

Solutions

**CMR
INSTITUTE OF
TECHNOLOGY**

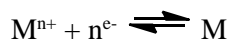


Sub:	Engineering Chemistry	Code:	15CHE22
Date: <u>28/03/2017</u>	Duration: <u>90</u> mins	Marks: <u>50</u>	Sem: <u>II</u>
			Branch: <u>All</u>

Internal Assessment Test I – March 2017

1. (a) Derive Nernst equation for a single electrode potential in a galvanic cell. (05 Marks) (CO1, L3)

Solution: Consider an electrode assembly undergoing a spontaneous reaction.



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

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

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

n = moles of electrons, $F = C \text{mol}^{-1}$, $E = J C^{-1}$

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 JK⁻¹mol⁻¹), F (96500Cmol⁻¹) and T (298K) in eqn (8) we get

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

(b) What is fuel cell? Explain the differences between fuel cell and battery. (05 Marks)
(CO1, L4)

Solution: 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.

	Conventional batteries		Fuel Cells
1.	Anodic and cathodic compartments are preloaded and reaction products are retained in the battery.	1.	Permit continuous movement of fuel, oxidant and reaction products in and out of battery.
2.	They have definite amount of stored energy.	2.	They are only energy conversion devices, do not store any energy.
3.	As long as active components exist, battery continues delivering energy.	3.	As long as fuel and oxidant are supplied at respective electrodes, energy is available.
4.	Generally function at ambient temperatures without an active catalyst being employed.	4.	Generally work at higher temperature or in presence of an electrocatalyst.

2. (a) EMF of the concentration cell $\text{Ag}/\text{AgNO}_3 (\text{C}_1)//(\text{C}_2=0.2\text{M}) \text{AgNO}_3/\text{Ag}$ is 0.8 V. Calculate C_1 of the cell. If $\text{C}_1=\text{C}_2$, what is cell potential? (05 Marks) (CO1, L3)

Solution: Cell Reaction: $\text{Ag} \longrightarrow \text{Ag}^+ (\text{C}_1) + \text{e}^-$ (ANODE)

$\text{Ag}^+ (\text{C}_2) + \text{e}^- \longrightarrow \text{Ag}$ (CATHODE)

$n=1, E_{\text{cell}}=0.8\text{V}, \text{C}_2=0.2\text{M}, \text{C}_1=?$

Formula: $E_{\text{cell}} = 0.0591/n \log [C_2]/[C_1]$

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

Or, $0.8 = 0.0591 \log [0.2] - \log [C_1]$

Or, $\log [C_1] = -14.22$

Or, $C_1 = 5.81 \times 10^{-15}\text{M}$

If $\text{C}_1=\text{C}_2, E_{\text{cell}} = 0.0591/n \log 1=0$ (since $\log 1=0$).

(b) Explain construction and working of Li-ion battery. Mention its applications. (05 Marks) (CO1,L3)

Solution:

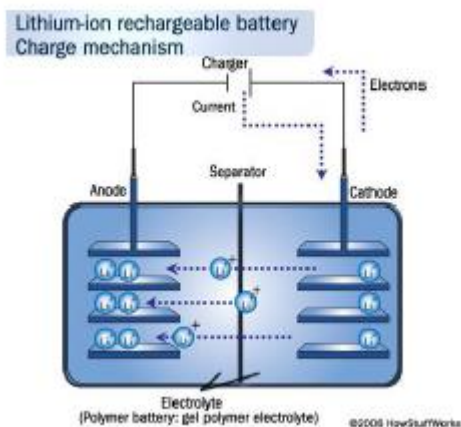
A lithium-ion battery is a member of a family of rechargeable battery types in which lithium ions move from the negative electrode to the positive electrode during discharge and back when charging.

Anode : Li-metal oxide , like lithium cobalt oxide

Cathode: carbon

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

Separator : polypropylene separator

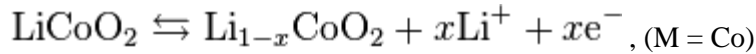


Type and Cell representation:

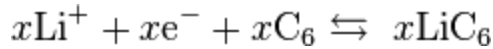
Li-ion battery is a secondary battery.

