

First/Second Semester B.E Degree Examination, June/July 2019 Engineering Chemistry (17CHE12/22)

Time: 3hrs Max. Marks: 100

Module-1

- 1. a. What is single electrode potential? Derive Nernst expression 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 298K. Given E $^{\circ}$ Fe=0.44V and E $^{\circ}$ Cu=0.34V (07 Marks)

Solution: 1a) *Single Electrode Potential*: Electrode potential is defined as the potential developed at the interface between metal and solution, when it is in contact with solutions of its ions.

Or

It is a measure of the tendency of the metal electrode to lose or gain electrons, when it is in contact with of its own ionic solution. It is represented as E.

Nernst Equation:

The potential of an electrode depends on concentration and temperature. In 1889, W. H. Nernst derived a quantitative relationship between electrode potential and concentration of electrolyte species.

Consider an electrode assembly undergoing a spontaneous reaction.

$$M^{n+} + n^{e-} \longrightarrow M$$

The equilibrium constant (Kc) is related to change in free energy by Vant Hoff equation as follows

$$\Delta G = \Delta G \circ + RT \ln Kc$$
 ----(1)

For above reaction
$$Kc = \frac{[M]}{M^{n+}}$$
 -----(2)

According to thermodynamics, decrease in free energy $(-\Delta G)$ represents maximum amount of work that can be obtained from a chemical reaction.

$$\Delta G = W_{\text{max}}$$
 (3)

Work done in electrochemical reaction depends on

(i) Number of coulombs of electricity that flow and (ii) Energy available per coulomb.

Number of coulombs = $n \times F$ (Where n = number of electrons involved in the cell reaction and F = Faraday constant)

Energy available per coulomb = E_{cell} (V) or JC^{-1}

When E_{cell} = maximum, work derived from cell is maximum.

Thus,
$$W_{max} = n x F x E$$
 -----(4)

 $n = moles of electrons, F = Cmol^{-1}, E = JC^{-1}$

Equating equations (3) & (4)

$$-\Delta G = n \times F \times E \text{ or }$$

$$\Delta G = -n \times F \times E$$
 (5)

Under standard conditions, when concentrations of all species is unity, standard free energy change is given by equation

$$\Delta G^{\circ} = -n \times F \times E^{\circ}$$
 (6)

Where E° is a constant called **standard electrode potential**. E° is the potential when a metal is dipped in 1M solution of its ions or when an inert electrode is in contact with a gas at a pressure of 1 atm at 298 K.

Therefore by substituting values of ΔG , $\Delta G \circ$ and Kc from equation (2), (5) and (6) into equation (1), we get

$$-nFE = -nFE^{\circ} + RT \ln \frac{[M]}{[M]^{n+1}}$$

$$-nFE = -nF E^{\circ} + RT \ln [M] - RT \ln [M^{n+}]$$

Dividing whole equation by -nF

$$\frac{-nFE}{-nF} = \frac{-nF E^{\circ}}{-nF} + \frac{RT \ln[M]}{-nF} - \frac{RT \ln[M]^{n+1}}{-nF}$$

$$E = E^{\circ} - \frac{RT \ln[M]}{nF} + \frac{RT \ln[M]^{n+1}}{nF}$$

Under standard condition [M] = 1,

$$\therefore E = E^{\circ} + \frac{RT \ln[\mathbf{M}^{n+}]}{nF} \qquad (7)$$

Converting natural log to base 10 in eqn (7) we get

$$E = E^{\circ} + \frac{RT \log[M^{n+1}]}{nF} \qquad (8)$$

Substituting the values for R (8.314 JK⁻¹mol⁻¹), F (96500Cmol⁻¹) and T (298K) in eqn (8) we get

$$E = E^{\circ} + \frac{0.0591 \log[\mathbf{M}^{n+}]}{n}$$

This is the mathematical representation of Nernst equation.

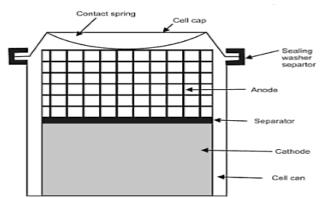
Solution: 1b) Battery is a device consisting of two or more galvanic cells arranged in series or parallel or both, that can generate electrical energy.

Nickel - Metal Hydride Battery

It is a good example for secondary battery which is also called as rechargeable battery.

Construction:

1. Anodic material - Metal hydride such as VH₂,



ZrH₂, TiH₂ etc with a hydrogen storage alloy such as LaNi₅, TiZr₂ etc. Anodic material permits reversible electrochemical storage and release of hydrogen (H2) during charging and **Fig. : Nickel** – *metal hydride battery*

discharging of battery and is corrosion resistant.

- 2. Cathodic material NiO(OH) nickel oxy hydroxide. (Highly porous Ni substrate into which Ni(O)OH is impregnated.
- 3. Electrode Porous nickel foil/grid on to which active materials are either coated or pasted.
- 4. Electrolyte Aqueous solution of KOH (30%).
- 5. Separator Synthetic non woven polypropylene is used, it serves the purpose of separator as well as electrolyte absorbent.

Cell Representation

The battery is represented as, MH₂/KOH (30%) / Ni (OH)₂, NiO(OH)

Working:

The cell reactions occurring during discharging (\rightarrow) and recharge (\leftarrow) are,

At anode:
$$MH_2(s) + 2OH^{-}(aq) \longrightarrow M(s) + 2H_2O(1) + 2e^{-}$$

At cathode:
$$2\text{NiO (OH) (s)} + 2\text{H}_2\text{O (l)} + 2\text{e}^{-1}$$
 $\text{Ni (OH)}_2(\text{s)} + 2\text{OH}^-(\text{aq.})$

Net cell reaction:
$$2\text{NiO (OH) (s)} + \text{MH}_2$$
 $2\text{Ni (OH)}_2 + \text{M}$

During discharging process, at anode MH_2 reduces to M & at cathode Ni^{3+} reduces to Ni^{2+} . Finally the battery produces a potential of 1.35V.

Applications

Ni-MH battery is used in,

- 1. Electric razors, toothbrushes, cameras, pagers, cellular phones and laptop computer.
- 2. Medical instruments and equipments and also used in automotive batteries.

Solution: 1c)

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

$$Cu^{2+}(1M) + 2e \rightarrow Cu(s)$$

The Nernst equation is: Ecell = $E \approx 1 + 0.0591/n \log \left[Cu^{2+} \right] / \left[Fe^{2+} \right]$

E cell = E Cathode - E Anode

$$E \text{ cell} = 0.34 - (-0.44)$$

$$E cell = 0.78V$$

Ecell =
$$0.78 + 0.0591/2 \log 1/0.5$$

Ecell =
$$0.78 + 0.0295 \log 2$$

Ecell=
$$0.78 + 0.0295*0.3010$$

- 2. a. What is Battery? Explain primary and secondary batteries with examples. (06 Marks)
- b. Describe the construction and working of Lithium ion battery. Mention its applications. (07 Marks)
- c. What are concentration cells? Emf of the cell Cd/CdSO4(XM)//CdSO4(0,025M)/Cd at 28°C is 0.035V. Find the concentration of CdSU4 at the anode. Given R=8.314J/K/mol, F=96500C/mol (07 Marks)

Solution: 2a) Battery is a device consisting of two or more galvanic cells arranged in series or parallel or both, that can generate electrical energy.

