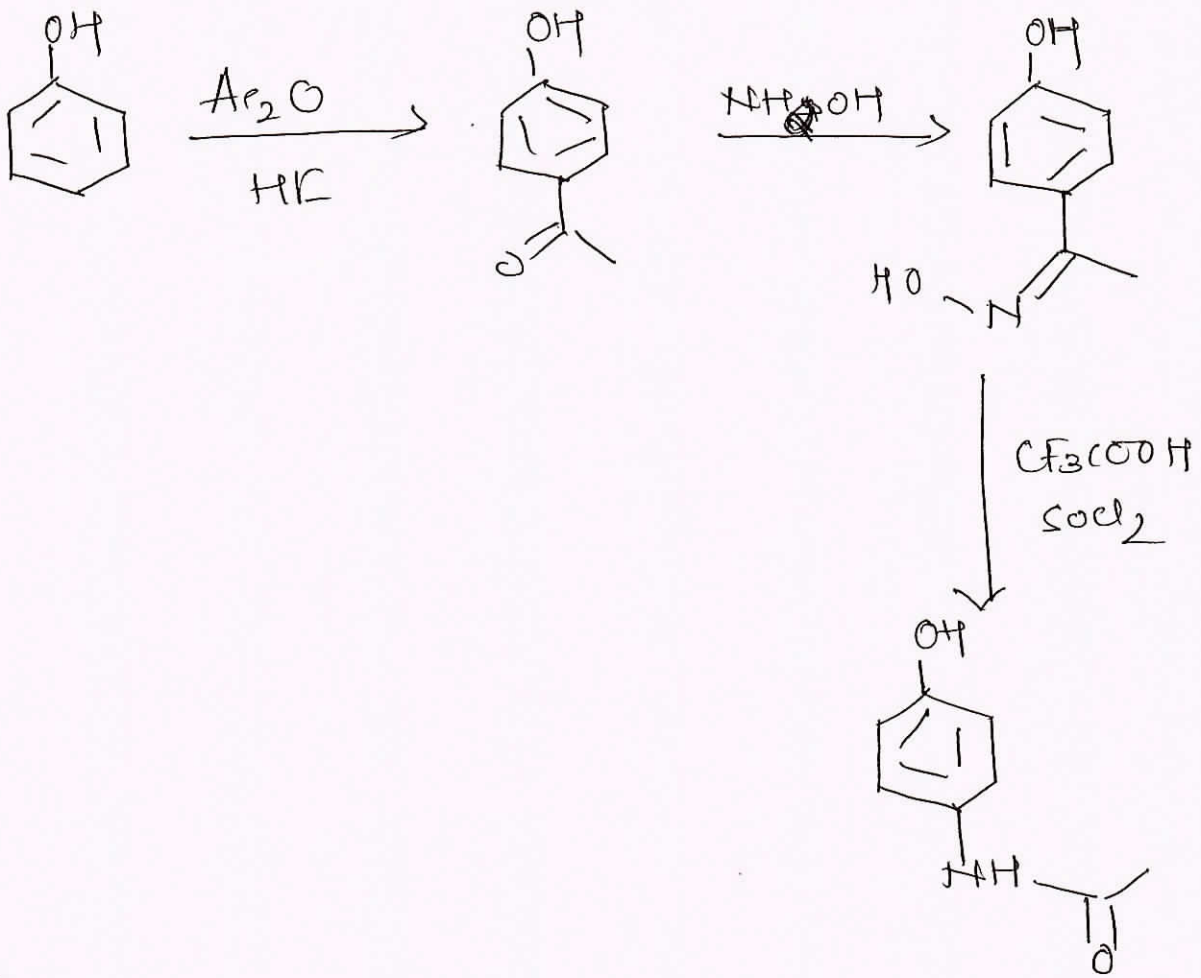


b) Explain the Synthesis of Paracetamol by conventional and green route from Phenol (4 marks).

