CBCS SCHEME

USN ☐☐☐☐☐☐☐☐☐☐   **18CHE12/22**

First/Second Semester B.E. Degree Examination, Dec.2019/Jan.2020
Engineering Chemistry

Time: 3 hrs.   Max. Marks: 100

Note: *Answer any FIVE full questions, choosing ONE full question from each module.*

Module-1

1 a. Define Free Energy. Derive Nernst equation for single electrode potential. **(07 Marks)**
  b. What are Reference Electrodes? Describe the construction and working of Calomel electrode. **(06 Marks)**
  c. Explain the construction and working of Ni – Metal Hydride battery. Give the reaction during charging and discharging mode. Give any two applications. **(07 Marks)**

OR

2 a. Describe the construction and working of Lithium – ion battery. Give its applications. **(07 Marks)**
  b. Write a note on Primary , Secondary and Reserve batteries. **(06 Marks)**
  c. What are Concentration Cells? EMF of the cell $Ag/AgNO_3(C_1)$ // $AgNO_3$ $(C_2 = 0.2m)$ / Ag is 0.8V. Calculate C_1 of the cell. **(07 Marks)**

Module-2

3 a. What is Corrosion? Explain the Electrochemical theory of corrosion by taking iron as an example. **(07 Marks)**
  b. Explain i) Differential Metal Corrosion ii) Pitting Corrosion. **(07 Marks)**
  c. What do you mean by metal finishing? Mention any five technological importances. **(06 Marks)**

OR

4 a. Define and explain any two terms :
    i) Polarisation   ii) Decomposition potential   iii) Over voltage. **(06 Marks)**
  b. What is Electroless Plating? Explain the Electroless plating of copper. **(07 Marks)**
  c. Explain the process of Galvanization. **(07 Marks)**

Module-3

5 a. What is Knocking? Explain the mechanism. **(07 Marks)**
  b. On burning 0.96 grams of solid fuel in bomb calorimeter the temperature of 3500 grams of water increased by 2.7^0C water equivalent of calorimeter and latent heat of steam are 385 grams and 587 cal/gram respectively. If the fuel contains 5% H_2 , calculate its gross and net calorific value. Specific heat of water = 4.187 kJ/kg K. **(06 Marks)**
  c. What are Fuel Cells? Describe the construction and working of $CH_3OH – O_2$ fuel cell. **(07 Marks)**

OR

6 a. What are Solar Cells? Explain the construction and working of a typical P.V. Cell. **(07 Marks)**
  b. Explain the production of solar grade Si by Union Carbide Process. **(07 Marks)**
  c. Write a note on : i) Power alcohol   ii) Unleaded petrol. **(06 Marks)**

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Module-4

7 a. What are the main sources, effects and control of lead pollution? **(07 Marks)**
   b. Mention the various causes, effects and disposal methods of e – waste. **(07 Marks)**
   c. 50 mℓ of an industrial sewage has consumed 11.5 mℓ of 0.4N $K_2Cr_2O_7$ solution for complete oxidation. Calculate C.O.D of industrial sewage. **(06 Marks)**

OR

8 a. Explain the activated sludge treatment of sewage water. **(07 Marks)**
   b. What is Desalination? Describe the desalination of seawater by reverse Osmosis process. **(07 Marks)**
   c. Write a note on Ozone depletion. **(06 Marks)**

Module-5

9 a. Explain the theory, Instrumentation and Application of Calorimetry. **(06 Marks)**
   b. What is Potentiometric titration? Explain the principle involved in Potentiometric titration. **(07 Marks)**
   c. Write a note on Fullerene. Mention its application. **(07 Marks)**

OR

10 a. What are Nano – materials? Give their synthesis by Sol – gel techniques. **(07 Marks)**
    b. Write a note on Graphenes. Mention their applications. **(07 Marks)**
    c. Explain the theory and applications of Atomic Absorption Spectroscopy. **(06 Marks)**

* * * * *

Module - 1

1 Define free energy. Derive Nernst equation
a for single electrode potential (7mark)

Free energy:
It is the energy released by a spontaneous reaction which can be utilized for doing some useful work. **1M**

Nernst equation for single electrode potential
An equation which tells the relationship amongst three quantities —
a) System temperature
b) Electrode potential
c) Molar concentration of ionic species. It was derived by Nernst in 1889. Hence it is called as Nernst equation.

Nernst considered spontaneous reduction electrode reaction:

$$M^{n+} + ne^- \rightleftharpoons M$$
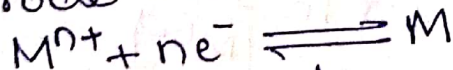
when this reaction is spontaneous, there must be decrease in free energy of system ($-\Delta G$) and it is equal to maximum work done by the system (Wmax) **1M**

$$-\Delta G = Wmax$$
$$-\Delta G = (nF)E$$
$$\Delta G = -(nF)E \quad \text{———(1)}$$ **1M**

where ——

'nF' is the coulombs of charge that is transferred during the reaction.

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

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

'E' is the electrode potential. (V)

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

$$\Delta G = -nFE^\circ \qquad\qquad\qquad —(2)$$

where 'E°' is standard electrode potential. Change in free energy is related to equilibrium constant of the reaction, Keq, by Van't Hoff reaction isotherm.

$$\Delta G = -RT \ln Keq + RT \ln Q \qquad —(3)$$

where, Q is the reaction quotient
'R' is the molar gas constant
and T is the temperature of the system in K
Also standard change in free energy, ΔG° is given by

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

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

By definition, $[M] = 1$, substitution of ΔG and ΔG° in equation (4)

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

Divide the whole equation by $-nF$

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

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

Substituting the values of $R = 8.314\ J\ mol^{-1}\ K^{-1}$ and $F = 96500\ C\ mol^{-1}$

$$E = E^\circ + \frac{0.0591}{n} \log [M^{n+}] \qquad —(8)$$

at 298K, (7) & (8) is Nernst equation

1M

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1M

1b | What are reference electrodes? Describe the construction and working of calomel electrode. (6M)

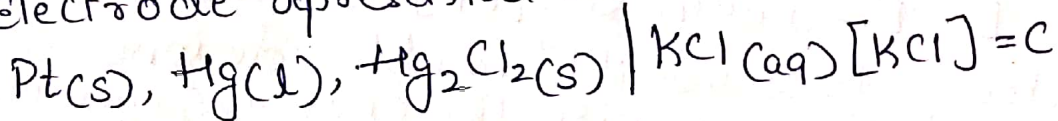Reference electrode:

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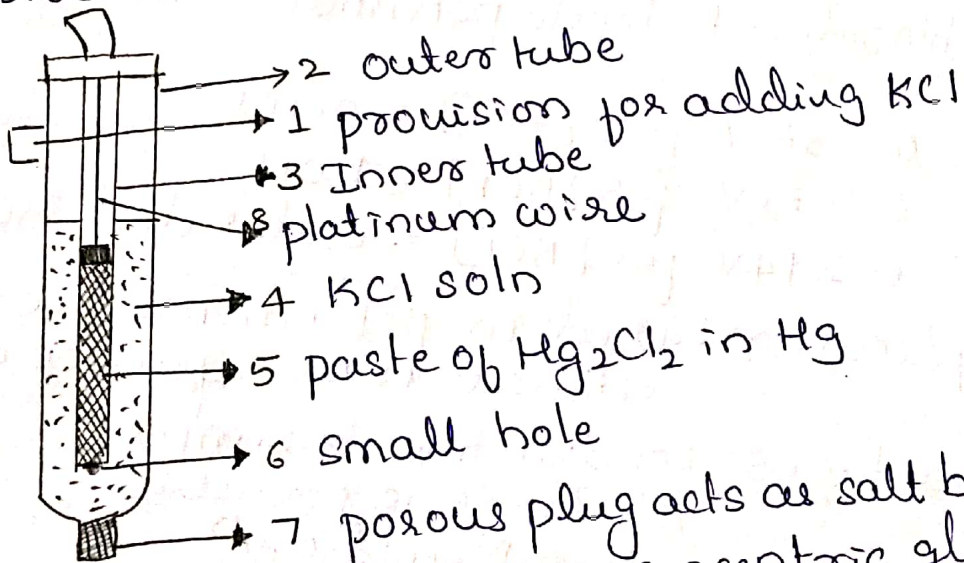
       Ex: Calomel, SHE, Ag-AgCl

Construction and Working of calomel electrode

→ Calomel electrode is secondary reference electrode.

→ Electrode representation   1M

$$Pt_{(s)}, Hg_{(l)}, Hg_2Cl_{2(s)} \mid KCl_{(aq)} [KCl] = C$$

→ Construction

→ 2 outer tube
→ 1 provision for adding KCl
→ 3 Inner tube
→ 8 platinum wire   1M
→ 4 KCl soln
→ 5 paste of Hg_2Cl_2 in Hg
→ 6 small hole
→ 7 porous plug acts as salt bridge

The electrode consists of two concentric glass tubes.

The inner tube contains a paste of Hg_2Cl_2 in Hg

The outer tube contains a soln of KCl

A little of Hg along with platinum wire in tube helps the external contacting of electrode.

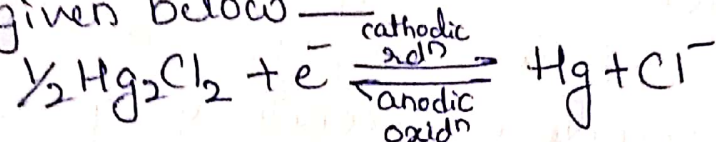A small hole at the bottom of the inner tube establishes contact with KCl in the outer tube.

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A hole at the bottom of the outer tube with a porous plug attached helps in establishing contact with the external analyte.
→ There is provision for adding more KCl

Working

Depending on potential of 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 —

$$\frac{1}{2} Hg_2Cl_2 + \bar{e} \underset{\substack{\text{anodic} \\ \text{oxid}^n}}{\overset{\substack{\text{cathodic} \\ \text{red}^n}}{\rightleftharpoons}} Hg + Cl^- \qquad 1M$$

Electrode potential equation

$$E = E^° - 0.0591 \log [Cl^-] \text{ at } 298 K \qquad 1M$$

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
0.279 V for [KCl] = 1.0 N
0.244V for [KCl] = Saturated KCl

Application: Used in potentiometric estimation as reference electrode $\qquad 1M$

Advantages: Construction is simple
Electrode is portable
Obeys Nernst equⁿ

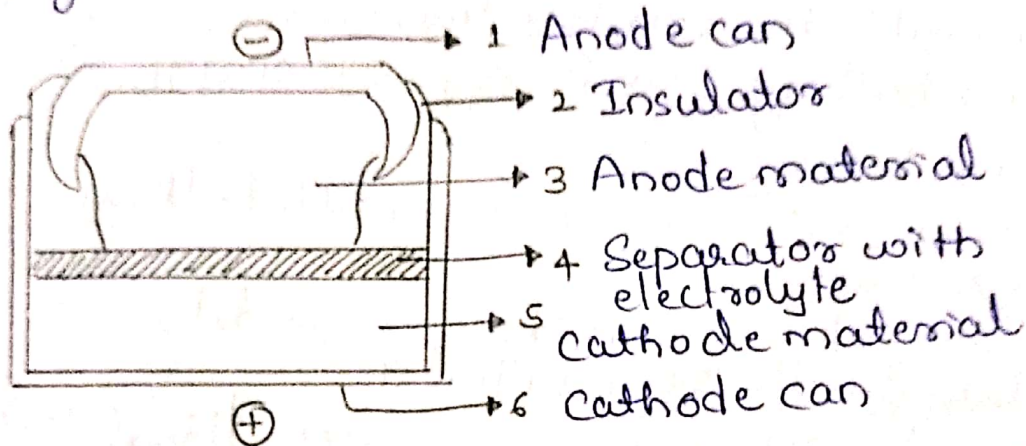Limitation: Mercury is poisnous in nature
Cannot be used beyond 60°C

| 1c | Explain construction and working of Ni-MH₂ battery. Give the reaction during charging and discharging (7M) mode. Give any two applications. |

4

Ni – Metal hydride battery

→ It is secondary rechargeable battery. Acts as galvanic cell during discharge & electrolytic cell during recharge.