$\text{LiMO}_2 / \text{electrolyte}$ (lithium salt in an organic solvent) / C

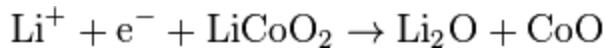
The positive electrode half-reaction is:



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

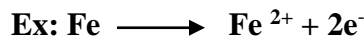
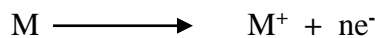
- *Portable devices* like mobile phones and smartphones, laptops and tablets, digital cameras and camcorders, electronic cigarettes, handheld game consoles and torches (flashlights).
- Li-ion batteries are used in tools such as cordless drills, sanders, saws
- *Electric vehicles*

Li-ion batteries are used in telecommunications applications.\

3. (a) Demonstrate how electrochemical theory of corrosion can explain rusting of iron. (05 Marks) (CO2, L2)

According to electrochemical theory, corrosion of metals takes place due to the formation of anodic and cathodic regions on the same metal surface or when two metals are in contact with each other in the presence of a conducting medium.

AT ANODE:



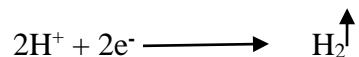
At cathode:

Since metal cannot be reduced further, metal atoms at the cathodic region are not affected.

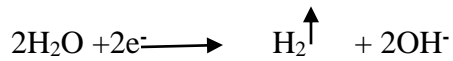
Therefore, cathodic reaction depends on the nature of the electrolyte.

There are three possible ways in which the reduction can take place.

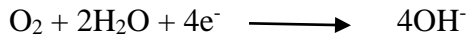
(a) If the solution is deaerated and acidic, the cathodic reaction involves evolution of hydrogen.



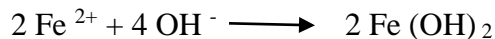
(b) If the solution is deaerated and almost neutral the cathodic reaction involves evolution of hydrogen gas and hydroxyl ions.



(c) If the solution is aerated and almost neutral the alkaline oxygen or water are reduced to OH^- ions.



Corrosion of iron produced Fe^{2+} ions and OH^- ions at the anode and cathode sites respectively. These ions diffuse towards each other. Since small Fe^{2+} ions diffuse more rapidly than OH^- ions. Their combination occurs more commonly near cathodic region.

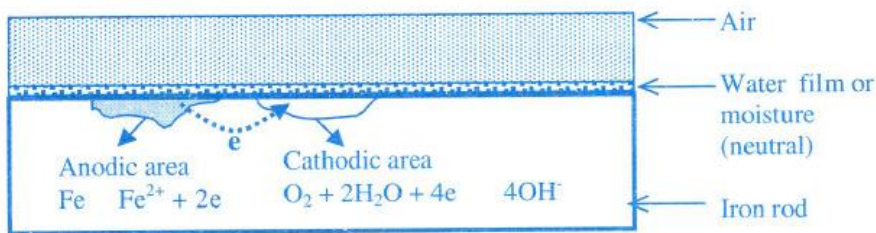


(Ferrous hydroxide)

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



[Rust]



(b) What is metal finishing? Mention the technological importance of metal finishing. (05 Marks) (CO3, L1)

Solution: 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

4. (a) Explain the following characteristic of a battery:

(i) Voltage (ii) Capacity (iii) Energy Efficiency (06 Marks) (CO1, L4)

Solution: (i) Voltage: The voltage of a battery is given by the equation,

$$E_{\text{cell}} = (E_c - E_A) - |\eta_A| - |\eta_C| - i R_{\text{cell}}$$

Where, E_c and E_a are the electrode (reduction) potential of cathode and the anode respectively, η_A , η_C are the over-potentials at the anode and the cathode respectively and iR_{cell} is the internal resistance.

To derive maximum voltage from a battery

- (a) The difference in the electrode potentials must be high.
- (b) The electrode reactions must be fast so as to minimize the overpotential.
- (c) The internal resistance of cell must be low.

The electrode system should be such that the active mass at the positive electrode depletes readily and that at the negative electrode increase easily. This minimize the overpotential at the cathode and anode. The cell should be appropriately designed so as to minimize internal resistance. This can be achieved by keeping the electrodes close to each other and also by using an electrolyte of high conductivity.

(ii) Capacity: Capacity is the charge or amount of electricity that could be obtained from battery and is given in ampere hours (Ah). It depends on size of battery and is given by Faraday's relation

$$C = \frac{(wnF)}{M}$$

w = mass of active material

M = Molar mass of active material

Therefore amount of active materials actually consumed during discharge determines capacity of battery. Capacity can also be measured by finding for a fixed current discharge (i amperes), time taken for battery to reach minimum voltage, E_{cell}^{min} when cell is said to be dead as shown in Fig. 2.2.