Primary batteries: In primary batteries, the net cell reaction is not completely reversible and hence these are not reachargble.

For example: Zn – MnO2, Li-MnO2 batteries etc.

2. Secondary batteries: In secondary batteries, the net cell reaction is completely reversible and hence these are rechargeable.

For example: Lead storage battery, Ni – Cd battery etc.

3. Reserve batteries: One of the key components i.e. electrolyte, in reserve batteries is incorporated into the battery when required. When one of the key components is separated from remainder, chemical reaction between cell components (self discharge) is prevented and battery can be stored for a long period of time.

For example: Mg-AgCl, Mg-CuCl, Zinc – Silver oxide reserve batteries, etc.

Solution: 2b) Lithium Ion Battery:

A lithium-ion battery is a member of a family of rechargeable battery types in which lithium ions move from the negative electrode to the positive electrode during discharge and back when charging.

Anode: Li-metal oxide, like lithium cobalt oxide

Cathode: carbon

Separator: polypropylene separator

Electrolyte: lithium salts (LiCl, LiBr) in organic carbonate solvents(ethylene carbonate)

Type and Cell representation:

Li-ion battery is a secondary battery.

LiMO₂/ electrolyte (<u>lithium salt</u> in an <u>organic solvent</u>) / C

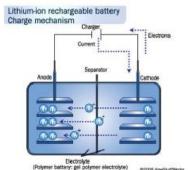
Working: The positive electrode half-reaction is:

$$\text{LiCoO}_2 \leftrightarrows \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + x\text{e}^-_{\text{,(M = Co)}}$$

The negative electrode half reaction is:

$$x \text{Li}^+ + x \text{e}^- + x \text{C}_6 \leftrightarrows x \text{LiC}_6$$

The overall reaction has its limits. Over discharge supersaturates lithium cobalt oxide, leading to the production of lithium oxide, possibly by the following irreversible reaction:



$$\text{Li}^+ + \text{e}^- + \text{LiCoO}_2 \rightarrow \text{Li}_2\text{O} + \text{CoO}$$

It is used in

- 1. *Portable devices* like mobile phones and smart phones, laptops and tablets, digital cameras and camcorders, electronic cigarettes, handheld game consoles and torches (flashlights).
- 2. Li-ion batteries are used in tools such as cordless drills, sanders, saws
- 3. Electric vehicles
- 4. Li-ion batteries are used in telecommunications applications.

Solution: 2c) Concentration Cell: It is an electrochemical cell in which two identical electrodes immersed in same ionic solution but of different concentration. Ex: Copper concentration cell

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

Where C_2 = Concentration of electrolyte at cathodic compartment = 0.025 M

 C_1 = Concentration of electrolyte at anodic compartment = XM

E = 0.035V

n = 2

T=28+273=301K

Substituting the above values in above formula,

0.035 = [(2.303*8.314*301)/2*96500] log 0.025/X

 $0.035 = [5763.289/193000]\log(0.025) - \log X$

 $0.035 = [0.0298](-1.6021) - \log X$

 $X=1.674*10^{-3}M$

Module-2

- 3.a. Discuss the following types of corrosion: (i) Differential metallic corrosion (ii) Waterline corrosion. (06 Marks)
- b. What is corrosion? Illustrate electrochemical theory of corrosion taking iron as an example.

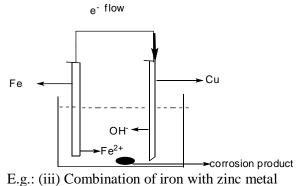
(07 Marks)

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

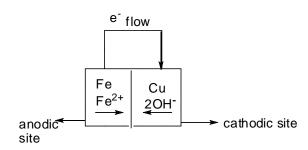
Solution: 3a) (1) Differential metallic corrosion [galvanic corrosion]

When two dissimilar metals are in contact with each other, a potential difference is setup resulting in a galvanic current. A metal placed high in the electrochemical series is said to be anodic with respect to the one placed below it. E.g.: Fe is anodic to Cu, Ni, and Sn (tin) (since E.P of Fe is -0.44V & Cu is +0.34V). Fe acts as cathode when it is in contact with Zn, Mg. (since E.P of Zn is -0.76V & Mg is -2.37V). Fe corrodes when it is in contact with Cu and Ni; but Zn and Mg corrode when these are in contact with Fe. The rate of differential metal corrosion depends primarily on the amount of the current passing from anode to cathode i.e.; on the difference in electrochemical potential, higher the difference faster is the rate of corrosion.

E.g.: (i) When iron and copper are in contact with an aerated solution of NaCl. A current flows between the two electrodes spontaneously and electrons flow from Fe to Cu, indicating that Fe is the anode and Cu is the cathode. The reaction that takes place is same as the reaction discussed under electrochemical theory.



E.g.: (ii) Combination of iron with copper metal



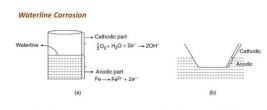
Fe
$$\longrightarrow$$
 Fe $^{2+}$ + 2e⁻ (Anodic)
 $^{1}/_{2}$ O₂ + H₂O + 2e⁻ \longrightarrow 2OH⁻ (Cathodic)
Overall:

Fe
$$^{2+}$$
 + 2 OH $^{-}$ Fe (OH) $_2$ (Ferrous hydroxide)
2Fe (OH) $_2$ + O $_2$ + (n-2) H $_2$ O \longrightarrow [Fe $_2$ O $_3$.nH $_2$ O] [Rust]

(2) Water line 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 and gets corroded while the part above the water is exposed to higher oxygen concentration of the atmosphere thus part of the metal below the water act as cathode and free from corrosion. A distinct brown line is formed just below the water line due to deposition of rust.

E.g.: Water storage steel tanks, Ocean going ship, Water lifting pipes under water.

Though ocean going ships undergo differential aeration corrosion, ships sunk under water are free from corrosion as the difference in oxygen concentration between top and bottom of the ship is negligibly small as ship is exposed to almost uniform concentration of air and hence doesn't undergo differential aeration corrosion.



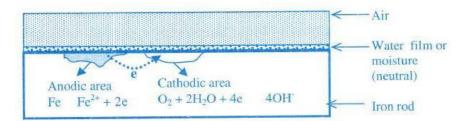
Waterline corrosion: (a) Water storage tank and (b) ocean going ship

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$$\frac{1}{2}$$
 O₂ + H₂O + 2e⁻ → 2OH⁻ (Cathodic)
Overall:
Fe ²⁺ + 2 OH - → Fe (OH) ₂
(Ferrous hydroxide)
2Fe (OH) ₂ + O₂ + (n-2) H₂O → [Fe₂O₃.nH₂O] [Rust]

Solution: 3b) Corrosion: It is defined as the destruction of metal or alloys by the surrounding environment through chemical or electrochemical changes.

<u>Electrochemical theory of corrosion:</u> Most of the corrosion problems are best explained on the basis of electrochemical theory.



