First Semester B.E Degree Examination, Dec.2018/Jan 19
Engineering Chemistry (18CHE12/22)
Time: 3hrs   Max. Marks: 100

Module-1

1. a. Define terms: (i) Free energy (ii) Entropy (iii) Cell Potential.   (06 Marks)
b. For the cell, Fe/Fe2+(0.01M)//Ag+(0.1M)/Ag, write the cell reaction and calculate the emf of cell at 298K, if standard potentials of Fe and Ag electrodes are -0.44V and +0.8V respectively.
(07 Marks)
 c. What are Secondary batteries? Explain the construction and working of Nickel-metal hydride (Ni-MH) battery. Mention its applications.   (07 Marks)

Solution: 1a) (i) <u>Free energy:</u> 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 ($\Delta G^o = \Delta H^o - T\Delta S^o$) (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.

(ii) <u>Entropy:</u> Entropy is the measure of a system's thermal energy per unit temperature that is unavailable for doing useful work. The amount of entropy is also a measure of the molecular disorder, or randomness, of a system.

(iii) <u>Cell Potential</u>: The cell potential, Ecell, is the measure of the potential difference between two half cells in an electrochemical cell. The potential difference is caused by the ability of electrons to flow from one half cell to the other. The cell potential (Ecell) is measured in voltage (V), which allows us to give a certain value to the cell potential.

Solution: 1b) . $Fe(s)/Fe^{2+}(0.01M)//Ag^+(0.1M)/Ag$

$Fe \rightarrow Fe^{2+}(0.01M) + 2e-$

$[Ag+ (0.1M) + e- \rightarrow Ag(s)]*2$
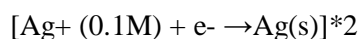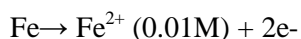
The Nernst equation is: Ecell = E°cell + 0.0592/2 log $[Ag^+]^2/[Fe^{2+}]$

E°cell = E°Cathode - E°Anode

E°cell = 0.80- (-0.44)

E°cell = 1.24V

Ecell = 1.24 + 0.0295 log $(0.1)^2/0.01$

Ecell= 1.24 + 0.0295log (0.01)/(0.01)

Ecell = 1.24V

Solution: 1c) 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.

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 VH_2, ZrH_2, TiH_2 etc with a hydrogen storage alloy such as $LaNi_5$, $TiZr_2$ etc. Anodic material permits reversible electrochemical storage and release of hydrogen (H_2) during charging and
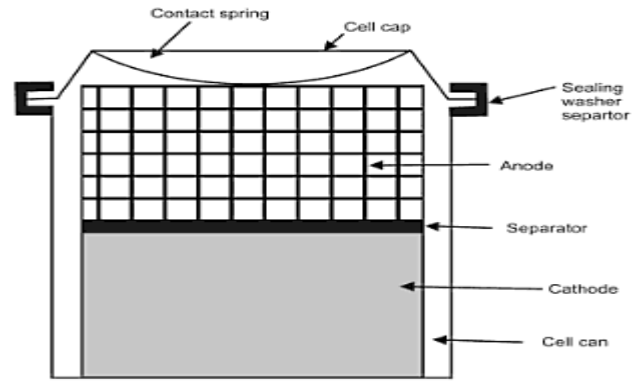
Fig. : Nickel – metal hydride battery

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.
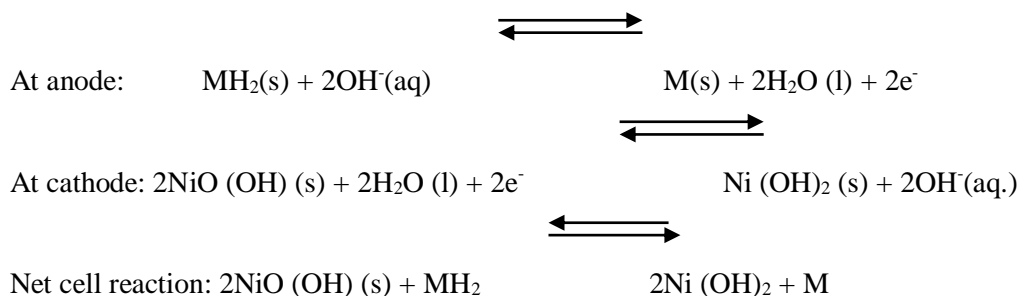
4. Electrolyte – Aqueous solution of KOH (30%).

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,

At anode: $MH_2(s) + 2OH^-(aq)$ $\rightleftarrows$ $M(s) + 2H_2O (l) + 2e^-$

At cathode: $2NiO (OH) (s) + 2H_2O (l) + 2e^-$ $\rightleftarrows$ Ni $(OH)_2 (s) + 2OH^-(aq.)$

Net cell reaction: $2NiO (OH) (s) + MH_2$ $\rightleftarrows$ $2Ni (OH)_2 + M$

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.**

Advantages

1. High energy density, power density and typical cycle life is 500 cycles (less than Ni-Cd battery).
2. Environmentally friendly (No cadmium mercury or lead).
3. No maintenance is required and rapid recharge capability.

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. Define Primary, Secondary and Reserve batteries with examples. **(06 Marks)**
b. What are concentration cells? The cell potential of copper concentration cell, Cu(s)/CuSO4 (0.005M)//CuSO4 (xM)/Cu(s) is 0.0295V at 25C. Calculate the value of x. **(06 Marks)**
c. Explain the construction and working of glass electrode giving its application in determination of pH of solution. **(08 Marks)**

Solution: 2a) 1. 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) 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

Construction: It consists of two copper electrodes immersed in copper sulphate solutions of different concentrations C_1 and C_2 is as shown in the fig.

