First/Second Semester B.E. Degree Examination, June/July 2019
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. What is single electrode potential? Derive Nernst's equation for single electrode potential. **(06 Marks)**

b. What are batteries? Demonstrate the construction and working of Ni-MH battery, mention its applications. **(07 Marks)**

c. What voltage will be generated by a cell that consists of an iron electrode immersed in 0.5M FeSO4 solution and a copper electrode immersed in 1M CuSO4 solution at 298 K. Given $E^{o}_{Fe} = -44$ V and $E^{o}_{Cu} = 0.34$ V. Write the cell representation and cell reactions. **(07 Marks)**

OR

2 a. What is Battery? Explain primary and secondary with examples. **(06 Marks)**

b. Describe the construction and working of Li-ion battery. Mention its applications. **(07 Marks)**

c. What are concentration cells? Emf of the cell Cd | $CdSO_4$ (XM) | | $CdSO_4$ (0.025M) | Cd at 28°C is 0.035 V. Find the concentration of CdSO4 at anode. Given R = 8.314 J/K/mol, F = 96500 C. **(07 Marks)**

Module-2

3 a. Discuss the following types of corrosion:
i) Differential metallic corrosion ii) Water line corrosion **(06 Marks)**

b. What is corrosion? Illustrate electrochemical theory of corrosion taking iron as an example. **(07 Marks)**

c. What is electroless plating? Outline the electroless plating of copper. **(07 Marks)**

OR

4 a. Explain the factors affecting the rate of corrosion:
i) Nature of corrosion product ii) Ratio of anodic to cathodic areas **(06 Marks)**

b. What is meant by metal finishing? Highlight any five technological importance of metal finishing. **(07 Marks)**

c. What is electroplating? Discuss the electroplating of chromium. **(07 Marks)**

Module-3

5 a. What are fuel cells? Describe the construction and working of Methanol-Oxygen fuel cell. **(06 Marks)**

b. Describe the experimental determination of calorific value of solid fuel using Bomb Calorimeter. **(07 Marks)**

c. 0.95 g of coal sample (C = 93%; H_2 = 6% and ash 1%) was subjected to combustion in Bomb calorimeter. Mass of water taken in the calorimeter was 2.6 kg and the water equivalent of calorimeter was 0.75 kg. The rise in temperature was found to be 3.2°C. Calculate the gross and net calorific values of the sample. Latent heat of steam = 2457 kJ/kg/°C and S = 4.187kJ/kg/°C. **(07 Marks)**

OR

6 a. Explain the preparation of solar grade silicon by union-carbide process. **(06 Marks)**

b. What are pv-cells? Illustrate the construction and working of a typical pv-cell. **(07 Marks)**

c. What is knocking? Explain the mechanisms of knocking. Mention its ill effects. **(07 Marks)**

Module-4

7 a. Outline the softening of water by ion-exchange method. **(06 Marks)**

b. What are the sources, effects and control of lead pollution? **(07 Marks)**

c. Define COD. In a COD test, 30.6 cm^3 and 15.5 cm^3 of 0.05N FAS solution are required for blank and sample titration respectively. The volume of the test sample used was 25 cm^3. Solve the COD of the water sample solution. **(07 Marks)**

OR

8 a. What is Desalination? Describe the process of reverse osmosis of water. **(06 Marks)**

b. What is boiler corrosion? Explain the boiler corrosion with CO_2, O_2 and $MgC\ell_2$. **(07 Marks)**

c. Define COD. Illustrate the determination of COD of waste water sample. **(07 Marks)**

Module-5

9 a. Describe the synthesis of nano-material by sol-gel technique. **(06 Marks)**

b. Discuss the theory and instrumentation of conductometry. **(07 Marks)**

c. Outline the theory, instrumentation and applications of colorimetry. **(07 Marks)**

OR

10 a. Explain size dependent properties of nano material:

i) Surface area

ii) Electrical

iii) Optical properties **(06 Marks)**

b. Write a note on fullerenes. Mention its properties and applications. **(07 Marks)**

c. What are nanomaterials? Explain the synthesis of nanomaterial by chemical vapour deposition method. **(07 Marks)**

VTU – Question Paper with Answers.

18CHE12 June/July – 2019

Note: Answer any five full questions.

Module 1

1.a What is Single electrode potential Derive Nernst Equation for Single Electrode Potential. (06 Marks)

Answer: Single Electrode Potential: It can be defined as the Potential developed at the interface between the metal and solution when it is in contact with a solution of its own ions.

Nernst Equation for Single Electrode Potential.

Nernst equation gives a relationship between single electrode potential and standard electrode potential through concentration of metal ions at particular temperature.

The decrease in free energy ($-\Delta G$) represents the maximum amount of work that can be obtained from a chemical equilibrium.

$$-\Delta G = W_{max} \quad \text{——— (1)}$$

$$W_{max} = nFE \quad \text{——— (2)}$$

Where $n \rightarrow$ no. of electrons

$E \rightarrow$ Electrode potential

$F \rightarrow$ faraday Constant

Under standard Condition

$$-\Delta G^\circ = nFE^\circ \quad \text{——— (3)}$$

Where $-\Delta G^\circ$ = Decrease free energy under standard Condition

E° = Standard Electrode potential

Consider a reversible Electrode reaction

$$M^{n+} + ne^- \rightleftharpoons M \quad \text{——— (4)}$$

According to Vanthoff's reaction Isotherm

$$-\Delta G = -\Delta G^\circ - RT \ln K_e \quad \text{——— (5)}$$

Where Ke - Equilibrium Constants.

Substitute the Values of Ke, we have

$$-\Delta G = -\Delta G^{\circ} - RT \ln \frac{[M]}{[M^{n+}]} \quad \text{---(6)}$$

Substitute the Value of ΔG & $-\Delta G^{\circ}$.

$$nFE = nFE^{\circ} - \frac{RT}{} \ln \frac{[M]}{[M^{n+}]} \quad \text{---(7)}$$

Divide the equation (7) by nF.

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]} \quad \text{---(8)}$$

For Solid Metal Concentration is unity, so that $[M] = 1$

Then we have.

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]} \quad \text{---(9)}$$

$$E = E^{\circ} + \frac{RT}{nF} \ln [M^{n+}] \quad \text{---(10)}$$

$$E = E^{\circ} + 2.303 \frac{RT}{nF} \log [M^{n+}] \quad \text{---(11)}$$

Substitute the Value $R = 8.314\ J/K/mol$

T=298K F=96500 C/Mol

$$E = E^0 + \frac{0.0591}{n} \log [M^{n+}] \quad \text{--- (12)}$$

Nernst Equation for emf of cell.

$$E_{cell} = E^0_{cell} + \frac{0.0591}{n} \log \left[\frac{\text{Species at Cathode}}{\text{Species at Anode}} \right]$$

b) What are batteries? Demonstrate the Construction and working of Ni-MH battery. Mention its applications.

Ans:

A term battery refers to two or more cells connected in series or parallel.

Nickel-Metal hydride battery is rechargeable

construction and working

Anode Material : A metal hydride such as VH_2, ZrH_2 or TiH_2 containing hydrogen storage metal alloys such as $LaNi_5$ or TiNi

