

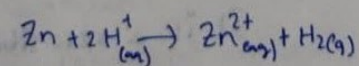
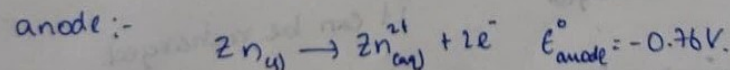
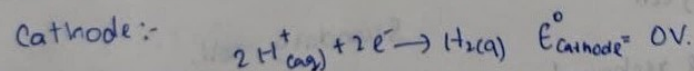
Part-A

- 1) Electrochemical cell:- It is a device that can generate electrical energy from the chemical energy.
- 2) Electrolytic cell:- It is a device that converts electrical energy into chemical energy.
- 3) Salt bridge is used to maintain the charge balance between cathode and anode.
- 4) The electromotive force is the maximum potential difference between two electrodes of a galvanic or voltaic cell.
It is represented by the anode and cathode are separated by two bars or slashes which represent a salt bridge.
- 5) Batteries are cells that produce electric current.
They are classified into two types, Primary and Secondary Batteries.
- 6)

Primary cell	Secondary cell.
1) It can't be recharged	It can be recharged.
2) It is an irreversible cell	It is a reversible cell.
Ex:- Alkaline batteries, dry cells	ex:- Lithium-ion battery and nickel-Cadmium.

- 7) The charging reaction converts the lead sulfate at the negative electrode to lead. and converts lead to leadoxide at positive electrode.
The discharging reaction converts the lead to lead sulfate at ^{negative} positive electrode and converts leadoxide to lead at positive.
- 8) The advantages of Li-ion batteries mean that these batteries have high energy density, self-discharge. and low maintenance. It is used in Solar Power storage, Reliable and lightweight Marine performance and portable power packs.
- 9) The potential of a half-reaction measured against SHE under standard conditions is called standard electrode potential.

In a galvanic cell at cathode it should be Standard Hydrogen electrode and at anode it should be Zn electrode. when the circuit is closed, the voltmeter indicates a potential of 0.76 V.



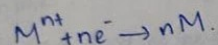
$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode} = 0.76V.$$

(2)

When the electrodes in contact with their ions are arranged on the basis of the values of their standard (electrode) reduction potential standard oxidation potential, the resulting series is called Electrochemical Series.

It is used to determine the reducing and oxidizing strengths, calculation of E° in electrochemical cell. and Predicting the Feasibility of Redox Reaction.

1) Consider a metal M:



work done for movement of electron

$$W_{\text{red}} = n F E_{\text{red}}$$

Gibbs free energy (ΔG) is equal to maximum useful work done in a process

$$\Delta G = -n F E_{\text{red}} \dots (1)$$

ΔG° and E_{red}° are the values at there standard conditions.

$$\Delta G^\circ = -n F E_{\text{red}}^\circ \dots (2)$$

And also,

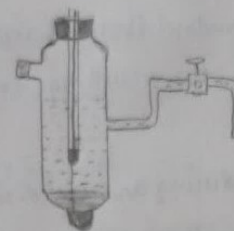
$$\Delta G = G^\circ + RT \ln K \dots (3)$$

Substituting (1) and (2) in eq-(3)

$$-n F E_{\text{red}} = -n F E_{\text{red}}^\circ + RT \ln K$$

$$\Rightarrow E_{\text{red}} = E_{\text{red}}^\circ - \frac{RT}{nF} \ln \frac{[M]^n}{[M^{n+}]} \quad \left(\text{where } K = \frac{[M]^n}{[M^{n+}]} \right)$$

$$\Rightarrow E_{m/m} = E_{m/m}^\circ - \frac{2.303 RT}{nF} \log \frac{[M]^n}{[M^{n+}]}$$



Calomel electrode is the mercury-mercurous chloride electrode. It consists of glass vessel having bent side tube. Pure mercury is placed at the bottom of the tube. Which is covered with a paste of mercury-mercurous chloride.

The remaining cell is filled with 1N or 0.1N or saturated KCl. A platinum wire is sealed into a glass tube is dipped into mercury layer is used to provide the external electrical contact. The side tube is used for making electrical contact with a salt bridge. It is represented as $Hg(l)/Hg_2Cl_2(s)/Cl^-$. The calomel electrode can act as anode or cathode depending on the nature of other electrode of cell.

13) Corrosion is the decay of metal when it is exposed to the elements in the environment.

Causes of corrosion,

metal corrodes when it reacts with another substance such as oxygen, hydrogen, an electrical current or even dirt and bacteria. Corrosion can also happen when metals like steel are placed under too much stress causing the material to crack.

Disadvantages,

- 1) Weakens material
- 2) loss, contamination and deterioration of appearance of material.

he ratio of the volume of the oxide formed to the volume of the metal consumed is called Pilling-Bedworth rule.

5) Liquid metal corrosion is primarily a physical form of attack on the metal substrate rather than a chemical effect.

14) Dry Corrosion:- It occurs when there is no water or moisture to aid the corrosion and the metal oxidises with the atmosphere alone.

Wet Corrosion:- It occurs through electron transfer, involving two processes, oxidation and reduction. The other metal, liquid or gas which gains the electrons is called the cathode.

17) Cathodic protection (CP) is a technique used to control the corrosion of a metal surface by making it the cathode of an electrochemical cell.

Sacrificial anodic protection:-

One type of cathodic protection system is the sacrificial anode.

The anode is made from a metal alloy with a more active voltage than the metal of the ~~surface~~ structure it is protecting.