→ Construction

Cell representation $Ni, MH_2 | KOH (30\%) | NiOOH Ni$ →1M

where, MH_2 is metal hydride with a hydrogen storage material.

- 1 Anode can
- 2 Insulator
- 3 Anode material
- 4 Separator with electrolyte
- 5 Cathode material
- 6 Cathode can

→1M

1) Anode material: MH_2 such as VH_2, ZrH_2, TiH_2 etc with a hydrogen storage alloy such as $LaNi_5$, $TiZr_2$, $TiNi$ etc.

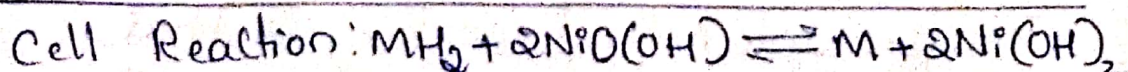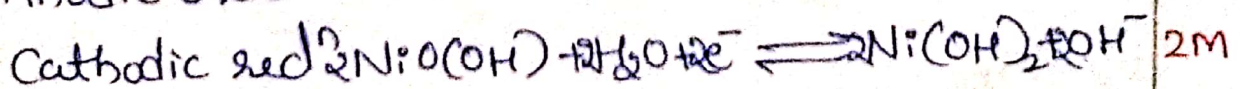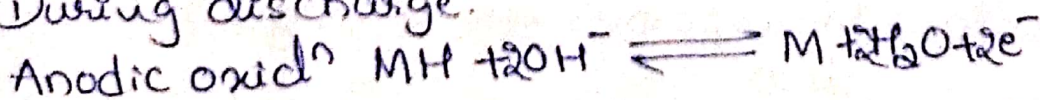2) Cathode material: $NiO(OH)$ – Nickel oxy hydroxide

3) Electrodes: are made of porous Ni-foil or grid onto which the active materials are either coated or pasted.   1M

4) Electrolyte: Aqueous solution of KOH (30%)

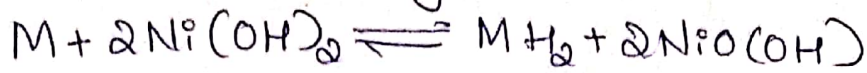5) Separator: Synthetic non-woven polypropylene is used.

Working:

During discharge:

Anodic oxid^n $MH + 2OH^- \rightleftharpoons M + 2H_2O + 2e^-$

Cathodic red^n $2NiO(OH) + 2H_2O + 2e^- \rightleftharpoons 2Ni(OH)_2 + 2OH^-$ 2M

Cell Reaction: $MH_2 + 2NiO(OH) \rightleftharpoons M + 2Ni(OH)_2$

5

Reactions are reversed during recharge with opposite polarity.

$$M + 2Ni(OH)_2 \rightleftharpoons MH_2 + 2NiO(OH)$$

Cell potential: $1.25 - 1.35V$

1M

Applications:
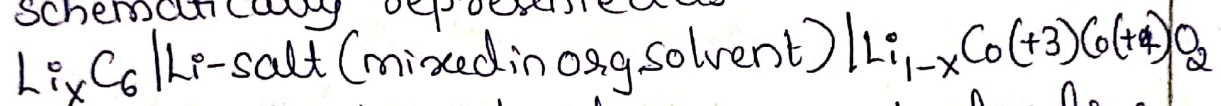Used in electric cars, medical instruments, laptop computers, digital cameras.

1M

2a. Describe the construction and working of Li-ion battery. Give its applications (7M)

Li-ion battery
→ It is secondary rechargeable battery.
→ Construction
Li-ion cell when in charged condition is schematically represented as

$$Li_xC_6 | Li\text{-salt (mixed in org. solvent)} | Li_{1-x}Co(+3)_6(+4)O_2$$

However, actual construction refers to loading of crystallised carbon at anode and lithium cobalt oxide at cathode. Cu and Al are used as current collectors.

1M

$$Cu, C_6 \left| \begin{array}{c} LiPF_6, LiBF_4, LiClO_4 \\ \text{in org. solvent} \end{array} \right| LiCoO_2, Al$$
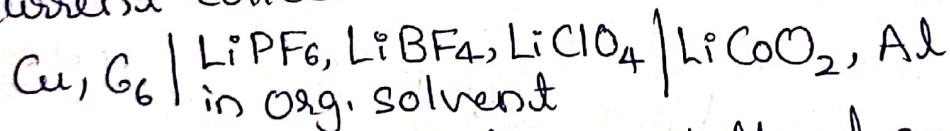
Anodic material: highly crystallised specialty carbon

Cathodic material: $LiCoO_2$

Electrolyte: $LiPF_6, LiBF_4, LiClO_4$ in organic solvent such as ether or mixed organic solvent.

Separator: Microporous - polypropylene is used

1M

Working:
The principle behind working is that, during charge, lithium ion in the cathode
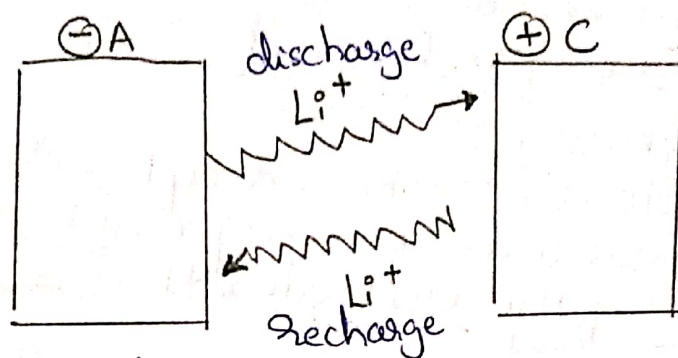
6

($LiCoO_2$) 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).
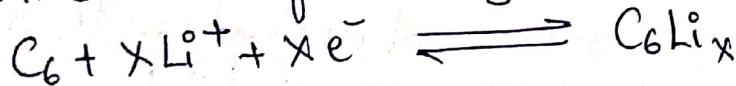

Charging Reactions
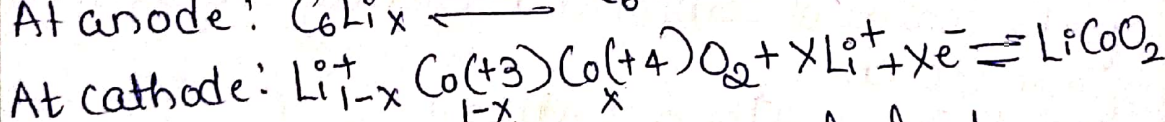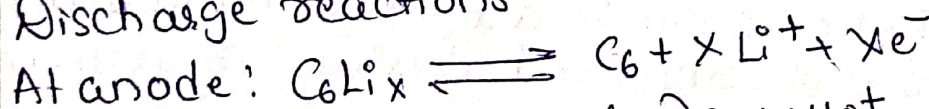
At anode of electrolytic cell (Cathode of galvanic cell),

$$LiCoO_2 \rightleftharpoons Li^+_{(1-x)} Co_{1-x}^{(+3)} Co_x^{+4} O_2 + XLi^+ + Xe^-$$
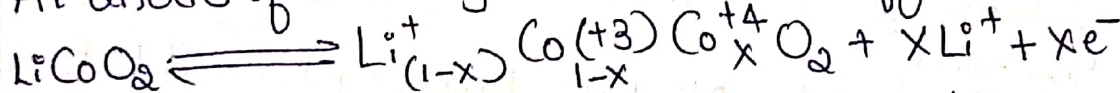
At cathode of electrolytic cell (anode of galvanic cell)

$$C_6 + XLi^+ + Xe^- \rightleftharpoons C_6Li_x$$

Discharge reactions

At anode: $C_6Li_x \rightleftharpoons C_6 + XLi^+ + Xe^-$

At cathode: $Li^+_{1-x} Co_{1-x}^{(+3)} Co_x^{(+4)} O_2 + XLi^+ + Xe^- \rightleftharpoons LiCoO_2$

Cell reaction during charge and discharge:

$$C_6 + LiCoO_2 \rightleftharpoons C_6Li_x + Li^+_{1-x} Co_{1-x}^{+3} Co_x^{+4} O_2^-$$
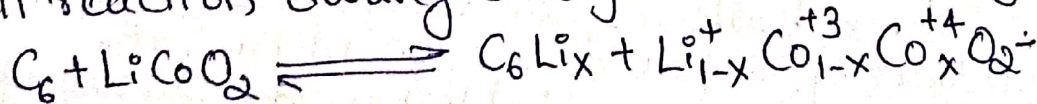
Cell potential 3.7V

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

1M

3M

1M

7

2b Write a note on primary, secondary and reserve batteries. (6M)

1) **Primary batteries:**
   → Irreversible, to be discarded on discharge
   → Function as galvanic cells during discharge
      Eg: $Zn-MnO_2$ battery, $LiMnO_2$ battery
   → These are designed for discharge alone
   → Attempt to recharge these cells results in explosion or fire-hazard.

   } 2M

2) **Secondary batteries:**
   → Reversible, are recharged after discharge from an external source of emf by reversal of polarity of the electrodes. thus, are redischargeable.
   → The cell functions as galvanic cell during discharge and as electrolytic cells during recharge.
      Ex: $Pb-H_2SO_4$, $Ni-MH_2$ battery, $Ni-Cd$ battery

   } 2M

3) **Reserve 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 electric energy.
      Ex: $Pb|acid|PbO_2$ battery
   These batteries can be activated by the insertion of isolated component and the battery is made available fore the discharge. Generally electrolyte component is isolated. Following are the examples of reserved batteries
   Water activated i) $Mg|sea\ water|AgCl, Ag$
   Acid activated ii) $Pb|acid|PbO_2$ battery
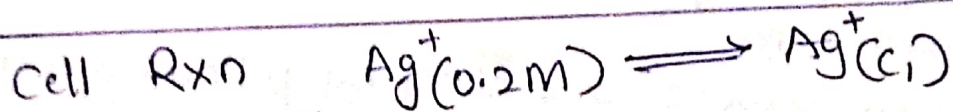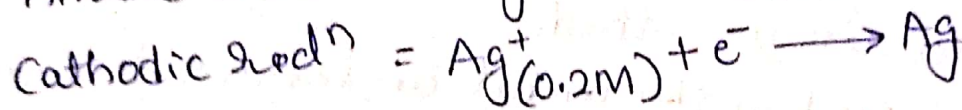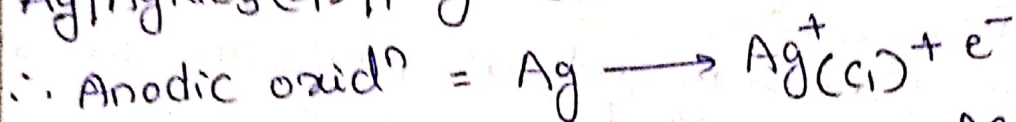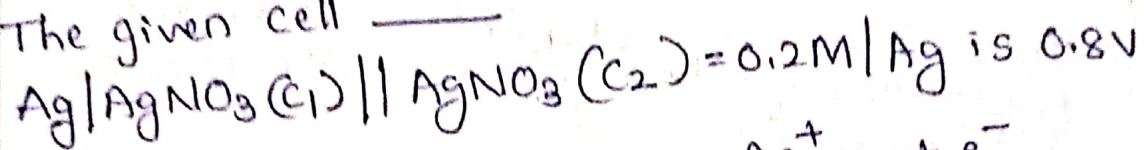   Alkali activated iii) $Zn|KOH|Ag_2O$ battery

   } 2M

8

2c) What are concentration cells? EMF of cell $Ag|AgNO_3(c_1)||AgNO_3(c_2)=0.2m|Ag$ is 0.8V Calculate G of Cell. (7M)

Concentration cell

A cell is constructed by the combination of two electrodes made of same chemical substance but with changing concentration of the electrolyte or electrode's concentration cell. There are two types of concentration cells electrode and electrolyte concentration cells.