EMF of concentration cell can be determined by using following formula:

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

Concentration Cell

Under standard condition (T=25C=298K)**,**

$$E_{cell} = \frac{0.0591}{n} \log C_2/C_1$$

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

C_1 = Concentration of electrolyte at anodic compartment = 0.005M

E = 0.0295V
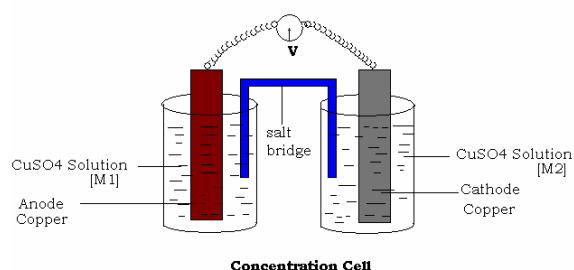
n = 2

Substituting the above values in above formula,

0.0295= 0.0591/2 log x/0.005

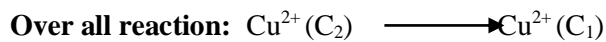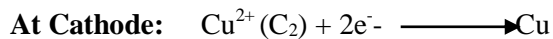0.0295= 0.0295 [log x-log (0.005)]

1= [log x- (-2.301)]

-1.3010=log x

x= antilog (-1.3010)

x= 0.05M

Thus, the value of x=0.05M.

Cell Reaction

At anode: $\quad$ Cu $\longrightarrow$ Cu^{2+} (C_1) + 2e-

At Cathode: $\quad$ Cu^{2+} (C_2) + 2e- $\longrightarrow$ Cu

Over all reaction: Cu^{2+} (C_2) $\longrightarrow$ Cu^{2+} (C_1)
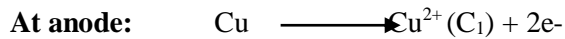
Solution: 2c) Glass Electrode

Construction: The glass electrode consist of glass tube, the bottom of the glass tube is glass bulb covered with glass membrane made up of special glass of low melting point and high electrical conductivity (SiO_2,Na_2O,Al_2O_3 etc., and it allows only H^+ ions). Glass bulb consists of 0.1 N HCl (Assume concentration is C_2) and Ag/AgCl electrode it serves as internal reference electrode as shown in fig. The glass electrode is dipped into any solution containing H^+ ions then glass electrode develops potential called as glass electrode potential. It is represented as E_G.

Then, $E_G = E_b + E_{Ag/AgCl} + E_{assy}$ …………….. (1)

Where, E_b= Boundary potential

$\qquad$ $E_{Ag/AgCl}$ = Potential due to Ag/AgCl

$\qquad$ E_{assy}= asymmetric potential when $C_1 = C_2$

Boundary potential (E_b); It is a potential developed across the glass membrane when concentration of the solution inside and outside the glass membrane are different.

Mathematically it is represented as, $E_b = E_1 - E_2$

$\qquad$ Where, E_1= Potential due to H^+ present inside the bulb (Unknown solution)

$\qquad\qquad$ E_2 = Potential due to H^+ present in outside solution (Unknown solution)

According to Nernst equation

$= E^o + \dfrac{0.0591}{n} \log C_1 - (E^o - \dfrac{0.0591}{n} \log C_2)$

$= \dfrac{0.0591}{n} \log C_1 - \dfrac{0.0591}{n} \log C_2$

Where, $C_2 = 0.1$ M and n = 1 (H^+)

$= \dfrac{0.0591}{n} \log C_2 - K$ **or**

$= K + \dfrac{0.0591}{n} \log C_1$

Glass selects only H^+ ions ignoring other ions.

Hence $\quad$ $C_1 = H^+$

$E_b = K + 0.0591 \log [H^+]$

Where, $\log [H^+] = -pH$

$E_b = K - 0.0591pH$ --------------------(2)
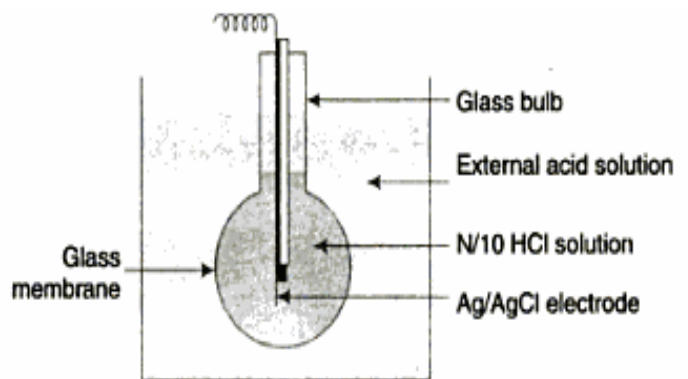
Substituting eqn (2) in (1)

$E_G = K - 0.0591pH + E_{Ag/AgCl} + E_{assy}$

$E_G = E^o_G - 0.0591pH$

Where, E^o_G = Standard glass potential

$\qquad\qquad = K + E_{Ag/AgCl} + E_{assy}$

Advantages of Glass electrode;

Combined Glass Electrode

1. It can be employed in presence of strong oxidizing /reducing substances and metal ions.
2. It does not get poisoned easily.
3. It can be used in unbuffered solution and can be adopted for measurements with very small quantities of solution.

Determination of pH using glass electrode or calomel electrode

To determine the pH of given solution, glass electrode is dipped in a solution whose pH has to be determined. It is combined with a saturated calomel electrode through a salt bridge.

Determination of pH by glass electrode.
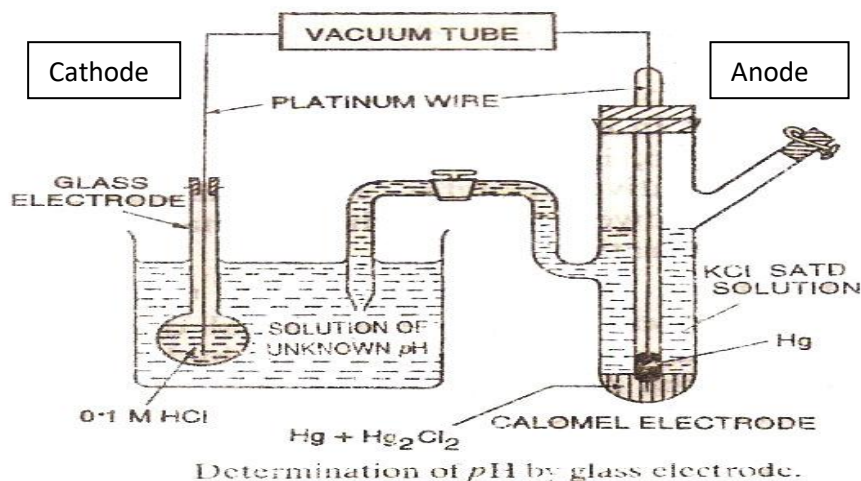
Cell assembly representation:

Hg / Hg$_2$Cl$_2$ / Cl$^-$ // Unknown solution / glass membrane / 0.1N HCl / AgCl / Ag

From the EMF, the pH of the solution is calculated as below:

$E_{cell} = E_{right} - E_{left}$

$E_{cell} = E_{glass} - E_{cal}$

$E_{cell} = (E^{\circ}_{G} - 0.0591 \text{ pH}) - E_{cal}$

$E_{cell} = E^{\circ}_{G} - 0.0591 \text{ pH} - E_{cal}$

$pH = \dfrac{E^{\circ}_{G} - E_{cal} - E_{cell}}{0.0591}$

$pH = \dfrac{K - E_{cell}}{0.0591}$ $K = (E^{\circ}_{G} - E_{cal})$

Module-2

3.a. Define corrosion. Describe the electrochemical theory of corrosion by taking rusting of iron as an example. **(07 Marks)**

b. Explain (i) Waterline corrosion (ii) Pitting corrosion **(06 Marks)**

c. What is electroless plating? Explain electroless plating of Nickel. **(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.
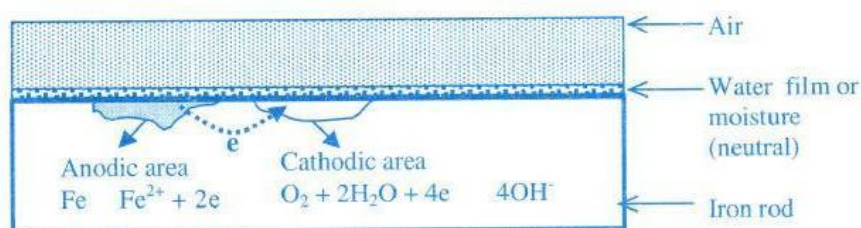
(i) According to electrochemical theory, corrosion of metals takes place due to the formation of minute

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**.

$$M \longrightarrow M^+ + ne^-$$

Ex: $Fe \longrightarrow Fe^{2+} + 2e^-$
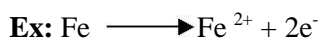
(iii) The electrons flow from the anodic to cathodic area and at the cathodic region, reduction takes place. Since metal cannot be reduced further, **metal atoms at the cathodic region are unaffected by the cathodic reaction**. Some constitutions of the corrosion medium take part in the cathodic reaction. 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.

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

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

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$
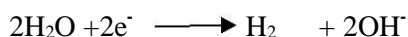
(iii) If the solution is deaerated and acidic, the H^+ ions are reduced to H_2

$$2H^+ + 2e^- \longrightarrow H_2 \uparrow$$
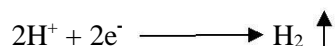
(iv) The electrons liberated at the anodic region migrates to the cathodic region constituting corrosion current, the metal ions liberated at the anode and some anions liberated at the cathode diffuse towards each other through the conducting medium-range and form a corrosion products.

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 $Fe(OH)_2$.

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

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

$$2Fe(OH)_2 + O_2 + (n-2) H_2O \longrightarrow [Fe_2O_3.nH_2O] \text{ [Rust]}$$
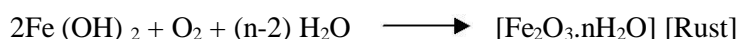
Solution: 3b) (i) Waterline corrosion:

 (i)The water line corrosion takes place due to the formation of differential oxygen concentration cells.

(ii)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.

Ex: Water storage steel tanks

Ex: Ocean going ship

Ex: 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.

At anodic region: Fe $\longrightarrow$ Fe^{2+}

At cathodic region: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

$$2Fe + O_2 + 2H_2O \longrightarrow 2Fe^{2+} + 4 OH^-$$
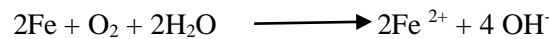
(ii)Pitting corrosion:

(i)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.

At anodic region: Fe $\longrightarrow$ Fe^{2+}

At cathodic region: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

$$2Fe + O_2 + 2H_2O \longrightarrow 2Fe^{2+} + 4 O$$
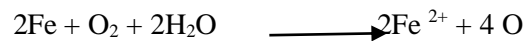
Solution: 3c) *Electroless-plating:* Deposition of metal or alloy over a conducting or non-conducting substrate surface by **chemical reduction of the metal ions by use of reducing reagent** and without the use of electrical energy is called electroless-plating.

Electroless-plating is generally autocatalytic in nature. Schematically, it can be represented as,   Metal ions + Reducing agent $\xrightarrow{\text{catalytically active surface}}$ Metal atom + Oxidized product

Electroless-plating of Nickel:

Electroless nickel (EN) plating is a process for depositing nickel alloy onto a substrate by electrochemical reactions.

Typically, the constituents of an EN solution are:

1. A source of nickel ions (nickel sulfate)

2. A reducing agent (Sodium hypophosphite NaH_2PO_2. H_2O)

3. Suitable complexing agents (organic acids like lactic acid)

4. Stabilizers (Thiourea)

5. Brighteners (Thiourea)

6. Exaltants (Lactates, Succinates)

Reactions:

Cathode: $Ni^{2+} + 2e^- \rightarrow Ni$

Anode: $H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2H^+ + 2e^-$

Overall reaction: $Ni^{2+} + H_2PO_2^- + H_2O \rightarrow Ni + H_2PO_3^- + 2H^+$

Applications:

The most common form of electroless nickel plating produces a nickel-phosphorus alloy coating. The phosphorus content in electroless nickel coatings can range from 2% to 13%. It is commonly used in engineering coating applications where wear resistance, hardness and corrosion protection are required. Applications include oilfield valves, rotors, drive shafts, paper handling equipment, fuel rails, and optical

surfaces for diamond turning, door knobs, kitchen utensils, bathroom fixtures, electrical/mechanical tools and office equipment. It is also commonly used as a coating in electronics printed circuit board manufacturing, typically with an overlay of gold to prevent corrosion. This process is known as electroless nickel immersion gold.

Due to the high hardness of the coating, it can be used to salvage worn parts. Coatings of 25 to 100 micrometers can be applied and machined back to the final dimensions. Its uniform deposition profile means it can be applied to complex components not readily suited to other hard-wearing coatings like hard chromium.