- (i) According to electrochemical theory, corrosion of metals takes place due to the formation of minute galvanic cells over the surface of metal. Thus anodic and cathodic regions are formed on the same metal surface or when two metals are in contact with each other in the presence of a conducting medium.
- (ii) At the anodic region oxidation reaction takes place and the **metal gets converted into its ions by** liberating electrons. Consequently, **metal undergoes corrosion at the anodic region**.

M
$$\longrightarrow$$
 M⁺ + ne⁻
Ex: Fe \longrightarrow Fe²⁺ + 2e⁻

Fe \longrightarrow Fe $^{2+}$ + 2e (Anodic)

- (iii) The electrons flow from the anodic to cathodic area and at the cathodic region, reduction takes place. Since metal cannot be reduced further, metal atoms at the cathodic region are unaffected by the cathodic reaction. Some constitutions of the corrosion medium take part in the cathodic reaction. There are three possible ways in which the reduction can take place.
- (i) If the solution is aerated and almost neutral, oxygen is reduced in presence of water to OH- ions according to the equation.

$$\frac{1}{2}$$
 O₂ + H₂O + 2e⁻ \longrightarrow 2OH⁻

(ii) If the solution is deaerated and almost neutral the cathodic reaction involves formation of hydroxyl ions with evolution of hydrogen gas.

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

(iii) If the solution is deaerated and acidic, the H⁺ ions are reduced to H₂

(iv) The electrons liberated at the anodic region migrates to the cathodic region constituting corrosion current, the metal ions liberated at the anode and some anions liberated at the cathode diffuse towards each other through the conducting medium-range and form a corrosion products.

Corrosion of iron produced Fe 2+ ions and OH- ions at the anode and cathode sites respectively. These

ions diffuse towards each other and produce insoluble Fe (OH)₂.

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

$$2\text{Fe (OH) }_2 + \text{O}_2 + (\text{n-2}) \text{ H}_2\text{O} \longrightarrow [\text{Fe}_2\text{O}_3.\text{nH}_2\text{O}] [\text{Rust}]$$

Solution: 3c) Electroless plating: Deposition of metal or alloy over a conducting or non-conducting substrate surface by **chemical reduction of the metal ions by use of reducing reagent** and without the use of electrical energy is called electroless-plating. Electroless-plating is generally autocatalytic in nature. Schematically, it can be represented as,

The driving force for electroless-plating is autocatalytic redox reaction. Some of the object surfaces are active by themselves. However, some others are to be activated by certain pre-treatment. Al, Fe, Cu, Zn, brass, etc. can be plated directly. Stainless steel need be activated by immersion into 1:1 H_2SO_4 . Mg-alloys are given a thin coating of Zn and Cu. Non-metallic (non-conductors or insulators) plastics, glass, ceramic, quartz, etc. are sensitised by treatment with acidified $SnCl_2$ and then with acidified $PdCl_2$. Treatment with $SnCl_2$ leaves a thin layer of $SnCl_2$ and later treatment with acidified $PdCl_2$ leads to deposition of Pd. $SnCl_2 + PdCl_2 \longrightarrow Pd + SnCl_4$

Electroless plating of copper:

Substrate surface needs to be cleaned by suitable cleansing methods (solvent degreasing, acid pickling, alkali pickling, mechanical polishing, etc.). However, when the object is non-conducting or insulator material such as, plastics, PCBs, glass, etc. it needs to be activated by treatment with acidified $SnCl_2$ and then with acidified $PdCl_2$.

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

Following bath compositions are used for plating.

Constituents	Amount	Purpose
CuSO ₄	12 g/L	Provides metal ions
н-сно	8 g/L	Reducing reagent
Rochelle salt	14 g/L	Complexing agent
NaOH	15 g/L	Provides alkaline medium
EDTA	20 g/L	Exaltant & complexing agent
pН	11.0	
Temperature	25°C	

Reactions:

Oxidation of reducing reagent: $2HCHO + 4OH^{-} \longrightarrow 2HCOO^{-} + 2H_{2}O + H_{2} + 2e^{-}$

Reduction of metal ion over object surface : $Cu^{2+} + 2e^{-} \longrightarrow Cu$

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

Applications: Metalizing PCBs, producing through-hole connections, for plating on non-conductors, As a base before electroplating.

- 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)

Solution: 4a)(i) Nature of the corrosion product

The nature of the corrosion product largely decides the rate of further corrosion. The corrosion product formed on the surface of the metal may or may not act as a protective layer.

- (a) The nature of the oxide layer largely decides the rate of further corrosion. If its compositin is stoichiometric, highly insoluble and non poroes with low ionic and electrical conductivity, the layer acts as protective film and prevent further corrosion. For eg. Al, Ti and Cr develops such a layer on their surface and become passive to further corrosion. Stainless steel (18% Cr, 8% Ni) builds up a thin but a highly protective film of Cr₂O₃ which resist attack in a highly corrosive environment. Metals such as Zr and Mo not only form such protective layer but are also capable of self repairing the oxide films when it is damaged. Hence these metals are extremely resistant to corrosion.
- (b) If the oxide layer is non stoichiometric, highly porous, soluble, unstable, it can not control further corrosion. In such cases the fresh metal surface is continuously exposed to corrosion environment and corrosion takes place continuously. Eg. Fe and Zn

(ii) The ratio of anodic and cathodic areas

The rate of corrosion largely depends on the relative size of anode and a cathode.

(a) If the metal has a small anodic and large cathodic area (i.e; the ratio of anode to cathode is small) then the corrosion is more intensive and faster in rate. This is explained as follows

At anode oxidation takes place and electrons areas liberated. At the cathode these electrons consumed when the anode is smaller and cathode region is large, the electrons liberated at the anode, are rapidly consumed, at the cathode region. This process makes the anodic reaction to take place faster .thus increasing the corrosion rate.

(b) If the cathode is smaller, the consumption of electrons will be slower and the corrosion reaction as a whole will be slower.

Ex: A broken coating of tin on iron surface, tin is cathodic to iron and the small exposed part of iron acts as anodic region and rest of the large tin coated surface acts as cathodic region. Because of small ratio of anodic to cathodic area, the corrosion rate is very high, on the other hand Zn plating on Fe gives an anodic coating to iron (Zn is above Fe in electrochemical series). Thus even if Zn plating peels off at some point, Fe does not get corroded.

Solution: 4b) Definition: Process of surface modification by way of deposition of another metal or metal alloy or polymer or ceramic or oxide layer to bring about intended better surface characteristics is known as metal finishing.

Technological Importance:

Technological significance of metal finishing refers to imparting following different characteristics:

- (i) Better corrosion resistance,
- (ii) Better hardness, strength, wear / abrasion resistance, etc.
- (iii) Better thermal conductance or resistance or reflectance, etc.
- (iv) Better optical reflectance,
- (v) Better electrical conductance or insulation, etc.

Solution: 4c) Electroplating: The process of deposition of a thin and uniform layer of metal or metalalloy on to the electrically conducting object surface by electrolysis is known as electroplating.