Cathodic Material

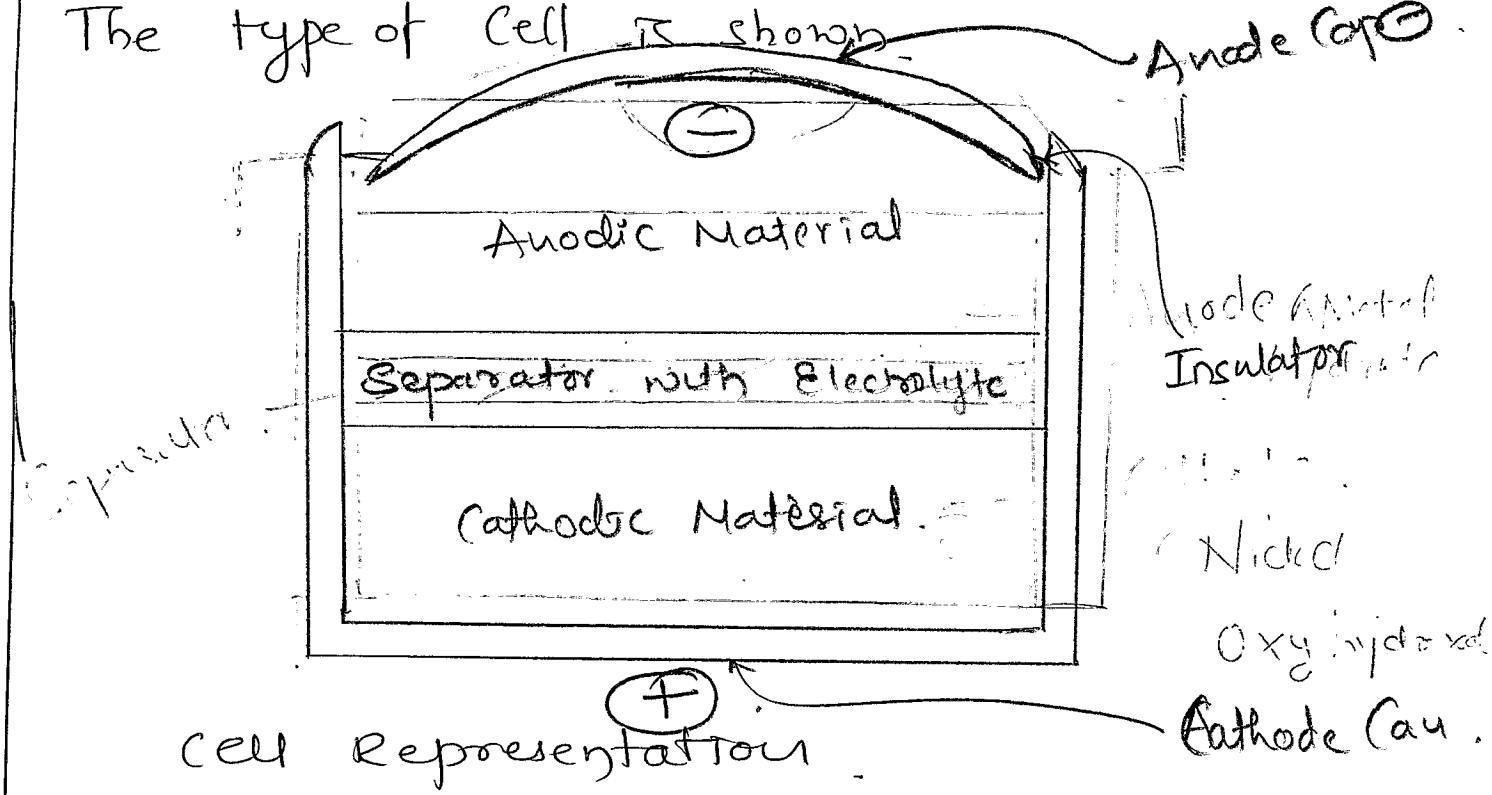
Cathodic Material

It's Nickel oxy hydroxide NiO(OH). The electrode materials are coated or pasted on Nickel wire gauze grids.

Electrolyte: Aqueous KOH solution

The electrodes are separated by a porous Separator soaked in KOH solution

The type of Cell is shown



Cell Representation

$$MH_2 | KOH\ (5\text{-}35\ M) || Ni(OH)_2 | NiO(OH)$$

Half cell reactions during discharge and charge

At Anode $MH_{2(s)} + 2OH^-_{(aq)} \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} M_{(s)} + 2H_2O_{(l)} + 2e^-$

At Cathode

$$2NiO(OH)_{(s)} + 2H_2O_{(l)} + 2e^- \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} 2Ni(OH)_{2(s)} + 2OH^-_{(aq)}$$

Net Cell Reactions:

$$MH_{2(s)} + 2NiO(OH)_{(s)} \rightleftharpoons M_{(s)} + 2Ni(OH)_{2(s)}$$

The cell has cell potential of 1.25 to 1.35V

During charging the reactions at the electrodes are reversed.

Applications:

1) Used in space craft since it can be used directly with pressurized hydrogen.

2) Used in Cellular phones, Computers, and other

3) Used in Electrical Vehicles.

1 c) What voltage will be generated by a cell that consists of a an iron electrode immersed in 0.5M $FeSO_4$ solution and a copper electrode immersed in 1M $CuSO_4$ solution at 298K. Given $E^{\circ}_{Fe} = -0.44V$ and $E^{\circ}_{Cu} = 0.34V$ What is the cell representation and cell reactions. (07 marks)

Given

$E^{\circ}_{Fe^{2+}} = -0.44V$ and $E^{\circ}_{Cu} = 34V$,

$E^{\circ}_{Cu^{+2}} > E^{\circ}_{Fe^{+2}}$

Cell Scheme

$Fe(s) | FeSO_4 (0.5M) || CuSO_4 (1M) | Cu(s)$

cell reactions

$Fe \longrightarrow Fe^{2+}(0.5M) + 2e^-$

$Cu^{2+}(1M) + 2e^- \longrightarrow Cu$

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

$(1M) \qquad (0.5M)$

Formula for calculation of Potential

$$E_{cell} = [E^{\circ}_R - E^{\circ}_L] + 2.303 \frac{RT}{nF} \log \frac{[\text{Reactant}]}{[\text{Products}]}$$

$$= [0.34 - (-44)] + 2.303 \times \frac{8.314 \times 298}{2 \times 96500} \log \frac{[1]}{[0.5]}$$

$$E_{cell} = 0.78 + \frac{0.0591}{2} \log 2$$

$$= 0.78 + 0.02955 \times 0.301$$

$$= 0.7888\ V$$

(4)

2a. What is Battery? Explain primary and Secondary batteries with examples. (6Marks).

Ans: A battery refers to two or more cells connected in series or parallel.

(1) Primary Batteries

Primary batteries can be used only once because the chemical reactions that supply electric current are irreversible. The electric current available depends on the quantity of active materials present. They have limited shelf life and are discharged continously with fairly high efficiencies. They are not to be charged

Examply: Leclanche dry battery, Zinc Air battery.

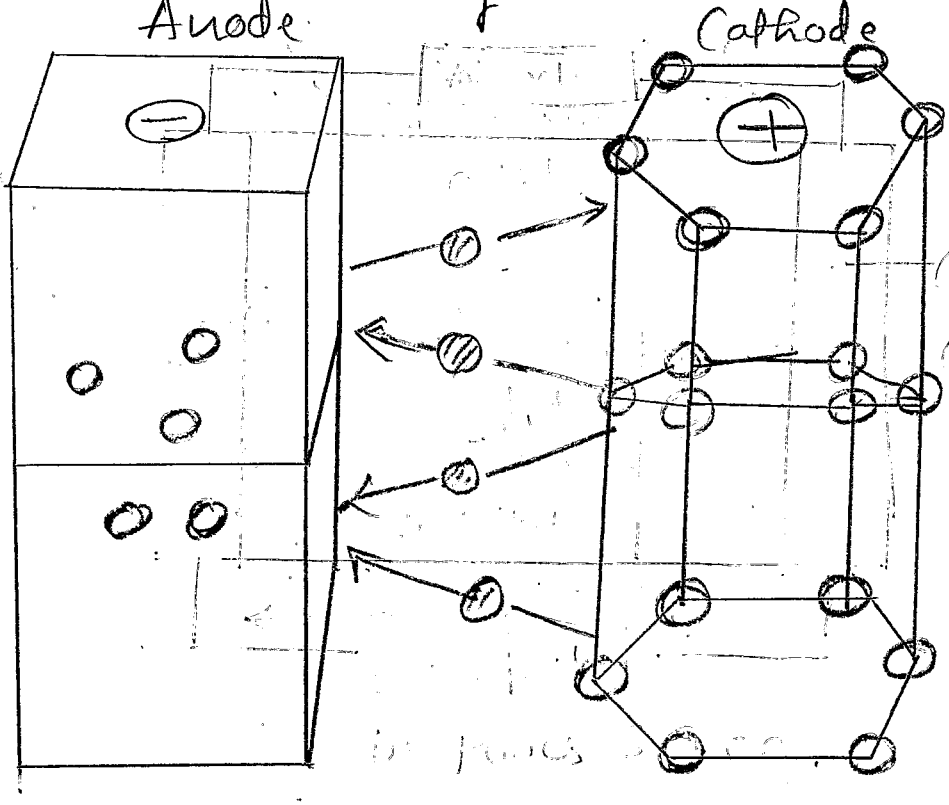
(2) Secondary Batteries

Secondary Batteries are also known as rechargeable batteries or accumulators and the chemical reactions are reversible

They can be charged with the help of an external source of electricity. The charge-discharge cycle (cycle life) can be repeated several hundred times and those batteries can be built into giant generators with high capacities.

