

Module-1

1. a. Define Free Energy. Derive Nernst expression for single electrode potential.

(07 Marks)

b. What are reference electrodes? Describe the construction and working of calomel electrode. (06 Marks)

c. Explain the construction and working of Nickel-metal hydride (Ni-MH) battery. Give the reaction during charging and discharging mode. Give any two applications. (07 Marks)

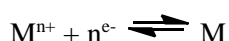
Solution: 1a) Free energy: The thermodynamic free energy is the amount of work that a thermodynamic system can perform. The free energy is the internal energy of a system minus the amount of energy that cannot be used to perform work.

The Gibbs free energy is a thermodynamic potential that can be used to calculate the maximum of reversible work that may be performed by a thermodynamic system at a constant temperature and pressure (isothermal, isobaric). The Gibbs free energy ($\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$) (J in SI units) is the maximum amount of non-expansion work that can be extracted from a thermodynamically closed system (one that can exchange heat and work with its surroundings, but not matter); this maximum can be attained only in a completely reversible process.

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.



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

$$\Delta G = \Delta G^\circ + RT \ln K_c \text{ -----(1)}$$

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

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

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

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 $J C^{-1}$

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

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

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

Equating equations (3) & (4)

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

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

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

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

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 , ΔG° and K_c from equation (2), (5) and (6) into equation (1), we get

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

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

Dividing whole equation by $-nF$

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

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

Under standard condition $[M] = 1$,

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

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

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

Substituting the values for R ($8.314 \text{ JK}^{-1}\text{mol}^{-1}$), F (96500 Cmol^{-1}) and T (298K) in eqn (8) we get

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

This is the mathematical representation of Nernst equation.

Solution: 1b) Reference Electrodes: These are the electrodes, used to determine the potentials of unknown electrodes.

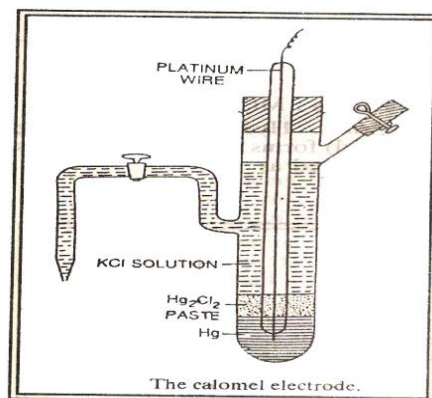
They are of two types; 1. **Primary Reference Electrodes:** These are the electrodes whose potentials are known from the method of construction. Ex: Standard hydrogen electrode (SHE).

2. **Secondary Reference Electrodes:** These are the electrode whose potential is known or constant and stable does not vary with temperature. Ex: Calomel electrode

Calomel electrode

It is a metal-metal insoluble salt electrode is also called as secondary reference electrode.

Construction: Electrode consists of glass tube. The bottom of the glass tube is filled with pure mercury (Hg) on which a calomel paste (Hg + Hg₂Cl₂) is placed. The remaining part of the glass tube is filled with sat. or std KCl Solution. It also contains side tube serves as salt bridge and a platinum wire is dipped into the mercury so that it serves as electrical contact.



Half cell representation: The calomel electrode is represented as, KCl /HgCl₂, Hg

Working: (a). When it acts as anode (oxidation): 2Hg + 2Cl⁻ → Hg₂Cl₂ + 2e⁻

(b). When it acts as cathode (reduction): Hg₂Cl₂ + 2e⁻ → 2Hg + 2Cl⁻

The electrode potential of the calomel electrode is mainly dependent on the concentration of KCl used, Electrode potential is calculated using Nernst equation,

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

E = 0.344V, for [KCl] = 0.1N; E = 0.281V, for [KCl] = 1.0N; E = 0.242V, for [KCl] = saturated KCl

Applications:

1. It is used as secondary reference electrode in all potentiometric determinations.
2. Used in glass or combined electrode to determine the pH of the unknown solution.

Solution: 1c) 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

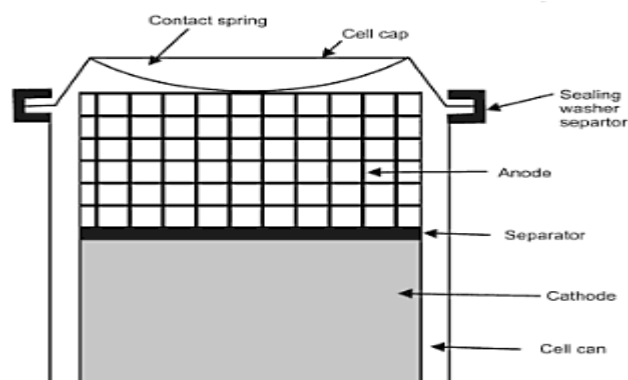


Fig. : Nickel – metal hydride battery

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%).

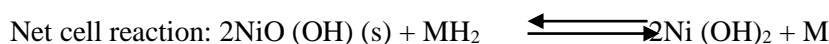
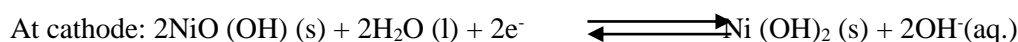
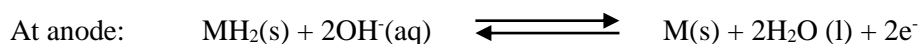
5. Separator – Synthetic non – woven polypropylene is used, it serves the purpose of separator as well as electrolyte absorbent.

Cell Representation

The battery is represented as, $MH_2/KOH (30\%) / Ni (OH)_2, NiO(OH)$

Working:

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



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.