Electroplating of Chromium:

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

• A thin coating of chromium is porous and thicker coating leads to cracking. Therefore, Cr-plating over steel is applied with an undercoat of copper and nickel. Copper is known to offer better finishing. Coverage of nickel and hence chromium is better with copper below. Also, lower thickness of nickel can be opted with an undercoat of copper. Chromium gives decorative & pleasing finish, nickel offers corrosion resistance and copper extends good coverage and better adhesion.

Bath composition
$$CrO_3$$
 (chromic acid): $H_2SO_4 = 100$: 1 ratio $45 - 60\,^{\circ}C$ Current density $100 - 200\,\text{mA/cm}^2$ Current efficiency $17 - 21\,^{\circ}$ Insoluble lead- Pb-Sb alloy or Pb-Sn alloy (with lead oxide coating) Cathode material Reaction at anode $H_2O \longrightarrow \frac{1}{2}O_2 \uparrow + 2H^+ + 2e^-$ Reaction at cathode $Cr^{3+} + 3e^- \longrightarrow Cr$

• There is a complex sequence of reactions which control the concentration of Cr^{3+} in the plating bath. Sulfate ion is said to catalyse the conversion of Cr^{6+} into Cr^{3+} and PbO_2 catalyses the conversion of Cr^{3+} into Cr^{6+} .

$$CrO_{3} + H_{2}O \longrightarrow H_{2}CrO_{4} \longrightarrow 2H^{+} + CrO_{4}^{2-}$$

$$2H_{2}CrO_{4} \longrightarrow H_{2}Cr_{2}O_{7} + H_{2}O \longrightarrow 2H^{+} + Cr_{2}O_{7}^{2-} + H_{2}O$$

$$Cr_{2}O_{7}^{2-} + 14H^{+} + 6e^{-} \xrightarrow{sulfateion(SO_{4}^{2-})} 2Cr^{3+} + 7H_{2}O$$

$$Cr^{3+} + 3O_{2} \xrightarrow{lead\ oxide(PbO_{2})} 2CrO_{3} + 6e^{-}$$

Chromium plating is a hard, attractive coating, with low coefficient of friction exhibiting wear resistance, abrasion resistance and also good corrosion resistance (with an undercoat of nickel and copper).

Applications:

- Decorative chromium provides a durable finish on cycles, automobiles, furniture, household fittings, aircraft, surgical and dental instruments.
- Hard chromium is mostly used in industries in the making of gauzes, dies, cutting tools, piston rings, and cylinder liners, crankshafts of marine and aero engines, bearings, hydraulic rams and in printing industry.
- Black chromium is used in optical instruments, machine tools and electronic parts. It is also used in non-glare finishes on automobiles, and as an efficient coating for solar energy collectors.

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. 0.95g of coal sample (C= 93%, H_2 = 6% and ash =1%) was subjected to combustion in a 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 = 2454kJ/kg and S = 4.187kJ/kg C. (07 Marks)

Solution: 5a) Fuel cells are the galvanic cells which convert chemical energy of a fuel- oxidant system directly into electrical energy by oxidation of fuel at anode and reduction of oxidant at cathode. *Or*

A fuel cell is a device that converts the chemical energy of a fuel (hydrogen, natural gas, methanol, gasoline, etc.) and an oxidant (air or oxygen) into electricity.

Methanol-oxygen fuel cell: It is good example for liquid fuel cell.

Construction: Methanol – oxygen fuel cell consist of

- 1. Anode It is a porous platinium (Pt) electrode.
- 2. Cathode It is a porous platinium (Pt) electrode.
- 3. Electrolyte Aqueous sulphuric acid (H₂SO₄)
- 4. Active components: (a) Fuel Methanol mixed with sulphuric acid supplied at anode.
 - (b) Oxidant Pure oxygen is supplied at cathode.
- 5. Adjacent to cathode towards electrolyte side, a semi permeable membrane is inserted to allow the diffusion of H⁺ ions, but disallow the diffusion of methanol and its direct oxidation at cathode.

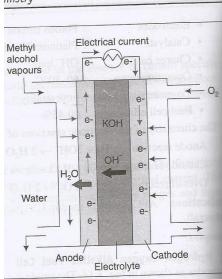


Fig: Methanol – oxygen fuel cell

Working:

Anode Reaction: $CH_3OH(1) + H_2O(1) \longrightarrow CO_2(g) + 6H^+(aq) + 6e^-$

Cathode Reaction: $3/2 O_2(g) + 6 H^+(aq) + 6e$ \longrightarrow $3 H_2O(1)$

Overall Cell Reaction: $CH_3OH(1) + 3/2 O_2(g) \longrightarrow CO_2(g) + 2 H_2O(1)$

Solution: 5b) Experimental determination of calorific value of solid fuel: Bomb Calorimeter:

Principle: A known weight of the sample (solid or liq fuel) is burnt completely in excess of oxygen. The liberated heat is absorbed by the surrounding water and the calorimeter. Thus the heat generated during the combustion of fuel is equal to the heat absorbed by water and copper calorimeter. The GCV of fuel is calculated from the data.

Construction

The calorimeter consists of a stainless steel bomb. It has an airtight screw lid valve for introducing oxygen inside the bomb. It also has an electrical ignition coil for the initiation of combustion of fuel. The bomb is placed in a large well insulated Cu calorimeter. The calorimeter is equipped with a mechanical stirrer for dissipation of heat and a thermometer to read accurately the temperature rise.

Working

A known wt. of fuel (solid or liq) is placed in a small stainless steel crucible. The crucible is placed inside the bomb. The bomb is sealed airtight by the lid. The sealed bomb is placed in a large well insulated copper Calorimeter. The known mass of water is taken inside calorimeter. The water is continuously stirred by the mechanical stirrer. The initial temp of the water is carefully measured. Thebomb is filled with oxygen and the combustion of fuel is initiated by passing electric current. As the sample burnt in the bomb, heat is liberated and it is absorbed by surrounding water and calorimeter. The temperature of water gradually rises and attains the maximum value. The maximum temp is carefully noted.

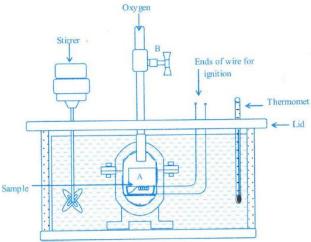


Fig. Bomb Calorimeter

Observation and calculation

Mass (wt) of the fuel = m (kg)

Mass of the water taken in calorimeter = W_1 (kg)

Water equivalent of calorimeter = W_2 (kg)

Initial temp. of water = T_1 °C

Final temp. of water = T_2 °C

Specific heat of water = s (4.18 KJ Kg⁻¹ °K)

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

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

Where, 'GCV' is gross calorific value of the fuel.

GCV =
$$\frac{(W_1 + W_2)(T_2 - T_1) 4.187}{m}$$
 KJ kg⁻¹

And, net calorific value,

$$NCV = GCV - 0.09 \times H \times L_v \times J \times g^{-1}$$
 (2)

Where, H is the percentage amount of hydrogen in the fuel and $L_v = 587 \times 4.187 \text{ kJ kg}^{-1}$ (2454) kJ/kg) is the latent heat of condensation of steam.