Examples: Lead-Acid battery, Nickel-Metal hydride battery.

2b Describe the Construction and Working of Li-ion battery. Mention its applications. (7 Marks)



Anode: Lithium intercalated Carbon or Graphite. Metal Matrix Composit or polymer.

Anode Current Collector: Copper foil

Cathode: Partially Lithiated transition metal Oxides of nickel, Cobalt and Manganese Li_yNiO_2, Li_yCoO_2 and $Li_yMn_2O_4$.

Cathode Current Collector: Aluminium foil

Cell Reactions

At Anode

$$Li_xC_6 \underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftharpoons}} 6C + xLi^+ + xe^-$$

At Cathode

$$Li_{(1-x)}CoO_2 + xLi^+ + xe^- \underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftharpoons}} LiCoO_2$$

Overall Reaction

$$Li_{(1-x)}CoO_2 + Li_xC_6 \underset{\text{Charging}}{\overset{\text{Discharging}}{\rightleftharpoons}} 6C + LiCoO_2.$$

The unit cells are cylindorical and of jelly-roll design, useally of the same size as nicad (Ni-Cd) cells. The open circuit voltage is about 4.1V. Self discharge rate is about 10% per month.

Applications

For Portable telephones, Computers, Camcorders etc.

2c) What are concentration cells & EMF of the cell $Cd|CdSO_4(XM)||CdSO_4(0.025M)|Cd$ at 25°C is 0.035V. Find the Concentration of $CdSO_4$ at anode Given R = 8.314 J/K/mol F = 96500 C.

Ans: Concentration cells are those in which both the anode and the cathode are made up of the same element (metal or non-metal) in contact with the solutions of the same electrolyte, but different Concentrations.

$Cd|CdSO_4(xN)||CdSO_4(0.025M)|Cd$

$C_1 = x \quad C_2 = 0.025\,M$

$T = 25 + 273\,K = 298\,K.$

$F = 96500$

$n = 2.$

$E_{cell} = 0.035\,V.$

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

$$0.035 = \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \times \log\frac{[0.025]}{x}$$

$$0.035 = \frac{0.0591}{2}\log\frac{0.025}{x}$$

$$0.035 = 0.02955 \log\frac{0.025}{x}$$

$$1.184 = \log\frac{0.025}{x}$$

$$\text{Ant}(1.184) = \frac{0.025}{x}$$

$$15.27 = \frac{0.025}{x}$$

$$x = 1.637 \times 10^{-3}\,M$$

$$C_1 = 1.637 \times 10^{-3}\,M$$

3a. Discuss the following types of Corrosion

i) Differential Metal Corrosion

ii) Waterline Corrosion

Ans: Differential Metal Corrosion

When two dissimilar metals are in contact with each other a potential difference is set up resulting in a galvanic current. The two metals differ in their tendencies to undergo oxidation, the one which with lower electrode potential or the more active metals acts as anode and the one with higher electrode potential acts as cathode. The anodic metal undergoes corrosion and the cathodic metal is generally unattacked.

At the Anode (less O_2 concentration)

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

At the Cathode (More O_2 Concentration)

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

$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$$

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

$\longrightarrow [Fe_2O_3 \cdot 3H_2O]$ rust.

Example :

(1) Steel pipes joined to Copper plumbing undergo galvanic Corrosion, Since steel acts as the anode

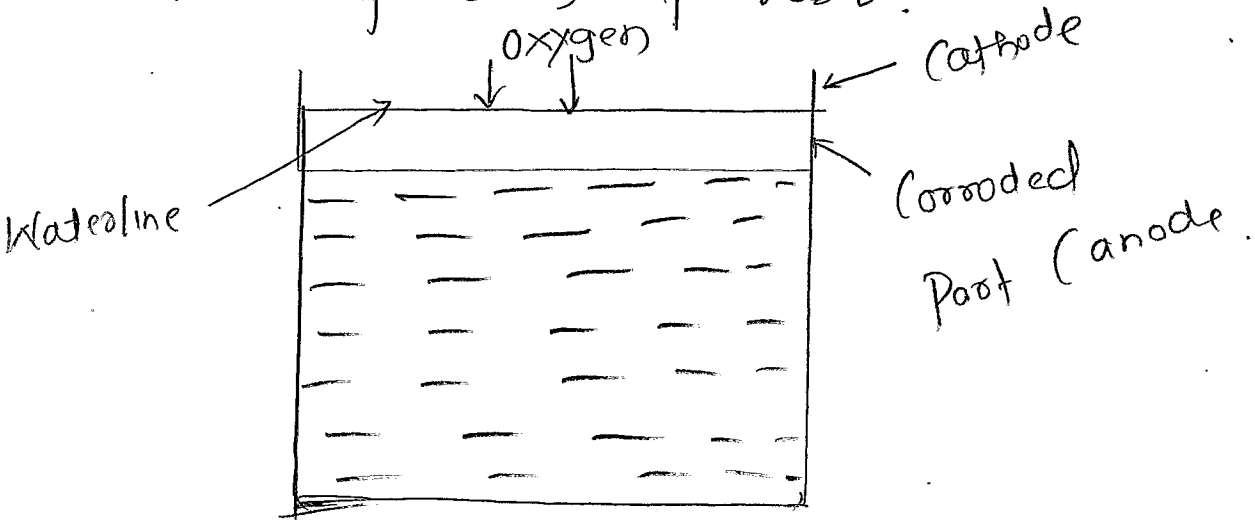
(2) Steel Screws or rivets used on copper sheet, or screws and washers of unlike metals

(3) Steel propelles shaft in Bronze bearing.

Waterline Corrosion

Waterline Corrosion is a case of differential aeration corrosion. the water line Corrosion takes place due to the formation of differential oxygen Concentration Cells. The part of the metal below the water line is exposed only to dissolved oxygen (acts as anode) while part of above the water.

is exposed to higher oxygen concentration (acts as cathode) of the atmosphere. A distinct brown line is formed below the water line due to deposition of rust.



At the Anode
(less O_2 concentration)

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

At the Cathode
(More O_2 concentration)

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

$$Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2$$

$$2Fe(OH)_2 + \tfrac{1}{2}O_2 + H_2O \longrightarrow Fe_2O_3 \cdot 3H_2O$$

rust.

2b) What is Corrosion & illustrate electrochemical theory of corrosion taking iron as an example. (07 marks)

Ans:- According to Electrochemical theory of corrosion of the metal take place due to the formation of anodic and cathodic regions on the same metal surface in the presence of a conducting medium

Corrosion is a defined as the distruction and consequent loss of metals through chemical or electrochemical attack by the Environment.

Corrosion reactions

At the Anodic region iron is liberating Fe^{2+} ions and electrons.

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

At the Cathodic region

The Chemical species present in the surrounding of cathode undergoes reduction by accepting electrons coming through metal.

from the anodic region. Depending on the surrounding medium, there are four possible reduction reactions at the cathodic region.

1. Hydrogen liberation takes place in the absence of oxygen

a) In acidic medium and in the absence of oxygen the cathodic reaction is

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

b) In neutral or alkaline medium and in the absence of oxygen hydroxide ions are formed with simultaneous liberation of hydrogen

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

2. Absorption of Oxygen takes place in the presence of Oxygen.

a) In acidic medium and in the presence of oxygen

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

b) In Neutral or alkaline medium and in presence of oxygen hydroxide ions are formed by the following reaction

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

Corrosion of Iron produces Fe^{2+} and $\bar{O}H$ ions at the anode and cathode sites respectively.

These ions diffuse towards each other to produce insoluble $Fe(OH)_2$.

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

In an oxidizing environment it is oxidized to ferric oxide and the yellow rust is hydrated ferric oxide.

$$2Fe(OH)_2 + 1/2O_2 + H_2O \rightarrow 2[Fe_2O_3 \cdot 3H_2O]$$

In the presence of limited oxygen ferrous oxide is converted into magnetic oxide of iron (Fe_3O_4) and is known as black rust.

c) What is electroless plating & outline the electroless plating of Copper (07 Marks) (9)

Ans:

Definition : Electroless plating is the controlled deposition of a continous film of a metal from its salt solution on a catalytic active surface of the substrate by a suitable reducing agent without the use of electrical energy.

The base of a printed circuit board is a plastic material such as epoxy or phenolic polymer or a glass fiber reinforced polymer composite.

In the manufacture of double sided PCB, the board is clad on either side with thin electroformed copper foils. Then both sides of copper clad board are printed with etch resistant circuit patterns.