2. a. Describe the construction and working of Lithium ion battery. Give its applications. (07 Marks)

b. Write a note on primary, secondary and reserve batteries with examples. (06 Marks)

c. What are concentration cells? Emf of the cell $Ag/AgNO_3(C1)//AgNO_3(C2= 0.2M)/Ag$ is 0.8V. Calculate C1 of the cell. (07 Marks)

Solution: 2a) 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

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

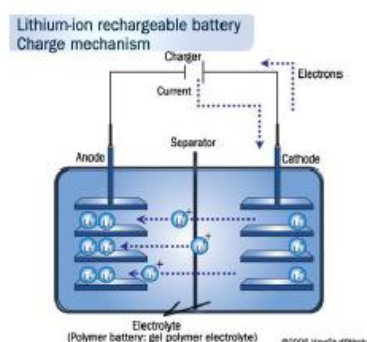
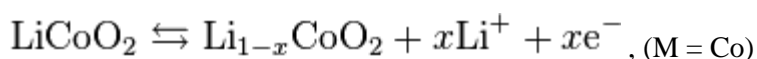
Separator : polypropylene separator

Type and Cell representation:

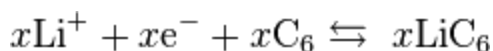
Li-ion battery is a secondary battery.

$LiMO_2 / \text{electrolyte (lithium salt in an organic solvent)} / C$

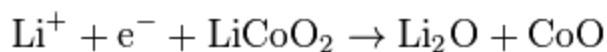
Working: The positive electrode half-reaction is:



The negative electrode half reaction is:



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:



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: 2b) Primary batteries: In primary batteries, the net cell reaction is not completely reversible and hence these are not rechargeable.

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: 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 = 0.2 M

C_1 = Concentration of electrolyte at anodic compartment

$$E = 0.8\text{V}$$

$$n = 1$$

Substituting the above values in above formula,

$$0.8 = [0.0591/1] \log 0.2/C_1$$

$$0.8 = [0.0591] \log(0.2) - \log C_1$$

$$0.8 = [0.0591](-0.6989) - \log C_1$$

$$14.2289 = -\log C_1$$

$$C_1 = 0.6 \times 10^{-14} \text{ M}$$

Module-2

3.a. What is corrosion? Explain the electrochemical theory of corrosion by taking iron as an example.

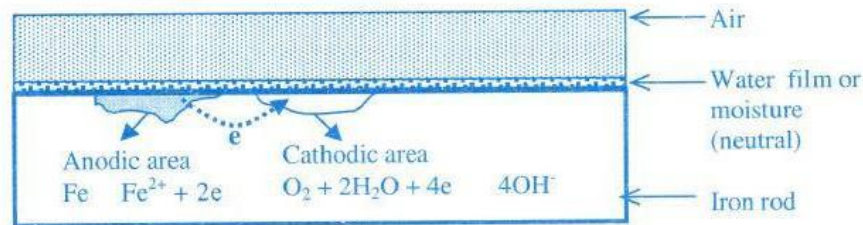
(07 Marks)

b. Explain: (i) Differential metal corrosion (ii) Pitting corrosion. (06 Marks)

c. What do you mean by metal finishing? Mention any five technological importances. (07 Marks)

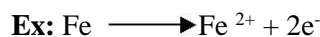
Solution: 3a) Corrosion: It is defined as the destruction of metal or alloys by the surrounding environment through chemical or electrochemical changes.

Electrochemical theory of corrosion: 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**.



(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 constituents of the corrosion medium take part in the cathodic reaction. There are three possible ways in which the reduction can take place.

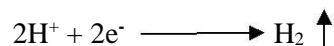
(i) If the solution is aerated and almost neutral, oxygen is reduced in presence of water to OH⁻ ions according to the equation.



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

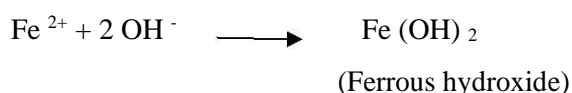


(iii) If the solution is deaerated and acidic, the H⁺ ions are reduced to H₂

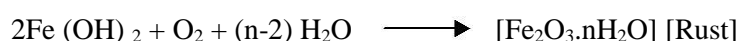


(iv) The electrons liberated at the anodic region migrates to the cathodic region constituting corrosion current, the metal ions liberated at the anode and some anions liberated at the cathode diffuse towards each other through the conducting medium-range and form a corrosion products.

Corrosion of iron produced Fe²⁺ ions and OH⁻ ions at the anode and cathode sites respectively. These ions diffuse towards each other and produce insoluble Fe(OH)₂.



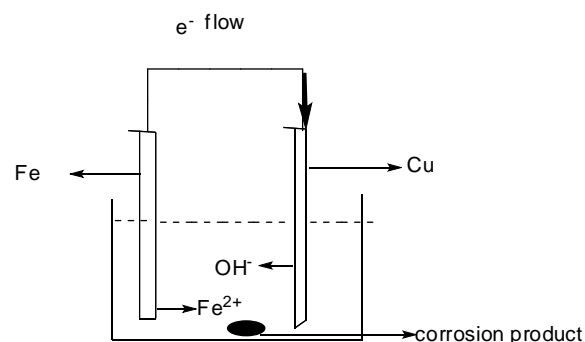
In an oxidizing environment, it is oxidized to ferric oxide and the rust is hydrated ferric oxide.



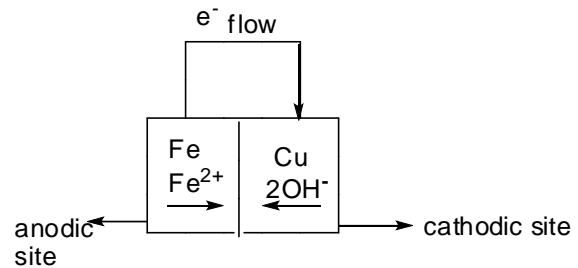
Solution: 3b) (1) Differential metal corrosion [galvanic corrosion]

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.