Solution: 5c)

Given, m =
$$0.95 \times 10^{-3} \text{ kg}$$

 W_1 = 2.6 kg
 W_2 = 0.75kg
 $(T_2 - T_1)$ = 3.2°C
 $\%\text{H}$ = 6
s = $4.187 \text{ kJ kg}^{-1} \text{ C}^{-1}$
 L_q = 2457 kJ/kg

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

$$= [(2.6 + 0.75) (3.2) 4.187]/0.95 \times 10 - 3$$

$$= 47246.99 \text{ kJ kg}^{-1}$$

$$NCV = GCV - 0.09 \text{ x } \% \text{H x L}_v$$

$$= 47246.99 - 0.09 \text{ x } 6 \text{ x } 2457$$

$$= 47246.99 - 1326.78$$

$$= 45920.21 \text{ kJ/kg}$$

- 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 mechanism of knocking. Mention its ill effects. **(07 Marks)**

Solution: 6a) Preparation of Solar Grade Silicon by union carbide process:

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

Si + 3 HCl
$$\longrightarrow$$
 HSiCl₃ + H₂

Trichlorosilane

Si + 4 HCl \longrightarrow SiCl₄ + 2H₂

Tetrachlorosilane

• Tetrachlorosilane is converted to trichlorosilane by treating with hydrogen at 1000°C.

$$SiCl_4 + H_2 \longrightarrow HSiCl_3 + HCl$$

• Trichlorosilane is passed through ion exchange resin containing quaternary ammonium salts to give dichlorosilane and tetrachlorosilane. Dichlorosilane subsequently forms trichlorosilane and silane (silicon tetra hydride).

2HSiCl₃
$$\longrightarrow$$
 H₂SiCl₂ + SiCl₄
3H₂SiCl₂ \longrightarrow SiH₄ + 2HSiCl₃

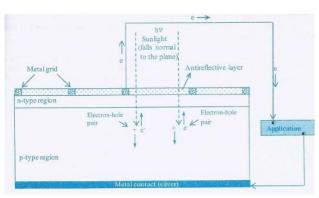
Tetrachlorosilane is hydrogenated again to trichlorosilane and trichlorosilane is again passed
through ion exchange resin. The process is continued to get silane (silicon tetra hydride). Silicon
hydride or silane obtained above is further purified by distillation. Silane is passed into a reactor
containing heated silicon seed rods. Silane gets pyrolysed to form polysilicon (semiconductor
grade silicon).

$$SiH_4 \longrightarrow Si + 2H_2$$

Solution: 6b) PV-cell: A photovoltaic cell is a device used to convert solar light incident on it to electrical energy. Each PV cell is very small, and a series of combination of such solar cell give rise to modules. Modules are designed to supply electricity at a certain voltage. The current produced is directly dependent on how much light strikes the module.

Construction & Working of PhotoVoltaic Cells-

- PhotoVoltaic Cells consist of a semiconductor diode (p-n junction) made of a silicon.
- It has two electrical contact, on one of its sides, a mettalic grid is used and on the other side a layer of noble metal (such as Ag) is used.
- The metal grids permits the light to fall on the diode between the grid lines.
- Electromagnetic radiation consists of particle called photon (hv). They carry a
 _{Eig. Photovoltaic cells}
 certain amount of energy given by the Plank quantum equation. E = hc/λ, Where, h = Planck's constant, c = velocity of light, λ = wavelength of the radiation
- The electromagnetic radiation (sunlight) falls normal to the plane of the solar cell, the photons which possess energy sufficient to overcome the barrier potential are absorbed, electrons are ejected and electron-hole pairs are formed.
- The electrons move towards the n-region (as it is positively charged). The electrons are driven into the external circuit and used for various applications or appliances.



Solution: 6c) Knocking: 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 fuel in an internal combustion (IC) engine.

Following are the reasons for knocking to happen:

Higher compression ratio (CR) beyond the optimum level

Lower octane gasoline.

Formation of highly reactive intermediates (peroxides), which lead to explosive reactions.

Petrol Knocking: Petrol engine is spark ignited engine. Gasoline is burnt to produce energy.

During knocking,

Petrol is vaporised and vapour is mixed with air.

The petrol air mixture is drawn into combustion chamber (Suction stroke).

The petrol air mixture is compressed (Compression stroke).

The mixture is ignited by a spark from spark plug and burnt.

 \Box The gases produced by the combustion reaction expand.

☐ Expansion causes the piston to move i.e. kinetic energy is produced.

☐ When the flame front (after ignition) moves at optimum speed, fuel is burnt smoothly and completely.

☐ When the flame front moves slowly, products of initially burnt fuel, exert pressure on un-burnt fuel-air mixture. Due to build up of pressure, temperature will also increase.

☐ All the un-burnt fuel is ignited ahead of the flame front. This produces thermal shock waves (explosive combustion) which hit the cylinder walls and piston; resulting in a characteristic metallic sound called "knocking" or "pinking".

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

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)

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

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

The unstable peroxides decompose readily to give a no. of gaseous compounds. This give rise to pressure waves which knocks.

Disadvantages of knocking:

Normal combustion:

- Produces undesirable rattling noise.
- Increased fuel consumption and lowered power output.
- Cause mechanical damage of engine parts because of overheating.
- Unpleasant driving.

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 cm³ and 15.5 cm³ of 0.05 N FAS solution are required for blank and sample titration respectively. The volume of the test sample used was 25 cm³. Calculate the COD of the sample solution. (07 Marks)

Solution 7a)

Water softening is the process of reducing the dissolved salts of Ca, Mg and Fe in water, thus reducing the hardness of water and making it soft.

In this method, softening of water is done by exchanging the ions causing hardness of water with desired ions from an ion exchange resin.

Ion exchange resin is a cross-linked organic polymer having some ionisable group. It may be of two types depending upon the nature of the ionisable group.

- Cation exchange resin or cation exchanger: These resins have acidic group as the ionisable group such as -SO₃H, -COOH, -H₂PO₃ group. These resins contains replaceable hydrogen (H+) ion and they exchange cationic portion of salts with H+.
- Anion exchange resin or anion exchanger: These resins have basic group which are capable
 of exchanging their OH- group with the anion present in water. They have group like -NH₂, NHCH₃, -OH groups.

Process: In this process cations and anions are packed in separate column. Hard water is first passed through cation exchange resin where cations like Ca²⁺, Mg²⁺ are removed from hard water by exchanging H+ ions as follows.

$$RH + M^{+} \longrightarrow RM + H^{+}$$

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

Where R is part of resin, M+ is monovalent ion like Na+ and M2+ is divalent ion like Ca2+, Mg2+.

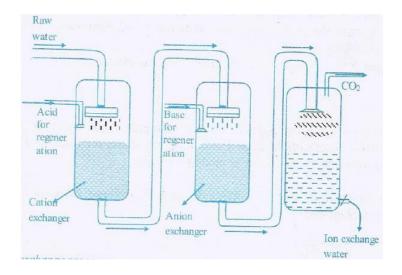
The cation free water is passed through another tank having anion exchanger, which absorbs all the ions present in water and leave behind the water molecules.

$$ROH + X^{-} \longrightarrow RX + OH^{-}$$

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

Where X- and X2- represent the anion such as Cl⁻, NO₃⁻, SO₄²-

Thus the cation and anion impurities in water are replaced by an equal number of H⁺ and OH⁻ ions respectively.