Ans. Synthesis of Paracetamol from Phenol



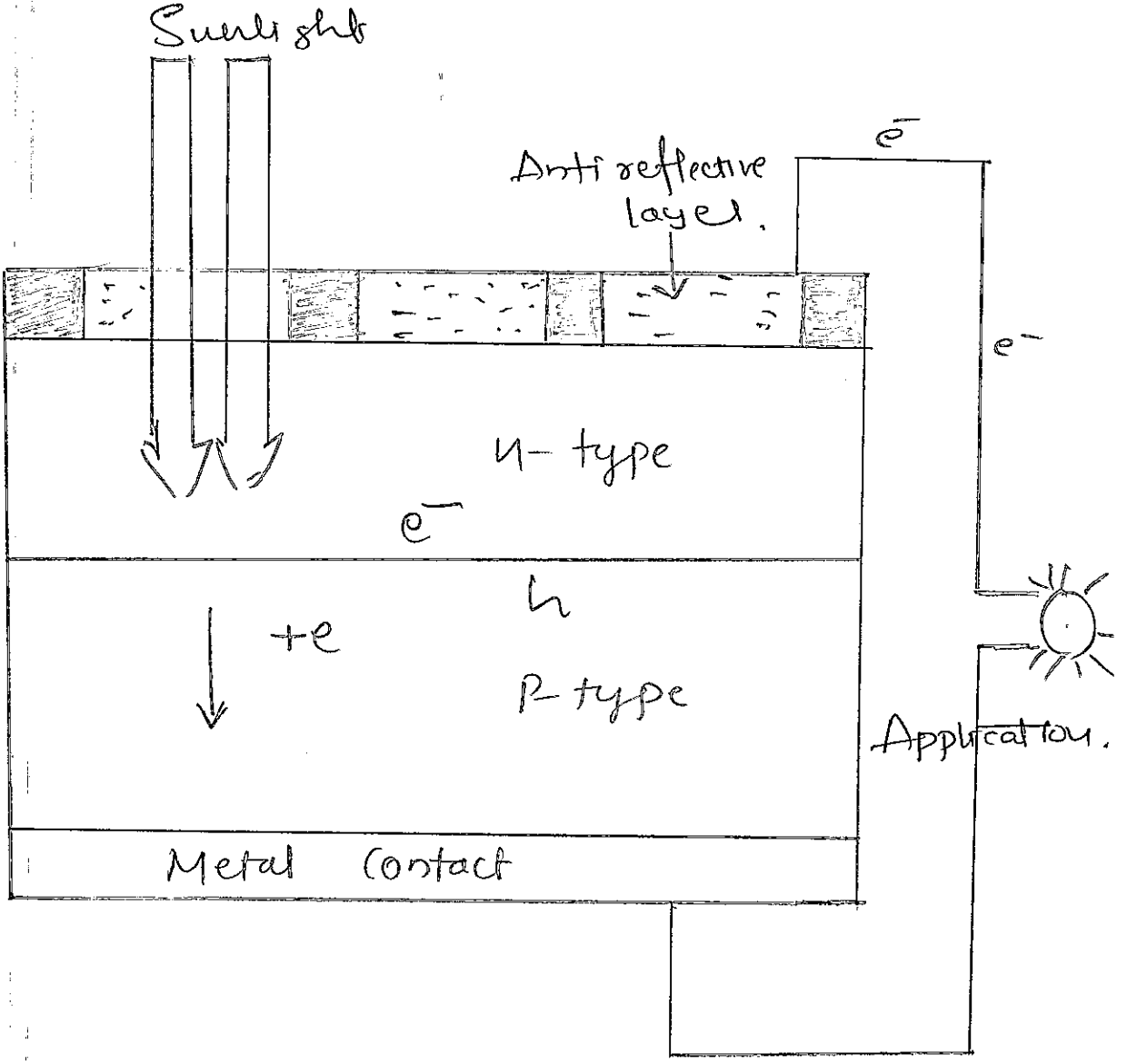
Green Synthesis



Q.8c Explain the construction and working of Photovoltaic Cells (6 Marks).

Ans: Photovoltaic cells or solar cells are made out of semiconductors which have the capacity to absorb light. When n-type and p-type semiconductor are brought together a semiconductor diode is formed. The semiconductor diode

separates and collects the carriers and conducts the generated electrical current preferentially in a specific direction.