18) Impressed current cathodic protection is a corrosion protection system consisting of sacrificial anodes connected to an external power source. The external power source, often a DC power supply, provides the current necessary to drive the electrochemical reaction required for cathodic protection to occur.

1a) Galvanization is the process of applying a protective zinc coating to steel or iron in order to prevent premature rust and corrosion. Application are:-

1. To galvanized sheet metal.
2. To galvanized house-hold items such as buckets, tubs and other containers.
3. To galvanized machine parts, tools, ships, tanks and wires.

2a) Hot-dip galvanizing is the process of coating fabricating steel by immersing it in a bath of molten zinc.

Tinning the tip extends the life of the tip by preventing oxidation and corrosion, but it also causes the solder wire to melt and flow more easily over the part. joining, making the overall soldering process go smoothly.

21) Electroplating is the process of applying a metal coating on another piece of metal through an electro-deposition process. In electroplating, the deposited metal becomes part of the existing product with the plating/coating.

Q. What is electroplating?

Ans: Electroplating:

Electroplating is the process of coating metals & non-metals, to change their surface properties such as to improve the appearance, and corrosion or chemical attack. Electroplating is the electro-deposition of metal, by means electrolysis over surface of metals, alloys or non metals.

PART - B [LONG ANSWER QUESTIONS]

1. What is galvanic cell? Explain the construction of galvanic cell with electrode reactions.

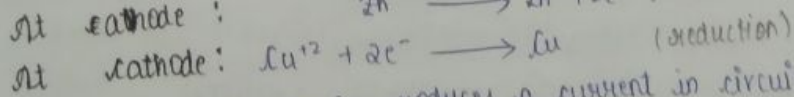
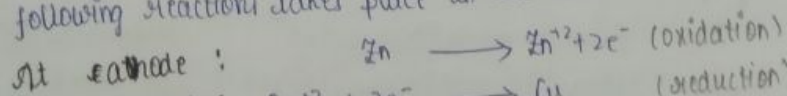
Galvanic cell: Galvanic cell is a device in which chemical energy is converted into electrical energy. These cells are called electrochemical cells or voltaic cells. Daniel cell is an example for galvanic cell.

Construction of galvanic cell:

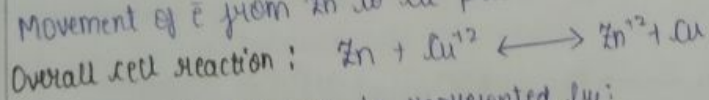
This cell is made up of two half cells. One is oxidation or anodic half cell. The other is reduction or cathodic half cell. The first half cell consists of 'Zn' electrode dipped in $ZnSO_4$ soln and second half cell consists of Cu electrode dipped in $CuSO_4$ solution. Both the half cells are connected externally by metallic conductor. And internally by "salt bridge", it is a U-tube containing concentrated soln of KCl or NH_4NO_3 in agar-agar gel contained porous pot. It provides electrical contact between two solutions.

Electrode reactions:

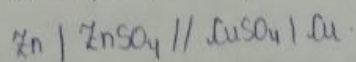
The following reactions takes place in the cell:



Movement of e^- from Zn to Cu produces a current in circuit.



The galvanic cell can be represented by:



The passage of e^- from one electrode to other causes the potential difference between them which is called emf.

2. Compare between a cell and a battery. Write the classification of batteries with examples.

Ans: Batteries:

When two or more electrochemical cells are electrically interconnected, each of which containing two electrodes and an electrolyte is called a battery. Batteries are classified into two categories depending on their recharging capabilities. Batteries are classified into 2 types:

1] Primary cell 2] Secondary cell.

Classification of batteries:

Primary batteries

These are non-rechargeable & are meant for single use and to be discarded after use.

Ex: 1] Alkaline Manganese

2] Zinc Carbon

3] Button

Cell: combination of electrode & electrolyte
Battery: combination/series of cells.

Secondary batteries

These are rechargeable, which are designed to be recharged & used multiple times.

Ex: 1] Lead Acid

2] Nickel Cadmium

3] Nickel Metal Hydride

4] Lithium ion.

3. Explain the construction and working of lead-acid battery. Write the discharging, charging reactions and limitations of lead acid battery.

Construction and working of lead-acid battery:

→ It consists of lead-antimony alloy coated with lead dioxide (PbO_2) as cathode and spongy lead as anode.

→ The electrolyte is a 20% solution of H_2SO_4 .

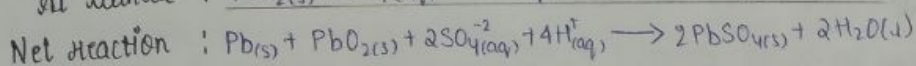
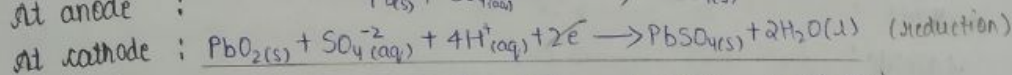
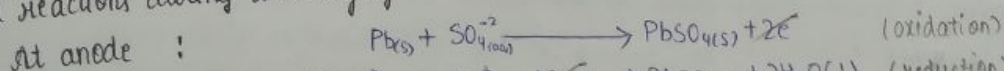
→ The storage cell can operate both as voltaic cell and electrolytic cell.

→ It acts as voltaic cell when supplying energy and as a result eventually becomes rundown. The cell operates as electrolytic cell when being recharged.