It is also used extensively in the manufacture of hard disk drives, as a way of providing an atomically smooth coating to the aluminum disks, the magnetic layers are then deposited on top of this film, usually by sputtering and finishing with protective carbon and lubrication layers; these final two layers protect the underlying magnetic layer (media layer) from damage should the read / write head lose its cushion of air and contact the surface.

Its use in the automotive industry for wear resistance has increased significantly. However, it is important to recognize that only End of Life Vehicles Directive or RoHS compliant process types (free from heavy metal stabilizers) may be used for these applications.

Advantages:

1. Does not use electrical power.
2. Even coating on parts surface can be achieved.
3. No sophisticated jigs or racks are required.
4. There is flexibility in plating volume and thickness.
5. The process can plate recesses and blind holes with stable thickness.
6. Chemical replenishment can be monitored automatically.
7. Complex filtration method is not required
8. Matte, semi-bright or bright finishes can be obtained.

Disadvantages:

1. High cost of chemicals.
2. Waste treatment cost is high due to the speedy chemical renewal.
3. Porous nature of electroless plating leads to inferior material structure compared to electrolytic processes.

4. a. What is meant by metal finishing? Mention (any five) technological importance of metal finishing. **(06 Marks)**

b. Explain the process of: i) Galvanizing ii) Anodizing of Al. **(07 Marks)**

c. What is electroplating? Explain electroplating of chromium. Mention why chromium cannot be used as anode. **(07 Marks)**

Solution: 4a) 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.

   (vi) Building up material or restoration

   (vii) Manufacturing printed circuit boards, capacitors, contacts, etc.

  (viii) Electrotyping (e.g., gramophone records)

   (ix) Electroforming or reforming of articles,

   (x)   Electrochemical machining, electropolishing and electrochemical etching, etc.

There are five important techniques of metal finishing:

   (i)   Electroplating of metals or alloys by use of electricity / electrolysis

   (ii) Electroless plating of metals or alloys by use of reducing agents

   (iii) Immersion plating [by replacement reactions]

   (iv) Chemical conversion plating by oxidation & deposition of metal compound from an oxidising bath.

   (v)   Electrophoretic painting on electrically charged surfaces like car bodies

Solution: 4b) (i) Galvanizing: 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 fort best adhesion property.

(iv) Finally the base metal is dipped into the zinc at 430-470^{0}C.

(v) The excess zinc is removed from the surface by rolling or wiping etc.
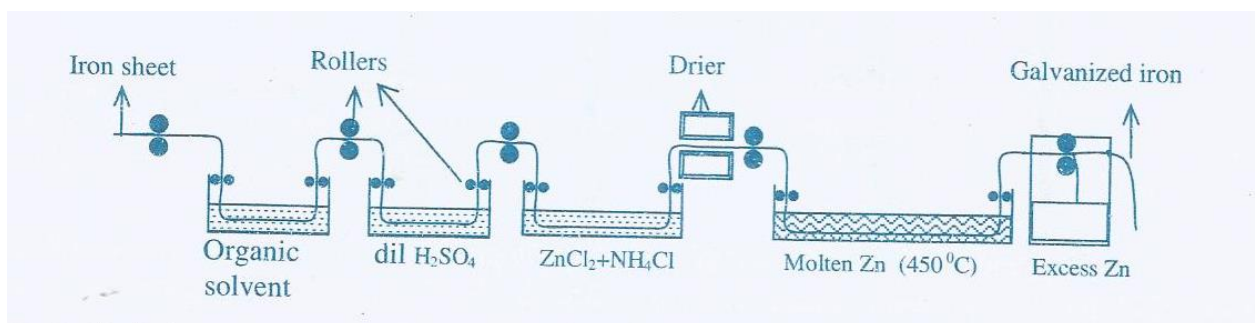
These steps are diagrammatically shown in Fig below….

Fig: Galvanization of Iron

(ii) Anodizing of Al:

(i) Some metals like Al, Mg, Ni etc and their alloy due to "passivation effect" exhibits much higher corrosion resistance than expected from its position in the galvanic series.

Anodizing is a process in which a protective passive oxide film is artificially (chemically or electrochemically) produced on certain metals. It is also called as anodic oxidation process.

Process:

In this method base metal is made as anode, in an electrolytic bath of suitable composition and passing direct electric current. The most commonly used baths are chromic acid, sulfuric acid, phosphoric acid, oxalic acid etc and lead in general used as a cathode.

When we apply external EMF, at anode oxidation takes place (Al $\longrightarrow$ Al^{3+} + 3e$^-$). The Al^{3+} gets combined with the oxygen and formed Al$_2$O$_3$ on the anode. This oxide layer is a porous. The strength and corrosion resistance of the anodized film can be increased by sealing, which involves dipping the metal in boiling water or steam or metal salt solution. This treatment changes porous alumina at the surface of the coating into monohydrate (Al$_2$O$_3$.H$_2$O), which occupies more volume thereby the pores are sealed. This coating provides good adherence for paints and dyes.

This process is carried out as follows:

The article is degreased, polished and connected to the anode. Steel or copper is made the cathode. The electrolyte consists of 5-10% chromic acid. The temperature of the bath is maintained at 35°C. A potential is applied and gradually increased from 0-40 V during first 10 min. Anodizing is continued for 20 min at 40 V. After 20 min, the potential is increased to 50 V and held at this temp for 5 min. An opaque oxide layer is obtained. For higher thickness, 10% sulphuric acid is used as the electrolyte at 22°C and a potential of 24 V. The article is dyed by immersing for about 20 min in a sol of the dye at 50-60°C. Finally the article is treated with ni acetate followed by boiling water.

Applications: Because of its attractive finish and environmentally safe nature anodized aluminum is one of the most widely used industrial, commercial and domestic materials. It is used in providing attractive, minimum maintenance, highly durable exteriors. It is also used in computer hardware, exhibit displays, and scientific instruments and in a range of home appliances.