A typical Silicon photovoltaic cell is composed of thin poly crystalline silicon wafer consisting of an ultra-thin layer Phosphorous doped. &(n-type) silicon on top of the boron doped (p-type) silicon.

Hence P-N junction is formed. A metallic grid forms one of the electrical current contacts of the diodes and allows light to fall on the semiconductor between the grid lines as shown in the figure. An antireflective layer between the grid lines increases the amount of light transmitted to the semiconductor. The cells other electrical contacts is formed by a metallic layer on the back of the solar cell.

PV cell works on the principle of Photovoltaic cell $E=h\nu$. When light radiation falls on the P-N junction diode, electron-hole pairs are generated by the absorption of the radiation. The electrons are drifted to and collected at the n-type end. and holes are drifted to p-type end. When these two ends are electrically connected through a conductor, there is flow of current between the two ends through

external circuit. The Photoelectric current is produced.

Q9

a) Explain the theory, instrumentation and applications of flame Photometry (7marks)

Ans:

Instrumentation : The flame photometer consists of the following basic components

Source of the flame : A burner in the flame photometer is the source of the flame The temperature of the flame is one of the critical factors in flame photometry.

Nebulizes : Nebulizer is used to send homogeneous solution into the flame at a balanced rate.

Optical System : The Optical system consists of convex mirror and convex lens. the convex mirror transmits the light emitted -

from the atoms and also helps to focus the emissions to the lens. The lens helps to focus the light on a point or slit.

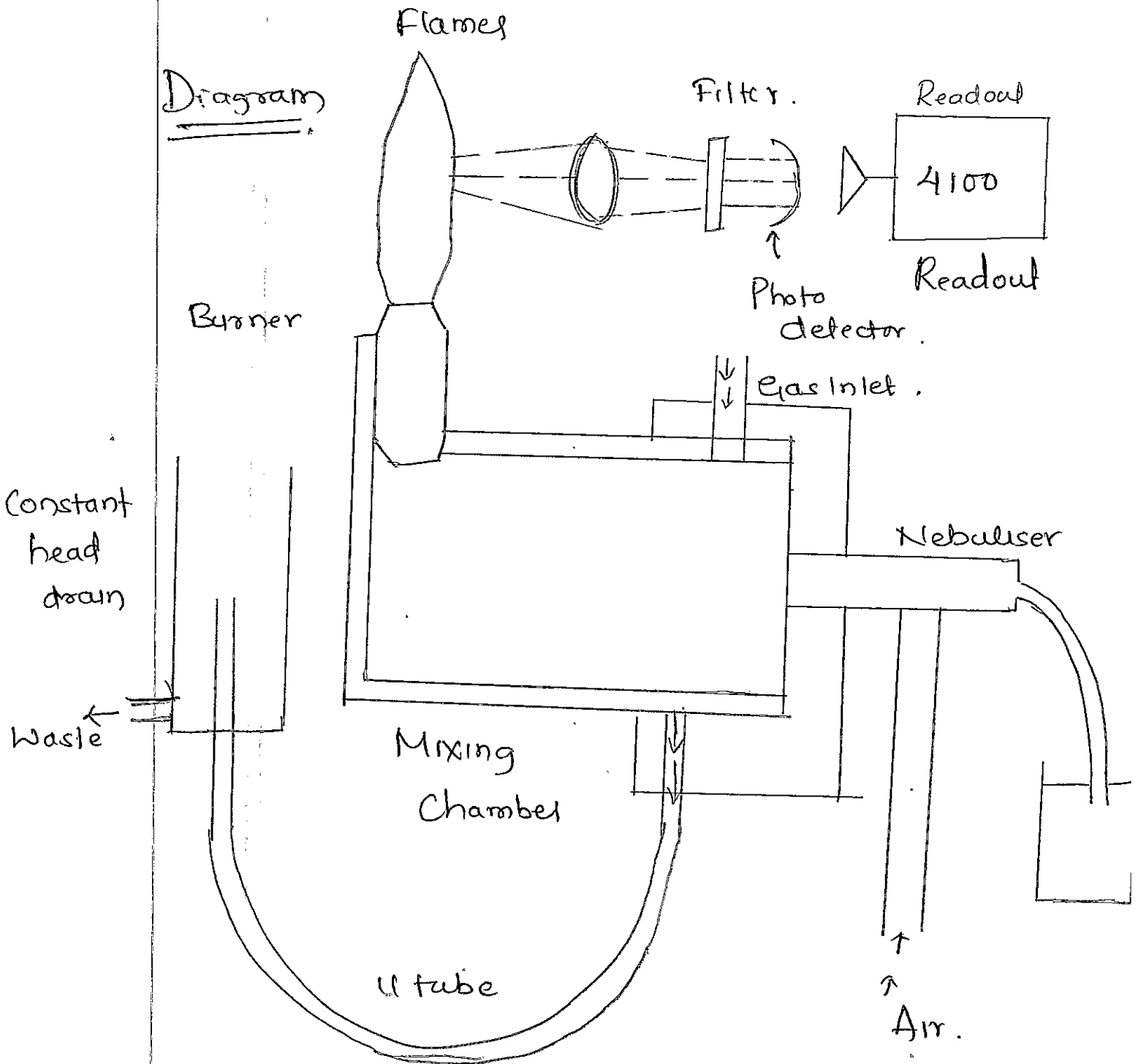
Sample colour filters :