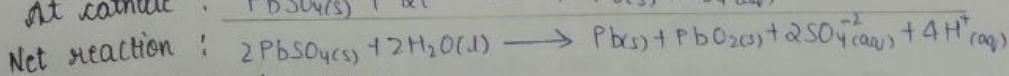
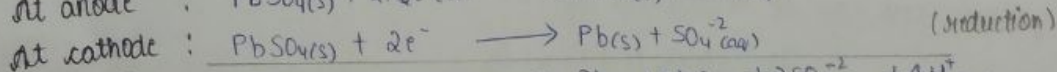
→ The cell consists of a series of Pb-plates (-ve plates) and PbO_2 plates (+ve plates) connected in parallel. The plates are separated from adjacent one by insulators like wood, rubber or glass fiber.

Anode: Pb-Plate (+ve plate) Cathode: PbO_2 Plate (+ve plate) Electrolyte: 20% of H_2SO_4 .

Cell reactions during discharging:



Cell reactions during recharging:



Limitations of lead acid battery:

The lead storage cells are used to supply current for electrical vehicles, gas engine ignition, telephone exchanges, electric trains, mines, laboratories, hospitals, automobiles, broadcasting & power stations.

4. Compare primary and secondary cells. Explain the construction of lithium ion battery with relevant reactions. Mention its applications.

Ans:

Primary cell

- 1] Cell reaction is irreversible.
 - 2] Must be discarded after use.
 - 3] Functions as galvanic cell.
 - 4] Have relatively short shelf life.
 - 5] Can't be used as storage devices.
- Ex: Dry cell, Alkaline cell and

Secondary cell

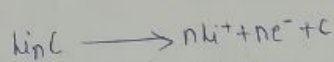
- 1] Cell reaction is reversible.
 - 2] May be recharged.
 - 3] Functions as galvanic & electrolytic cell.
 - 4] Have long shelf life.
 - 5] Can be used as energy storage devices.
- Ex: Lead acid storage cell, Li-ion, Ni-cd battery

Construction of lithium ion battery:

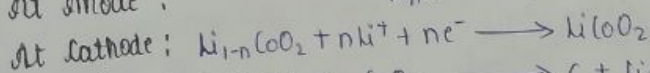
- Lithium ion cell is a secondary cell.
- It can be recharged.
- Anode is a intercalated lithium compound such as layered lithium cobalt(III) oxide - LiCoO_2 .
- Cathode is lithium doped graphite.
- The liquid electrolyte consists of complex lithium compound such as lithium hexafluoro phosphate dissolved in an organic solvent such as dimethyl carbonate.
- Provide light weight, high energy density power sources for variety of devices.

Reactions:

At Anode:



At Cathode:



Cell reaction (discharging): $\text{Li}_n\text{C} + \text{Li}_{1-n}\text{CoO}_2 \longrightarrow \text{C} + \text{LiCoO}_2$

Cell reaction (recharging): $\text{C} + \text{LiCoO}_2 \longrightarrow \text{Li}_n\text{C} + \text{Li}_{1-n}\text{CoO}_2$

Applications:

- Lithium ion batteries are commonly used for portable electronics and electric vehicles and are growing in popularity for military and aerospace applications.
- Used in mobile phones, notebook PC's, cameras, camcorders, MP3, PDA's
- Used in power tools such as cordless drills, sanders, saws and variety of garden equipment including whipper-snippers and hedge trimmers.
- Secondary non-aqueous lithium batteries provide reliable backup power to load equipment in a network environment of tele-communications provider.

5. Explain the construction and working principle of dry cell with reactions.

Ans: Dry cell:

- Dry cell consists of a cylindrical zinc container which acts as an anode.
- A graphite rod is placed in the center.

- The graphite rod does not touch the base and it acts as cathode.
- The graphite rod is surrounded by powdered MnO_2 and carbon.
- The remaining space b/w cathode and anode is filled with a paste of NH_4Cl and ZnCl_2 .
- The graphite rod is fitted with a metal cap and the cylindrical cell is sealed at the top with a pitch.

Anode : Zinc (Zn)

Electrolyte : NH_4Cl , ZnCl_2 , MnO_2

Cathode : Carbon Rod (Graphite)

EMF : 1.5V

Reactions :

The reactions takes place in the cell are :

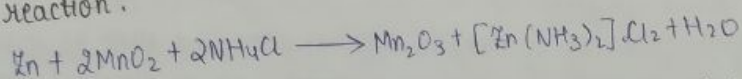
At anode : $\text{Zn} \longrightarrow \text{Zn}^{+2} + 2\text{e}^-$ (oxidation)

At cathode : $2\text{MnO}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \longrightarrow \text{Mn}_2\text{O}_3 + 2\text{OH}^-$ (reduction)

$2\text{NH}_4\text{Cl} + 2\text{OH}^- \longrightarrow 2\text{NH}_3 + 2\text{Cl}^- + 2\text{H}_2\text{O}$

$\text{ZnCl}_2 + 2\text{NH}_3 \longrightarrow [\text{Zn}(\text{NH}_3)_2]\text{Cl}_2$ (diamine dichloro zinc)

Net redox reaction :



6. Derive Nernst equation. Explain how it can be utilized to find the emf of an electrolyte concentration cell.

Nernst equation: It gives the relationship b/w electrode potentials and concentration of electrolyte solutions.