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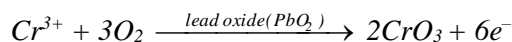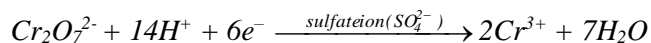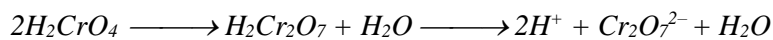
Electroplating of Chromium:

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

- 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$_2$SO$_4$ = 100: 1 ratio
Temperature	45 – 60 ^{o}C
Current density	100 – 200 mA/cm^2
Current efficiency	17 – 21 %
Anode material	Insoluble lead- Pb-Sb alloy or Pb-Sn alloy (with lead oxide coating)
Cathode material	Surface cleaned object metal
Reaction at anode	H$_2$O $\longrightarrow$ ½ O$_2$ ↑ + 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+}.

$$CrO_3 + H_2O \longrightarrow H_2CrO_4 \longrightarrow 2H^+ + CrO_4^{2-}$$

$$2H_2CrO_4 \longrightarrow H_2Cr_2O_7 + H_2O \longrightarrow 2H^+ + Cr_2O_7^{2-} + H_2O$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \xrightarrow{sulfateion(SO_4^{2-})} 2Cr^{3+} + 7H_2O$$

$$Cr^{3+} + 3O_2 \xrightarrow{lead\ oxide(PbO_2)} 2CrO_3 + 6e^-$$

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, 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.

Chromium anode is not used because, the anode efficiency is nearly 100% and that of the cathode is only around 20% at the best. There will be increase in concentration of Cr^{3+} ions which results in poor quality electrodeposits (black deposits).

Module-3

5. a. Define calorific value of fuel. Explain the experimental determination of calorific value of solid/liquid fuel using Bomb calorimeter. **(08 Marks)**
b. What are fuel cells? Describe the construction and working of solid oxide fuel cell (SOFC).
(06 Marks)
c. What are solar cells? Explain the construction and working of photovoltaic cell. (06 Marks)
Solution: 5a) Calorific value of fuel: It is defined as the amount of heat released when unit quantity (unit mass or volume) of fuel is burnt completely in excess of air or oxygen.
Experimental determination of calorific value of 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 temp. 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. The bomb 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.
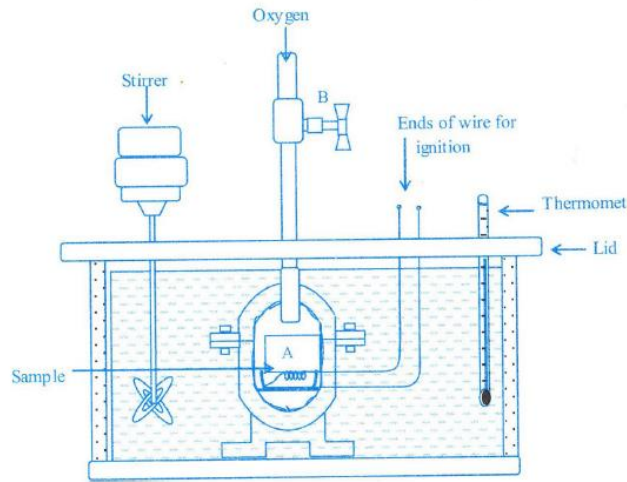

Fig. Bomb Calorimeter

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.

$$GCV = \frac{(W_1 + W_2)(T_2 - T_1)\,4.187}{m} \; KJ \; kg^{-1} \qquad \text{............(1)}$$

And, net calorific value,

$$NCV = GCV - 0.09 \times H \times L_v \; KJ \; kg^{-1} \qquad \text{............(2)}$$

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

Solution: 5b) Fuel Cell: 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.

Solid Oxide Fuel Cell (SOFC)

Introduction: A solid oxide fuel cell (or SOFC) is an electrochemical conversion device that produces electricity directly from oxidizing a fuel. Fuel cells are characterized by their electrolyte material, the SOFC has a solid oxide or ceramic electrolyte.
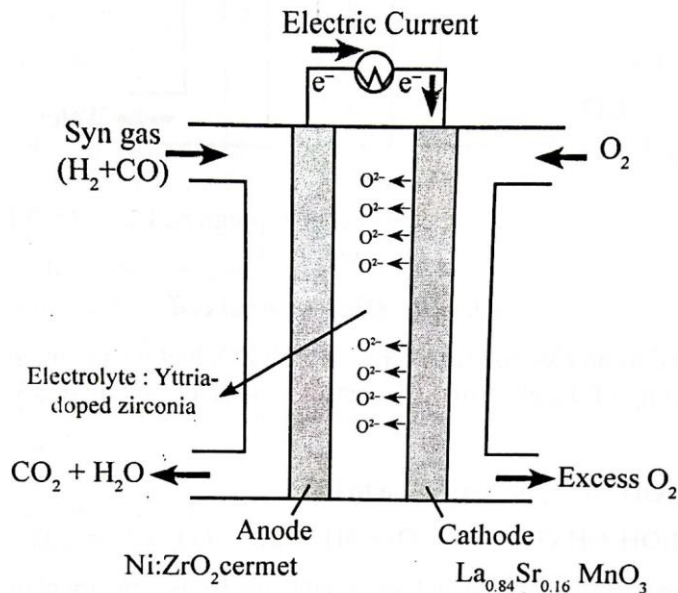
Fig : Solid Oxide fuel cell

Construction:

Anode : Porous electrode made up of Ni: ZrO_2
Cathode :
Fuel : H_2 solid
Electrolyte : Solid Yettria stabilized Zirconia
Electrodes : Carbon or metal based
Catalyst : Ceramic
Charge carriers : O^{2-} ions
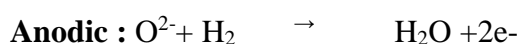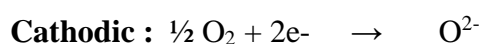Operating temperature : $1000°C$
Fuel cell efficiency : 50-60 %

Working :
Solid oxide fuel cells are a class of fuel cells characterized by the use of a solid oxide material as the electrolyte. SOFCs use a solid oxide electrolyte to conduct negative oxygen ions from the cathode to the anode. The electrochemical oxidation of the oxygen ions with hydrogen liberates H_2O and two electrons on the anode side. Electrons flow from the anode through the external circuit to the cathode.