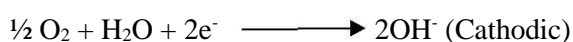
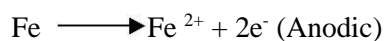
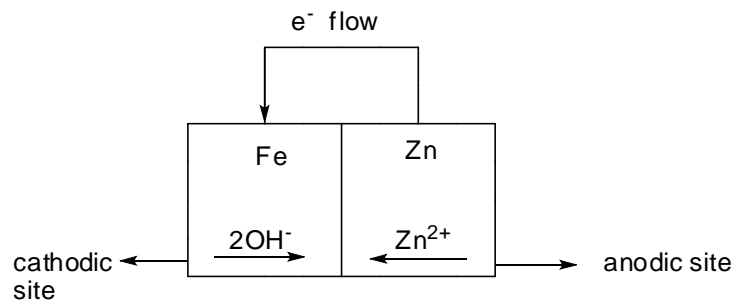
E.g.: (i) When iron and copper are in contact with an aerated solution of NaCl. A current flows between the two electrodes spontaneously and electrons flow from Fe to Cu, indicating that Fe is the anode and Cu is the cathode. The reaction that takes place is same as the reaction discussed under electrochemical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



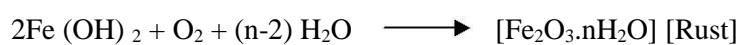
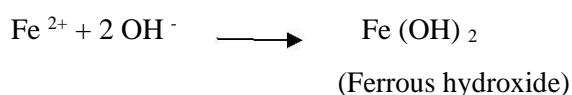
E.g.: (ii) Combination of iron with copper metal



E.g.: (iii) Combination of iron with zinc metal



Overall:

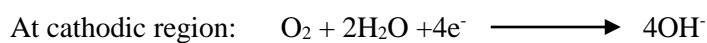


(2) Pitting corrosion

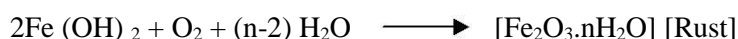
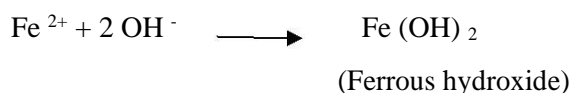
Pitting corrosion results when small particles of dust get deposited on a steel surface. The portion covered by the dust will not be well aerated compared to the exposed surface.

(ii) The covered portion thus becomes anodic with respect to the surface exposed. In the presence of electrolyte and moisture corrosion takes place in the form of pits thereby increasing the rate of corrosion because of formation of small anodic area.

Ex: Crack developed in tin coating on iron gives rise to a small anodic area and large cathodic area.



Overall:



Solution: 3c) 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.

4.a. Define and explain any two terms: (i) Polarization (ii) Decomposition Potential (iii) Overvoltage (06 Marks)

b. What is electroless plating? Explain the electroless plating of copper. (07 Marks)

c. Explain the process of galvanization. (07 Marks)

Solution: 4a) (i) Polarization: A process of variation in electrode potential due to change in concentration of ionic species at electrode surface by (i) slow diffusion of ions from the bulk of the electrolyte to the electrode or from the electrode towards the bulk (known as concentration polarization (ii) one or more of elementary steps of discharge (or evolution) of gases being slow at electrode surface (known as overvoltage polarization).

Electrode potential is a function of active mass or molar concentration of ionic species in the solution given by the Nernst equation:

$$E = E^{\circ} + \frac{2.303 RT}{nF} \log [M^{n+}]$$

For a reduction reaction at the cathodic surface, there is depletion in concentration of M^{n+} ions in the vicinity of cathodic surface. Until that time, ions diffuse from the bulk and re-establish the equilibrium, lower concentration of ionic species alters the electrode potential. Similar such phenomena can be seen at the anodic surface. This effect is known as concentration polarization. Polarization of electrodes depends upon

- (i) current densities applied
- (ii) nature of the electrode (i.e., composition, size, shape, etc.)
- (iii) nature of electrolyte, its concentration and conductivity
- (iv) agitation / temperature of the electrolyte
- (v) nature of the products formed at the electrode surfaces.

Concentration polarization can be minimised by

- (i) having larger electrode surfaces
- (ii) by optimised current densities
- (iii) lower concentrations of highly conducting electrolyte
- (iv) better agitation / higher temperature of the electrolyte

Knowledge of polarization helps one to realise the importance of agitation of electrolyte in order to minimise concentration polarization and thus, the expenses of electroplating. However, overvoltage cannot be eliminated.

(ii) Overvoltage:

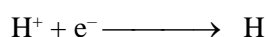
Overvoltage can be defined as excess voltage over the theoretical voltage (or reversible discharge potential) required to be applied for the continuous discharge / deposition of a substance at the electrode surface.

For example, decomposition potential of water over smooth platinum surfaces is 1.68 V. However, the theoretically calculated voltage (or reversible cell potential) is 1.23 V. Therefore, overvoltage is $1.68 - 1.23 = 0.45$ V.

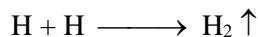
Explanation:

Evolution of hydrogen gas from a plating bath at cathodic surfaces involves

- (i) Diffusion of hydronium ion, H_3O^+ .
- (ii) Becoming H^+ ion and reduction to atomic hydrogen



- (iii) Diffusion of hydrogen atoms towards one another, their union to form molecules, few molecules forming the bubble and escape of hydrogen gas from the surface.



When any one or more of these processes is slow, there is variation of ionic concentrations near electrode surfaces and a change in the potential. As a fact, the third step, diffusion of atomic hydrogen and their union happens to be slow with energy consumption attributing to overvoltage.

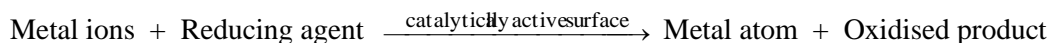
Overvoltage depends upon:

- (i) Nature and physical state of the electrode: Metals with smooth surfaces have relatively higher overvoltages. Mercury has highest overvoltage. Smooth-Pt has higher overvoltage than platinised Pt.
- (ii) Nature of the substance getting deposited: Overvoltages of different substances are different. For example, overvoltages of H_2 and O_2 over same smooth-Pt surface are different, say, 0.024 V and 0.721 V with a current density of 0.001 A/cm² at 25°C.

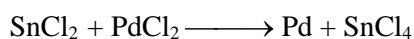
(iii) Current density at the electrode surface: Generally, increase in current density increases overvoltage.

(iv) Temperature of the electrolytic bath: Generally, increase in temperature decreases overvoltage.

Solution: 4b) 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,

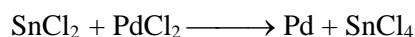


The driving force for electroless-plating is autocatalytic redox reaction. Some of the object surfaces are active by themselves. However, some others are to be activated by certain pre-treatment. Al, Fe, Cu, Zn, brass, etc. can be plated directly. Stainless steel need be activated by immersion into 1:1 H₂SO₄. 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 SnCl₂ and then with acidified PdCl₂. Treatment with SnCl₂ leaves a thin layer of SnCl₂ and later treatment with acidified PdCl₂ leads to deposition of Pd.