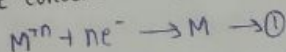
$$E_{\text{M}^{n+}/\text{M}} = E_{\text{M}^{n+}/\text{M}}^\circ - \frac{2.303RT}{nF} \log \frac{[\text{M}_{(\text{s})}]}{[\text{M}^{n+}_{(\text{aq})}]}$$

But at STP conditions $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$, $T = 298 \text{ K}$, $F = 96500 \text{ C}$. Then Nernst eqn becomes

$$= E_{\text{M}^{n+}/\text{M}}^\circ - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{[\text{M}]}{[\text{M}^{n+}]} \quad [\because \text{M}^\circ = 1] \Rightarrow \left[E^\circ - \frac{0.0591}{n} \log \frac{1}{[\text{M}^{n+}]} \right]$$

$$E_{\text{M}^{n+}/\text{M}} = E_{\text{M}^{n+}/\text{M}}^\circ + \frac{0.0591}{n} \log [\text{M}^{n+}]$$

Emf of an electrolyte concentration cell :



Nernst equation $E = E^\circ - \frac{0.0591}{n} \log K \rightarrow \text{②}$

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

$$E_{\text{M}^{n+}/\text{M}} = E_{\text{M}^{n+}/\text{M}}^\circ + \frac{0.0591}{n} \log [\text{M}^{n+}]$$

$$E_{\text{M}^{n+}/\text{M}} = E_{\text{M}^{n+}/\text{M}}^\circ + \frac{0.0591}{n} \log C \quad [\because [\text{M}^{n+}] = C]$$

$$\left[\because K = \frac{\text{M}}{\text{M}^{n+}} \Rightarrow E = E_{\text{M}^{n+}/\text{M}}^\circ - \frac{0.0591}{n} \log \frac{1}{[\text{M}^{n+}]} \quad [\because \text{M}^\circ = 1] \right]$$

7. What is electrochemical series? Explain the electrochemical series with its applications.

Ans: Electrochemical series:

When the various electrodes (metals) are arranged in the order of increasing value of standard reduction potential on hydrogen scale, then the arrangement is called electrochemical series.

When the various electrodes (metals) are arranged in the order of decreasing value of standard oxidation potential on hydrogen scale, then the arrangement is called e.c.s.

Applications of electrochemical series:

1. Calculation of standard emf of cell.
2. Relative ease of oxidation or reduction.
3. Displacement of one element by the other.
4. Hydrogen displacement behaviour.
5. Corrosion tendency of the elements.

8. What are reference electrodes? Describe the construction of calomel electrode. How the potential of calomel electrode varies with concentration of KCl.

Ans: Reference electrodes: Because of the inconveniences in the usage of hydrogen electrode like maintenance of accurate pressure, inconvenience in handling gas secondary electrodes were developed. Such electrodes are known as reference electrodes.

Construction of calomel electrode:

- It is a secondary-reference electrode.
- It is a mercury-mercurous chloride ($\text{Hg}-\text{Hg}_2\text{Cl}_2$) electrode.
- The calomel electrode is used as only reducing electrode i.e. as cathode only. It consists of a glass tube having a side tube on each side.
- One side tube acts as salt bridge and other is used to fill KCl solution.
- The high purity mercury is placed at the top of this tube and connected to the circuit by the means of Pt wire, sealed in glass tube.
- The surface of Hg is covered with a paste of mercurous chloride (calomel) & Hg in KCl soln.
- The electrolyte is the soln of KCl. The electrode is connected with the help of side tubes on the left through salt bridge with the other electrolyte whose potential has to be determined.

→ A Pt wire is sealed into glass tube which is in contact with Hg & electrode shown as $\text{Hg}, \text{Hg}_2\text{Cl}_{2(s)} / \text{KCl (saturated soln)}$. Potential of the calomel electrode depends on ^{the concentration of} KCl.

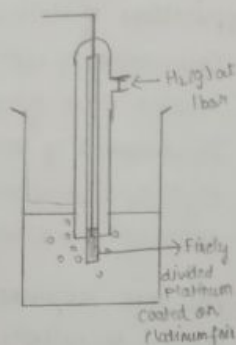
Concentration of KCl	0.1N	1.0N	Saturated	Representation of Calomel electrode
Electrode potential (V)	0.3335	0.2810	0.2422	$\text{Hg}, \text{Hg}_2\text{Cl}_{2(s)} (\text{Saturated soln})$

9. What is standard electrode potential. Describe the construction of standard hydrogen electrodes giving the diagram and electrode reaction.

Ans: Standard ^{electrode} ~~hydro~~ potential: It is the measure of tendency of a metallic electrode to lose or gain electrons, when it is in contact with a solution of its own salt of one molar concentration at 25°C.

Standard hydrogen electrode:

- It is used as primary reference electrode for measuring the emf of all other electrodes in their standard conditions.
- The emf of standard hydrogen electrode is 0.00 eV at all temp.
- Hydrogen electrode consists of hydrogen gas at one atmosphere in equilibrium with H^+ ions of 1 mole in a sol'n.
- Electrical contact of this electrode provided by an inert metal like platinum coated with platinum black.
- When this electrode is used as cathode then it is denoted by $H^+/H_2 (Pt)$.
- When it is connected with anode it is denoted with $(Pt) H_2/H^+$.



10. What is electrochemical cell? Explain the construction and functioning of Daniel cell.

Ans: Electrochemical cell: An electrochemical cell is device which converts chemical energy into electrical energy. Are commonly referred as voltaic or galvanic cell.