The given cell ——

$Ag|AgNO_3(c_1)||AgNO_3(c_2)=0.2M|Ag$ is 0.8V

∴ Anodic oxid^n = $Ag \longrightarrow Ag^+_{(c_1)} + e^-$

Cathodic red^n = $Ag^+_{(0.2M)} + e^- \longrightarrow Ag$

——————————————————————————

Cell Rxn $\quad Ag^+_{(0.2M)} \rightleftharpoons Ag^+_{(c_1)}$

$\boxed{n = 1}$

$E_{cell} = 0.8V$
$C_1 = ?$
$C_2 = 0.2M$
$n = 1$

$E_{cell} = \dfrac{0.0591}{n} \log \dfrac{C_2}{C_1} \qquad \because C_2 > C_1$

$0.8 = \dfrac{0.0591}{1} \log \dfrac{0.2}{C_1}$

$\dfrac{0.8}{0.0591} = \log \dfrac{0.2}{C_1}$

$13.53 = \log \dfrac{0.2}{C_1}$

$\dfrac{0.2}{C_1} = Antilog\,(13.53)$

$\dfrac{0.2}{3.38 \times 10^{13}} = C_1$

$C_1 = 0.0591 \times 10^{-13}\,M$

(margin markings: 1M, 2M, 1M, 1M, 2M)

Module-2

2. What is corrosion? Explain electrochemical theory of corrosion by taking iron as an example? (7M)

Corrosion:

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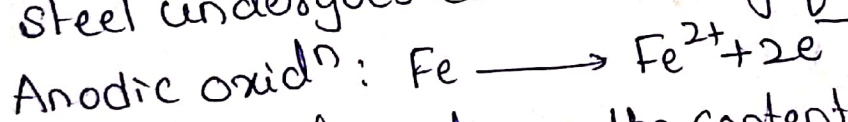
Electrochemical theory of corrosion.

→ This corrosion is characterised by the formation of small galvanic cells due to heterogeneities.

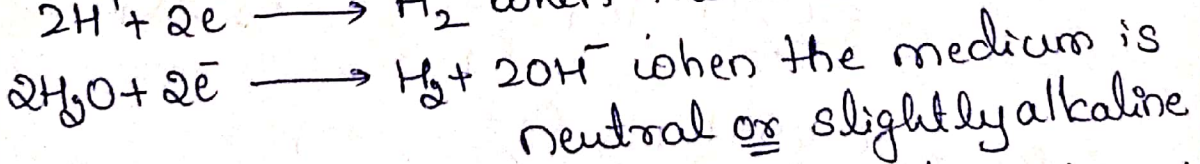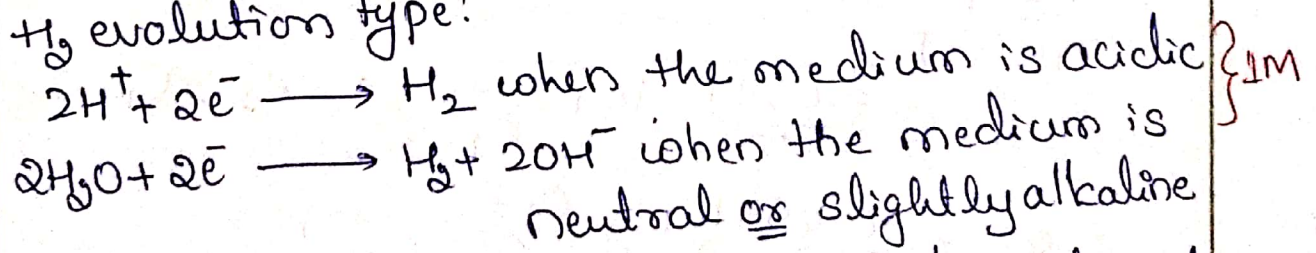→ part of the metal acts as anode and another part acts as cathode. } 1M

Anodic part of the metal undergoes destruction by oxidation

steel undergoes corrosion by following rxns

Anodic oxid^n: $Fe \longrightarrow Fe^{2+} + 2e^-$ } 1M

Reduction depends on the contents in the medium

Some important reactions are

H_2 evolution type:

$2H^+ + 2e^- \longrightarrow H_2$ when the medium is acidic } 1M

$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$ when the medium is neutral or slightly alkaline

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

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O_2 absorption type

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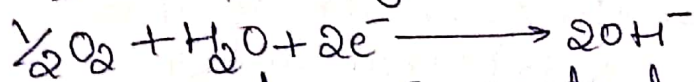
when medium is neutral or slightly alkaline

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

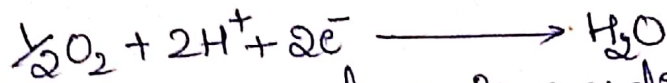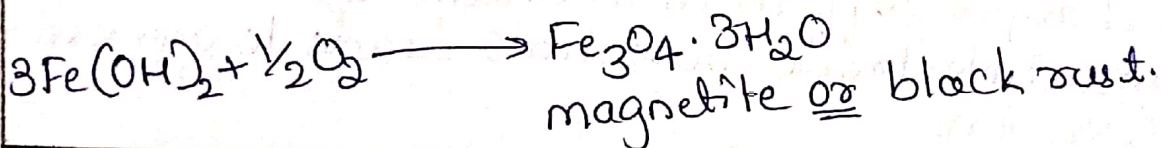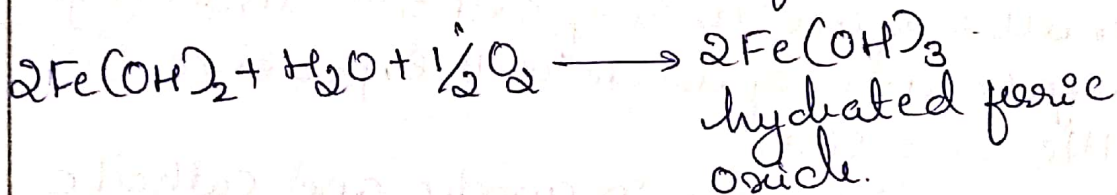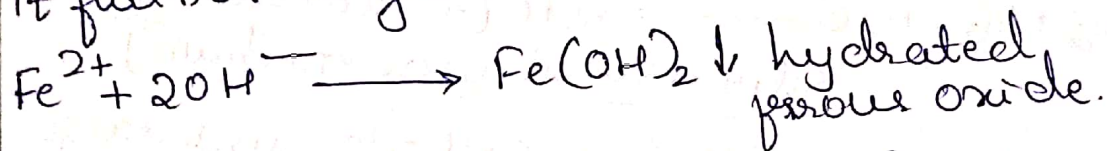when the medium is acidic & in presence of dissolved oxygen, DO

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.

$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2 \downarrow \text{ hydrated ferrous oxide.}$$

$$2Fe(OH)_2 + H_2O + \frac{1}{2}O_2 \longrightarrow 2Fe(OH)_3 \text{ hydrated ferric oxide.}$$

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

3b. Explain i) Differential metal corrosion & ii) pitting corrosion. (7M)

i) Differential metal corrosion or 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
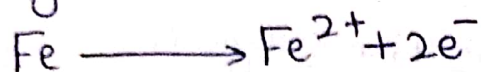
Anodic metal undergoes corrosion.
→ Driving force for the corrosion is the difference in electrode potentials of two metals.
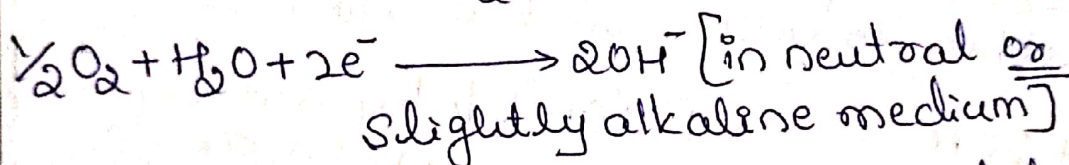
Ex:
Steel vessel with brass tap & brass vessel with steel tap } 0.5M

steel acts as anode and undergoes corrosion by oxidation

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

Cathodic reduction reaction depends on the medium

$$2H^+ + 2e^- \longrightarrow H_2 \quad [\text{in acidic medium}]$$

$$\frac{1}{2}O_2 + H_2O + 2e^- \longrightarrow 2OH^- \quad [\text{in neutral or slightly alkaline medium}]$$
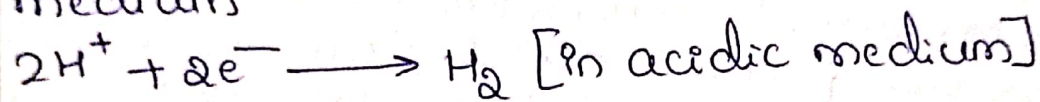
Small surface area of cathode and large surface area of anode will experience little corrosion.
→ Larger difference in anodic and cathodic metal electrode potentials leads to aggressive corrosion.

} 2

ii) Pitting Corrosion:
→ Corrosion of metals leading to the formation of pits or cavity or holes is called pitting corrosion
→ It is very aggressive, localised corrosion. It occurs when the metal is in contact with stagnant solution.
→ Momentary changes in O_2 concentration in the medium is the cause for corrosion.

} 1M

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Part of metal acts as anode which is exposed to less oxygenated area. and undergoes corrosion

steel corrodes at less oxygenated area

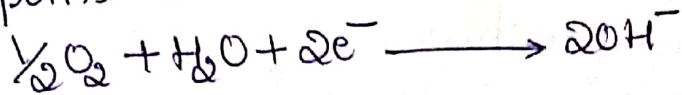as $Fe \longrightarrow Fe^{2+} + 2e^-$

Cathodic reduction at more oxygenated point as

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

In stagnant solution, Fe^{2+} ions at anodic area attract the oppositely charged ions say, Cl^- ions and form the salt $FeCl_2$. The salt on hydrolysis precipitates $Fe(OH)_2$ with generation of HCl. Corrosion of steel is promoted beneath the deposit. Also, acid formed accelerates the corrosion. Thus it is autocatalytic in nature. }1M

salt hydrolysis at anode:

$$FeCl_2 + 2H_2O \longrightarrow Fe(OH)_2\downarrow + 2HCl$$

small anode   large cathode   pit

0.5 M
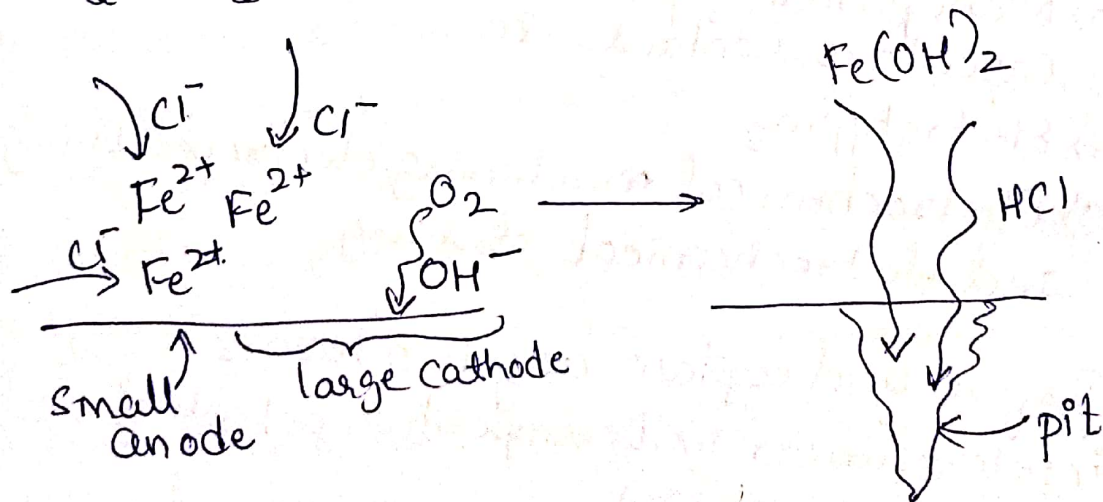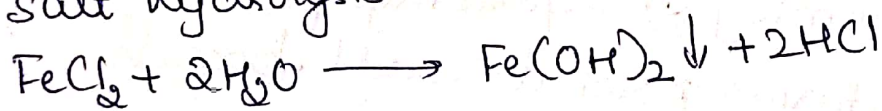
pitting corrosion can be minimized by avoiding stagnation of process solution in vessels, pipes etc.