Electroless plating of copper:

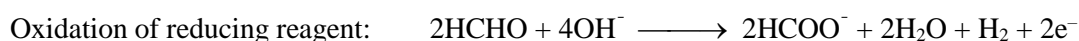
Substrate surface needs to be cleaned by suitable cleansing methods (solvent degreasing, acid pickling, alkali pickling, mechanical polishing, etc.). However, when the object is non-conducting or insulator material such as, plastics, PCBs, glass, etc. it needs to be activated by treatment with acidified SnCl₂ and then with acidified PdCl₂.



Following bath compositions are used for plating.

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

Reactions:



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

Solution: 4c) Galvanization: The process of coating a thin film of molten zinc on the base metal surface by hot dipping technique is called as galvanization. It is a method of anodic metal coating.

The process of galvanization is carried out as follows:

- (i) The base metal is first treated with organic solvent to remove grease or oil material present on it.
- (ii) It is further treated with dil. H_2SO_4 to remove rust or oxide layer present on it.
- (iii) The metal is then treated with flux of $ZnCl_2$ and NH_4Cl for best adhesion property.
- (iv) Finally the base metal is dipped into the zinc at $430-470^\circ C$.
- (v) The excess zinc is removed from the surface by rolling or wiping etc.

These steps are diagrammatically shown in Fig below:

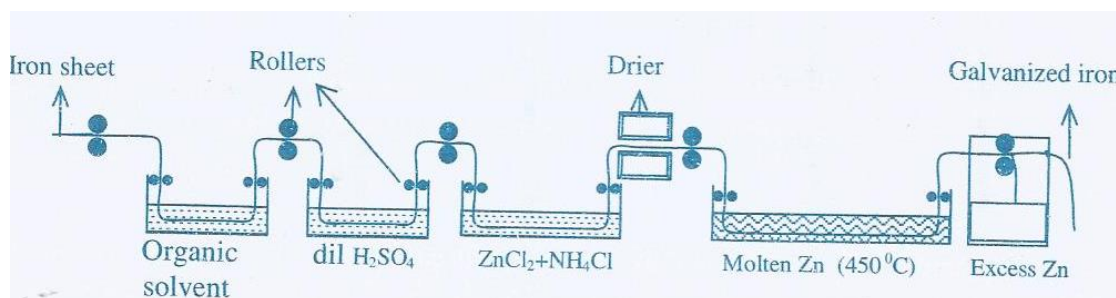


Fig:

Galvanisation of Iron

Module-3

5. a. What is knocking? Explain the mechanism. (07 Marks)

b. On burning 0.96g of solid fuel in bomb calorimeter the temperature of 3500gm of water increased by $2.7^\circ C$ water equivalent and latent heat of steam are 385 gm and 587 cal/gm, respectively. If the fuel contains 5% H_2 , calculate its gross and net calorific values. Specific heat of water = $4.187 kJ/kgK$. (06 Marks)

c. What are fuel cells? Describe the construction and working of Methanol Oxygen fuel cell.

(07 Marks)

Solution: 5a)

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.

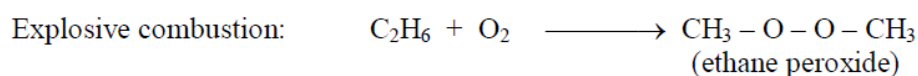
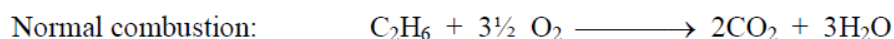
Petrol Knocking: Petrol engine is spark ignited engine. Gasoline is burnt to produce energy.

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.
- 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.



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

Disadvantages of knocking:

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

Remedies:

- Improved engine design.
- Optimised compression ratio.
- Use of higher octane gasoline.
- Use of anti-knocking reagents.

Solution: 5b)

Given, m	=	0.96x10 ⁻³ kg
W ₁	=	3500g = 3.5 kg
W ₂	=	385g = 0.385 kg
(T ₂ - T ₁)	=	2.7°C
%H	=	5
s	=	4.187 kJ kg ⁻¹ °C
L _q	=	2457 kJ/kg

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

$$=[(3.5 + 0.385) (2.7) 4.187] / 0.96 \times 10^{-3}$$

$$= 45749.51 \text{ kJ kg}^{-1}$$

$$\begin{aligned} \text{NCV} &= \text{GCV} - 0.09 \times \% \text{H} \times L_v \\ &= 45749.51 - 0.09 \times 5 \times 2457 \\ &= 45749.51 - 1105.65 \\ &= 44643.86 \text{ kJ/kg} \end{aligned}$$

Solution: 5c) 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 platinum (Pt) electrode.
2. Cathode - It is a porous platinum (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.

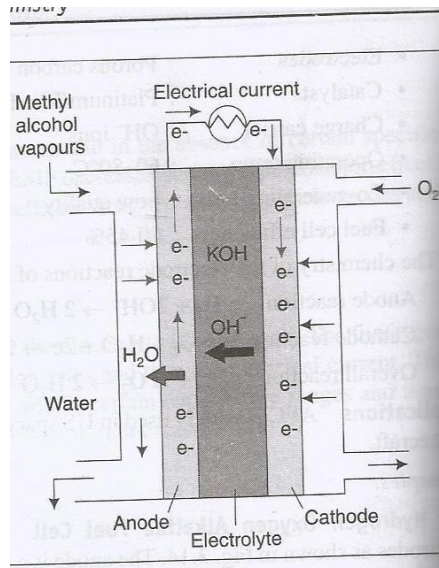
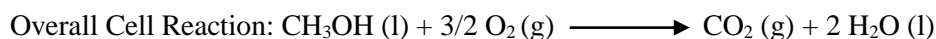
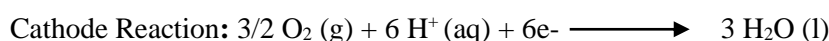
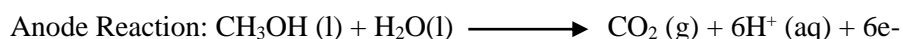