Reactions :

Cathodic : $\frac{1}{2} O_2 + 2e- \rightarrow O^{2-}$

Anodic : $O^{2-} + H_2 \rightarrow H_2O + 2e-$

Advantages: high efficiency, long-term stability, fuel flexibility, low emissions, and relatively low cost.

Disadvantage : high operating temperature which results in longer start-up times and mechanical and chemical compatibility issues.

Applications: It is used for large power plants and for industrial applications.

Solution: 5c) Solar cell: A solar cell (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
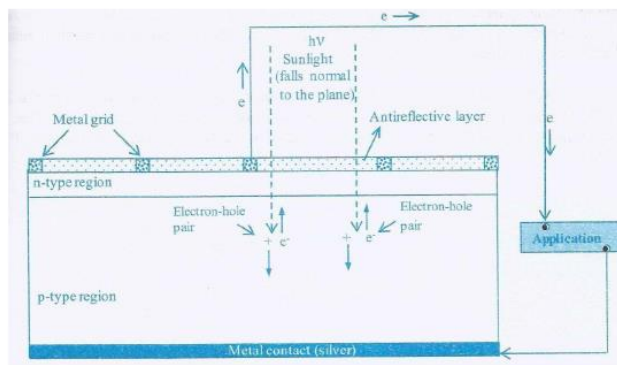

Fig. Photovoltaic cells

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.

6. a. Explain the preparation of solar grade Silicon by Union Carbide process.   (07 marks)
b. Write a note on (i) Power Alcohol (ii) Unleaded Petrol   (06 Marks)
c. 0.75g of coal sample (Carbon 90%, H2 5% and ash 5%) was subjected to combustion in a bomb calorimeter. Mass of water taken in calorimeter was 2.5 kg and the water equivalent of calorimeter is 0.65 kg. The rise in temperature was found to be 3.2°C. Calculate the higher and lower calorific values of the sample. Latent heat of steam = 2454kJ/kg and specific heat of water is 4.187kJ/kg/°C.   (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

$$Si + 3 HCl \longrightarrow HSiCl_3 + H_2$$
Trichlorosilane
$$Si + 4 HCl \longrightarrow SiCl_4 + 2H_2$$
Tetrachlorosilane
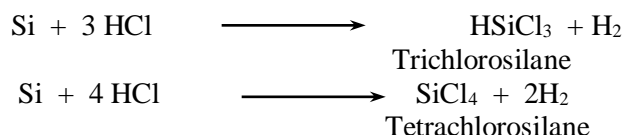
- Tetrachlorosilane is converted to trichlorosilane by treating with hydrogen at 1000°C.

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

- 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).

$$2HSiCl_3 \longrightarrow H_2SiCl_2 + SiCl_4$$

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

- 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).

$$SiH_4 \longrightarrow Si + 2H_2$$
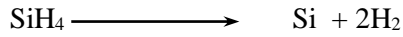
Solution: 6b)

(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.

Solution: 6c) Given, m =0.75g = 0.75x10^{-3} kg

W_1= 2.5 kg
W_2= 0.65kg
$(T_2 - T_1)$ = 3.2°C
%H = 5%
S = 4.187 kJ kg^{-1}·C^{-1}
L_q= 2454 kJ/kg

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

$$= \frac{(2.5 + 0.65)\,(3.2)\,4.187}{0.75 \times 10^{-3}}$$

$$= 56273.28 \text{ kJ kg}^{-1}$$

NCV = GCV – 0.09 x %H x L_v

= 56273.28 – 0.09 x 5 x 2454

= 56273.28 -1,104.3

= 55168.98 kJ/kg

Module 4

7. a. What are the causes, effects and disposal methods of e-wastes?   (07 Marks)
b. What are the sources, effects and control of lead pollution (Pb pollution). (07 Marks)
c. In a COD test 30.2 cm3 and 14.5 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)

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 penetrates 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

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: 7a)

. **Solution: 7b)**

Solution: 7c) Given, V = 25 mL, b = $30.2 cm^3$, a = $14.5 cm^3$, N_{FAS} = 0.05N

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

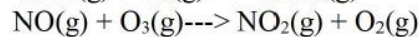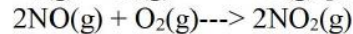= 0.05 X (30.2-14.5) X 8000/ 25 = 251.2 mg of O_2 /dm^3
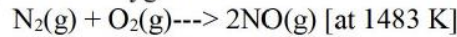
8. a. Explain the sources, effects and control of oxides of nitrogen.   **(07 Marks)**
b. Explain softening of water by ion exchange method.   **(07 Marks)**
c. Explain activated sludge treatment of sewage water.   **(06 Marks)**

Solution: 8a)

Dinitrogen and dioxygen are the main constituents of air.
$$N_2(g) + O_2(g) ---> 2NO(g) \text{ [at 1483 K]}$$
$$2NO(g) + O_2(g) ---> 2NO_2(g)$$
$$NO(g) + O_3(g) ---> NO_2(g) + O_2(g)$$

Sources:
- ❖ Vehicular emissions or automobile emissions
- ❖ Burning of coal in thermal power station
- ❖ When fossil fuel is burnt, dinitrogen and dioxygen combine to yield significant quantities of nitric oxide (NO) and nitrogen dioxide (NO_2).
- ❖ NO_2 is produced in small amounts by microbiological processes in soil.
- ❖ However significant amount of NO & NO2 are emitted in to the atmosphere by natural activity.

Ill effects:
- ❖ Causes respiratory problems
- ❖ NO_2 and other NO_x interact with water, oxygen and other chemicals in the atmosphere to form acid rain.
- ❖ The nitrate particles that result from NO_x make the air hazy and difficult to see though.(Visibility)
- ❖ NO_x in the atmosphere contributes to nutrient pollution in coastal waters.
- ❖ Accounts for global warming.
- ❖ Accounts for photochemical fog formation

Asthmatic bronchitis and DNA damage are caused due to the Hexavalent Chromium present.

Control:
- ❖ Fuel switching is the simplest and potentially the most economical way to reduce NOx emissions.
- ❖ Installation of burners especially designed to limit NOx formation can reduce NOx emissions by up to 50%.
- ❖ Selective catalytic reduction (SCR) is a post-formation NOx-control technology that uses a catalyst to facilitate a chemical reaction between NOx and ammonia to produce nitrogen and water.
- ❖ **Staged combustion.** Either air or fuel injection can be staged, creating either a fuel-rich zone followed by an air-rich zone or an air-rich zone followed by a fuel-rich zone.