The reflections from the optical systems pass through the slit and reach the filters. Filters will isolate the wavelength to be measured, from that irrelavant emissions,

Photodetector : The intensity of radiation emitted by the flame ~~pass through the slit and reach the filters. Filters will isolate the wavelength to be measured from that of irrelavant emissions~~. is measured by Photo detector. Here the emitted radiation is converted to an electrical signal with the help of Photo detector.

Determination of Sodium in water sample using flame photometer.

Diagram


Flames
Filter.
Readout
4100
Readout
Photo detector.
Burner
Gas Inlet.
Constant head drain
Nebuliser
Waste
Mixing Chamber
U tube
Air.

1. Prepare the following standard solution to construct calibration graph 0·2, 0·4, 0·6, 0·8, 1·0 mg Na in 100ml standard flasks from the 1000mg/L sodium standard solution, using deionized water as a diluent.

2) Select the sodium filter at 589 nm and aspirate the 1.0mg Na/100ml standard ~~solution~~ and adjust sensitivity control to obtain a reading of 100

3) Aspirate deionized water and adjusts the zero control to obtain zero reading

4) Asprate 1.0 mg Na/100ml standard Again re-adjust to 100

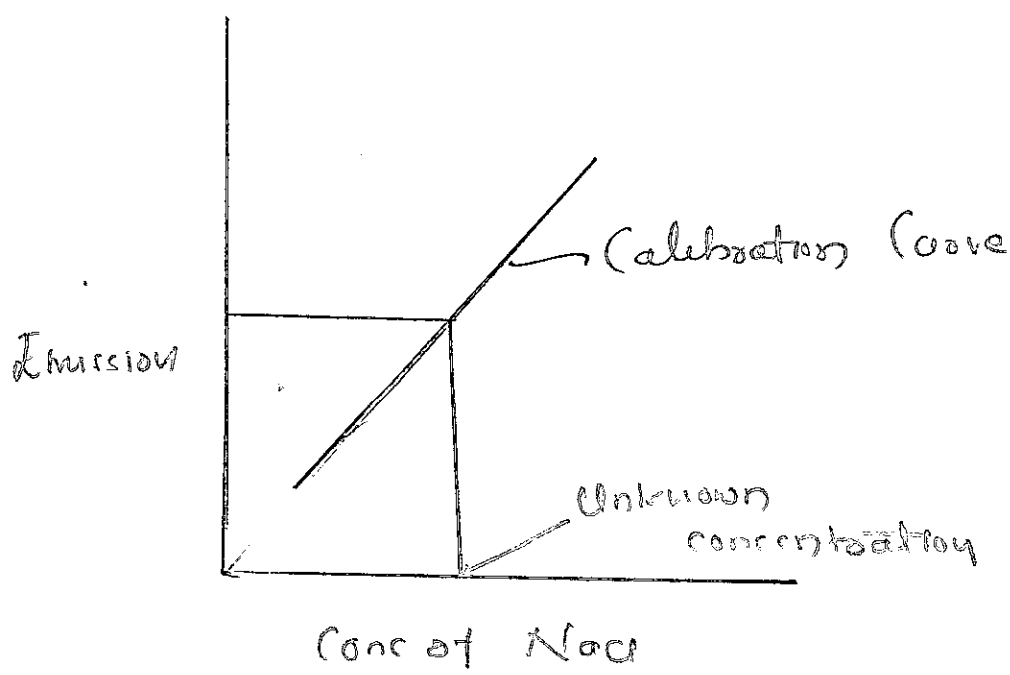
5) Aspirate deionized water again and re-adjusts if necessary to zero.