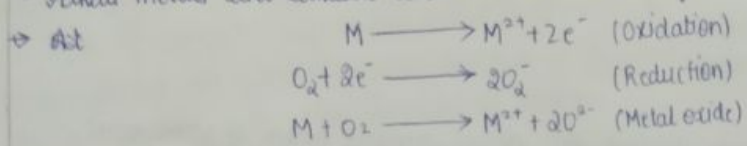
Construction and functioning of Daniel cell:

- Daniel cell is a typical example of galvanic cell.
- Daniel cell consists of a beaker containing copper rod dipped in $CuSO_4$ sol'n which is connected to another beaker containing zinc rod dipped in $ZnSO_4$ sol'n by a salt bridge.
- Salt bridge is an inverted U-tube containing saturated sol'n of some electrolyte such as KCl , KNO_3 , NH_4NO_3 which does not undergo chemical change during process.
- The saturated sol'n is generally taken in agar-agar jelly or gelatin.
- The salt bridge allows the flow of ions to pass through it when the flow of electric current takes place.
- It completes the electric circuit and maintains the electrical neutrality of two half cells solutions.
- When the circuit is completed, electric current flows through the external circuit as indicated by an ammeter.

11. What is oxidation corrosion and how does it take place? Describe the mechanism of oxidation corrosion.

Ans: Oxidation corrosion;

- This is carried out by the direct action of oxygen at low or high temperature on metals in absence of moisture.
- Alkali metals & alkaline earth metals are rapidly oxidized at low temperatures.
- At high temperatures all metals are oxidized (except Ag, Au, Pt).
- This is carried out by the direct action of oxygen at low or high temperatures on metals in absence of moisture.
- Alkali metals and alkaline earth metals are rapidly oxidized at low temperatures.



Mechanism of Oxidation corrosion:

Initially the surface of metal undergoes oxidation and the resulting metal oxide scale forms a barrier which restricts further oxidation. The extent of corrosion depends upon the nature of metal oxide.

a) If the metal oxide is stable, it behaves as a protective layer which prevents further corrosion.

Ex: The oxide films of Al, Sn, Pb, Cu, Cr, W, etc are stable and therefore further corrosion is prohibited.

b) If the metal oxide is unstable, the oxide layer formed decomposes back into metal and oxygen, oxidation corrosion is not possible.

Ex: Au, Pt doesn't undergo oxidation corrosion.

c) If the metal oxide layer is volatile, then the oxide layer volatilizes after formation and leaves the underlying metal surface exposed for further attack. This causes continuous corrosion which is extensive in Molybdenum oxide (MoO_3).



d) If the metal oxide layer is porous, the oxide layer formed has pores or cracks. In this case the atmospheric oxygen penetrates through the pores or cracks and corrodes the underlying metal surface. This causes continuous corrosion till conversion of metal into its oxide is completed.

12. Explain the rusting of iron with the help of electrochemical theory of corrosion?

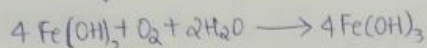
Ans: Rusting of iron is due to the absorption of oxygen. Rusting of iron in neutral aqueous sol'n of electrolytes in presence of atmospheric oxygen. Usually the surface of iron is coated with a thin film of iron oxide. If the film develops cracks, anodic areas are created on the surface. While the metal parts act as cathodes. It shows that anodes are small areas, while the rest metallic part forms large cathodes. The released e^- flow from anode to cathode through iron metal.

At anode: $\text{Fe} \longrightarrow \text{Fe}^{2+} + 2\text{e}^-$ (oxidation)

At cathode: $\frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \longrightarrow 2\text{OH}^-$ (reduction)

Overall reaction: $\text{Fe}^{2+} + 2\text{OH}^- \longrightarrow \text{Fe(OH)}_2$

If oxygen is excess, ferrous hydroxide is easily oxidized to ferric hydroxide



The product called yellow rust corresponds to $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$

13. Define corrosion. Explain dry corrosion and its mechanism.

Ans: Corrosion: The process of decay metal by environmental attack is known as corrosion.

There are two theories of corrosion.

- 1] Dry corrosion
- 2] Wet corrosion.

Dry corrosion:

This type of corrosion occurs mainly through the direct chemical action of atmospheric gases like O_2 , halogens, H_2S , SO_2 , N_2 or anhydrous inorganic liquid with the metal surface.

There are three types of chemical corrosion:

1] Oxidation corrosion

2] Corrosion due to other gases

3] Liquid metal corrosion.

This type of corrosion occurs in absence of moisture either by:

1] Oxidation corrosion: By direct action of dry oxygen (stable, unstable, porous, volatile)

2] Corrosion due to other gases: The attack by SO_2 , CO_2 , Cl_2 , etc. Degree of attack depends on formation of protective or non-protective films on metal surface on the basis on Pilling Bedworth rule.

$$\text{Specific volume ratio} = \frac{\text{Volume of metal oxide}}{\text{Volume of metal}}$$

3] Liquid metal corrosion: Due to the chemical action of flowing liquid metal at high temperatures on solid metal/alloy. The corrosion reaction involves either dissolution of a solid metal by a liquid metal or internal penetration of liquid metal into solid metal.

14. What is electrochemical corrosion? Describe the mechanism of electrochemical corrosion by hydrogen evolution and oxygen absorption.

Ans: Electrochemical corrosion/Wet corrosion:

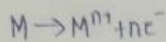
This type of corrosion occurs where a conducting liquid is in contact with the metal. This corrosion occurs due to the existence of separate anodic and cathodic parts, b/w which current flows through the conducting solution.