The water obtained after this process is ions free and called as ion exchanged water or deionized (demineralized) water.

Regeneration of spent catalyst: After some time when the resins are exhausted and loose their capacity to exchange ions, they need to be regenerated again. Regeneration is the reversal of the reaction taking place for ion exchange.

The cation exchange resin is regenerated by flushing it with hydrochloric acid

$$RM + H^{+} \longrightarrow RH + M^{+}$$
 $R_{2}M + 2H^{+} \longrightarrow 2RH + M^{2+}$

The anion exchange resin is regenerated by reacting it with sodium hydroxide.

$$RX + OH$$
 ROH + X'
$$R_2X + 2OH$$
 \longrightarrow $2ROH + X^2$

Solution: 7b)

Sources:

- The exhaust from automobiles which use lead tetraethyl as antiknocking agent-
- When TEL is used as antiknocking agent, lead is converted to halide and released into the atmosphere. This leads to increase in the concentration of lead in the atmosphere.
- Paint pigments: Litharge and red lead (oxides of lead) and lead chromate are used as pigments.
 These cause lead pollution
- Plumbing systems-lead pipes are used for plumbing and these may cause lead pollution.

Ill effects:

- Lead competes with calcium and enters the blood and bone marrow.
- The lead interferes in the manufacture of red blood corpuscles and abnormal multiplication of blood cells and thus leads to anemia and blood cancer in human beings.
- Lead enters the blood and various organs of the body including the brain and the leading to dysfunction of the kidney and damage to the brain.

Control: Use of unleaded petrol.

Lead contamination in drinking water is minimized by RO process.

Maintain soil pH 6.5 to avoid absorption of lead by plants, can be achieved by using composted leaves and manure.

Solution 7c)COD: It is defined as the amount of O_2 consumed in the complete chemical oxidation of organic and inorganic wastes present in 1 litre of waste water by using strong oxidizing agent, such as acidified $K_2Cr_2O_7$.

Given,
$$V = 25 \text{ cm}^3$$
, $b = 30.6 \text{ cm}^3$, $a = 15.5 \text{ cm}^3$, $N_{FAS} = 0.05 \text{N}$

COD of the sample =
$$\frac{N_{FAS} \times (b-a) \times 8 \text{ g dm}^{-3}}{V}$$

 $= 0.05 \text{ X} (30.6-15.5) \text{ X } 8000/25 = 241.6 \text{ mg of } O_2/\text{dm}^3$

Thus, COD of the water sample is 241.6 mg of O_2 /dm³.

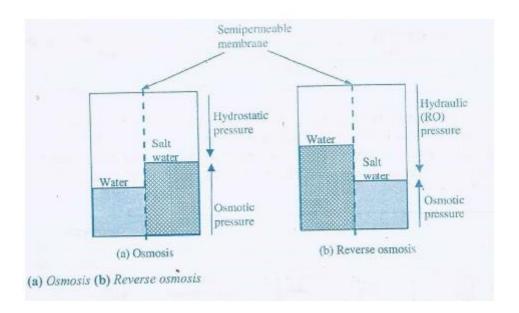
- 8. a. What is Desalination? Describe the process of reverse osmosis of water. (06 Marks)
- b. What is boiler corrosion? Explain the boiler corrosion with CO₂, O₂, MgCl₂. (07 Marks)
- c. Define COD. Illustrate the determination of COD of waste water sample. (07 Marks) Solution: 8a)

Desalination

The process of partial or complete demineralization of highly saline water such as the sea water is referred to <u>desalination</u>. In partial demineralization, the amount of dissolved salts reduced to such a level, that water is rendered potable.

Reverse Osmosis:

Osmosis is the physical movement of a solvent through a semi permeable membrane from lower concentration to higher concentration. When two aq. Solution of different concentration are separated by a semi-permeable membrane, water passes through the semipermeable membrane in the direction of more conc. solution as a result of osmotic pressure. (i.e. pressure exerted by this mass transfer is known as osmotic pressure).



This natural process may be reversed by applying a pressure on the brine side higher than that of the osmotic pressure, and then fresh water tends to flow from brine into fresh water. Thus the process, which reverses the natural spontaneous osmosis, is called reverse osmosis. The greater the pressure applied the more rapid is the diffusion.

Sea water exerts an O.P. of about 240 psi. Reverse osmosis can be effected by the use of pressure in the range of 410-510 psi.

Process: An R.O. unit is simple as shown in fig. given below.

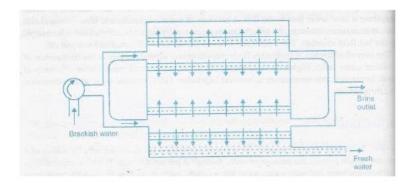


Fig: Reverse osmosis method of desalination

A series of tubes made up of porous material is lined on the inside with extremely thin film of cellulose acetate semi-permeable membrane. These tubes are arranged in parallel array in fresh water.

Brackish water is pumped continuously at high pressure through these tubes. Water flows from brackish water into fresh water. The flow of water is proportional to applied pressure which in turn depends on the characteristics of the film. Greater the number of tubes, larger is the surface area and hence more production of fresh water. Concentrated brine and fresh water are withdrawn through their respective outlets.

Advantages:

- 1. The energy requirements are low.
- Process is simple and continuous.
- 3. It involves no phase changes
- 4. Provides odorless, crystal clear water.
- 5. Easy to maintain

Disadvantages:

- 1. This method is not used on large scale production of fresh water
- 2. It is only successful in recovery of fresh water from brackish water

Solution: 8b)

Boiler Corrosion: It is the most serious problem created by the use of unsuitable water in boiler. It is largely due to presence of

- Dissolved Oxygen
- Dissolved CO₂
- · Acid from the dissolved salts
- Corrosion due to Dissolved Oxygen: When water containing O₂ is heated (350-450 °C)in the boiler, the free gas is evolved under high pressure of the boiler and attacks the boiler material and forms rust.

$$2Fe + O2 + 2H2O \longrightarrow 2Fe(OH)2$$

$$4Fe(OH)2 + O2 \longrightarrow 2(Fe2O3.2H2O)$$
(Rust)

 Corrosion due to CO₂: CO2 is present in the water either from the airor due to the presence of temporary hardness.

$$Mg(HCO_3)_2$$
 \longrightarrow $Mg(OH)_2 + 2CO_2$ $Ca(HCO_3)_2$ \longrightarrow $CaCO_3 + CO_2 + H_2O$

It dissolves in water to produce carbonic acid which is slightly acidic in nature and cause corrosion.

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

 Acids from the dissolved salts: Minerals acids are produced by the hydrolysis of salts like MgCl₂, FeCl₂ present in boiler feed water.

$$MgCl_2 + 2H_2O$$
 \longrightarrow $Mg(OH)_2 + 2HCl$
This acid reacts with iron to form rust.

$$Fe(OH)_2 + O_2$$
 \longrightarrow $2(Fe_2O_3. 2H_2O)$

Control of boiler corrosion: It can be controlled by removing O_2 , CO_2 , or any impurities from the feed water.