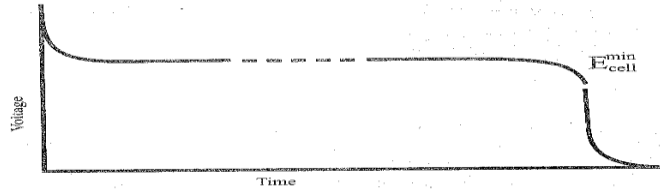


Fig. 2.2 Battery voltage against time at constant current discharge

Length of flat portion of curve is a measure of capacity of battery, longer the flat portion, better is the capacity.

(iii) Energy efficiency

Amount of energy released on discharge per unit energy input is referred to as energy efficiency.

$$\% \text{ Energy efficiency} = \frac{\text{amount of energy released during discharge}}{\text{amount of energy required for recharge}} \times 100$$

Batteries should have high energy efficiency.

It depends on rate of reaction, electron transfer, self discharge, capacity.

(b) Which type of corrosion control mechanism could be deployed to protect the underground crude oil pipeline and explain the method in detail? (04 Marks) (CO2, L5)

Solution: Sacrificial anode method can be deployed to protect the underground oil pipeline.

In this method, the base metal structure is converted into a cathode by connected it to a more active [higher up in galvanic series or less noble] metal. This active metal actually acts as an auxiliary anode. Mostly Zn, Mg, Al are the common auxiliary anodes used in this method. These metals being more active, acts as anode and undergo destruction and protect the metal structure.

Since the anode material sacrifice to protect the metal structure, the method is known as sacrificial anode method. After continuous use exhausted sacrificial anodes are replaced by new ones as and when required. Ex: A Mg block connected to buried oil storage tank.

5. (a) Explain the construction and working of methanol-oxygen fuel cell. List any two applications. (05 Marks) (CO1, L4)

Solution: It is good example for liquid fuel cell

Construction: Methanol – oxygen fuel cell consist of

Anode – It is a porous platinum (Pt) electrode.

Cathode - It is a porous platinum (Pt) electrode.

Electrolyte – Aqueous sulphuric acid (H₂SO₄)

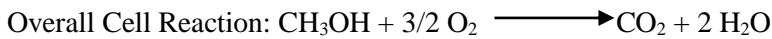
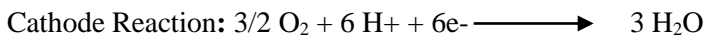
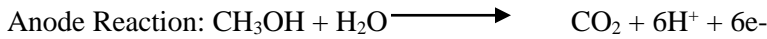
Active components: (a) Fuel – Methanol mixed with sulphuric acid supplied at anode. (b)

Oxidant – Pure oxygen is supplied at cathode.

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.

Working:

Cell reaction;

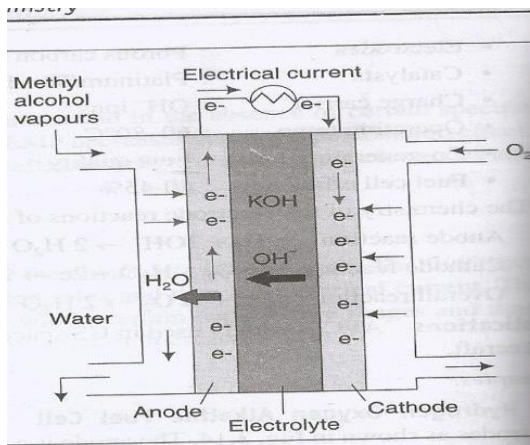


H₂O and CO₂ are formed do not harm the cell functioning because they are removed as and when they are formed.

Cell Potential : 1.2 V

Applications:

1. used in automobiles, military applications.
2. Power backup and portable instruments.