13

3c What to do you meant by metal finishing? Mention any five technological importance (6M)

Metal finishing

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. } 1M

Technological importance. [any 5]

1) Better corrosion resistance
2) Better hardness, strength, wear or abrasion resistance, impact resistance etc.
3) Better thermal conductance or resistance or reflectance
4) Better optical reflectance
5) Better electrical conductance or insulation

6) Electroforming or reforming of articles.
7) Manufacturing printed circuit boards, capacitors, contacts etc.
8) Electrotyping
9) Electrochemical machining, electropolishing and electrochemical etching.

5M

4a. Define and explain any two terms
i) polarisation ii) Decomposition potential
iii) Overvoltage. (7M)

i) Polarisation:

A process of which variation of electrode potential is observed due to change in concentration of ionic species at electrode

14

Surface by
i) Slow deffusion of ions from the bulk of the electrolyte to the electrode or from the electrode towards the bulk
ii) One of the elementary steps of discharge of gases being slow at electrode surface.

Polarisation of electrode depends on
i) Nature of the electrode
ii) Nature of the electrolyte, its concentration and conductivity
iii) Current densities applied
iv) Nature of the products formed at the electrode surfaces.
v) Agitation and temperature of the electrolyte

Concentration polarization can be minimized by
i) having larger electrode surfaces
ii) highly conducting electrolyte and at lower concentrations.
iii) By optimized current densities
iv) Better agitation and higher temperature of the electrolyte.

Overvoltage polarization is due to slow steps of gas discharge at electrode surface.

Ex:
Evolution of hydrogen gas discharge at electrode surface may involve following steps;
i) Diffusion of hydronium ion (H_3O^+) from the bulk.
ii) H_3O^+ ion getting split and becoming H^+ ion and H_2O.

iii) Electron transfer to H^+ ion and reduction to atomic hydrogen

iv) Diffusion of hydrogen atoms towards one another, their union to form molecules.

v) Few molecules forming the bubble and escape of hydrogen gas from the surface.

When any one <u>or</u> more of these processes is slow, there is variation of ionic concentrations near electrode surface and a change in the electrode potential. This is overvoltage polarization and cannot be eliminated because surface reactions tend to consume that extra energy and time for their occurence & continue to be slow.

Knowledge:
Knowledge of polarisation helps one to realise the importance of agitation of electrolyte inorder to minimise concentration polarisation and thus, the expenses of electroplating. However, overvoltage polariz^n cannot be eliminated.

2M

ii) Decomposition potential.
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 decomposition of water, a dilute solution of either an acid <u>or</u> alkali is electrolysed using smooth platinum electrodes. For the applied potential of less than 1.68V, there is initial surge of current which will drop to

16

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.

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 and oxygen at anode. A H_2-O_2 galvanic cell is formed with H_2 electrode acting as anode and O_2 electrode acting as cathode. This galvanic cell potential opposes the externally applied potential. Thus, a back e.m.f is produced. It may be noted that decomposition potential should overcome this back emf. **3M**

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 soln, a potential of 1.30V needs to be applied
Predicting the order in which the different substances, discharge or deposit at respective electrodes. **2M**

Ex: by 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,

Zn, Cd and Cu are made active anodes, their dissolution happens to be in the sequence; Zn, Cd and Cu.

iii) Overvoltage

For most of the metals, reversible discharge potential and the experimentally evaluated discharge potentials are identical. However especially for gaseous substances, the experimental discharge potentials are slightly higher than the reversible discharge potentials. This excess potential over the theoretical is referred to as overvoltage. **{1M}**

Overvoltage can be defined as excess voltage over the theoretical voltage required to be applied for the continuous discharge of a substance at the electrode surface.

Ex: decomposition potential of water over smooth platinum surfaces is 1.68 V. However the theoretically calculated voltage is 1.23 V. Therefore, overvoltage is 1.68 V − 1.23 V = 0.45 V

Total overvoltage is the sum of anodic overvoltage and cathodic overvoltage. Evolution of hydrogen gas ᵖatom a plating bath at cathodic surfaces involves. **{3M}**

i) Diffusion of hydronium Ion, H_3O^+ towards electrode surface

ii) its becoming H^+ ion; $H_3O^+ \longrightarrow H^+ + H_2O$

iii) reduction to atomic hydrogen $H^+ + \bar{e} \longrightarrow H \cdot$

iv) Diffusion of hydrogen atoms towards one another, their union to form molecules.

$$H + H \longrightarrow H_2$$
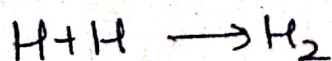
v) few molecules forming the bubble and escape of hydrogen gas from the surface.

Overvoltage depends on

i) Nature and physical state of the electrode; Metals with smooth surfaces have relatively higher overvoltages. Mercury has the highest overvoltage. Smooth-Pt has higher overvoltage than platinised Pt.

ii) Current density at electrode surface; Generally increase in current density increases overvoltage

iii) Temperature of the electrolytic bath; generally, increase in temperature decreases overvoltage.

A knowledge of overvoltage helps in having more convenient acidic plating bath for electroplating without liberation of H_2 gas during the plating process.
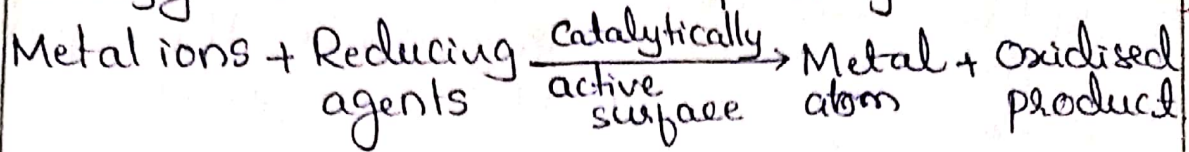
Ex: Zinc electroplating in acidic medium will not lead to liberation of H_2 gas. In a plating bath with $[Zn^{2+}] = 1.0 M$ and pH=4, the discharge potential of zinc is $-0.76 V$; and with an overvoltage of $0.70V$ on Zn, the discharge potential of hydrogen is $-0.236 V$ $-0.70V = -0.936 V$. Since, $-0.76 > -0.936 V$, zinc gets deposited preferential to hydrogen.

2M

4b | What is electroless plating? Explain the electroless plating of copper (7M)

Electroless plating:

P.T.O

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 electrical energy is called electroless plating.

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

Electroless plating of copper

Substrate surface needs to be cleaned by suitable, cleaning methods. 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 $PdCl_2$.
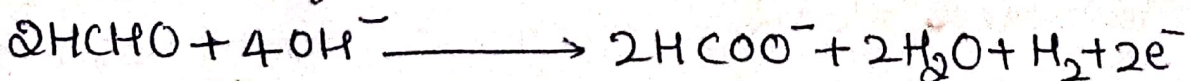
Bath composition

Constituents	Amount	Purpose
$CuSO_4$	12 g/L	provides metal ions
HCHO	8 g/L	Reducing agent
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

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

1M

3M

20

Reduction over object surface
$$Cu^{2+} + 2e^- \longrightarrow Cu$$
Overall reaction;
$$Cu^{2+} + 2HCHO + 4OH^- \longrightarrow Cu + 2HCOO^- + 2H_2O + H_2 \uparrow$$
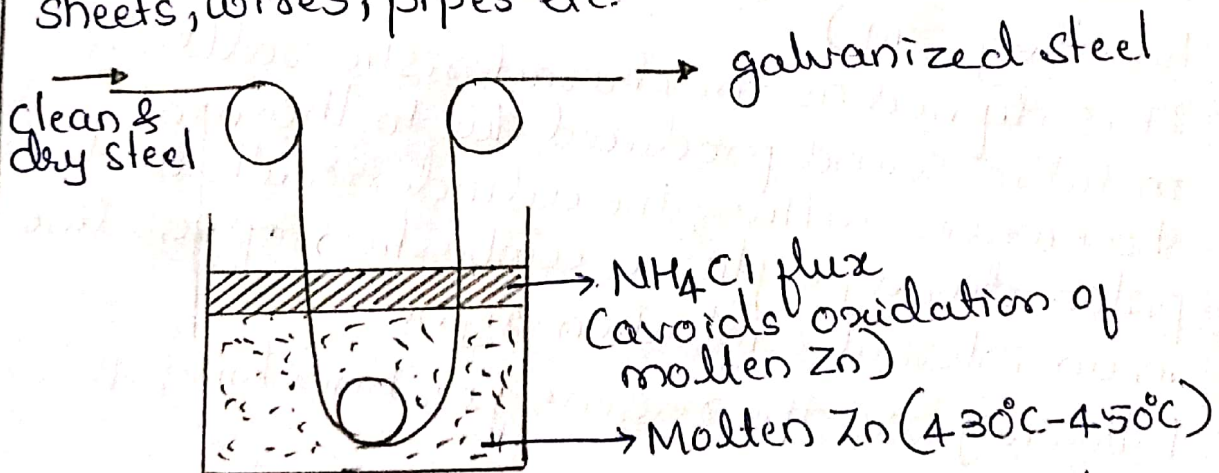
2M
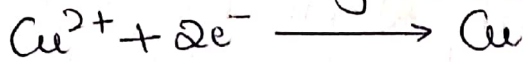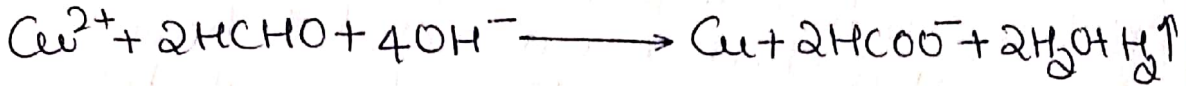
Applications
→ Establishing through hole connections on double sided PCBs
→ For plating on non-conductors or as a base before electroplating.

1M

4c. Explain the process of galvanization [1M]

Galvanization

It refers to hot depping method of coating of Znic over iron and control of corrosion. Coated zinc metal sacrifices itself in protecting the object metal from corrosion. The method is employed for continuous metal sheets, wires, pipes etc.

1M

Clean & dry steel

→ galvanized steel

→ NH₄Cl flux (avoids oxidation of mollen Zn)

→ Molten Zn (430°C-450°C)

1M

Object metal surface needs preparation; oil, grease, wax etc are removed by organic solvents
→ Then it is treated with hot dilute H_2SO_4 for removing the scales, washed with H_2O & air dried.
→ Clean and dry metal sheets are then immersed into a bath containing molten Zn. An ammonium chloride flux is used to avoid the oxidation

3M

21

of molten Zn.
→ Excessive Zn from the sheets drawn is removed and uniformity achieved by passing it between two regulated hot rollers.
→ Zn coated sheets are annealed to have firm bonding between the metals with better surface characteristics. And, what comes out is galvanized steel.