The composition of the electroless plating bath & the procedure given below.

Electroactive metal salt Solution	12g $CuSO_4$/litre.
Reducing agent	8g of HCHO per litre.
Buffes	14g Rochelle Salt +15g of NaoH.
Complexing Agent,	20g of EDTA pes litre.
pH	11.
Tempesatue	25°c

Electroless plating through the hole.

Reactions

Anodic Reaction

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

Cathodic Reactions.

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

Overall Reactions

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

4a. Explain the factors affecting the Rate of Corrosion 10

(1) Nature of Corrosion product.
(2) Ratio of Anodic to cathodic Area. (6marks)

Ans:

(1) Nature of Corrosion product.

The Corrosion product formed on the metal surface may or may not act as protective film

If the Corrosion product formed is insoluble, stable, uniform and non-porous. It acts as protective film preventing the further Corrosion

A thin, Invisible, impervious continuous film formed on the surface acts as a barrier between the metal and the Corrosion environment.

If the Corrosion product formed is soluble, unstable, porous and nonuniform, the corrosion continuous, Because in such cases the fresh metal surface is continuously exposed to the Corrosion environment.

In Oxidizing environment metals like aluminium, chromium, Titanium (passive metal)

etc are high passive as their oxides as corrosion products form protective films on the metal surface. Metal such as Fe, Zn, Mg etc. Do not form any protective film.

Ratio of Anodic and Cathodic Area

If a metal has a small anodic area and large cathodic Area ie. the ratio of anodic to cathodic area is small, then the corrosion is more intensive and faster. As this ratio decreases the corrosion rate increases.

At anode oxidation takes place and electrons are liberated. When the anode is smaller and cathode region is large all the electrons liberated at anode are rapidly consumed at cathode region. So rate of anodic reaction increases, corrosion rate also increases.

Eg: A broken coating of tin on iron surface enhances corrosion of iron / steel.

b) What is meant by Metal Finishing? Highlight any five technological Important of Metal Finishing. (7 marks) 11

Definition: Metal Finishing is the process Carried out to modify the surface properties of a metal by electro deposition of a layer of another metal on the substrate.

Technological Importance of Metal finishing.

* To impact corrosion resistant to metals
* To impact abrasion & wear resistance.
* To impact thermal resistance & Impact resistance
* To provide Electrical or Thermal Conducting Surface
* To offer to the surface a thermal or optical reflectivity.

4e. What is Electroplating? Discuss Electroplating of Chromium. (7 marks)

Defination: Electroplating - "Electroplating is the deposition of a metal, by electrolysis over the surface of a substrate, which may be another metal, alloy, polymer, ceramic or composite."

Chromium Plating	Decorative Chromium	Hard chromium
Anode	Insoluble anodes like Pb & Alloys like Pb-6% antimony Pb-7% Sn etc coated with PbO_2 are used.	Insoluble Anodes like Pb & Alloys like Pb.
Cathode	Pre-treated metal Object to be plated	Pre-treated metal object to be plated.
Bath Composition.	250g of Chromic acid (CrO_3). +2.5g of Conc H_2SO_4 (100:1) Chromic acid. and H_2SO_4.	-do-

	It should also contain 1g of trivalent Chromium (Cr^{+3}).	—do—
Current density.	150 – 430 mA/cm2	290 – 580 mA/cm2.
Operating Temperature	45 to 60°C	45 to 60°C
Current effiency	10 to 15%.	17 to 20%.

Reactions.

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{+3} + 7H_2O$$

$$Cr^{+3} + 3e^- \longrightarrow Cr.$$

Module (3).

5a. What are fuel cells, ? Describe the Construction and working of Methanol-oxygen fuel- cell. (06marks).

Ans A fuel cell is an electrochemical cell in which the energy of combustion of a fuel such as hydrogen, methane, carbon monoxide, Methanol etc. is directly converted to electrical energy.

Methanol—Oxygen Fuel Cell

Construction and working.

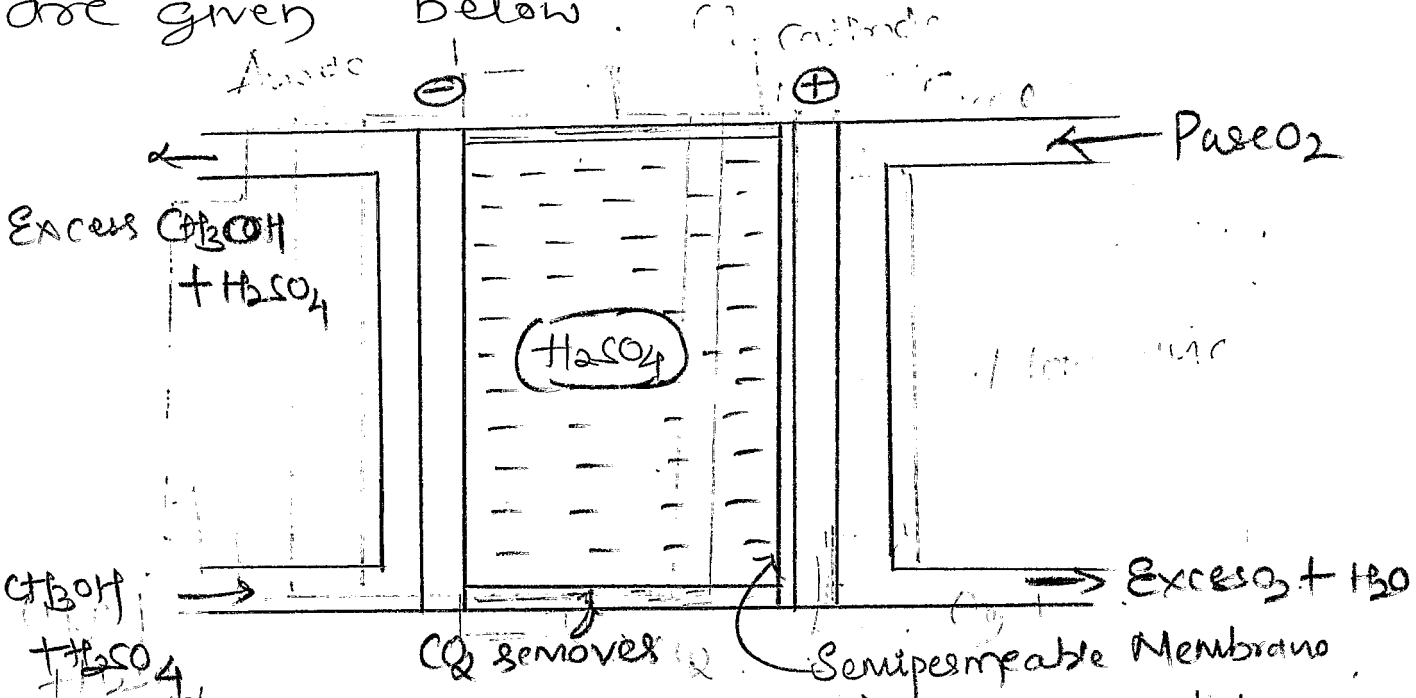
Anode: It is a porous nickel sheet on which platinum or palladium catalyst is deposited.

Cathode: It is a porous nicked sheet on which Silver is deposited.

Electrolyte: Sulphuric acid.

Methanol is circulated through the anode chamber and oxygen gas is circulated through the cathode. A membrane is inserted close to the cathode.

to minimize diffusion of methanol into the cathode thereby reducing the concentration of methanol near to cathode. The reaction are given below.