(b) Represent the cell formed by the coupling of two copper electrodes immersed in cupric sulphate solutions. Concentration of cupric ion in one solution is 100 times more concentrate than other. Calculate the cell potential at 300K. (05 Marks) (CO1, L3)

Solution: Cell representation is $\text{Cu} / \text{CuSO}_4 (C_1) // \text{CuSO}_4 (C_2=100C_1) / \text{Cu}$

Formula : $E_{\text{cell}} = 0.0591/n \log [C_2]/[C_1]$

Or, $E_{\text{cell}} = 2.303 RT/nF \log c_2/c_1$

$$= (2.303 \times 8.314 \times 300) / 2 \times 96500 \log 100c_1/c_1 \quad (n=2)$$

$$= 0.0595\text{V}$$

Anodic reaction : $\text{Cu} \rightarrow \text{Cu}^{+2} (c_1) + 2e^-$

Cathodic reaction: $\text{Cu}^{+2} (c_2) + 2e^- \rightarrow \text{Cu}$

6. (a) Describe the effect of the following factors on the rate of corrosion: (06 Marks) (CO2, L2)

(i) pH of the medium (ii) Nature of corrosion product (iii) Relative areas of anode and cathode.

Solution:

(i) pH of the medium: In general, the rate of corrosion is high when the nature of the environment is acidic.

(a) If the $\text{pH} < 3$, severe corrosion occurs even in the absence of air due to the continues evolution of hydrogen at the cathodic region.

(b) If the $\text{pH} > 10$, corrosion of the metal practically ceases, due to the formation of a protecting coating of hydrogen oxide of iron.

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

(a) The nature of the oxide layer largely decides the rate of further corrosion. If its composition is stoichiometric, highly insoluble and non porous with low ionic and electrical conductivity, the layer acts as protective film and prevent further corrosion. For eg. Al, Ti and Cr develops such a layer on their surface and become passive to further corrosion. Stainless steel (18% Cr, 8% Ni) builds up a thin but a highly protective film of Cr_2O_3 which resist attack in a highly corrosive environment. Metals such as Zr and Mo not only form such protective layer but are also capable of self repairing the oxide films when it is damaged. Hence these metals are extremely resistant to corrosion.

(b) If the oxide layer is non stoichiometric, highly porous, soluble, unstable, it can not control further corrosion. In such cases the fresh metal surface is continuously exposed to corrosion environment and corrosion takes place continuously. Eg. Fe and Zn

(iii) Relative areas of anode and cathode: The rate of corrosion largely depends on the relative size of anode and a cathode.

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

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

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

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

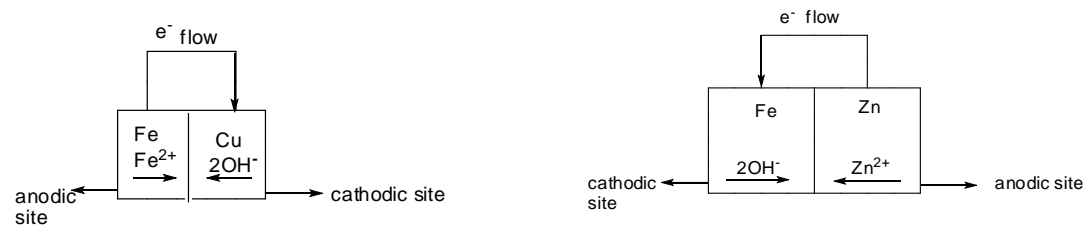
(b) Give reasons for the following:

(i) Iron corrodes when it is in contact with copper but not with zinc.

(ii) A pure iron rod half-immersed vertically in water starts corroding at the bottom. (04 Marks) (CO2, L3)

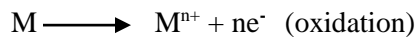
Solution: (i) This is a case of differential metal corrosion. When two dissimilar metals are in contact with each other, a potential difference is set up, resulting in a galvanic current. A metal placed high in the electrochemical series is said to be anodic with respect to the one placed below it. The 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.

When iron is in contact with copper, iron behaves as an anode owing to its lower reduction potential and thereby undergoes corrosion. While copper, being the cathode, remains unaffected. On the other hand, zinc is anodic to iron since it has a lower reduction potential and thus corrodes while iron remains unaffected.

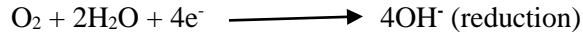


(ii) This is a case of differential aeration corrosion. The part of the pure iron rod exposed to higher oxygen concentration acts as the cathodic region since oxygen has a demand for electrons and hence can undergo reduction, and the part of the metal exposed to lower oxygen concentration (immersed in water) acts as an anodic region, consequently the poorly oxygenated region undergoes corrosion.