6) Repeat steps 4 and 5 if necessary to obtain 100 on the standard and zero on deionized water.

7) Aspirate the other standard solutions note the readings and plot a Calibration curve.

8) Measure the emission intensity for water sample and obtain the concentration from the graph as shown

9) Repeat the above calibration procedure with pottassium filter using standard solutions of the following concentrations 0.2, 0.4, 0.6, 0.8 and 1.0 mgK/100ml. prepared from the 1000mgl pottassium standard solution using deonized was as the diluent



Q9: Write the principles and requirement of titrametric analysis. (7 marks)

Ans: The volumetric method involves measurement of volumes of the reacting substances and concentration of substances are found out by volume determination.

Types of titration

(1) Acid Base titration OR Neutralization reaction

(2) Redox Reaction (FAS V/S $K_2Cr_2O_7$)

(3) Precipitation titration

(4) Complexometric titration (EDTA Method)

Terms used in titration

Titrant: Burette solution or standard solution

Analyte: The substance whose quantity or concentration is to be determined

Indicator: A chemical substance whose colour changes with chemical reaction and colour change corresponds to end point and completion of reaction.

Qc: In a COD test, 30.5 cm^3 and 15.5 cm^3 of 0.05 N FAS solution are required for blank & Sample titration respectively. The volume of test sample used was 25 cm^3 Calculate the COD of the Sample Solution (6 marks)

Ans:

P = Main titration Reading = 15.5 cm^3

Q = Blank titration Readings = 30.5 cm^3

Y = Normality of FAS = 0.05 N

Z = Volume of Sample taken = 25 cm^3

$$COD = \frac{8}{1000} \times (Q-P) \times Y \times \frac{10^6}{Z}$$

$$= 0.008 \times (30.5 - 15.5) \times 0.05 \times \frac{10^6}{25}$$

$$= 0.008 \times 15 \times 0.05 \times \frac{10^6}{25}.$$

$$= 0.006 \times \frac{10^6}{25}$$

$$= 240 \text{ ppm}$$

$$=$$

Q10 a) Explain the determination of hardness of water by EDTA method (7 Marks)

Ans:

Total hardness = Temporary hardness + Permanent hardness.

Estimation of Temporary hardness and Permanent hardness,

a) EDTA - (Ethylene diamine tetra acetic acid)

Principle: This is complexometric method It is in the from of its Sodium salt which yeilds the anion and this forms complex with Ca^{2+} and Mg^{2+} ions.

In order to determine the equavalent point (re-just Completion of metal-EDTA Complexe ~~formation~~) Indicator esiochrome black-T (EBT) an alcoholic solution blue dye is employed which forms an unstable wine red Complex with Ca^{2+} and Mg^{+2} ions. The Indicator is effective at about pH 10. When EBT is added

to hard water buffered to pH of about 10 (employing $NH_4OH - NH_4Cl$), a winered unstable complex is formed.

$$M^{2+} + EBT \xrightarrow{pH-10} M-EBT$$

Complex

$M^{2+} = Ca^{2+}$ or Mg^{2+}

Unstable winered.

during the course of titration against EDTA solution combines with M^{2+} (Ca^{2+} or Mg^{2+}) ions from stable complex M-EDTA and releasing free EBT. which instantaneously combines with M^{2+} ions still present in the solution.