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

Cathode $3/2\ O_2 + 6H^+ + 6e^- \longrightarrow 3H_2O$

Overall Reaction $CH_3OH + 3/2\ O_2 \longrightarrow CO_2 + 2H_2O$

5b Describe the Experimental determination of calorific value of solid fuel using Bomb Calorimeter. (7marks)

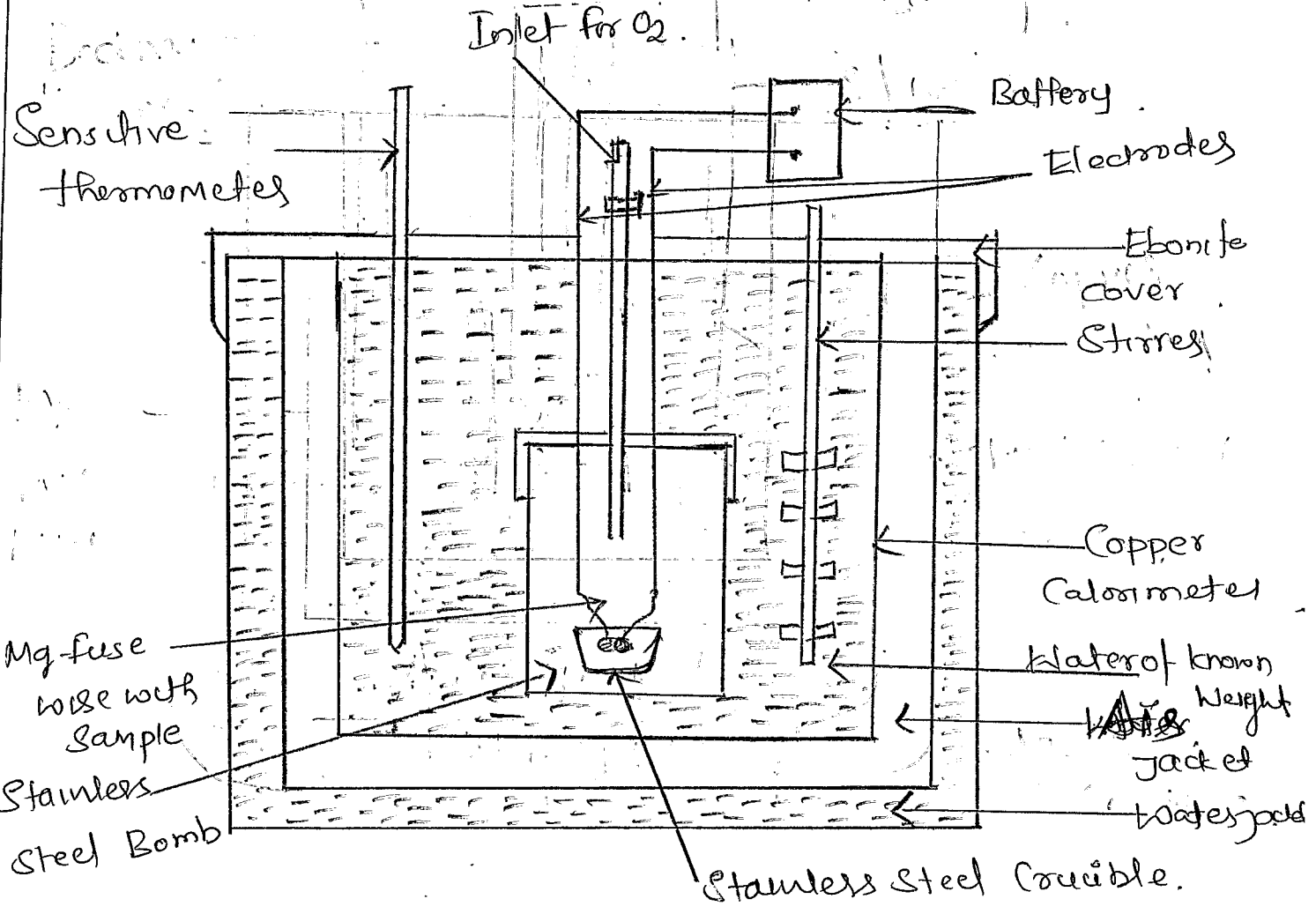
Ans: Pomciple: A known weight of the sample is burnt completely in excess of Oxygen

The liberated heat is absorbed by surrounding water and calorimetes. Thus the heat liberated during the combustion of fuel is equal to the heat absorbed by water and copper calorimeter. The higher calorific value of the fuel is calculated from the data.

Construction : The Bomb calorimeter consists of a cylindrical air tight stainless steel bomb, in which a known weight of fuel (solid or liquid) is taken in a small stainless steel crucible. The two electrodes connected with a magnesium fuse wire is introduced in a bomb for the initiation of combustion of fuel. Also there is an oxygen inlet valve.

The bomb is now immersed in a copper calorimeter containing a weighed mass of water. The copper calorimeter is equipped with a mechanical stirrer for dissipation of heat & thermometer to read accurately the temperature rise.

The colorimeter is surrounded by an insulated air jacket to minimize heat loss. Externally it is surrounded by a water jacket.



Working: The water is kept in constant agitation by the Mechanical Stirrer. The Initial temperature of the water is caretully measured. the fused Magnesium wire is placed in the fuel. The Bomb is filled with oxygen. The fuel is ignited by connecting the two electrodes to a source of electric current. As the sample burns in the bomb

heat is liberated and is absorbed by the surrounding water and the copper calorimeter. The temperature of water gradually increases the water in the calorimeter is stirred continuously during the combustion. When the temperature attains the maximum value (complete combustion) the maximum temperature is noted. The water equavalent of calorimeter is determined by burning a fuel of known calorific value. From the data obtained in the experiment calorific value is calculated.

Calculation

Mass of fuel = m kg

Initial temperature of water = t_1°C.

Maximum temperature of water = t_2°C.

Rise in temperature of water = $(t_2 - t_1)$°C = U°C

Mass of water in the calorimeter = W_1 kg

Water Equavalent of calorimeter = W_2 kg

If S is the gross calorific value of the fuel.

The Calorific Value Q is calculated from the equation

$$Q = \frac{S(W_1 + W_2)\Delta t}{m} \text{ KJ/kg}$$

Where $S = 4.184$ KJ/°C

Net Calorific Value.

= GCV − latent heat of water formed

= GCV − (0.09H × 587 × 4.184) KJ/kg.

5C 0.95g of Coal Sample (C = 93%. H_2 = 6%. and Ash = 1%) was subjected to combustion in Bomb Calorimeter... Mass of water taken in the Calorimeter was 2.6 kg and the water Equivalent of Calorimeter was 0.75 kg. The rise in temperature was found to be 3.2°C. Calculate the gross and net Calorific Value of the Sample. Latent heat of steam = 2457 KJ/kg and S = 4.187 KJ/kg/C.

Given: Mass of sample $m = 0.95g = 0.95 \times 10^{-3} kg$

$= 0.00095 kg$

Mass of water $= m_1 = 2.6kg$

Water Equavalent of Calorimeter $= 0.75kg$

the rise in temperature $(\Delta T) = T_2 - T_1 = 3.2°C$

$= 3.2K$

Latent heat of steam $= L_c = 2757 kJ/kg$.

Specific heat of water $= S = 4.187 kJ/kg/K$.

1. Hydrogen = 6 %

Formula for Calculation of HCV

$$GCV = \frac{(m_1 + m_2)\,\Delta T\, S}{m}$$

$$= \frac{(2.6 + 0.75)\,3.2 \times 4.187}{0.00095}$$

$$= \frac{3.35 \times 3.2 \times 4.18]}{0.00095}$$

$$= 47246.98 \text{ kJ/kg}$$

$$NCV = GCV - 0.09 \times C_v \times H.$$

$$= 47246.98 - (0.09 \times 2757 \times 6)$$

$$= 47246.98 - 1488.78$$

$$= 45,758.2 \text{ kJ/kg}.$$

6a. Explain the Preparation of Solar grade Silicon by union- carbide process. (06 Marks)

Ans: Production of Semiconductor grade Silicon (crystalline)

Matallurgical Grade silicon is produced in submerged electrical arc furnace. The furnace consists of a coucible containing Carbon and Silicon & an electric arc is struck. A high temperature is produced & Silica is reduced to elemental silicon with a typical purity of 98.5%.

$$SiO_2 + 2C \longrightarrow Si + 2CO$$

Elements less noble silicon such as Al, Ca & Mg are oxidised & slag is formed

$$4Al + 3SiO_2 \longrightarrow 3Si + 2Al_2O_3$$

$$2Ca + SiO_2 \longrightarrow Si + 2CaO$$

$$2Mg + SiO_2 \longrightarrow Si + 2MgO.$$

The Si obtained is 99% pure and is called metallic grade Silicon

Semiconductor grade Silicon is used for Solar cells. The purification of Metallic grade silicon to obtain Solar grade Silicon involves the following steps.

The metallic grade Silicon is treated with dry HCl gas at 300°C from trichloro Silane and a small amount of tetrachloro Silane. The mixture is distilled to get pure trichloro silane.

$$Si + 3HCl \longrightarrow HSiCl_3 + H_2$$

$$Si + 4HCl \longrightarrow SiCl_4 + 2H_2$$

Silicon tetrachloride is reduced with hydrogen at 1000°C in a reactor.