Fig: Methanol – oxygen fuel cell

Working:



6. a. What are Solar cells? Explain the construction and working of a typical P.V. cell. (07 Marks)

b. Explain the production of solar grade Silicon by Union Carbide process. (07 marks)

c. Write a note on (i) Power Alcohol (ii) Unleaded Petrol (06marks)

Solution: 6a) 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

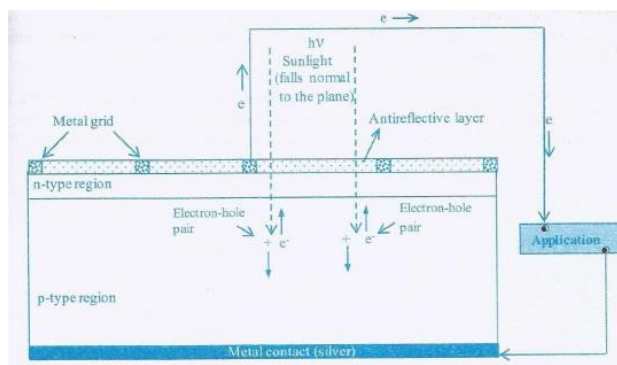


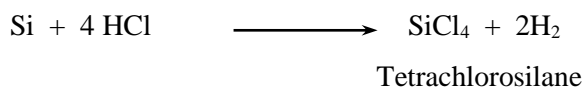
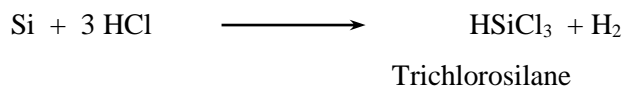
Fig. Photovoltaic cells

certain amount of energy given by the Plank quantum equation. $E = hc/\lambda$, Where, h = Planck's constant, c = velocity of light, λ = wavelength of the radiation

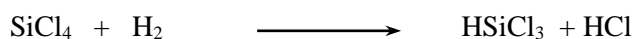
- The electromagnetic radiation (sunlight) falls normal to the plane of the solar cell, the photons which possess energy sufficient to overcome the barrier potential are absorbed, electrons are ejected and electron-hole pairs are formed.
- The electrons move towards the n-region (as it is positively charged). The electrons are driven into the external circuit and used for various applications or appliances.

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

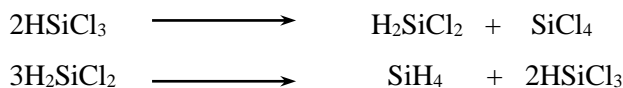
- Metallurgical grade silicon is heated to 300-350 °C and dry hydrogen chloride is passed. Trichlorosilane and a small amount of tetrachlorosilane are formed as given below



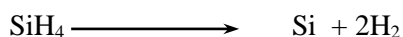
- Tetrachlorosilane is converted to trichlorosilane by treating with hydrogen at 1000°C.



- 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).



- 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).



Solution: 6c) (i) Power Alcohol: A blend containing **10 to 85% of ethanol and 15-90% of gasoline**, used as fuel is known as power alcohol. The addition of alcohol to petrol increases its octane number. Power alcohol is used as a fuel by blending with petrol in IC engine. It is also blended with diesel to form E-diesel. Power alcohol has calorific value of about 7000 cal/g and its octane no. is 90.

Advantages:

- Addition of alcohol to petrol increases octane number (octane number of ethanol is 112) and reduces knocking.
- Because of increased O.N., it can be used in engine with high CR, thus better power output is achieved.
- Because, alcohol contains oxygen, it is referred as oxygenate which assist better combustion efficiency. Also, VOC (volatile organic content) emissions are reduced or pollution is lessened.
- Alcohol can be synthesized from plants. Thus, especially, with higher proportion of alcohol, one has a sustainable fuel [an alternative to fast depleting fossil fuels].
- When synthesised, helps in improved economy of a country because imports are avoided.

Disadvantages:

- Lowers the calorific value of the fuel (two third that of gasoline).
 - Atomization is difficult because of high surface tension of alcohol.
 - Alcohol gets oxidised to acids and may corrode concerned engine equipment.
 - Modification of CR of the engine is required otherwise, power out put is reduced.
- (Gasoline engines generally have a CR of around 8 which need be increased to around 12).
- Alcohol as such has good affinity for water and as a result separation of alcohol and petrol layers takes place especially at low temperature. To avoid this blending agent such as benzene or toluene are used.
- (ii) **Unleaded Petrol:** An alternative to increase the octane rating of gasoline and employ higher CR or power output is to blend gasoline with compounds of higher octane rating. Gasoline or petrol with better anti-knock properties, however, without the presence of leaded compounds but with the presence of higheroctane blending reagents is called unleaded petrol.

Following are some blending reagents:

- Methyl tertiary butyl ether (MTBE)
- Ethyl tertiary butyl ether (ETBE)
- Methyl tertiary amyl ether
- Ethyl tertiary amyl ether
- Methanol
- Ethanol
- Isopropanol, etc.

All the above blending reagents have higher octane rating of nearly 100 or more. When blended with gasoline in proportions of more than 10% (unlike 0.1% of ethyl fluid) overall octane rating of the blend is increased and so is the anti-knock property of the blend.

Advantages:

1. Higher octane number, higher CR and higher power output with better anti-knock characteristics.
2. Better combustion efficiencies because blending agents are also oxygenates and lower the emissions of volatile organic contents.
3. Emission of leaded compounds is avoided safeguarding the health of living beings.
4. Catalytic converters are employable with vehicle exhaust lines and relatively safer combustion products are ensured.

Module 4

7. a. What are the main sources, effects and control of lead pollution. (07 Marks)

b. Mention the various causes, effects and disposal methods of e-wastes. (07 Marks)

c. 50 mL of industrial sewage as consumed 11.5 mL of 0.4N $K_2Cr_2O_7$ solution for complete oxidation. Calculate COD of the industrial sewage. (06 Marks)

Solution 7a)

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 Kidneys 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: 7b)

E Waste:

"E-waste" is a popular, informal name for electronic products attaining the end of their "useful life."