Solution: 8b)

<u>**Sources:**</u>
- • 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.

<u>**Ill effects**</u>:
- • 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.

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.

1. **Cation exchange resin or cation exchanger:** These resins have acidic group as the ionisable group such as $-SO_3H$, $-COOH$, $-H_2PO_3$ group. These resins contains replaceable hydrogen (H+) ion and they exchange cationic portion of salts with H+.
2. **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 $-NH_2$, $-NHCH_3$, $-OH$ 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 Ca^{2+}, Mg^{2+} are removed from hard water by exchanging H+ ions as follows.

$$RH + M^+ \longrightarrow RM + H^+$$
$$2RH + M^{2+} \longrightarrow R_2M + 2H^+$$
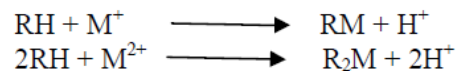
Where R is part of resin, M+ is monovalent ion like Na+ and M2+ is divalent ion like Ca2+, Mg2+.

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.
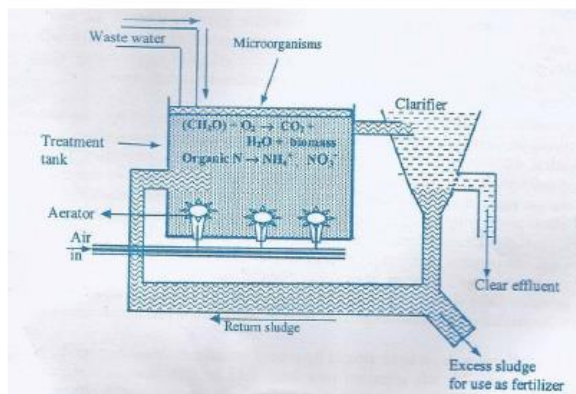
$$ROH + X^- \longrightarrow RX + OH^-$$
$$2ROH + X^{2-} \longrightarrow R_2X + 2OH^-$$
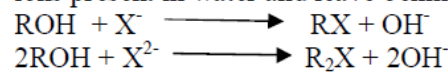
Where X- and X2- represent the anion such as Cl^-, NO_3^-, SO_4^{2-}

Thus the cation and anion impurities in water are replaced by an equal number of H^+ and OH^- ions respectively.
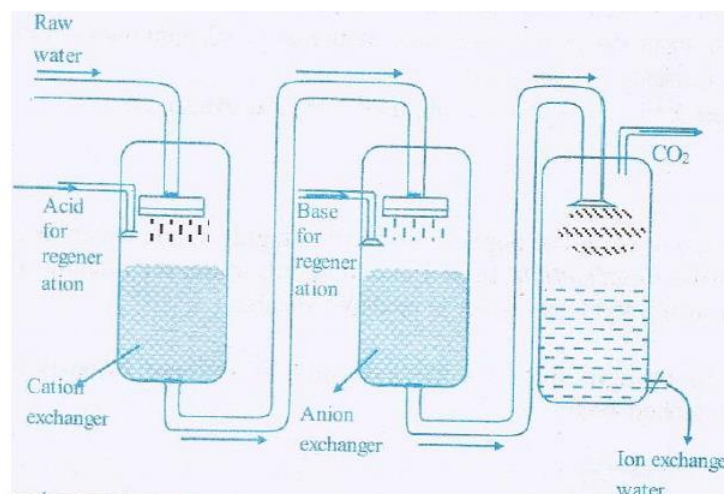
Solution: 8c)

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.

Module 5

9a. Explain the theory, instrumentation and application of atomic absorption spectroscopy.
(06 Marks)
b. Explain the theory and instrumentation of potentiometry. (07 Marks)
c. Write a note on Fullerene. Mention its application. (07 Marks)
Solution: 9a) 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 v is incident on a molecule, the molecule in the gaseous state E1absorbs a photon of energy hv, 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.

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.

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

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 mol dm-3. Let y mol dm-3 is the volume of titrant added at given instant and z 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 electode depends upon the concentration of ions of analyte.

A is a ref. electrode (Satuated calomel electrode), B is the indicator electrode and C is a mechanical stirrer. A known volume of the analyte is taken ia a beaker and its potential is determined by connecting
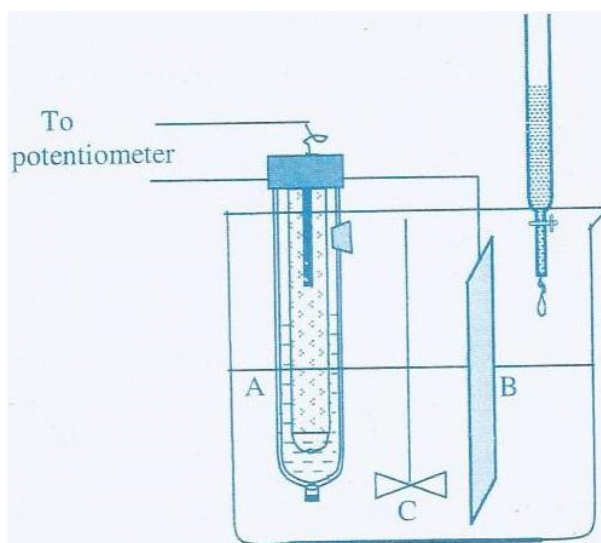
the assembly to a potentiometer. The titrant is added in increments of 1 mL and the potential is measured each time. Close to the equivalence point the potential tends to increase rapidly. A few readings are taken beyond the equivalence point. The equivalence point is determined by plotting change in 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 (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 Ω/m.
☐ They function as catalysts in organic reactions.

Buckminister Fullerene - C60

10. a. What are nano-materials? Explain the synthesis of nanomaterials by precipitation method.