Applications:
Roofing sheets, fencing wires, pipes etc $\quad$

Limitations:
Galvanized steel sheets are not used for making food containers because, they are known to form toxic substances with acidic food items and cause heath problems. $\quad$

Module-3

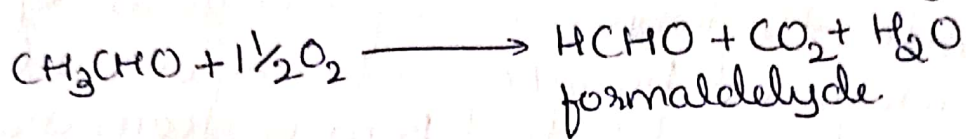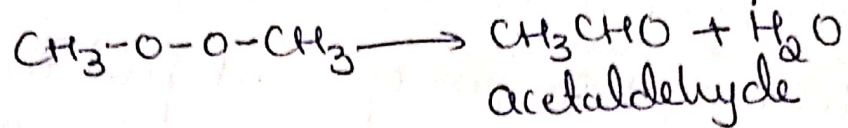5a What is knocking? Explain the mechanism knocking (7M)

It is defined as the characteristic rattling, metallic sound produced due to thermal shock waves hitting the cylinder walls and piston during explosive combustion of gasoline in an internal combustion engine $\quad$

Following are the reasons for knocking to occur.

1) Higher compression ratio beyond the optimum level
2) lower octane petrol or gasoline
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

Mechanism

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

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

$HCHO + O_2 \longrightarrow H_2O + CO_2$

[2M]
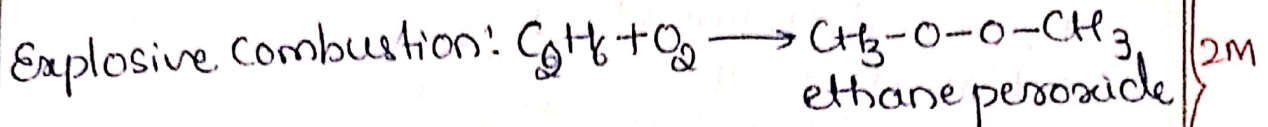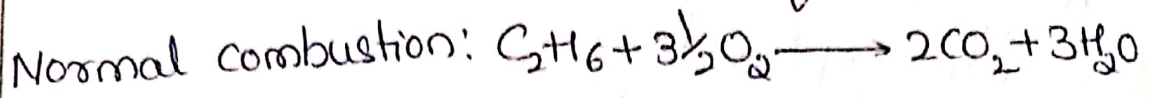
Above sequence of reactions occuring explosively result in release of instant energy or thermal shock waves which hit the cylinder walls and piston & produce knocking.

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 unburnt fuel air mixture. Due to build of pressure, temperature will also increase. All of the un-burnt fuel is ignited a-head of the flame front. This produces thermal shockwaves which hit the cylinder walls and piston; resulting in a characteristic

[3M]

metallic sound called knocking.

III effects
→ Mechanical damage of engine parts
→ noise pollution
→ Air pollution

Prevention of knocking
→ Improved engine design
→ optimized compression ratio
→ Use of antiknocking reagents

1M

5b) On burning 0.96 gms of solid fuel in bomb
calorimeter the temperature of 3500 grams of
water increased by 2.7°C water equivalent
of calorimeter and latent heat of steam are
385 grams and 587 cal/gram respectively. If
the fuel contains 5% H_2, calculate its gross and
net calorific value. Specific heat of water = 4.187
KJ/kg/K. [6M]

Solution:
$m = 0.96 \, g \Rightarrow 0.00096 \, kg$

$w_1 = 3500 \, g \Rightarrow 3.5 \, kg$

$w_2 = 385 \, g \Rightarrow 0.385 \, kg$

$\Delta T = 2.7°C \Rightarrow 2.7 \, K$

$L_v = 587 \, cal/gram \Rightarrow 587 \times 4.187$

$\Rightarrow 2457.769 \, KJ/kg$

1M

$H\% = 5$

$GCV = ?$

$NCV = ?$

$GCV = \dfrac{(w_1 + w_2) \Delta T S}{m}$

$= \dfrac{(3.5 + 0.385) \, 2.7 \times 4.187}{0.00096}$

1M

24

$$= \frac{43.919}{0.00096}$$

$$= 45,749.5 \ KJ/kg$$

$$NCV = GCV - 0.09 H \times L_v$$

$$= 45,749.5 - 0.09 (5) \times 2457.769$$

$$= 45,749.5 - 1105.99$$

$$= 44,643.51 \ KJ/kg.$$

5c | what are fuel cells ? Describe the construction and working of $CH_3OH - O_2$ fuel cell (7M)

Fuel cells

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

Methanol - oxygen fuel cell

Construction:

This fuel cell is represented as

Porous C (dispersed with pt), $CH_3OH + H_2SO_4$ | $H_2SO_4 (aq)$ | O_2, porous C dispersed with Pt
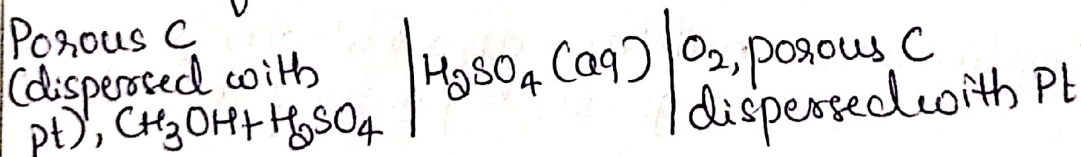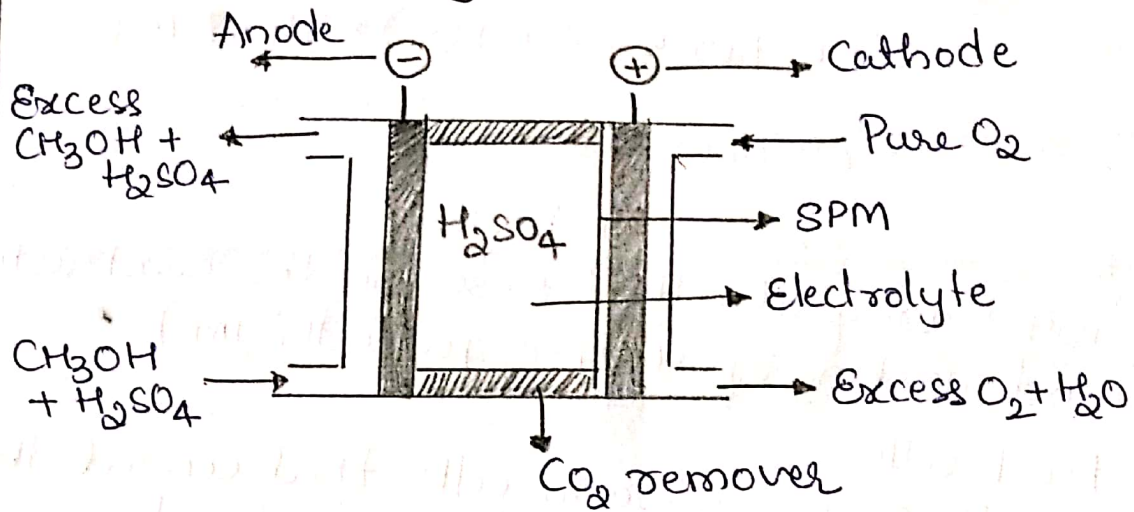
The cell consists of

Anode: Porous C with dispersed pt

Cathode: Porous C with dispersed Pt
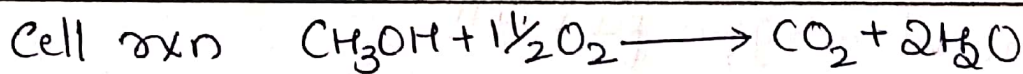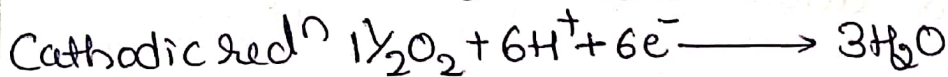
Electrolyte: Aq. H_2SO_4

Active components: Fuel: methanol mixed with H_2SO_4 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-oxidation directly at cathode.

working:

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

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

Cell rxn $CH_3OH + 1\frac{1}{2}O_2 \longrightarrow CO_2 + 2H_2O$
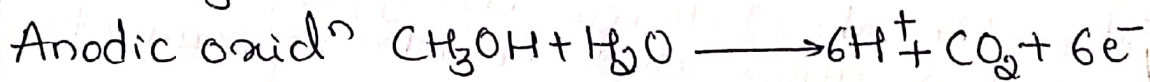
Cell potential 1.2V

Applications: military applications & large-scale power production

6a What are solar cells? Explain the construction and working of typical PV cell [7M]

Solar cells:
These are devices that convert solar energy into electrical energy from semi - conductors.   }1M

P.T.O

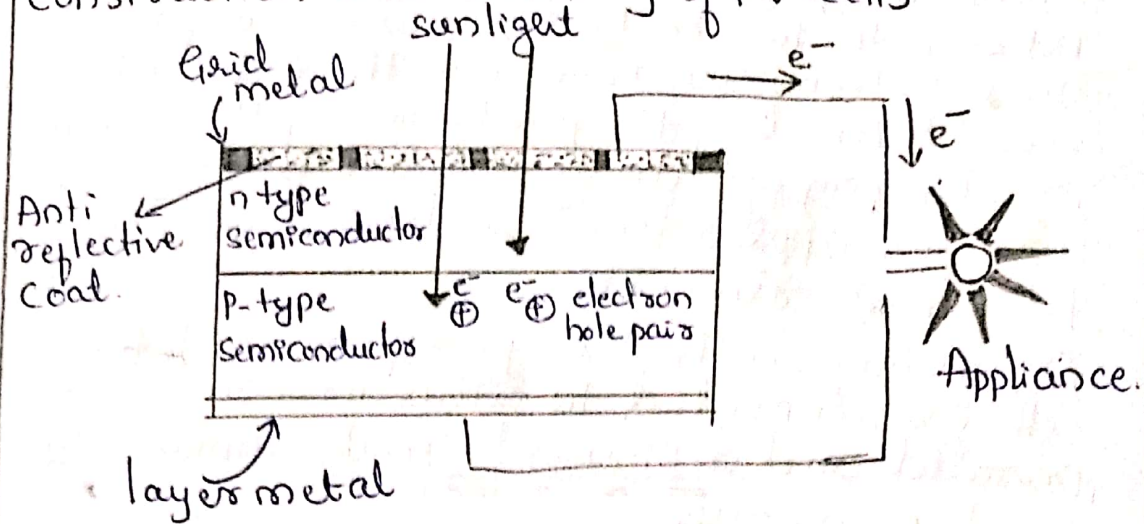## Construction and working of PV cells

Construction:

1. Photovoltaic cell is made of a semiconductor diode (p-n junction)

2. The diode has two electrical contacts:
A grid metal contact is used top side and a layer metal contact on the bottom side. Grid metal or layer metal contact is generally made by silver.

3. The metal grid permits the light to fall on the diode between the grid lines.

4. An antireflective coat (Si_3N_4 - silicon nitride or TiO_2 - titanium dioxide) is used between the grid lines to increase the efficiency of light absorbance or energy conversion.

Working:

1 when electromagnetic radiation having energy sufficient to overcome the barrier potential falls normal to the surface of p-n junction, electron-hole pairs are formed.

2. The electrons move towards the n-region and holes move towards p-region

27

3. when an appliance or battery is connected between the two contacts, circuit is completed and electrons are driven into the 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 to either in series or parallel and designed to make modules or panels or arrays.

Importance:
→ No moving parts, no wear & tear, no sound or operate silently and render little maintainance cost.