At anode: (less oxygen concentration)



At cathode: (more O₂ concentration)

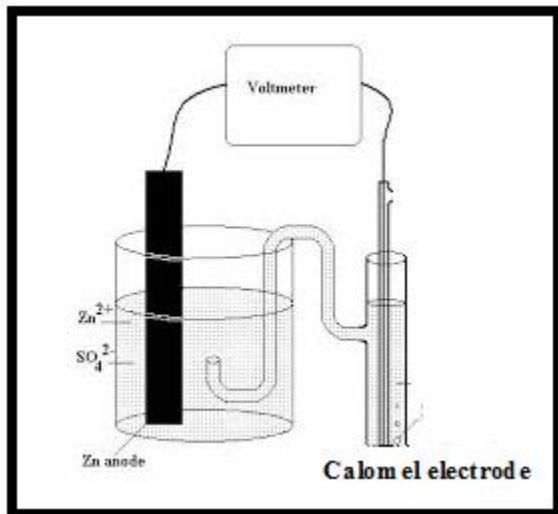


Corrosion of metals occurs due to the formation of oxygen concentration cell due to uneven supply of air on the metal surface is known as differential aeration corrosion.

7. (a) What is secondary reference electrode? Explain the determination of electrode potential of an unknown electrode using calomel electrode. (05 Marks) (CO1, L4)

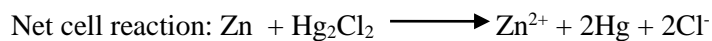
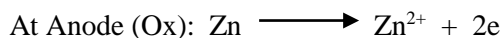
Solution: These are the electrode whose potential is known or constant and stable does not vary with temperature. Ex: 1. Calomel electrode 2. Silver-silver chloride electrode

The given electrode, say zinc electrode, is coupled with saturated calomel electrode as in the figure. Since the reduction potential of zinc electrode less than that of calomel electrode, zinc acts as anode and calomel as cathode.



The cell assembly is represented as, $\text{Zn} / \text{ZnSO}_4 (1 \text{ M}) // \text{KCl (satd)} / \text{Hg}_2\text{Cl}_2 / \text{Hg}$

Cell reactions:



The EMF of the cell assembly is,

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

$$= E_{\text{cal}} - E_{\text{Zn/Zn}^{2+}}$$

$$1.002 = 0.242 - E_{\text{Zn/Zn}^{2+}}$$

$$E_{\text{Zn/Zn}^{2+}} = 0.242 - 1.002$$

$$E_{\text{Zn/Zn}^{2+}} = -0.76 \text{ volt.}$$

(b) What is anodic metal coating? Describe galvanization process of corrosion prevention with a proper labeled diagram. (05 Marks) (CO2, L2)

Solution: The metal coating which is anodic to the base metal is called anodic metal coating. In order to protect the metal from corrosion, any metal which is higher up in the galvanic series such as Zn, Mg, etc are coated on iron (base metal). The characteristic feature of anodic coating is that the base metal on which the coating is done will not get corroded even if the coating falls at some places. This is due to the formation of large anodic and small cathodic areas.

GALVANIZATION: 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 $430\text{-}470^\circ\text{C}$.
- (v) The excess zinc is removed from the surface by rolling or wiping etc.

These steps are diagrammatically shown in Fig below:

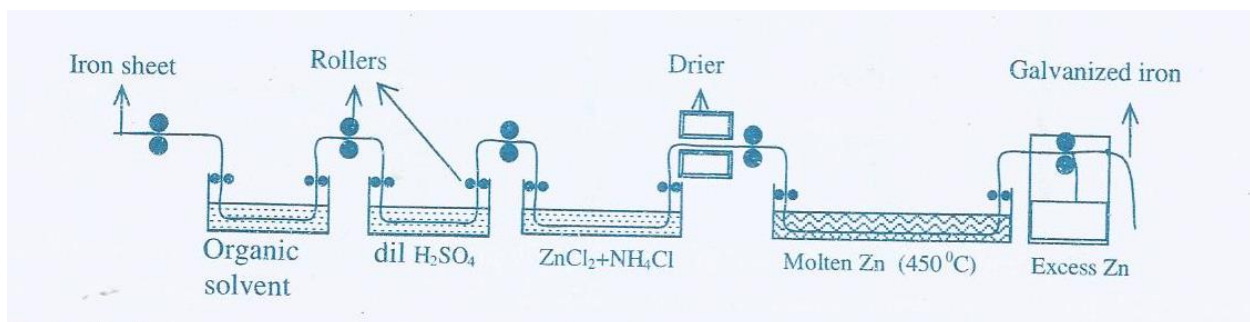


Fig: Galvanisation of Iron