"E-wastes are considered dangerous, as certain components of some electronic products contain materials that are hazardous, depending on their condition and density. The hazardous content of these materials poses a threat to human health and environment. The discarded computers, televisions, VCRs, stereos, copiers, fax machines, electric lamps, cell phones, audio equipment and batteries if improperly disposed can penetrate into soil and groundwater.

Constituents of e-Waste:

- Circuit Boards- these include heavy metals like lead and cadmium
- Batteries- these include cadmium
- Cathode ray tubes- they contain lead and barium oxide
- Brominated flame retardant in coated on circuit boards, cables, and PVC
- Copper cables and plastic coated computers release toxic dioxins and furan when burnt
- Flat screens contain mercury
- Old capacitors contain PCB

When burn these produce dioxin, which causes problems of reproduction, destruction of the immune system, and regulatory hormones are damaged too.

e-Waste disposal:

- a) Reuse b) recycle c) land fill d) incineration

Solution 7c).

Given, $V_{\text{water}} = 50 \text{ mL}$, $N_{K_2Cr_2O_7} = 0.4N$, $V_{K_2Cr_2O_7} = 11.5 \text{ mL}$

$$\text{COD} = (N_{K_2Cr_2O_7} * V_{K_2Cr_2O_7} * 8000) / V_{\text{water}}$$

$$\text{COD} = (0.4 * 11.5 * 8000) / 50 = 736$$

Thus, COD of the water sample is 736 mg of O_2 /dm³.

8. a. Explain activated sludge treatment of sewage water.

(07 Marks)

b. What is Desalination? Describe the desalination of sea water by reverse osmosis process. (07 Marks)

c. Write a note on ozone depletion. (06 Marks)

Solution: 8a)

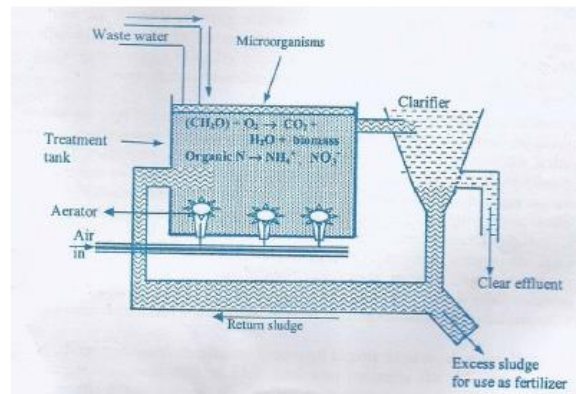


Fig. Activated sludge process

(b) Secondary(Biological) treatment (Activated sludge process).

- The waste water after the primary treatment is allowed to flow into large tanks where biological treatment is carried out.
- *Activated sludge* containing microorganisms (from a previous operation) is sprayed over the water. The microorganisms present in the sludge form a thin layer and thrive on the organic wastes in the sewage.
- Air is passed vigorously from the centre of the tank in order to bring good contact between the organic wastes and bacteria in presence of air and sunlight. Under these conditions, aerobic oxidation of organic matter occurs.
- The sludge formed is removed by settling or filtration. A part of the sludge is reused and the rest is used as fertilizer.
- The residual water is chlorinated to remove bacteria and finally discharged into running water or used for watering plants. The activated sludge process operates at 90-95 % efficiency of BOD treatment.

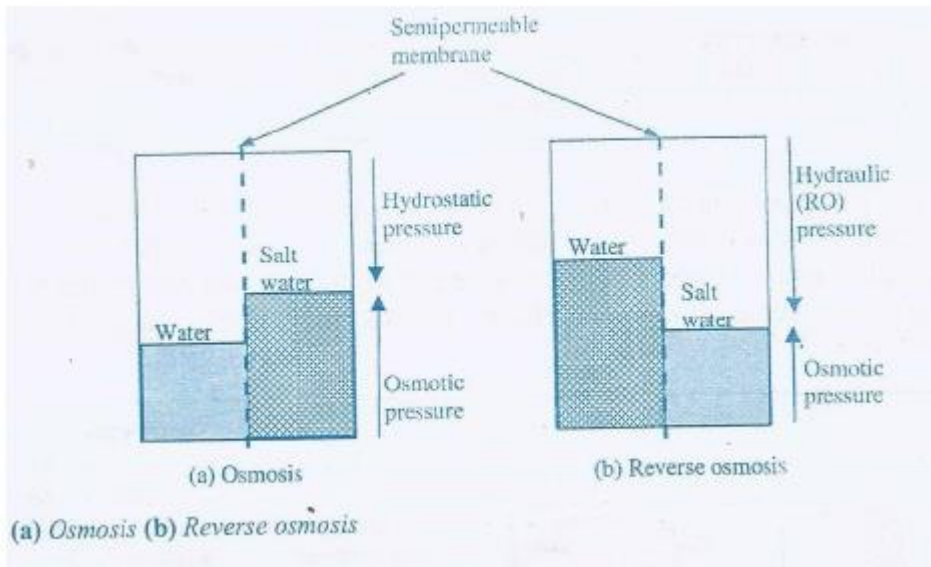
Solution: 8b)

Desalination

The process of partial or complete demineralization of highly saline water such as the sea water is referred to desalination. 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.