2.5M

6b. Explain the production of solar grade si by Union Carbide process [7M]

Preparation of silicon for use in photovoltaic cells involve several steps,

1st step:
Preparation of Metallurgical Grade Silicon from Naturally occuring quartz
   A mixture of quartz (SiO_2) and carbon is struck by an electric arc in an electric arc furnace using carbon electrodes
$$SiO_2 + 2C \xrightarrow{>1500°C} Si + 2CO$$
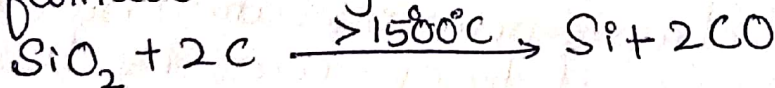
CO oxidizes to give CO_2.
Silicon is obtained in the mollen state and is contaminated with aluminium, calcium and magnesium
   The impurities are removed as slag by the addition of silica. Following reactions take place.

2M

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

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

Step II:
Synthesis of Silane from silicon
→ Metallurgical grade silicon is heated to 300-350°C and dry hydrogen chloride gas is passed. Trichlorosilane and a small amount of tetra--chlorosilane are formed as given below

$$Si + 3HCl \xrightarrow[350°C]{300-} HSiCl_3 + H_2$$
Trichlorosilane

$$Si + 4HCl \longrightarrow SiCl_4 + 2H_2$$
Tetrachlorosilane
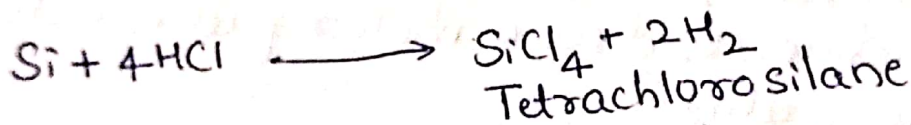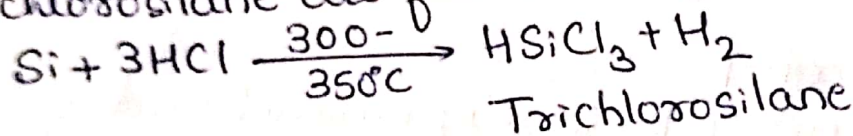
Tetrachlorosilane is converted to trichlorosilane by treating with hydrogen at 1000°C.
$$SiCl_4 + H_2 \xrightarrow{1000°C} HSiCl_3 + HCl$$
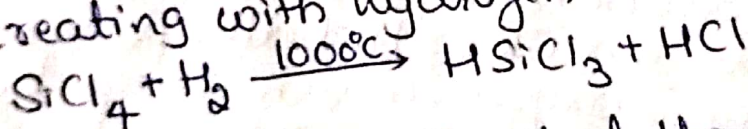
Trichlorosilane is converted through a column bed filled with an ion exchange resin containing quaternary ammonium salts as catalyst to give dichlorosilane and tetrachlorosilane. Dichlorosilane subsequently forms silane & trichlorosilane.

$$2HSiCl_3 \longrightarrow H_2SiCl_2 + SiCl_4$$

$$3H_2SiCl_2 \longrightarrow SiH_4 + 2HSiCl_3$$

3M

29
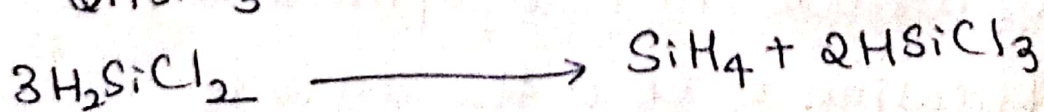
Tetrachlorosilane is hydrogenated again to trichlorosilane and trichlorosilane is again passed through ionexchange resin. The process is continued to get silane.

Step III : Purification of silicon hydride

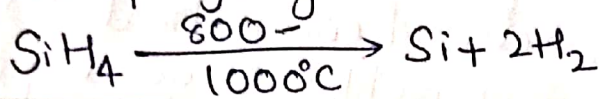Silicon hydride or silane obtained above is further purified by distillation. Silane is passed into a reactor containing hot silicon seed rods. This method is called Union carbide process. Silane gets pyrolysed at higher temp to form polycrystalline silicon.

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

2M

6c | Write a note on i) power alcohol ii) Unleaded petrol

i) Power alcohol

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

1M

Advantages:
→ Increases octane number and reduces knocking, higher CR with better power output
→ Alcohol contains oxygen, which assist better combustion efficiency. VOCs are reduced

1M

disadvantages
→ Lowers the calorific value, atomization is difficult because of higher surface tension of alcohol

→ Alcohol readily gets oxidized to acids and may corrode engine equipment.

1M

→ Modification of CR of the engine is required.

30

ii) Unleaded petrol

Gasoline or petrol with better anti-knock properties, however, without the presence of leaded compounds but with the presence of higher octane blending reagents is called unleaded petrol.

Blending agents used are —
i) Methyl tertiary butyl ether (MTBE)
ii) Ethyl tertiary butyl ether (ETBE)
iii) Methyl tertiary amyl ether
iv) Ethyl tertiary amyl ether

Advantages:

→ Higher octane number, higher CR and higher power output with better antiknock characteristics.

→ Better combustion efficiency is achieved because blending agents are also oxygenates and lower the emissions of volatile organic contents.

→ Emission of leaded compounds is avoided safeguarding the health of living beings.

→ Catalytic converters are employable with vehicle exhaust lines and relatively safer emissions are ensured.

Module 4

7a. What are the main sources, effects and control of lead pollution. [7M]

Sources of lead

→ Manufacture of lead acid batteries for motor vehicles

→ Through TEL (tetra ethyl lead) is banned, what was emitted earlier still remains in the soil

→ Smelting of metals

→ Drinking water delivered through lead pipes joined with lead solder may contain lead

III effects of lead

i) Toxic to kidneys, decreased mental ability weakness, headache, abdominal cramps, diarrhea and anemia. Instills neurological and cardiovascular problems, behavioral problems and learning deficiencies.

iii) Affects blood forming mechanisms and the peripheral nervous system and damages immune system.

iv) Long term exposure to lead can cause permanent kidney and brain damage.

v) Lead to reduced growth/reproductive rates in plants & animals,

Control of lead

Lead pollution can be controlled by

i) Avoiding lead containing products

ii) Recycling lead coherene essential

iii) Designing lead smelting plants to avoid the exposure of lead to air.

7b Mention the various causes, effects and disposal methods of e-waste. [7M]

It is important to know the characteristics of waste for adopting suitable disposal method.

i) Hazardous waste components
        Electronic waste will contain a large amount of hazardous components in various

sizes and shapes which need to be removed for separate treatment. Flame retardants are used to prevent or delay a developing fire in the e-components. Nearly 12% of all plastics and about 55% of all consumer e-component equipment are treated with flame retardants.

ii) Material composition:
Electronic components contain various metals, metalloids and non metals such as copper, aluminium, steel, nickel, zinc, indium gallium, selenium etc including some toxic metals like mercury, beryllium, lead, cadmium, arsenic, antimony etc. attached to or covered with various plastics, glass and ceramics. Noble metals like gold, silver, platinum etc. are used as contact materials due to their chemical stability and conducting properties. **4M**

Disposal of ewaste
i) Reuse: Has the first priority by extending the lifespan of a secondary market.
ii) Remanufacturing: Used products are dissembled, cleaned, repaired or refurbished reassembled, and qualified for new equipment. **3M**
iii) Recycle: Selective dis-assembly by hazardous or valuable waste for specific treatment and upgrading or refining the useful materials like precious metals for further use by chemical or metallurgical processes.

7c 50mL of an industrial sewage has consumed 11.5mL of 0.4N $K_2Cr_2O_7$ solution for complete oxidation. Calculate COD of industrial sewage. [6M]

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Given

$z = 50\,mL$

$(Q-P) = 11.5\,mL$

$Y = 0.4\,N\ K_2Cr_2O_7$

$COD = ?$

$$COD = \frac{8}{1000} \times Q-P \times Y \times \frac{10^6}{z} \quad \cdots\cdots ppm$$

$$= \frac{8}{1000} \times 11.5 \times 0.4 \times \frac{10^6}{50}$$

$$= 7.36 \times 10^{-4} \times 10^6$$

$$= 7.36 \times 10^2$$

$$= 736\ ppm\ \underline{or}\ mg/L$$

<u>or</u>

$1000\,mL$ of $1N$ FAS $= 8g\ O_2$

$\dfrac{1000\,mL}{1000}$ of $1N$ FAS $= \dfrac{8}{1000}\,g\ O_2$

$1\,mL$ of $1N$ FAS $= 0.008g\ O_2$

$(Q-P)\,mL$ of YN FAS $= \dfrac{8}{1000} \times Q-P \times Y$

Express it interms of ppm

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

$$= \frac{8}{1000} \times (11.5) \times 0.4 \times \frac{10^6}{50}$$

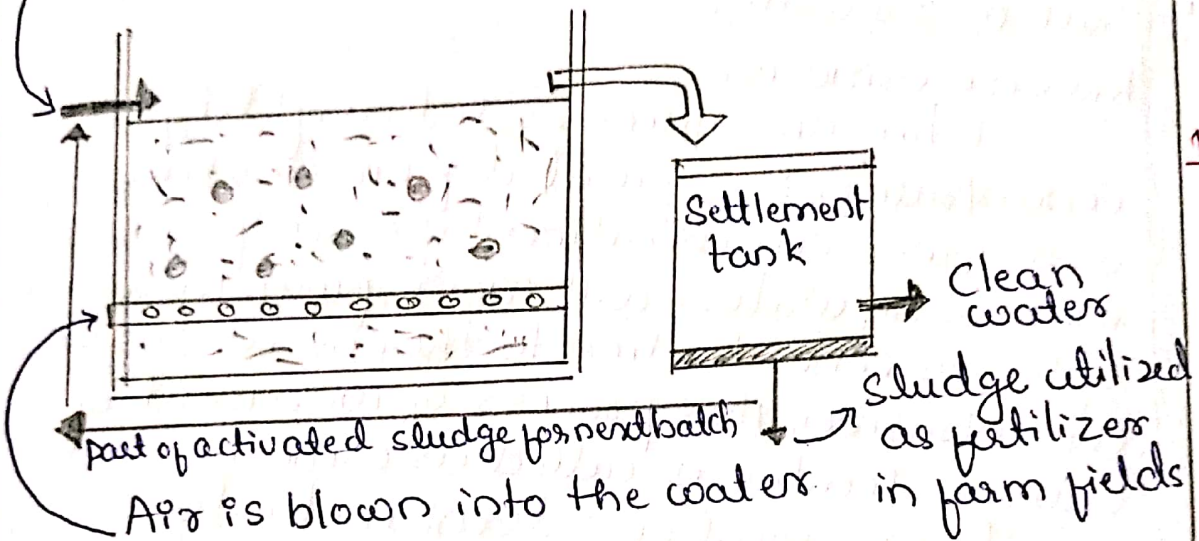$$= 736\,ppm$$

8a | Explain the activated sludge treatment of sewage water [7M]

Activated sludge treatment.

It is also called as secondary - treatment. Removal of biologically oxidizable impurities from water.

Polluted water after primary treatment with activated sludge.