→ At anodic area, oxidation reaction occurs thereby destroying the anodic metal either by dissolution or formation of compounds. Hence corrosion always occurs at anodic parts.

Mechanism of wet corrosion:

→ Electrochemical corrosion involves flow of e^- b/w anode and cathode.

→ The anodic reaction involves dissolution of metal liberating free e^-

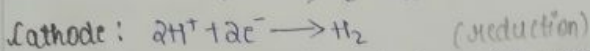


→ The cathodic reaction consumes e^- with either evolution of hydrogen or absorption of oxygen which depends on the nature of corrosive environment.

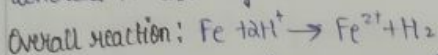
Evolution of hydrogen:

This type of corrosion occurs in acidic medium.

Ex: Considering the metal Fe, anodic reaction is dissolution of iron as ferrous ions with liberation of electrons.



The e^- s released flow through the metal from anode to cathode, whereas H^+ ions of acidic solution are eliminated as hydrogen gas.



This type of corrosion causes displacement of hydrogen ions from the solution by the metal ions. All metals above hydrogen in electrochemical series have a tendency to get dissolved in acidic solution with simultaneous evolution of H_2 gas. The anodes are large areas, whereas cathodes are small areas.

Absorption of oxygen:

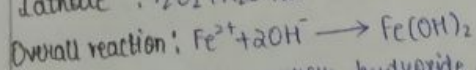
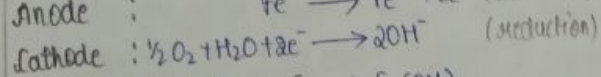
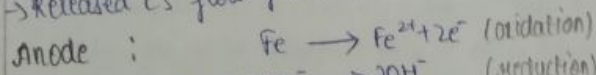
→ For example, rusting of iron in aqueous solution of electrolytes in presence of atmospheric oxygen.

→ Usually the surface of iron is coated with thin film of iron oxide.

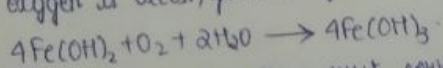
→ If the film develops cracks, anodic areas are created on the surface.

→ While metal part acts as cathode. It shows that anodes are small ^{areas} parts, while the rest metallic part forms large cathodes.

→ Released e^- s flow from anode to cathode through iron metal.



If oxygen is excess, ferrous hydroxide is easily oxidized to zinc hydroxide.



The product called yellow rust corresponds to $Fe_2O_3 \cdot 3H_2O$.

15. Describe the role of nature of oxide formed in oxidation corrosion. State and explain.

Pilling-Bedworth rule.

Ans: Role of nature of oxide formed in oxidation corrosion:

- 1) If metal oxide is stable - behaves as protective layer - (prevent corrosion)
- 2) If metal oxide is unstable - layer formed decomposes back into metal and oxygen (not protective)
- 3) If metal oxide is volatile - volatilizes & leaves the metal surface exposed (cont. corrosion)
- 4) If metal oxide is porous - pores & cracks are formed (cont. corrosion till conversion of metal into oxide is completed)

Pilling - Bedworth Rule:

When the oxide film is sufficiently porous so that the diffusion of cation M^+ and anion O^{2-} takes place smoothly then oxidation corrosion takes place continuously. It describes the porous and non-porous nature of metallic oxide which is formed during corrosion. According to this rule specific ratio calculated as follows:

$$\text{Specific volume ratio} = \frac{\text{volume of metal oxide}}{\text{volume of metal}}$$

- If the SVR is smaller, then oxidation corrosion takes place, here oxide films are sufficiently porous for diffusion of M^+ and O^{2-} .
- If SVR is more than 1, then it will be non-porous.

$$R_{PB} = \frac{V_{\text{oxide}}}{V_{\text{metal}}} = \frac{M_{\text{oxide}} \cdot \rho_{\text{metal}}}{n \cdot M_{\text{metal}} \cdot \rho_{\text{oxide}}}$$

- If volume of metallic oxide is equal or greater in volume to metal surface, then metal surface is compact, non-porous, protective.

Ex: Cu, In, Al, Ni, Cr forms oxides whose volume is greater than volume of metal.

- If volume of metallic oxide is less than the volume of the metal surface, the oxide is porous, non-protective.

Ex: Alkali and alkaline earth metals - Li, Na, K, Mg.

16. Describe the process of galvanization of iron. How does it prevent the corrosion of iron and mention its applications.

Ans: Galvanizing:

Galvanizing is a process in which the iron article is protected from corrosion by coating it with a thin layer of zinc. At first iron or steel is cleaned by pickling with dil. H_2SO_4 at a temperature range of $60^\circ - 90^\circ C$ for 15-20 minutes. Therefore, it removes scale, rust and other impurities present. Then after dipped molten zinc in the bath at $425 - 450^\circ C$ to prevent it from oxide formation, the surface of bath is covered with a flux (NH_4Cl). When the iron piece is taken out it is coated with a thin layer of zinc & to remove excess zinc, it is passed through a pair of hot rollers; lastly, it is annealed at a temperature of $450^\circ C$.

Applications of galvanizing:

- It is widely used for protecting iron exposed to the atmosphere, as in the case with roofs, wire fences, pipes and articles fabricated from galvanized sheets like buckets, tubes.
- Galvanized ware is not used for keeping eatables because of the solubility of zinc.
- The popularity of galvanizing is due to the low cost of zinc.
- Easy application and the anodic protection offered by the zinc.