Trichlorosilane, thus obtained is passed through fixed bed columns containing quaternary amonium ion exchange resin as catalyst. Trichloro silane gets converted into dichloro silane.

$$2HSiCl_3 \longrightarrow H_2SiCl_2 + SiCl_4$$

The products are separated by distillation tetrachlorosilane is recycled to the hydrogenation reactor.

Dichlorosilane is passed through a second fixed bed column filled with quaternary ammonium ion exchange resin. Dichlorosilane converted to silane.

$$3H_2SiCl_4 \longrightarrow SiH_4 + 2HSiCl_3$$

6b What are PV cells? Illustrate the construction and working of a typical PV-cell.

Ans: Photovoltaic cells or solar cells as they are often referred to are semiconductor devices that convert sunlight into direct current electricity on illumination".

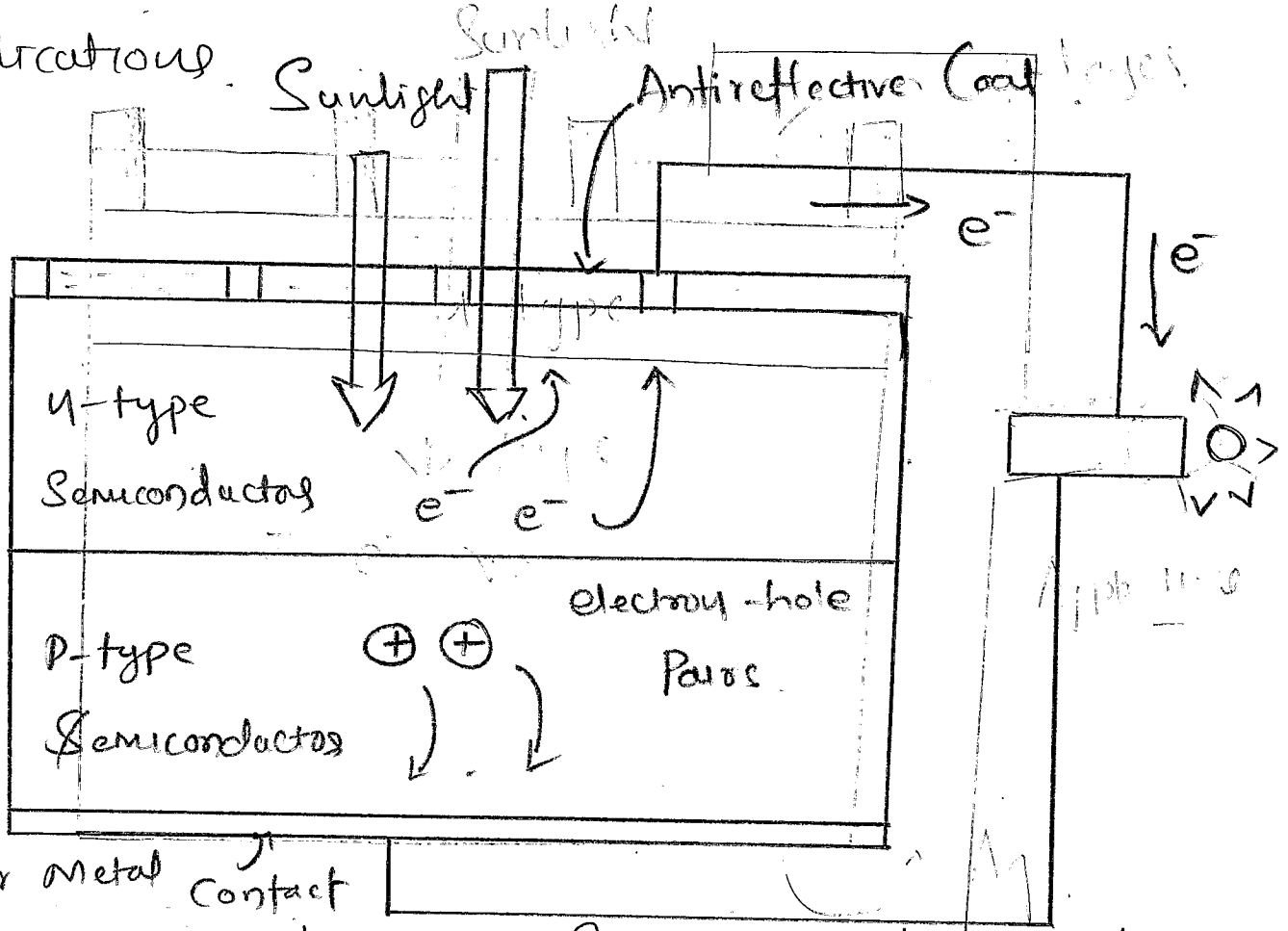
Construction of a photovoltaic cells & its working.

Solar cells consist of p-n junction formed from a semi-conductor diode obtained when n-type and p-type semiconductor are brought together to form a metallurgical junction. the diode has two electrical contacts one of which is in the form of metallic grid and the other is a layer of nobler metal on the back of the solar cell. The metallic grid allows light to fall on the semiconductor between the grid lines to increase the amount of light transmitted through the front to the cell

All electromagnetic radiations including sunlight consist of particles called photons. the photons carry a certain amount of energy given by $E = h\nu$.

When electromagnetic radiation is incident normal to plane of the solar cell, the photons which possess energy sufficient to overcome the barrier potential are absorbed &

and electron-hole pairs are formed. electrons are driven out into the external circuit & could be stored and used for various applications.



6C What are knocking? Explain the Mechanisms of knocking. Mention its ill effects (07 marks)

Ans:

Knocking is the explosive combustion of petrol-air mixture beyond a certain compression ratio which produces shock waves in IC Engine which hit walls of the cylinder and piston producing a rattling sound.

Mechanism of knocking

Under normal conditions there is slow oxidation of the fuel during which oxygen combines with a few hydrocarbons molecules and activates them by forming peroxides. The activated molecules combine with other hydrocarbon molecules and a chain reaction is set up resulting in smooth combustion. Knocking occurs if the chain reactions proceeds at too fast rate. The unstable peroxides formed decompose exposively giving rise to pressure waves, which knock against the Engine walls. The normal and explosives combustion of a fuel (eg C_2H_6) may be represented as follows.

$$C_2H_6(g) + \frac{7}{2}O_2 \longrightarrow 2CO_2 + 3H_2O$$

$$CH_3 - CH_3 + O_2 \longrightarrow CH_3 - O - O - CH_3$$

Ethane Peroxide

$$CH_3 - O - O - CH_3 \longrightarrow CH_3CHO + H_2O,$$

$$CH_3CHO + 3/2\,O_2 \longrightarrow HCHO + CO_2 + H_2O$$

$$HCHO + O_2 \longrightarrow H_2O + CO_2$$

iii) effects

1) It produces undesirable rating noise
2) It increases fuel consuption
3) It results in decreased power output.
4) It cause mechanical damage due to overheating to engine parts such as Spark plug, pistoy and engine walls and reduces the life of engine
5) The driving becomes rather unpleasant.

7a. Outline the Softening of water by ion-exchange method. (06 Marks).

Ans: An elegant way to soften water is to remove all the associated metal ions and their counter anions from water. This is accomplished with the effluent Synthetic ion-exchange resins. the utility of ion exchange resin rests with its ability to be used and reused, high efficiency economical cost and long useful life.

Function of cation exchanger, commercially significant cation exchange resins are sulfonated copolymers of styrene and divinyl benzene. They are represented as RH and

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

$$2RH + Mg^{2+} \longrightarrow R_2Mg + 2H^+$$

Function of Anion Exchanger: The anion exchanger resins are copolymers of styrene and divinyl benzene containing active quaternary amino groups. The resins are represented as

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

$$2ROH + SO_4 \longrightarrow R_2SO_4 + 2OH^-$$

As cations replaced by H^+ ions and anions by OH^- ions, the net reaction is introduction of water in place of metal salts present in water.

7b) What are the sources, effects and control of lead pollution (7 marks).

Ans: (a) Sources: The most common source of lead poisoning is dust and chips from old paint.

2) Lead comes metal smelting, lead-Acid battery manufacturing and other factories that use lead

(b)

Effects: (1) Depending upon the level of exposure lead can adversely affect the nervous system, kedney function, immune system, cardiovascular system

(2) Affects oxygen carrying capacity of blood.

control. (1) Lead Smelting plants should design their storage piles in a way that the movements of lead materials are minimised to lessey exposure to wind and air

(2) Elimination of lead contamination in drinking water by processes such as

reverse osmosis, distillation and filtration using Carbon filters.