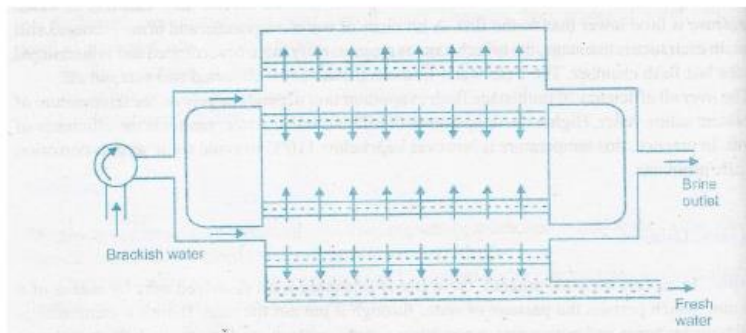


Fig: Reverse osmosis method of desalination

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.
2. Process is simple and continuous.
3. It involves no phase changes
4. Provides odorless, crystal clear water.
5. Easy to maintain

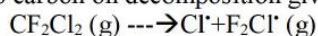
Disadvantages:

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: 8c)

Destruction or depletion of Ozone Layer:

A Chloro Fluoro carbon on decomposition gives Chlorine free radical



- i) The chlorine radical then react with stratospheric ozone to form chlorine monoxide radicals and molecular oxygen. $\text{Cl}^\bullet (\text{g}) + \text{O}_3 (\text{g}) \rightarrow \text{ClO}^\bullet (\text{g}) + \text{O}_2 (\text{g})$
- ii) Reaction of chlorine monoxide radical with atomic oxygen produces more chlorine radicals. $\text{ClO}^\bullet (\text{g}) + \text{O} (\text{g}) \rightarrow \text{Cl}^\bullet (\text{g}) + \text{O}_2 (\text{g})$

(iii) The chlorine radicals are continuously regenerated and cause the breakdown of ozone. Thus, CFCs are transporting agents for continuously generating chlorine radicals into the stratosphere and damaging the ozone layer

Coolants, Aerosols, and Refrigerators are main source for ChloroFluro carbons

Effects of depletion of ozone layer:

- With the depletion of ozone layer, more uv radiation filters into the troposphere. uv radiations lead to ageing of skin, cataract, sunburn, skin cancer, killing of many phytoplankton's, damage to fish productivity etc.
- The plant protein gets easily affected which leads to the harmful mutation of cells, increase in uv radiations damage paints and fibers, causing them to fade faster.

Control of ozone depletion:

Ozone depletion can be controlled by using hydro chloro fluoro carbons and hydro fluoro alkanes in place of CFCs. These contain more hydrogen in their molecule and undergo oxidation readily.

Module 5

9. a. Explain the theory, instrumentation and applications of colorimetry. (06 Marks)
b. What is potentiometric titration? Explain the principle involved in potentiometric titration. (07 Marks)
c. Write a note on fullerene. Mention its application. (07 Marks)

Solution: 9a) 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 (I_a), a portion is reflected (I_r) and the remainder is transmitted (I_t), then,

$$I = I_a + I_r + I_t$$

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

$$I = I_a + I_t$$

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.

Properties:

1. These are highly resistant to water, solvent, acids and alkali.
2. Cured epoxy resin have more toughness, adhesion and heat resistance.
3. They have good insulating properties.
4. They have good skid resistance and adhesion resistance.

Applications:

1. They are widely used as structural adhesives because of their excellent chemical resistant and good adhesion.
2. They are used for laminating materials.
3. Used in skid resistance flooring and highway surfacing.

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
$$I_t = I_o 10^{-\epsilon ct}$$

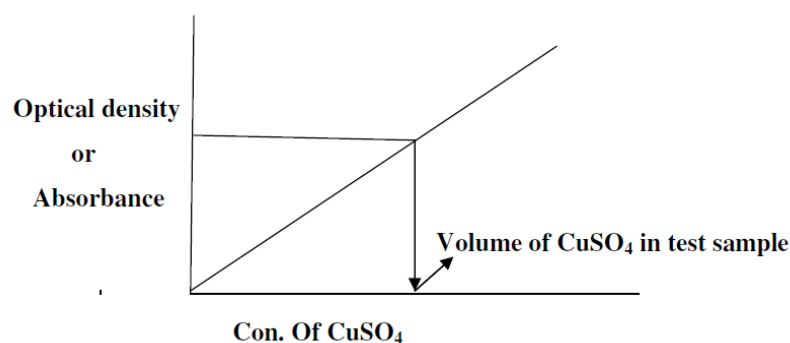
where ϵ called *molar absorptivity* or *molar absorption coefficient*, is a constant for a given substance at a given wavelength. If c is expressed in mol. dm^{-3} and t in centimeters, ϵ has the unit $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$.

The above equation can be written as

$$\log \frac{I_o}{I_t} = \epsilon ct \quad \text{Or} \quad A = \epsilon ct$$

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.



Solution: 9b)

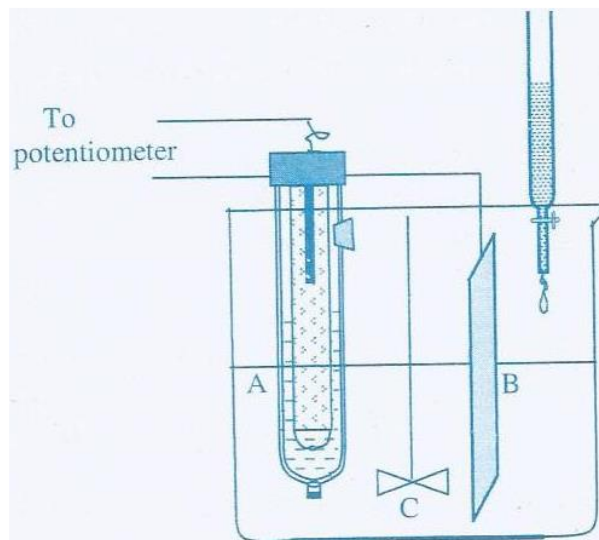
Potentiometry is the determination of concentration of a solution by measuring the e.m.f.

Theory:

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

$$E = E^0 + \frac{0.0591}{n} \log [M^{n+}]$$

Thus, the potential of an electrode E depends upon the concentration of the ion M^{n+} to which it is reversible. In potentiometric titration the potential is measured. The potential developed is a function of the concentration of the ions of the analyte. Assume the concentration of the analyte to be $x \text{ mol dm}^{-3}$. Let $y \text{ mol dm}^{-3}$ is the volume of titrant added at given instant and $z \text{ mol}$ of the product is formed under above conditions. The value of z will change throughout the course of titration because y is being changed continuously. If an indicator electrode is placed in the solution the potential will vary throughout the titration. Initially the change in potential will be small. At the equivalence point, there will be a steep rise in the potential. Beyond the equivalence point, there will be no significant change in the potential. The equivalent point can be determined by plotting change in potential against volume of titrant added.