1. Removal of O2:

- 1. First it is removed by deaeration. Removal of dissolved gases from boiler feed water is called deaeration. Several types of deaerator are available for this purpose.
- Deoxygenation can also be carried by using chemicals such O₂ scavangers to the boiling water.
 - In low pressure boilers, the removal of oxygen is effected by adding a 3-5% solution of sodium sulphite to boiling water.

$$2 \text{ Na}_2\text{SO}_3 + \text{O}_2 \longrightarrow 2\text{Na}_2\text{SO}_4$$

 In High pressure boilers the removal of oxygen is done by treatment with a very small amount of hydrazine.

$$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O$$

The reaction is complete in a few seconds and no trace of hydrazine remains as it is completely converted into nitrogen.

2. Removal of CO2:

- 1. Mechanical removal can be done by deaeration.
- 2. Chemical removal can be done by treating with lime or NH₄OH

$$Ca(OH)_2 + CO_2$$
 \longrightarrow $CaCO_3 + H_2O$
 $2NH_4OH + CO_2$ \longrightarrow $(NH_4)_2CO_3 + H_2O$

3. Removal of acidic impurities: Finally acidic impurities can be removed by treatment of water with alkaline NH₄OH.

Solution: 8c)

Definition

It is defined as the amount of O₂ consumed in the complete chemical oxidation of organic and inorganic wastes present in 1 litre of waste water by using strong oxidizing agent, such as acidified K₂Cr₂O₇.

Characteristics of COD parameter

- · It is a satisfactory, quantitative method for measuring total organic load.
- · It is preferable to BOD as the results are reliable.
- Rapidly measurable parameter and needs about 3 hours for completion.
- In general COD>BOD since both biodegradable and non-biodegradable organic load are completely oxidized.
- It is represented in mg dm⁻³ or ppm

Determination of COD

The principle of the method is the oxidation of organic matter using chemical oxidizing agents such as acidified potassium dichromate in the presence of a catalyst such as silver sulphate (which catalyzes the oxidation of organic matter) and mercuric sulphate (which combines with chloride ions present in water thus preventing its interference).

A typical reaction representing the oxidation of organic matter is given below.

$$3CH_2O + 16H^+ + 2Cr_2O_7^{2-} \xrightarrow{\text{Ag}_2SO_4} 4Cr^{3+} + 3CO_2 + 11 H_2O$$

The method consists in adding excess of a standard solution of potassium dichromate acidified with sulphuric acid to a known volume of effluent sample and back titrating the excess of potassium dichromate against a standard solution of ferrous ammonium sulphate using ferroin indicator. COD values are also expressed in mg dm⁻³

Method: To a measured volume of waste water sample taken in a flask, add 10 cm³ of std. K₂Cr₂O₇ solution followed by 30 cm³ of 6N H₂SO₄. Add 1 g of Ag₂SO₄ followed by 1 g of Hg₂SO₄. Attach a reflux condenser and reflux the contents for 2 hours. Cool and titrate the excess unreacted K₂Cr₂O₇ against ferrous ammonium sulphate solution using ferroin as indicator till the bluish green colour turns sharply to reddish brown. Let the volume of FAS required be 'a' cm³. Perform a blank titration without taking water sample. Let the volume of FAS required for blank titration be 'b' cm³.

Calculations:

Volume of FAS required for the (reacted K₂Cr₂O₇) sample = b-a cm³ Normality of FAS solution = N_{FAS}

Volume of waste water sample = V cm³

Normality of water x vol. of water = Normality of FAS x vol. of FAS

Normality of water sample =
$$\frac{\text{Normality of FAS x vol. of FAS}}{\text{Vol of water}}$$

$$= \frac{N \times (b-a)}{V}$$

COD of the sample =
$$\frac{N \times (b-a) \times 8 \text{ g dm}^{-3}}{V}$$

hemical resistant

(06 Marks)

$$= \frac{N \times (b-a) \times 8000 \text{ mg dm}^{-3}}{V}$$

Module 5

9. a. Describe the synthesis of nano-material by sol-gel technique.

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

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

Solution: 9a)

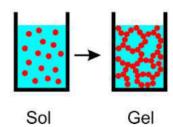
This is a colloidal process in which dispersions have two phases, a dispersed phase with particles having colloidal dimensions ($< \mu m$) and a dispersion medium. The process can be used to obtain metal and metal oxide nanocrystals with controlled particle sizes.

Sols are solid particles formed by hydrolysis of metal precursors and are dispersed in the solution medium. The commonly used metal precursors are their (i) alkoxides [M(OR)_n]and (ii) salts (MX), and

should have the tendency to form gels. Examples of M(OR)_n, where –OR is an alkoxide group, may be methoxides, ethoxides, propoxides of Al, Fe, Ti, Zn, and salts like FeCl₃, MnCl₂, AlCl₃, Zn(NO)₃ etc.

For nanomaterial synthesis, the process involves:

- (i) Hydrolysis of precursors
- (ii) Condensation and polycondensation to form particles
- (iii) Allowing gelation to occur (ageing)
- (iv) Drying of gel to obtain solid material, followed by its sintering to form nanoparticles



The important reactions in the process:

- (i) Hydrolysis of metal salt through de-protonation $M(H_2O)_n^{Z^+} \rightarrow [M(H_2O)_{n-2} (OH)_2]^{(Z-2)^+} + 2H^+$
- (ii) Condensation-polymerisation of the hydroxide intermediate $\begin{array}{c} M(H_2O)_n^{Z^+} + [M(H_2O)_{n-2} \, (OH)_2]^{(Z-2)^+} \rightarrow [M(H_2O)_{n-1}M(OH)_2]^{(ZZ-2)^+} + (H_2O)_{n-1} \\ \text{poly-condensed sol} \\ [M(OH)_2M(H_2O)_{b-1}]^{(2Z-2)^+} \xrightarrow{\text{$gelation}$} \text{sol-gel} \xrightarrow{\text{(ii)sintering}$} \\ (M-OH-M \ bonds) \end{array}$

When an alkoxide is used, the important reactions are:

$$Si(OR)_4 + 4 H_2O \rightarrow Si(OH)_4 + 4ROH (alcoholysis)$$

 $Si(OH)_n + Si(OH)_n \rightarrow (Si-O-Si)_n + nH_2O$

The material can be used to prepare nanocrystals, films and fibres.

Solution: 9b) Principle: Ohm's law states that the current i (amperes) flowing in a conductor is directly proportional to the applied electromotive force, E (volts), and inversely proportional to the resistance R (ohms) of the conductor. $i = \frac{E}{D}$

The reciprocal of the resistance is called the conductance. The resistance of a homogeneous material of uniform cross section with an area of a sq. cm. And length 1 cm is given by

$$R = \frac{\rho \times 1}{a}$$
; $k = C [Va]$

where r is the specific resistance. The reciprocal of the specific resistance is termed the specific conductance, ρ . It is the conductance of a cube of material 1 cm in length and 1cm in cross section.