17. Explain the process of tinning in corrosion control with its applications.

Ans: Tinning:

The process of coating tin over the iron or steel articles to protect it from corrosion is known as tinning. In this process, first, iron sheet is treated in dil. H_2SO_4 (pickling) to remove any oxide film if present. A cleaned iron sheet is passed through a bath molten flux like zinc chloride, then through molten tin and finally through a suitable vegetable oil. Lastly it is passed over rolls to adjust the thickness of the tin layer, which may be about 0.002 mm thick.

Applications:

- Tinning of mild steel plates is done mostly for the requirements of the food stuff industry.
- Tin is a nobler metal than iron, therefore, it is more resistance to chemical attack.

18. What is cathodic protection? Explain the sacrificial anodic protection method of controlling corrosion and write its applications.

Ans: Cathodic protection:

The cathodic protection of metals is used to control corrosion metals where it is impartibly to alter the nature of the corrosion medium. The principle involved in this method is to protect metals & alloys from corrosion by making them completely cathodic. Since there will not be any anodic area on the metal, therefore corrosion does not occur.

The following are two types of cathodic protection.

a) Sacrificial anodic protection

b) Impressed current cathodic protection.

Sacrificial anodic protection method:

- In this method, metal structure can be protected from corrosion by connecting it with wire to a more anodic metal.
- As this more active metal is sacrificed in process of saving metal from corrosion, it is known as sacrificial anode.
- The metals which are commonly used as sacrificial anodes are Mg, Zn, Al and their alloys.

Applications of sacrificial anodic protection:

1. Protection of underground cables and pipelines from soil corrosion
2. Protection of ships and boat hulls from marine corrosion
3. Prevention of rusty water by inserting Mg sheets or rods into domestic water boilers/tanks

19. Explain the impressed current method of cathodic protection with a neat diagram and write its applications.

Ans: Impressed current cathodic protection:

An impressed current is applied to convert the corroding metal from anode to cathode. The applied current is in opposite direction since to nullify the corrosion current.

This can be accomplished by applying sufficient amount of direct current source like battery or rectifier to an anode like graphite, high silica iron, stainless steel or platinum buried in soil or immersed in corrosion medium & connected to corroding metal structure which is to be protected.

In imp. current cathodic protection, \bar{e} are supplied from an external cell, so that the object itself becomes cathodic and not oxidized.

Applications:

This type of cathodic protection has been applied to buried structures such as tanks and pipelines, transmission line-towers, marine piers, laid-up ships, etc. since their operating and maintenance costs are less, they are well suited for large structures and long term operations.

20. Illustrate the reactions involved in electroplating of copper with a neat diagram and write the advantages of electroplating.

Electroplating of copper over metal object:

- The metal object, to be plated is first treated ^{with} dil HCl or dil H_2SO_4
- The cleaned object is the made cathode of an electrolytic cell & pure copper plate as anode. $CuSO_4$ & dil- H_2SO_4 sol'n are taken as electrolyte.
- When current is passed from battery through sol'n Cu dissolves in electrolyte & deposits uniformly on the metal object.

Chemical reactions:

At anode: $Cu \rightarrow Cu^{2+} + 2e^-$

At cathode: $Cu^{2+} + 2e^- \rightarrow Cu$ deposited on base metal.

Advantages of electroplating:

This process is widely used in automobiles, aircrafts, plating for decoration. Also used in refrigerators, jewellery, radios, cameras, typewriters, umbrellas, watches, plating on nonmetals etc.

Conditions for electroplating of Cu over metal object:

Anode / Coating metal: Pure copper plate

Cathode / Base metal: Metal object

Electrolyte: $CuSO_4$ and dil H_2SO_4

Temperature: $40-45^\circ C$

Current: $30-40 mA/cm^2$

Part-C-(Problem solving and critical thinking questions)

1. Calculate the emf of voltaic cell $\text{Fe} | \text{Fe}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu}$. Given the electrode potentials of copper and iron are 0.34 volt and -0.44 volt respectively.

A. given $\text{Fe} | \text{Fe}^{2+}(\text{aq}) || \text{Cu}^{2+}(\text{aq}) | \text{Cu}$

$$E^\circ_{\text{Cu}} = 0.34\text{V} \quad E^\circ_{\text{Fe}} = -0.44\text{V}$$

$$\text{emf} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$= 0.34\text{V} - (-0.44\text{V})$$

$$= 0.78\text{V}$$

2. Calculate the EMF of a cell if the reduction potentials of the cell are -0.763V and 0.337

A. $E^\circ_{\text{anode}} = -0.763\text{V}$ $E^\circ_{\text{cathode}} = 0.337\text{V}$.

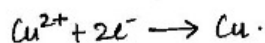
$$\text{emf} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

$$= 0.337\text{V} - (-0.763\text{V})$$

$$= 1.1\text{V}$$

3. Calculate the electrode potential of the copper wire dipped in 0.1M CuSO_4 solution at 25°C . The standard reduction electrode potential of copper is +0.34V.

A. $E^\circ_{\text{Cu}} = 0.34\text{V}$; $T = 25^\circ\text{C}$; $C = 0.1\text{M CuSO}_4$.



$$\text{Now } E = E^\circ + \frac{0.0591}{n} \log_{10} [\text{Cu}^{2+}]$$

$$E = 0.34 + \frac{0.0591}{2} \log_{10} [0.1]$$

$$= 0.34 + 0.02955 \times (-1)$$

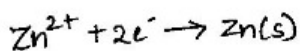
$$= 0.34 - 0.02955$$

$$E = 0.31045\text{V}$$

4. Calculate the electrode potential of the zinc rod dipped in 0.1M ZnSO_4 solution at 25°C . The standard reduction electrode potential of zinc is -0.76V .