Instrumentation: A potentiometer consists of a reference electrode, an indicator electrode and a device for measuring the potential. The emf of indicator electrode depends upon the concentration of ions of analyte.

A is a ref. electrode (Saturated calomel electrode), B is the indicator electrode and C is a mechanical stirrer. A known volume of the analyte is taken in a beaker and its potential is determined by connecting the assembly to a potentiometer. The titrant is added in increments of 1 mL and the potential is measured each time. Close to the equivalence point the potential tends to increase rapidly. A few readings are taken beyond the equivalence point. The equivalence point is determined by plotting change in potential against the volume of the titrant.

Application of Potentiometric Titrations:

- (i) Acid – Base titrations (ii) Redox Titrations (Oxidation reduction titration) (iii) Precipitation Titration

Solution: 9c)

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 (T_c) of doped fullerites increases with curvature of fullerenes cages, ie. as cluster size is reduced from C₆₀ to C₃₆, C₂₈ and C₂₀, their T_c increases.
- The index of refraction for fullerenes is 2.2 at 600 nm and they have a resistivity of 10¹⁴ Ω/m.
- They function as catalysts in organic reactions.



Buckminster Fullerene - C₆₀

10. a. What are nano-materials? Give their synthesis by Sol-Gel Techniques. (07 Marks)

b. Write a note on graphene. Mention their applications. (07 Marks)

c. Explain the theory and application of atomic absorption spectroscopy. (06 Marks)

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

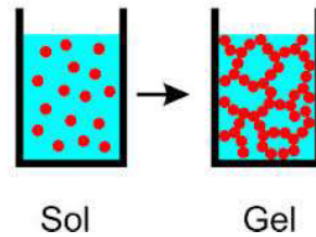
This is a colloidal process in which dispersions have two phases, a dispersed phase with particles having colloidal dimensions (< μm) and a dispersion medium. The process can be used to obtain metal and metal oxide nanocrystals with controlled particle sizes.

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 $FeCl_3$, $MnCl_2$, $AlCl_3$, $Zn(NO)_3$ etc.

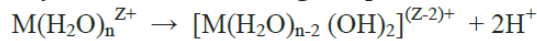
For nanomaterial synthesis, the process involves:

- (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

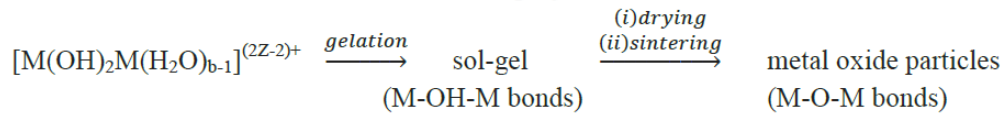
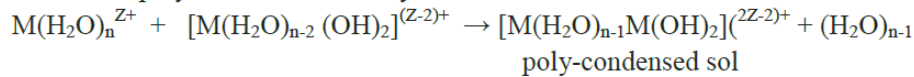


The important reactions in the process:

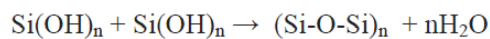
- (i) Hydrolysis of metal salt through de-protonation



- (ii) Condensation-polymerisation of the hydroxide intermediate



When an alkoxide is used, the important reactions are:



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

Solution: 10b)

Graphene is a one-atom-thick layer of carbon atoms arranged in a hexagonal lattice. It is the building-block of Graphite (which is used, among others things, in pencil tips), but graphene is a remarkable substance on its own - with a multitude of astonishing properties which repeatedly earn it the title “wonder material”.

Graphene is the thinnest material known to man at one atom thick, and also incredibly strong - about 200 times stronger than steel. On top of that, graphene is an excellent conductor of heat and electricity and has interesting light absorption abilities. It is truly a material that could change the world, with unlimited potential for integration in almost any industry.

Graphene is indeed very exciting, but producing it is not easy, especially if you are aiming towards high-quality sheets. Several companies are producing Graphene today in small volumes (most companies are using CVD based processes), and there's a lot of research going into developing new ways to mass produce the material in an affordable manner.

Applications:

- touchscreens (for LCD or OLED displays)
- transistors
- computer chips
- batteries
- energy generation
- supercapacitors
- DNA sequencing
- water filters

- antennas
- solar cells
- Spintronics-related products

Solution: 10c)

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

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

The absorption of radiation would bring about an increase in the energy of the molecule. The energy gained by the molecule is directly proportional to the wavelength of radiation. The increase in the energy of the molecule leads to the electronic excitations where electrons jump to higher energy levels. A particular wavelength that a given molecule can absorb depends upon the changes in vibrational, or rotational or electronic states.

When a monochromatic radiation of frequency ν is incident on a molecule, the molecule in the gaseous state E_1 absorbs a photon of energy $h\nu$, it undergoes a transition from lower energy level to higher energy level.

A detector is placed to collect the radiation after interaction with the molecule which shows that intensity has reduced. With wide range of frequencies, the detector shows the energy has been absorbed only from the frequency.

$$\nu = (\Delta E)/h$$

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

The energy difference between the levels is given as,

$$\Delta E = E_2 - E_1 = h\nu = hc/\lambda.$$

The instrument used for recording a spectrum is known as spectrometer or spectrophotometer.

In the atomic absorption spectrometer, the source of radiation in the spectrometer is the tungsten filament emitting white light or hydrogen discharge lamp. The radiation from the source is directed by some device (for example in this case a mirror) on the sample. The radiation then passes through an analyser (the grating in this case), which selects the frequency reaching the detector at any given time. The signal from the detector passes then to a recorder which is attached to the analyser so as to produce a trace of the absorbance of varying frequencies.

Atomic absorption spectroscopy has various applications in various fields.

- One of the major applications of atomic absorption spectroscopy is for the determination of structural elucidation of various substances. This technique is more beneficial as a very small quantity of substance is required for analyzing.
- Atomic absorption spectroscopy can be used to analyze water for its metal quantity if present.
- Atomic absorption spectroscopy is used in many pharmaceutical manufacturing processes where small quantities of catalyst remain in the final product.
- Atomic absorption spectroscopy can also be used in biological tissues such as blood, liver, brain tissue, muscle tissue and fluids for analyzing metals.