(M-EBT) Complex + EDTA $\longrightarrow$

Winered

[M-EDTA] complex + EBT

Stable Complex Blue.

Thus winered to blue colour marks the end point of titration.

Calculation:

$1000\ cm^3$ of 1M EDTA = 100g of $CaCO_3$

Therefore, ____ cm^3 of ____ M EDTA

$$= \frac{100 \times \quad \times}{1000} \text{ g } CaCO_3$$

= ____ g of $CaCO_3$

25 cm^3 of hard water solution ____ g of $CaCO_3$

Therefore, $10^6\ cm^3$ of hard water contains

$$= \frac{\quad \times 10^6}{25} = \text{____ ppm of } CaCO_3$$

Q10

b) Define the following units of standard solution

(i) Molarity: The Molarity (M) of a solution is defined as the number of moles of solute dissolved in one litre of solution.

Molarity = $\frac{\text{Weight of Solute}}{\text{Molar mass of Solute} \times \text{Volume of Solution in L}} \times 1000$.

Normality : Normality is the number of gram equavalent of solute in one litre of Solution

Normality = $\frac{\text{Gram Eq wt}}{\text{Volume of Solute in L}}$

PPM : One ppm is equavalent to Something per litre of water (mg/L)

Q 10c : Explain the theory and instrumentation of potentiometry (7 marks).

Potentiometric titration : A Method of determining concentration of a solution by measuring EMF is called potentiometry.

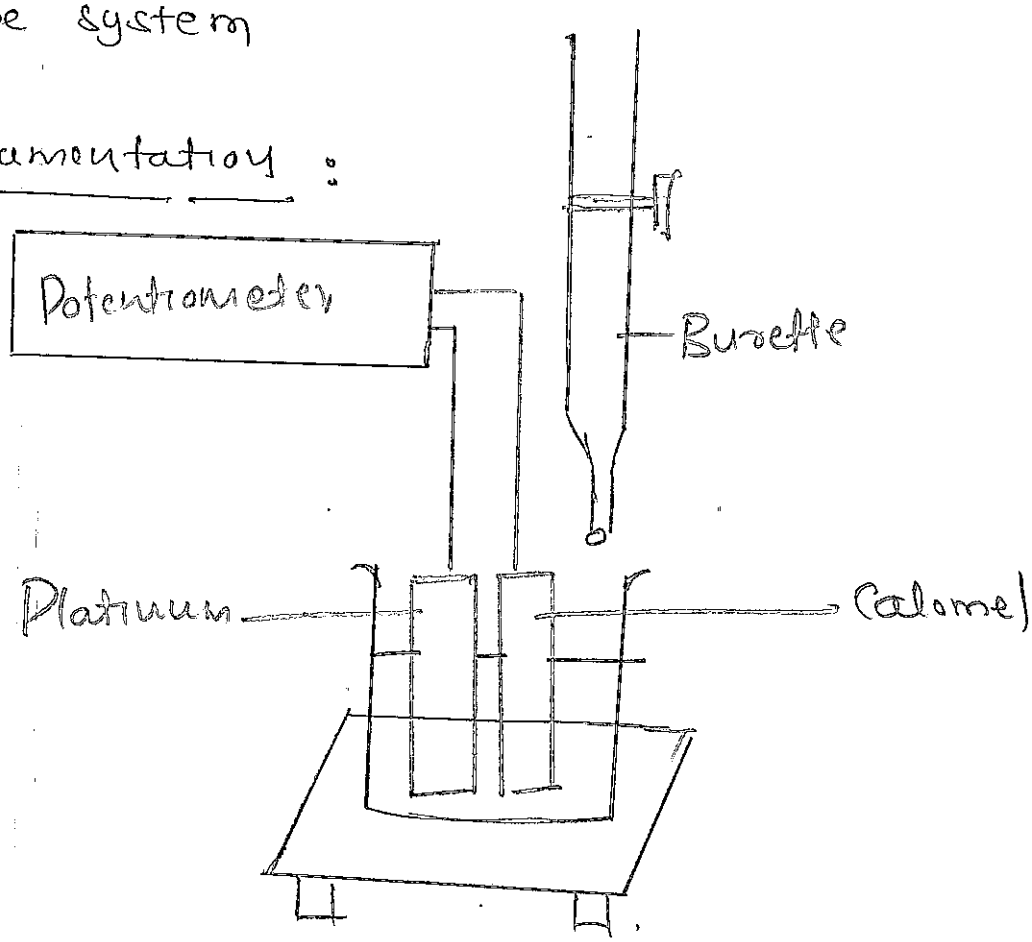
Principle : Redox titration can be carried out potentiometrically using platinum and calomel electrode. Potentiometry is based on Nernst eqn.