(07 Marks)

b. Explain the synthesis of nano materials by sol gel technique. **(07 Marks)**

**c. Explain the theory and instrumentation of conductometry.** **(06 Marks)**

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

The method employs mixing of reagents to get an insoluble material as a precipitate. For preparation of nanosized particles by this method, the reagents to be mixed are introduced at critical supersaturation limit. *For example, when AgNO3 is mixed with NaCl, a precipitate of AgCl is formed. White BaSO4 precipitate is formed when BaCl2 is mixed with H2SO4.*

The process involves (i) nucleation and (ii) growth of nuclei to form a particle. During nucleation few molecules come together and aggregate to form several nuclei. In the growth phase, smaller precipitates dissolve and get deposited on the bigger ones. This is Ostwald's ripening. Bulk precipitates of the size of μm to mm are generally formed when saturation concentration is reached and in absence of a controlled reaction. For nano-sized particles, the reagents are mixed at critical supersaturation limit, beyond which nucleation begins.

Preparation of nano-sized AgBr from AgNO3 and NaBr solutions: A double jet precipitation apparatus is used to prepare nanoparticles of AgBr by solution precipitation using equimolar AgNO3 and NaBr solutions. The apparatus allows to regulate particle concentration, temperature, rate of reagent addition and mode of mixing for the reaction.

The reagents are introduced through fine tubes into the apparatus in regulated pulses and a mixing device is used that is attached to a high speed motor shaft and rotates at controlled speed of 2000 rpm . The rate of reagent addition through fine tubes is controlled using a remote pump. One of the reagents (0.01 M AgNO3) is introduced above the inlet zone of the mixing device, while NaBr (0.01 M) is added below. The solution concentration is kept high (> 0.5 M) and the temperature of the system maintained at 70 0C. Baffles are present around the mixing device that inhibits the vertical rotation of the contents in the vessel. At high rates of reagent addition, supersaturation is obtained at the introduction point leading to highnucleation rate for the particle formation. Supersaturation is relieved by stirring at regulated speed and the resulting emulsion will have particles of 7-60 nm AgBr. The use of capping agents and re-dispersion will stabilize the prepared nanoparticles.
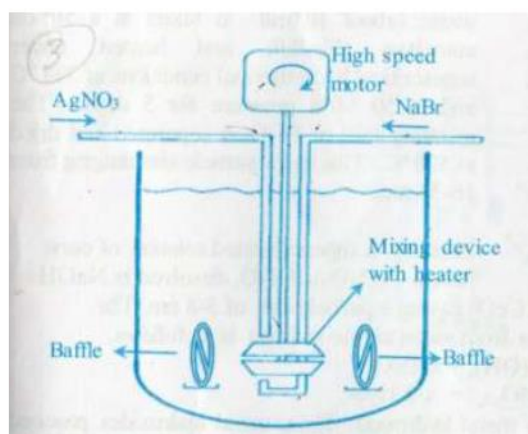
**Fig: Precipiation method**

Solution: 10b) (i) Sol-Gel:

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 $FeCl_3$, $MnCl_2$, $AlCl_3$, $Zn(NO)_3$ etc.
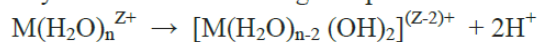
For nanomaterial synthesis, the process involves:
(i) Hydrolysis of precursors
(ii) Condensation and polycondensation to form particles
(iii) Allowing gelation to occur (ageing)
(iv) Drying of gel to obtain solid material, followed by its sintering
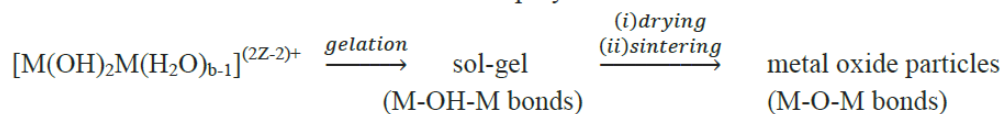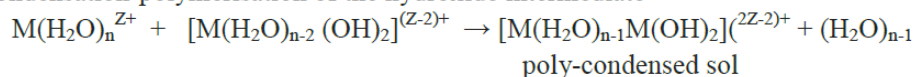   to form nanoparticles

Sol   Gel
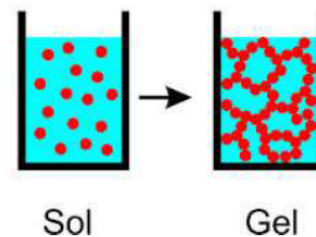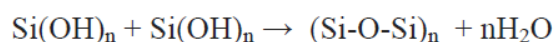
The important reactions in the process:
(i) Hydrolysis of metal salt through de-protonation
$$M(H_2O)_n^{Z+} \rightarrow [M(H_2O)_{n-2}(OH)_2]^{(Z-2)+} + 2H^+$$

(ii) Condensation-polymerisation of the hydroxide intermediate
$$M(H_2O)_n^{Z+} + [M(H_2O)_{n-2}(OH)_2]^{(Z-2)+} \rightarrow [M(H_2O)_{n-1}M(OH)_2]^{(2Z-2)+} + (H_2O)_{n-1}$$
poly-condensed sol

$$[M(OH)_2M(H_2O)_{b-1}]^{(2Z-2)+} \xrightarrow{gelation} \text{sol-gel} \xrightarrow[(ii)sintering]{(i)drying} \text{metal oxide particles}$$
(M-OH-M bonds)   (M-O-M bonds)

When an alkoxide is used, the important reactions are:

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

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

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

Solution: 10c)

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.

$$i = \frac{E}{R}$$

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 l cm is given by

$$R = \frac{\rho \times l}{a}; \quad k = C\,[l/a]$$

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
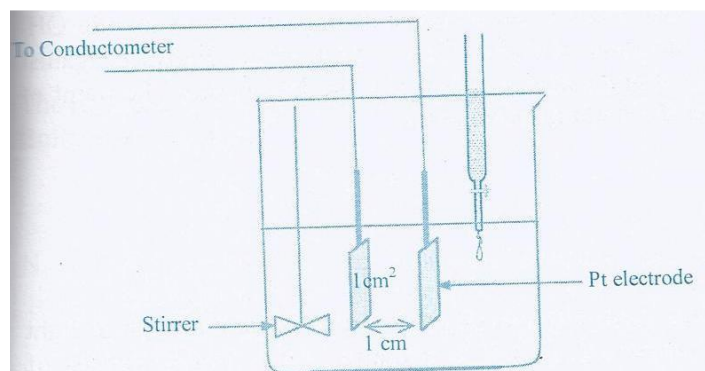

Fig: Conductometric Titration Unit