7c Define COD. In a COD test 30.6 cm^3 and 15.5 cm^3 of 0.05N FAS solution are required for blank and Sample titration respectively. The volume of the test Sample used was 25 cm^3. Solve the COD of the water Sample Solution. (07 Marks)

Definition

Any COD is the amount of oxygen equavalent used while oxidizing the Chemically oxidisable impurities in the water, with the strong Chemical Oxidant, $K_2Cr_2O_7$ in acid medium. It is expressed in mg/dm^3 or ppm.

Problems: $P = 15.5 cm^3$ $Q = 30.6 cm^3$

$Y = 0.05N$.

Main titration reading = $P = 15.5 cm^3 = 15.5 mL$

Blank titration reading = $Q = 30.6 m^3$ 30.6 mL

Con strength of FAS = $Y = 0.05$

Sample taken = Z = 25 cm3.

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

$$= 0.008 \times (30.6 - 15.5) \times 0.05 \times \frac{10^6}{25}$$

$$= 0.008 \times 15.1 \times 0.005 \times \frac{10^6}{25}$$

$$= 24.16 \text{ ppm}$$

8a What is Desalination? Describe the process of reverse osmosis of water (06 Marks)

The process of removal of dissolved salts (demineralization) from sea water to the extent that water becomes usable is described as desalination or desating.

Procedure: A series of tubes made up of porous material is lined on the inside with extremely thin film of cellulose acetate Semipermeable Membrane. These tubes are arranged in parallel array in fresh water. Brackish water is pumped continuously at high pressure (> 25 atm) through these tubes. Water flows from brackish water into fresh water. The flow of water is proportional to applied pressure which inturn depends on the characteristics of the film. (06) 40

The film may rupture under excessive pressure. Further, greater the number of tubes, larger the surface area more production of fresh water.

8b What is boiler Corrosion? Explain the boiler Corrosion with CO_2, O_2 and $MgCl_2$. (07 marks)

Ans

Definition of Boiler Corrosion, Corrosion occurs in Boilers due to major reasons Dissolved oxygen, Dissolved CO_2 and Dissolved Salts like $MgCl_2$.

(1) Corrosion due to Dissolved oxygen (O_2).

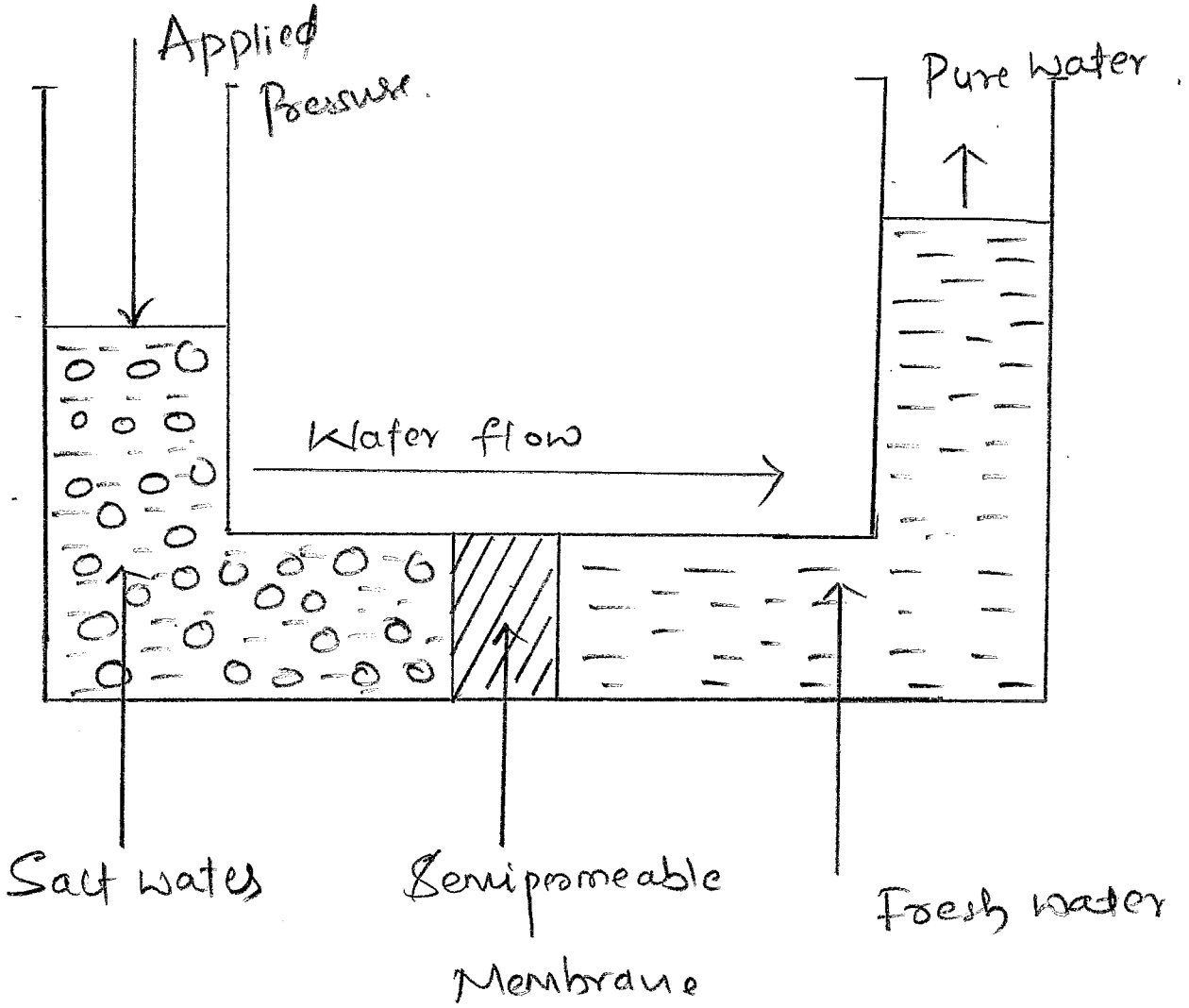
$$4Fe + 6H_2O + 3O_2 \longrightarrow 4Fe(OH)_3 \text{ [rust]}$$

dissolved oxygen presence in water causes corrosion.

(2) Due to presence of CO_2.

Salts like Calcium bicarbonate on heating produces CO_2, CO_2 dissolved in water to form

Diagram for Reverse Osmosis.



carbonic acid which corrodes the boiler metal.

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2.$$

Corrosion due to $MgCl_2$.

Dissolved salts like $MgCl_2$ cause acid formation. This will be prevented by

$$MgCl_2 + 2H_2O \longrightarrow Mg(OH)_2 + 2HCl$$

(corrosive acid).

8c Define COD. Illustrate the determination of COD of water sample. (07 Marks)

Ans: COD is the amount of oxygen equivalent used while oxidizing the chemically oxidisable impurities in the water with strong chemical Oxidant $K_2Cr_2O_7$ in acid medium. It is expressed in $mg \cdot dm^3$ or ppm

Determination of COD

A known volume of the waste water sample is refluxed with excess of $K_2Cr_2O_7$ solution in H_2SO_4 medium and in the presence of $AgSO_4$ & $HgSO_4$. Ag_2SO_4 catalyses the oxidation of straight chain organic compounds, aromatic compounds and pyridine. $HgSO_4$ avoids the interference of Cl^- ions forming soluble complex with them. In the absence of $HgSO_4$, Cl^- ion precipitates silver ion as AgCl.

Reactions

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3(O)$$

$$2FeSO_4 + H_2SO_4 + (O) \longrightarrow Fe_2(SO_4)_3 + H_2O$$

$$K_2Cr_2O_7 + 6FeSO_4 + 7H_2O \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Fe_2(SO_4)_3 + 7H_2O$$

9a Describe the Synthesis of nano-materials by sol-gel technique (8 Marks)

The sol-gel process, involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous net work phase (gel).

Sol-gel processing refers to the hydrolysis and ~~concentration of~~ condensation of alkoxide based precursers such as $(OEt)_4$. The reaction involved in the sol-gel chemistry based on the hydrolysis and condensation of metal alkoxides M(OR) can be described below

$$MOR + H_2O \longrightarrow MOH + ROH \quad \text{(Hydrolysis)}$$

$$MOH + ROM \longrightarrow M-O-M + R-OH$$

(condensation)

(5)

Sol gel method of synthesizing nanomaterials is very popular. The sol-gel process can be characterized by a series of distinct steps.