Settlement tank

Clean water

sludge utilized as fertilizer in farm fields

part of activated sludge for next batch

Air is blown into the water

1M

The waste water after the primary treatment is allowed to flow into large tanks where biological treatment is carried out. Activated sludge rich in aerobic bacteria, is added to the water. Micro-organisms present in the sludge thrive on the organic wastes in the sewage. Air is blown vigorously from the bottom of the tank in order to agitate the water and to have better contact of oxygen and organic wastes with aerobic bacteria. Aerobic oxidation removes the organic load in waste water. The sludge formed is removed by settlement or sedimentation. A part of the sludge is used as activated sludge for next batch of feed water and the rest is

3M

Used as activated sludge process operates at 90-95% efficiency of BOD treatment. }3M

8b. What is Desalination? Describe the desalination of seawater by reverse osmosis process.[7M]
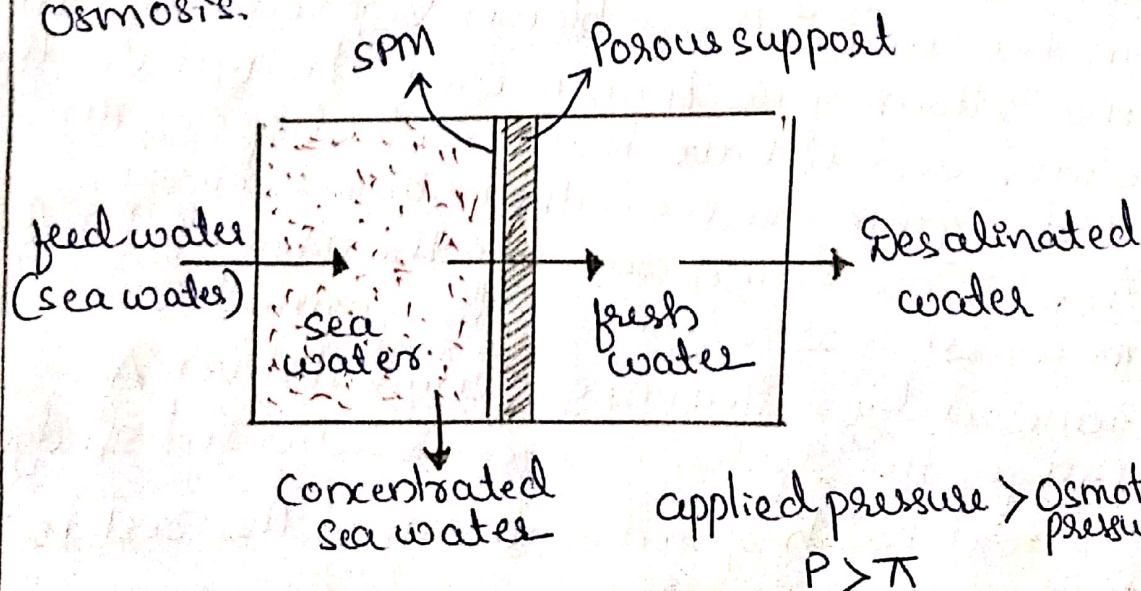
Desalination:

It is process of partial or complete demineralization of highly saline water such as sea water.

Reverse osmosis:

When an aqueous solution of higher concentration is separated from another with lower concentration by a semipermeable membrane, water will move from the region of lower concentration to the one at higher concentration. This process of movement of water molecules is called as osmosis.

The movement of solvent molecules through the semipermiable 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. }1M

feed water (sea water) → | sea water | SPM ↑ | Porous support | fresh water | → Desalinated water

Concentrated sea water

applied pressure > Osmotic pressure

$P > \pi$ }1M

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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 semi permeable membrane is reversed. This is termed as reverse osmosis. This method when applied to brackish water or seawater 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
→ Poly methacrylate
→ Polyimide
→ 100-150 μm in thickness with 0.0001-0.01μm 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 effected for brackish water by the used pressures up to 250-400 psi and for sea water, by use of pressure 600-1000 psi. Important components of the reverse osmosis unit are semi permeable membrane and a high pressure pump.

Reverse osmosis has advantage of removal of all pollutants including microorganisms. However, there is a disadvantage that desalinated water will not have been the required minerals. for good health.
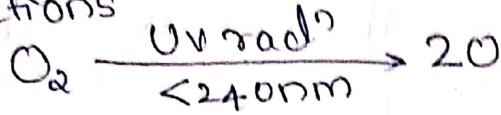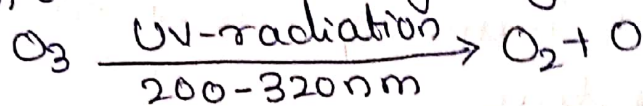
8c Write a note on ozone depletion [6M]

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

Ozone formation:
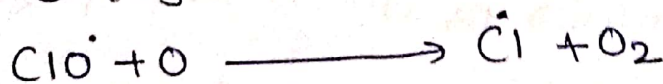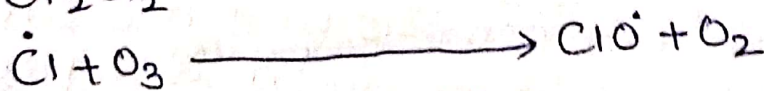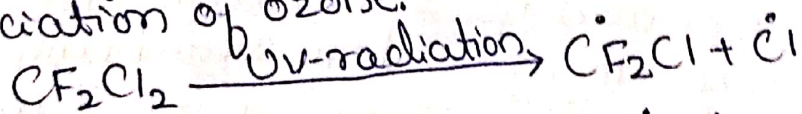It is formed in air by following reactions

$$O_2 \xrightarrow[<240nm]{UV\ rad^n} 2O$$

$$O_2 + O \longrightarrow O_3$$

Also, ozone is destroyed by

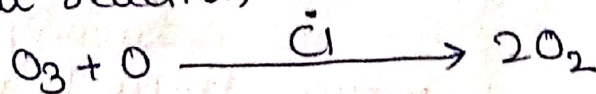$$O_3 \xrightarrow[200-320nm]{UV-radiation} O_2 + O$$

Ozone depletion
Chlorofluorocarbons: 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.

$$CF_2Cl_2 \xrightarrow{UV-radiation} \overset{\cdot}{C}F_2Cl + \overset{\cdot}{C}l$$

$$\overset{\cdot}{C}l + O_3 \longrightarrow Cl\overset{\cdot}{O} + O_2$$

$$Cl\overset{\cdot}{O} + O \longrightarrow \overset{\cdot}{C}l + O_2$$

Overall reaction

$$O_3 + O \xrightarrow{\overset{\cdot}{C}l} 2O_2$$

Ill effects of ozone depletion

1) UV radiations cause skin cancers and affect the immune system.

1M

2M

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ii) Absorbance of UV radiations by cornea and eye lens causes photo keratitis and cataracts. UV radiations kill microorganisms and thereby affect the dynamic biological balance on the earth. } 2M

Control of ozone depletion

Use of hydrochlorofluro carbons (HCFCs) and hydrofluoro alkanes (HFAs) in place of CFCs. These compounds with one or more hydrogen atoms are susceptible to degradation. In HFAs, there are no chlorine atoms and are not ozone destroyers. But these chemicals are greenhouse gases. Use of propane and butane as freezers is more useful. } 1M

Module-5

9a. Explain theory, instrumentation, and application of colorimetry. (6M)

Colorimetry:

Principle: Change in the colour intensity with changing sample or sample concentration and corresponding quantitative change in absorbance of light is the principle behind colorimetric analysis.

It is based on Beer-Lambert's law states that "when a monochromatic beam of light passes through a solution, the rate of decrease in light intensity with concentration and thickness of light absorbing medium.
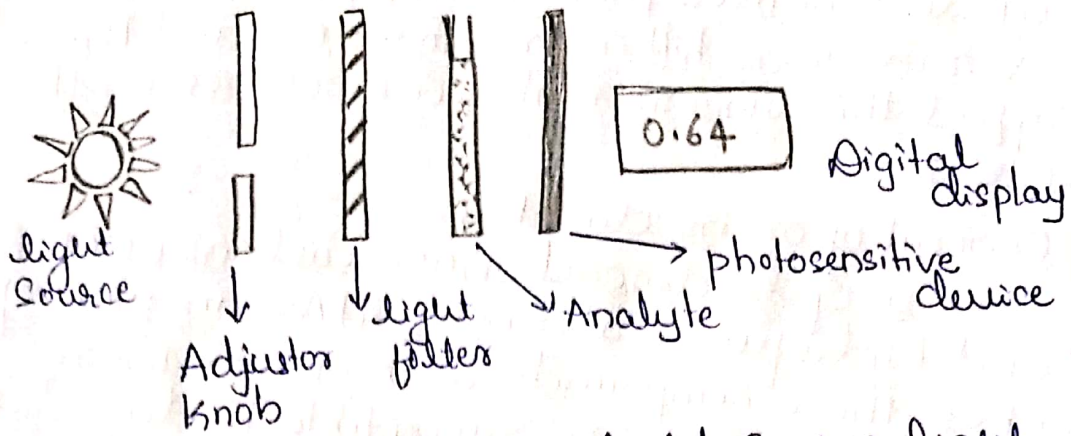
$$Absorbance (A) = \epsilon c t$$

where t is kept constant, Absorption (A) is proportional to the concentration 'c'

ϵ is molar absorptivity constant $L\,mol^{-1}cm^{-1}$. } 2M

Instrumentation:

light source → Adjustor Knob → light filter → Analyte → photosensitive device → 0.64 Digital display

Colorimeter consists of a light source, light intensity adjuster knob, a light filter, slot for standard or test solution in a cuvette and a photosensitive device to measure the transmittance or absorbance and display a unit. The colorimeter responds to the changes in concentration of standard solutions or analyte.

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

9b. What is potentiometric titrations? Explain the principle involved in potentiometric titrations [7M]

Potentiometric titrations

   A titration in which the end point or equivalence point is determined by measurement of cell potential and such titrations are called as potentiometric titrations.

Principle.

change in the electrode potential with changing ionic species or their molar concentration and corresponding quantitative change in cell potential is the principle behind potentiometric analysis.

When a metal M is immersed in a solution containing its own ions M^{n+}, the electrode potential is given by Nernst equation

$$E = E^\circ + \frac{0.0591}{n} \log [M^{n+}] \text{ at } 298 K$$

3M

A suitable indicator electrode and a reference electrode are coupled and dipped in the analyte to construct a galvanic cell.

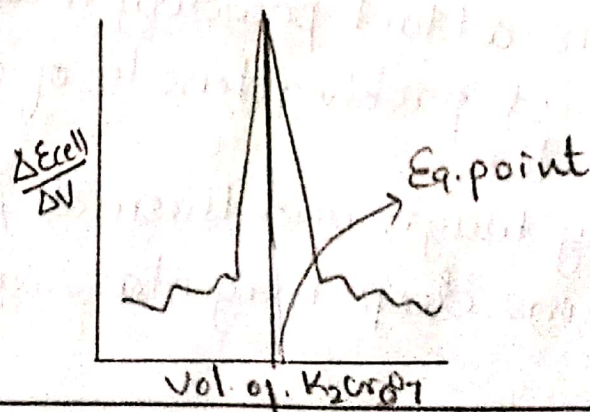→ Cell potential measured is a function of the concentration of the ions in the analyte.

→ Cell potential changes abruptly at the equivalence point as the nature of ions changes abruptly.

→ From the equivalence points, the concentration of analyte can be determined.

→ Potentiometry is used to determine the equivalence points in ———
* Redox reactions
* Acid-base reactions
* Precipitation reactions

Ex: Estimation of FAS using std potassium dichromate solution by potentiometric method.

3M

Graph: y-axis labeled $\frac{\Delta E_{cell}}{\Delta V}$, x-axis labeled Vol of. $K_2Cr_2O_7$, with peak labeled Eq. point

9c Write a note on Fullerene. Mention its application.

Fullerene

→ An allotrope of carbon
→ The most famous form of fullerene is C_{60}
→ Discovered by H W Kroto and R S Smalley at Rice University, USA (1985).
→ Popularly known as Buckminister fullerene in honor of American architect buckminister Fuller

→ The C_{60} fullerene 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 $C_{70}, C_{72},$ $C_{74}, C_{76}, C_{80}, C_{82}, C_{84}.$

Properties:

→ No other element has such wonderful properties as carbon
→ Bucky balls are relatively cheap
→ In fullerenes, 12 pentagonal rings are necessary sufficient to effect the cage closure.
→ The most stable containing 60 atoms.
→ The diameter of the molecule 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
→ Highest packing density of all known structures.
→ Very tough and thermally stable.
→ Forms deep magenta solution in benzene

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The mean diameter of molecule is measured to be $7-10A°$ **1M**

The average carbon-carbon bond length for C_{60} is $1.44A°$, which lies between that of graphite and diamond.