A. $E^\circ_{\text{Zn}} = -0.76\text{V}$ (reduction) ; $T = 25^\circ\text{C}$; 0.1M of ZnSO_4 .

$\text{Zn} \rightarrow \text{Zn}^{2+} + 2e^-$ Now reduction reaction is



$\therefore E^\circ_{\text{Zn}}(\text{oxidation}) = 0.76\text{V}$; $E^\circ_{\text{Zn}}(\text{reduction}) = -0.76\text{V}$

$$E_{\text{Zn}^{2+}/\text{Zn}} = E^\circ_{\text{Zn}^{2+}/\text{Zn}} + \frac{0.0591}{n} \log_{10} [\text{Zn}^{2+}]$$

$$= -0.76 + \frac{0.0591}{2} \log_{10} [0.1]$$

$$= -0.76 - 0.02955$$

$$= -0.78955\text{V}$$

$$E = -0.79\text{V}$$

5. The standard reduction potentials of Zn^{2+}/Zn and Cu^{2+}/Cu are -0.76V and $+0.34\text{V}$ respectively. What is the emf of the cell?
 $\text{Zn(s)} | \text{Zn}^{2+} (0.05\text{M}) || \text{Cu}^{2+} (0.005\text{M}) | \text{Cu(s)}$.

A. given $\text{Zn(s)} | \text{Zn}^{2+} (0.05\text{M}) || \text{Cu}^{2+} (0.005\text{M}) | \text{Cu(s)}$

$$\text{emf} = E_{\text{cathode}} - E_{\text{anode}}$$

$$E_{\text{cathode}} = E_{\text{Cu}} = E^\circ_{\text{Cu}} + \frac{0.0591}{n} \log_{10} [\text{Cu}^{2+}] \quad \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$$

$$= 0.34 + \frac{0.0591}{2} \log_{10} [0.005] \quad E^\circ_{\text{Cu}} = 0.34\text{V}$$

$$= 0.272\text{V}$$

$$E_{\text{anode}} = E_{\text{Zn}} = E^\circ_{\text{Zn}} + \frac{0.0591}{n} \log_{10} [\text{Zn}^{2+}] \quad \text{Zn}^{2+} + 2e^- \rightarrow \text{Zn}$$

$$= -0.76 + \frac{0.0591}{2} \log_{10} [0.05] \quad E^\circ_{\text{Zn}} = -0.76\text{V}$$

$$= -0.7984\text{V}$$

$$\text{emf of the cell} = E_{\text{cathode}} - E_{\text{anode}} = 0.272\text{V} - (-0.798\text{V})$$

$$= 1.07\text{V}$$

6. What is the overall cell reaction for $\text{Zn(s)} | \text{Zn}^{2+}(0.2\text{M}) || \text{Ag}^+(0.002\text{M}) | \text{Ag(s)}$ and calculate the emf of the cell at 25°C .
The standard emf of the cell is 1.54V .

A. Cell reactions for $\text{Zn(s)} | \text{Zn}^{2+}(0.2\text{M}) || \text{Ag}^+(0.002\text{M}) | \text{Ag(s)}$

at anode: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$

at cathode: $2\text{Ag}^+ + 2\text{e}^- \rightarrow 2\text{Ag}$ (at cathode)

net reaction: $\text{Zn} + 2\text{Ag}^+ \rightarrow \text{Zn}^{2+} + 2\text{Ag}$ $n = 2\text{e}^-$

$$\text{Emf} = E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} \quad \text{at } T = 25^\circ\text{C}$$

$$= 1.54 - \frac{0.0591}{2} \log_{10} \frac{[0.2]}{[0.002]^2} \quad \because E^\circ_{\text{cell}} = 1.54\text{V}$$

$$= 1.54 - 0.1388$$

$$= 1.4011\text{V}$$

7. Why does a steel pipe in a large copper tank corrode and causing rapid destruction?

A. Iron or steel is anodic with respect to copper. When a steel pipe fitted in a large copper tank is exposed to atmosphere, galvanic corrosion starts and the anodic metal (iron or steel) starts corroding. Moreover, small sized steel pipes (anode) in a large sized copper tank (cathode) causes rapid and intense corrosion (or destruction) of steel pipe.

8. How is cathodic protection of iron different from its galvanization?

A. In cathodic protection, the iron object is made cathode by connecting it with a more reactive metal like Mg, Zn, etc. whereas in galvanisation, the iron object is protected from corrosion by coating it with zinc.

9. Galvanized container is not used for storage of food products, but tin coated container is used. Comment on the statement.

A. Galvanized containers cannot be used for storing acidic food stuffs as zinc reacts with food forming poisonous compounds because of the solubility of zinc.

Tin coated containers can be used for storing any food as tin is non toxic and protects metal from corrosion.

10. Iron does not rust if the zinc coating is broken in a galvanized iron pipe, but rusting occurs much faster if the tin coating over iron is broken.

A. Zinc is more electro-positive than iron. Therefore, as long as zinc is there on the iron pipe, zinc acts as anode and the iron as cathode. As a result, rusting of iron is prevented.

On the other hand, tin is less electro-positive than iron. Therefore, when tin coating over iron gets broken, iron acts as anode and gets oxidized. Thus even when tin is there, the exposed iron gets rusted.