9b Discuss the theory and Instrumentation of Conductometry. (07 marks)

Principles: According to Ohm's law current (i) flowing in a conductor is directly proportional to emf (E) and inversely proportional to Resistance R.

$$\text{Therefore } i = \frac{E}{R}.$$

The reciprocal of resistance is conductance it's expressed in ohm^{-1} mho

the resistance of a homogeneous material of uniform cross section with an area of 'a' sq cm and length 'l' cm is given by

$$R = \frac{\rho l}{a}.$$

Specific Conductance

Specific Conductance is the conductance of a solution present between two parallel electrodes of area 1cm2 which are kept 1cm apart.

$$K = \frac{1}{a} \times \frac{1}{R} \quad \left\{ \frac{1}{a} = \text{(cell constant)} \right.$$

Specific Conductance of an electrolytic solution at any temperature depends on ions present and hence varies with ion concentration. On dilution, specific Conductance decreases as no of ions per ml also decrease.

Instrumentation:

Conductometer consists of 2 platinum electrodes and a conductance measuring device. The two electrodes have unit area of cross section and are placed unit distance apart, the solution is taken in beaker. The system responds readily to change in conc of analyte. (52)

9c Outline the theory, Instrumentation and application of Colorimetry. (7marks)

Ans:

Theory

Principles is used to identify a substance The Beer Lamberts law relates the light absorbed with the chemical analysis.

Lamber's law:

It relates incident, absorbed and transmitted light "When monochromatic light passes through a transperent medium the rate of decrease in Intensity with the thickness of the medium is proportional to Intensity of light.

Beer's law

It states that "The intensity of transmitted light decreases exponentially as the Conc. of the medium

They $I_t = I_0 e^{-kc}$ where 'c' is the molar conc.

Combined Beer Lambeots law, written ay

$$I_t = I_0 e^{-kct}$$

$$I_t = I_0 e^{-\epsilon t}$$

k - constant
molar absorption
coefficient

$$\log\left(\frac{I_0}{I_t}\right) = \epsilon t$$

ϵt is called Beer-Lambeots law

$\left(\frac{I_0}{I_t}\right)$ is called optical density or absorption A.

$\frac{I_t}{I_0}$ = Transmitance T.

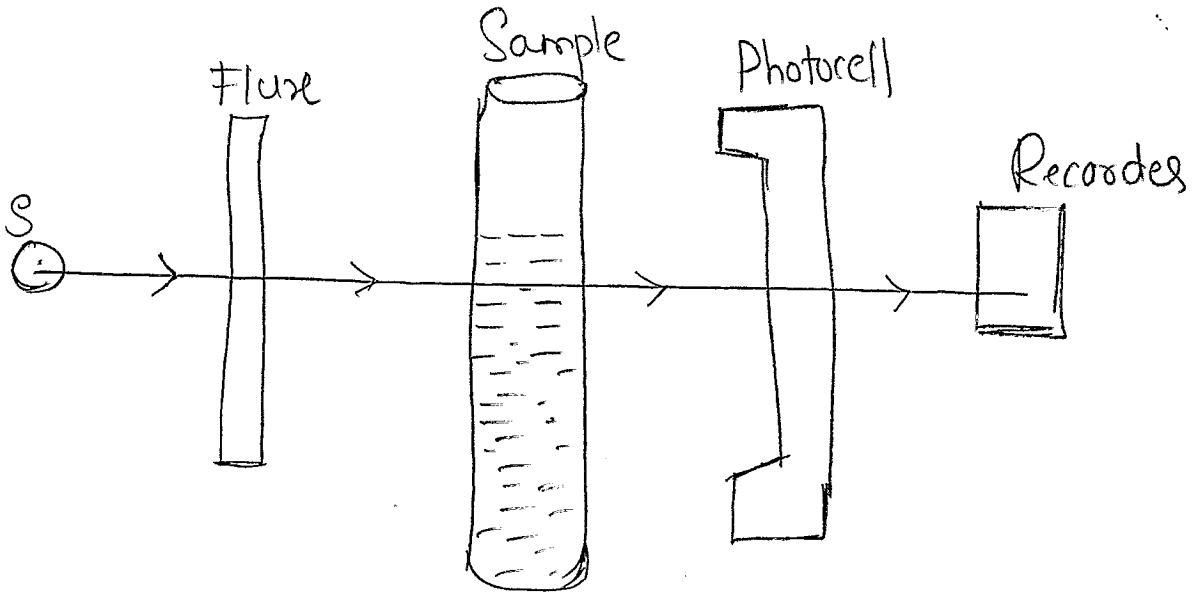
therefore relation between A T is given by

$$A = \epsilon t.$$

Instrumentation:

The essential part of photoelectric Colorimeter are a light sources, A light filter ~~containing~~ container for the solution

a photocell to receive the transmitted light. and some means for measuring the responce of the photocell. The blocks diagram given below.



10a Explain Size dependent properties of Nano material.

a) Surface Area b) Electrical c) Optical.

06 Marks

Ans.1) Surface Area:

Many physical and chemical properties of a material depend on its surface properties If a bulk material is subdivided into individual nano materials, the total volume remains the same. but the collective surface area is greatly increased

For Instant, the collective Surface area of a cube of $1 m^3$ Volume (each side of 1m) is $6 m^2$. If this cube is progressively cut into Smaller and Smaller Cubes of $1 nm^3$, one can get 10^{27} Cubes. The collective Surface area of 10^{27} cubes is 6000 Km^2. It means that Surface area is enormously increased on moving from bulk to nano scale.

Electrical properties

The electrical band in bulk material are continuous due to overlapping of orbitals of billions of atoms. But in the nano Size materials, very few atoms or molecules are present so the electronic bands Seperate (discrete) and the Separation between different electronic state varies with the Zinc of nano materials. Hence Some metals which are good conductors in bulk become Semiconductors and insulators as their size is decreased to nano level.

Optical properties

Nanoparticles often possess unexpected Optical properties as they are small enough to confine their electrons and produce quantum effects. The discrete electronic states of nanomaterials exhibit unique colors different from bulk materials.

The nano materials of different size can scatter radiation of different wavelength. Colors of few colloidal solution are due to this scattering effect.

Nanoparticles of metals exhibit unique Optical property called as surface Plasmon resonance. Size of metal nanoparticles is very much less than the wavelength of visible light. (400 - 780nm).

40b Write a note on fullerenes and it's applications. (07 marks)

Ans:

Fullerenes

Fullerenes are nanosized allotropes of Carbon having cage like structure. They are represented as C_{60} or C_{70} depending on the number of Carbon atoms present in the Case. Fullerenes are made by heating of graphite in an electric arc in the presence of inert gases such as helium or argon. The Sooty Material formed by the Condensation of Carbon vapour consists of mainly C_{60} with smaller quantity of C_{70} and traces of fullerenes containing even number of Carbon atoms upto 350 or above.

C_{60} molecule has a shape like soccer ball and is called Buckminster fullurene. It contains 20 six membered rings and 12 five membered rings.

All Carbons atoms are equal and are Sp^2 hybridised. The delocalized electrons in molecular orbitals give aromatic character to the molecule.

Applications:

+ In Optics, the fullerenes were proposed to use for the electro-photographical imaging Optical filters and nonlinear optical Materials.
+ In electronics they are used as molecular switchers, drode transisters, resisters for lithography, solar cell elements, magneto Optical recorders, photo electronic devices.
+ In military sphere, the fullerenes are used as the optical and microwave absorption Coatings to prevent the aircraft and missiles from ~~radator~~ radar detection.

10c What are nanomaterials? Explain the Synthesis of nanomaterials by chemical Vapour deposition Method. (7 marks)

Ans: Nano-Materials are usually considered to be materials with at least one external dimension less than 100 nanometer. They may be from of particles, tubes, rods or fibres.

Vapour deposition Method.

In Vapour deposition Method, nano particles are synthesized from the gaseous Phase by a chemical reaction or decomposition of precursors at high temperature. In this Method precurser is vapourised and mixed with a inert carrier gas like N_2 and the mixture is fed into the reactor. Producing a product which is deposited over the Substrate. The by products and left overs from the reactions are passed on the gas phase

which are easily removed from reaction chamber. Reaction is often catalyzed by the catalyst present on the substrate.

In CVD proper choice of precurser is very much important. Precurser used should be highly pure and stable at room temperature. It must react clearly over the substrate without any side reactions. Most commonly used precursers are halides carbonyls, organometallics and hydrides of metals. By CVD Method it is possible to produce almost any metal and non-metallic materials as well as compounds such as oxides, carbides, nitrids and many others.