Instrumentation

• Conductometer consists of two platinum electrodes and a conductance measuring device.

- The two electrodes have unit area of cross section and are placed unit distance apart. They are dipped in the electrolyte solution taken in the beaker.
- The assembly responds rapidly to the changes in the concentration of the analyte under test.
- A simple arrangement of conductometric titration is depicted in figure. The solution to be titrated is taken in the beaker, titrant is added from a burette and the solution is stirred. The conductance is measured after the addition of the titrant at intervals of 1 mL

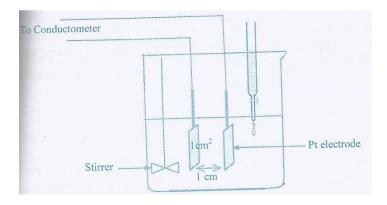


Fig: Conductometric Titration Unit

Solution: 9c) It is an analytical technique used for determination of conc. of compound in a solution. It is used for those solution which are coloured or which gives a colour when mixed with a suitable reagents. A measure of the variation of the color of a solution with change in concentration of the solute forms the basis of colorimetry.

Theory: When a monochromatic radiation of intensity I is passed through a solution of a sample under investigation taken in a cell, a portion of the radiation is absorbed (Ia), a portion is reflected (Ir) and the remainder is transmitted (It), then,

$$I = Ia + Ir + It$$

For a glass cell, Ir is negligible and therefore the above equation reduces to

$$I = Ia + It$$

Colorimetric estimation is based on the Beer-Lambert law.

Beer Lambert's Law: According to this the amount of light absorbed is directly proportional to the conc. and path length of solution.

Combining equations for Beer's law and Lambert's law, equation for Beer-Lambert's law can be written obtained;

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

Or
$$I_t = I_0 10^{-\epsilon ct}$$

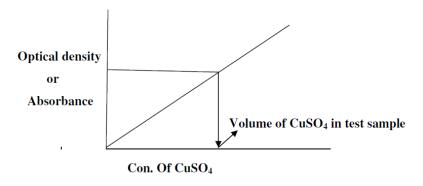
where \in called *molar absorptivity* or *molar absorption coefficient*, is a constant for a given substance at a given wavelength. If c is expressed in mol. dm⁻³ and t in centimeters, \in has the unit dm³mol⁻¹cm⁻¹.

The above equation can be written as

$$\log \frac{I_o}{I_c} = \epsilon ct \qquad \text{Or} \qquad A = \epsilon ct$$

This equation is referred to as Beer-Lambert's law.

If the path length of the cell is kept constant, then, absorbance A is proportional to the concentration c.



10. a. Explain size dependent properties of nano-material:

(i) Surface Area (ii) Electrical (iii) Optical Properties

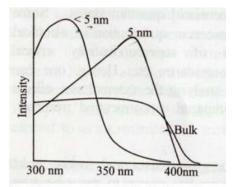
(06 Marks)

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

c. What are nano-materials? Explain the synthesis of nano-material by chemical vapour deposition method. (07 Marks)

Solution: 10a) (i) Surface Area: Nanomaterials have high surface to volume ratio and so exhibit good catalytic activity. For example, nano-structured metal clusters (Pd clusters) show improved catalytic properties for hydrogenation. Such clusters are integral part of cortex catalysts (heterogeneous type), where the active catalytic material is supported on solid oxide surface. These catalysts have improved life time and better catalytic activity. Nanomaterials can be used to construct efficient electrodes for fuel cells and in enantioselective catalysis where chiral modifiers are immobilised on the surface of metal particles.

- (ii) Electrical: When conducting materials are separated by a highly insulating material of nanoscale thickness, the charge particle violates the classical mechanical principles of carrier conduction. It penetrates the high potential barrier or impedance, much higher than the kinetic energy of the particle and cause charge transport through the structure. This nanoscale phenomena is called electron tunnelling and is attained when a particle with lower energy is able to exist on the other side of an energy barrier with high potential energy.
- (iii) Optical properties: Optical properties are connected with the electronic structure. A change in crystal size brings about changes in electronic structure and bandgap (electrons are more restricted in movement in nano-sized particles) leading to changes in absorption or luminescence behavior of the material. Example: Bulk gold appears yellow in colour, whereas nanosized Au appears red. In ZnO, the luminescence spectra shows blue-shift as particle size reduces. ie.



Luminiscence spectra of ZnO with change in particle size. Wavelength of PL shifts towards lower wavelengths (blue shift) with size.

The wavelength of the emitted light shifts towards lower wavelengths.

Solution: 10b) Fullerenes are clusters made of carbon and are zero dimensional solids. They are allotropes of carbon with the formula C-60 and have 60 C atoms arranged spherically. They are also called Bucky balls and have truncated icosahedrons structure with 20 hexagonal and 12 pentagonal rings forming the symmetry.

Fullerenes have particle size of 2 nm, density of 1.65g/cm3 and sublimes at 800K. The carbon atoms are sp2 hybridised, each carbon being bonded to three others in this material. Accordingly, there are two C-C bond lengths in fullerenes, the hexagonal bonds are shorter than pentagonal bonds.

They behave as soft electrophile and readily accept electrons during reactions. C60 structure can be easily hydrogenated, methylated and fluorinated. They form exohedral complexes in which an atom or group is attached to the outside of the cage, as well as endohedral complexes in which an atom is trapped inside the cage structure.

Synthesis: Fullerenes are prepared by creating an electric arc between two carbon or graphite electrodes in an inert gas atmosphere, when a black powder in the form of soot is produced. 10% of the soot is made up of C-60. They can be extracted from the soot by solvation in small amounts of toluene. After extraction, solvent is removed using a rotary evaporator, leaving behind a solid mixture of mostly C-60 with small amounts of larger fullerenes.

Bucky balls having more number of C atoms such as, 70, 76, 78, 84 etc arranged spherically have been isolated.

More properties:

□ Superconductivity is discovered in alkali doped fullerites at moderately high temperatures. □ Superconducting critical temperature (Tc) of doped fullerites increases with curvature of fullerenes cages, ie. as cluster size is reduced from C60 to C36, C28 and C20, their Tc increases. □ The index of refraction for fullerenes is 2.2 at 600 nm and they have a resistivity of $1014 \ \Omega/m$. □ They function as catalysts in organic reactions.



Buckminister Fullerene - C60

Solution: 10c) Nanomaterials: are nano-sized materials having atleast one physical dimension in the size range of 1-100 nm.

Chemical Vapor Deposition: In this method, the precursor material is vaporized, and the vapours are brought into contact with a hot surface of a reactor under supercritical conditions favouring nucleation of particles. The precursor material can be solid, liquid or gas at room temperature, but are delivered to the reactor as a vapour. In case of solids, they are sublimed by heating from an external source, and for liquids and volatile solids dissolved in solvents, precursors are bubbled out using inert gas. Vapours decompose in the hot zone and form particles that agglomerate. They are further swept by inert gas onto the surface of a cold finger, where they get condensed. The particles are scrapped into a collector at

regulated intervals. Due to high supersaturation that results in this method, it is typically used to synthesis NPs of metals in large scale.