$$E = E^{\circ} + \frac{0.059}{n} \log \frac{[\text{Oxidised form}]}{[\text{Reduced form}]}.$$

$$E = E^{\circ} + \frac{0.059}{n} \log \frac{[Fe^{+3}]}{[Fe^{2+}]}.$$

Where E° is the standard electrode potential of the system

Instrumentation :



Platinum Electrode : It is an indicator electrode used to measure the potential of the analyte solution comparing with that of reference electrode.

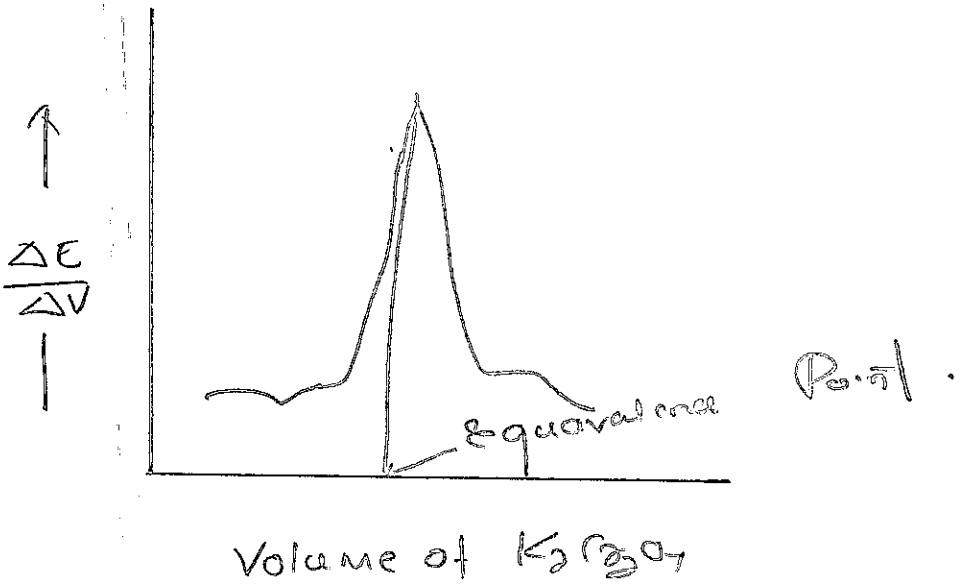
Calomel electrode: It's reference electrode and used for the determination of the analyte by maintaining the fixed potential,

Burette: standard $K_2Cr_2O_7$ solution

Beaker: The solution (FAS).

Procedure: Pipette out 25.0 cm^3 of ferrous ammonium sulphate solution into a clean beaker. Add a test tube of dilute sulphuric acid and immerse the platinum - calomel electrode assembly into the beaker containing the test solution. Connect the electrode to the potentiometer. Note down the emf of the cell before the addition of $K_2Cr_2O_7$. Now add 0.5 mL of $K_2Cr_2O_7$ from the semi micro burette. Allow the solution to mix well and measure the potential. Continue the procedure till a sudden rise in emf of the cell is observed. Take about 4-5 more readings. Plot a graph of $\frac{\Delta E}{\Delta V}$ vs volume of $K_2Cr_2O_7$ and calculate the volume

of $K_2Cr_2O_7$ consumed by FAS from the graph



Dr. Vinod Nails

HOD, Chemistry
& Dean, Academics.