Applications:
→ It is used in electrographic imaging solar cells, nonlinear optical films, magnato, optical recording.
→ It is widely used for the conversion of diamond.
→ Used as lubricants, adhesives, charge transfer complexes, etc.
→ It is, used in secondary batteries, fuel cell electrodes **2M**

10a what are Nano-materials? Give their synthesis by Sol-gel techniques.[7M]

→ It is a bottom up approach of synthesis of nanomaterials

→ The sol-gel process: a change from a liquid state to a gel state through polycondensation reactions. A sol is a stable dispersion of colloidal particles or polymers in a solvent. The particles may be amorphous or crystalline. A gel consists of a 3 dimensional continuous network of the sol particles, which encloses a liquid phase. **1M**

The sol-gel method involves the following steps.

1) Formation of different stable solutions of alkoxide or solvated metal precursors
$$MOR + H_2O \longrightarrow MOH + ROH \ (Hydrolysis)$$

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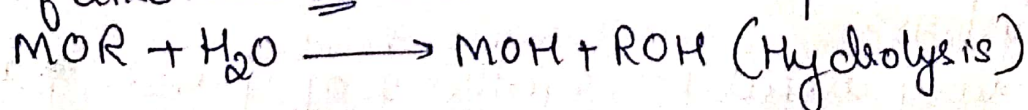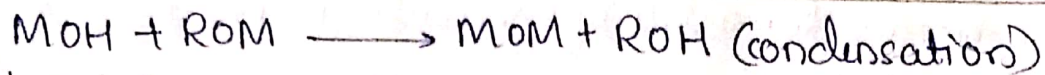
2) Gelation resulting from formation of an oxide or alcohol bridged networks by polycondensation reaction that results in dramatic increase in viscosity of the solution.

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

4) Drying of gel: Water and other volatile liquids are removed from gel network. The drying process has itself broken into four distinct steps:
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 supercritical or near supercritical 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 up to 800°C

6) Densification and decomposition of gels at higher temperature.

Advantages:

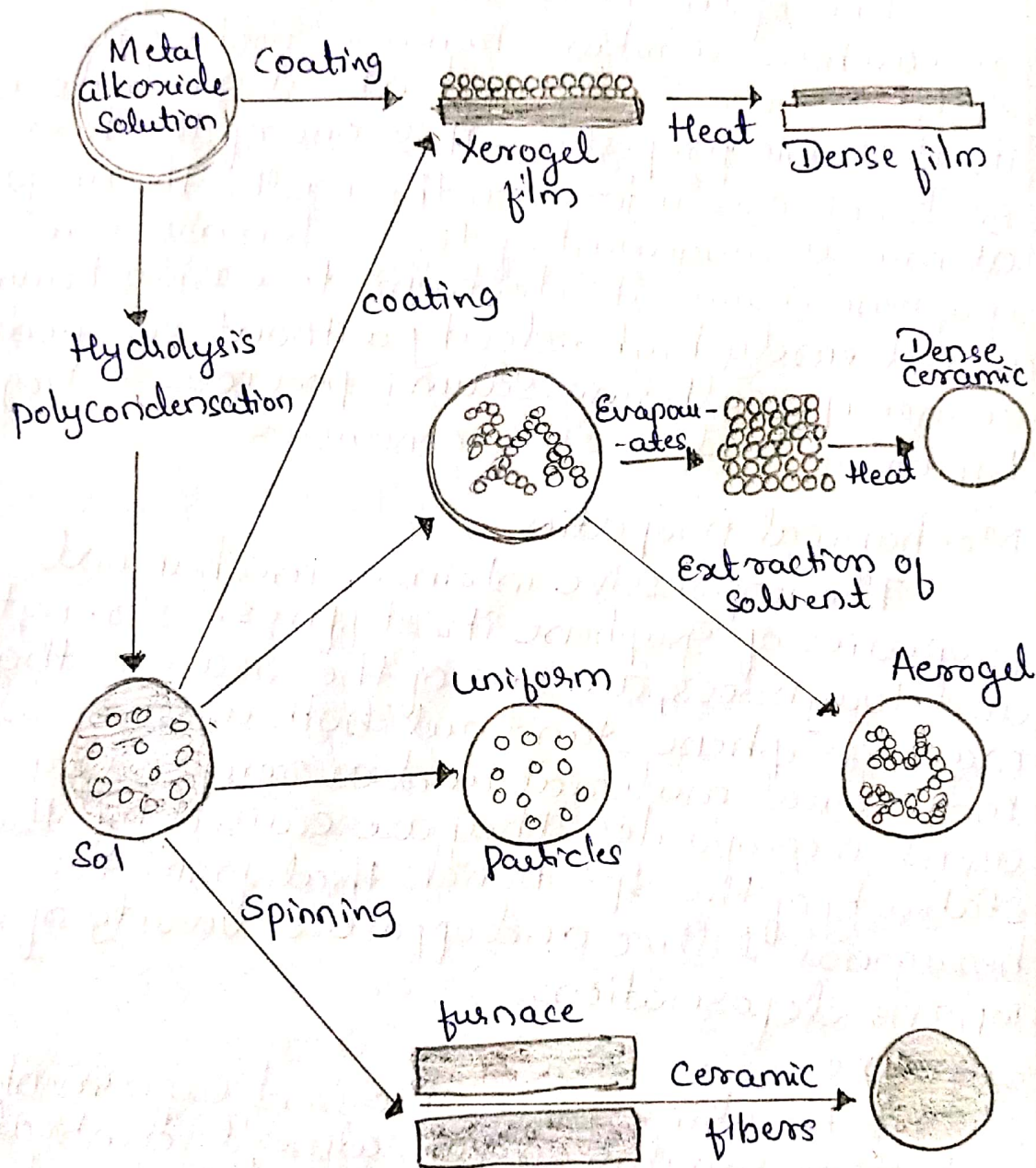It is very useful for synthesis of glasses, glass ceramics at lower temperature

3M

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→ Monosized nanoparticles are produced by this method.

→ No need for special or expensive equipment

→ Coatings and thin films, monoliths, composites, porous membranes, powders & fibers.

2M

1M

10b Write a note on Graphenes. Mention their applications. [7M]

Graphene is the name for an atom-thick honey comb sheet of carbon atoms. It is the building block for other graphitic materials

→ Harder than diamond yet more elastic than rubber; together than steel yet lighter than aluminium. Graphene is the strongest known material.

Properties:

→ **Electronic properties**

One of the reasons nanotechnology researchers working towards molecular electronics are so excited about graphene is its electronic properties. - It is one of the best electrical conductors on the earth. The unique atomic arrangement of the carbon atoms in graphene allows its electrons to easily travel at extremely high velocity without significant chance of scattering, saving precious energy typically lost in other conductors. **1M**

→ **Mechanical properties**

The impressive intrinsic mechanical properties of graphene, its stiffness, strength and toughness, are one of the reasons that make graphene stand out both as an individual material and as reinforcing agent in composites. They are caused by the stability of the sp² bonds that form the hexagonal lattice and oppose a variety of inplane deformations. **1M**

→ **Stiffness:**

The breaking force obtained experimentally and form simulation was almost identical and the experimental value of 2nd order elastic stiffness was equal to 340 ± 50 Nm⁻¹. This value corresponds to a Young's modulus of 1.0 ± 0.1 Tpa assuming an effective thickness of 0.335 nm. **1M**

→ **Strength:** Defect free, monolayer graphene is considered to be the strongest material

ever tested with a strength of 42 Nm⁻¹, which equates to an intrinsic strength of 130 GPa. {1M

→ Toughness

Fracture toughness, which is a property very relevant to engineering applications, is one of the most important mechanical properties of graphene and was measured as a critical stress intensity factor of 4.0 ± 0.6 MPa. }1M

Applications.

→ Used in solar cells
→ Used in rechargeable batteries a storage devices.
→ They are used as sensors.
→ Some of the most promising applications of graphene are in electronics (as transistors and interconnects) }2M

10c Explaen the theory and applications of Atomic absorption spectroscopy [6M]

Atomic Absorption spectroscopy (AAS) involves absorption of light by analyte that is atomic in the gas phase. These atoms of the analyte are usually produced in a flame from solute in aqueous solution.
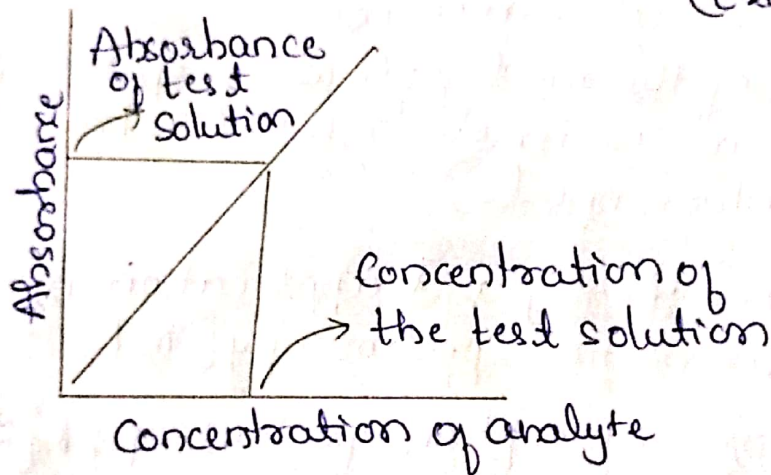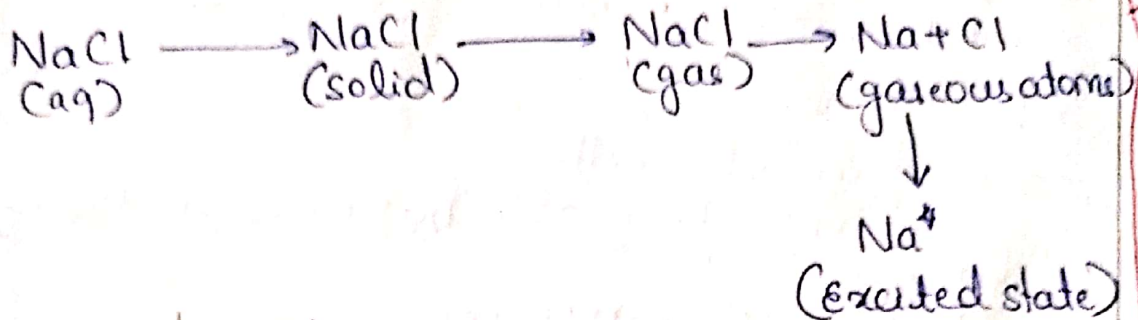
The aquous sample is drawn upto a mixing chamber through a capillary tube where it becomes ancerosol, is mixed with the fuel & air and drawn into the burner which converts the salt into atoms in the suitable flame. Flame itself in a way acts as sample holder. }3M

Absorption of light of characteristic wavelength (characteristic of the element under investigation) causes the atoms to enter into

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the excited state. Absorbance is measured using a photodetector after filtering the characteristic wavelength through a mono-chromator. The absorbance follows Beer's law and the analyte can be quantified.

Absorbance α concentration

Ex:

$$NaCl_{(aq)} \longrightarrow NaCl_{(solid)} \longrightarrow NaCl_{(gas)} \longrightarrow Na + Cl \text{ (gaseous atoms)}$$

$$\downarrow$$

$$Na^+ \text{ (Excited state)}$$

Concentration of analyte

Applications!

The atomic absorption spectrophotometer is used for the determination of metals in trace amounts from aqueous solutions such as water samples, biological, medical and pathological samples, pharamaceutical samples etc.

Prepared by Prof. S.S. Kulkarni.

19/7/21.

(Dear Academics)

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