Module 3

CONCEPT OF ELECTROCHEMISTRY

3.1 INTRODUCTION

Electrochemistry is a branch of chemistry which includes the study of chemical reactions brought about by electrical energy and of chemical reactions giving rise to electrical energy. It deals with qualitative and quantitative study of mutual conversion of chemical and electrical forms of energy. A device which carries out such conversions is called electrochemical cell. In the study of electrochemistry following two types of electrochemical cells are employed.

(a) **Electrolytic cell** : An arrangement in which electrical energy is used to bring about a desired chemical change. i.e., convert electrical energy into chemical energy. These cells are used in electrolysis of water in electrorefining of metals, electroplating of metals etc.

(b) **Galvanic cells** : An arrangement in which chemical energy is converted into electrical energy e.g., Daniel cell, lead storage battery, dry cell etc.

An electrochemical cell is a device consisting of two electrodes, each in contact with a solution of its own ions and transforms the free energy change of the redox reaction at the electrodes into electrical energy. In a redox reaction, the energy released in a reaction due to the movement of charged particles gives rise to a potential difference. The maximum potential difference is called the electromotive force (EMF) in volts. It should apparent form the above that the potential difference between the electrodes of a cell is the major of the tendency for the cell reaction to take place. The more positive is the cell potential, the greater is the tendency for the reaction to proceed to spontaneity.

Q.1 Classify various types of electrochemical cells with neat diagram.

Ans.: The electrochemical cells are classified as, (i) Voltaic cell (Galvanic celfy (ii) Electrolytic cell, (iii) Concentration cell, (iv) Fuel cell.

(i) Voltaic cell (Galvanic cell):

The free energy change in a galvanic cell must be negative and the potential difference of the electrodes (cell voltage) must be positive. Energy is released from spontaneous redox reaction. System does work on load/surrounding. In galvanic cell the free energy change of electrode redox reaction is converted into electric energy; that is $\Delta G = -nFE$. The examples of galvanic cells are primary irreversible cells (dry cells) and secondary cells (lead storage batteries).

Dissimilar metals

A galvanic cell
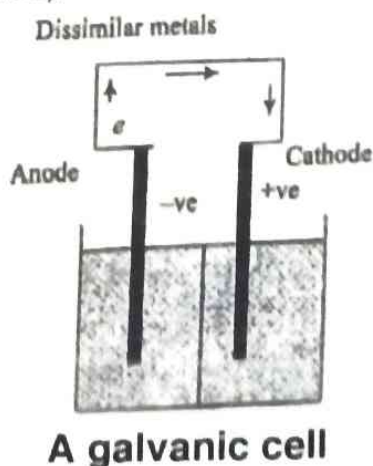
(ii) Electrolytic cell :

It is device in which electrical energy from an external source can be used to produce chemical reactions. Energy is absorbed to drive non-spontaneous redox reaction. Surroundings (power supply) do work on system (cell). In electrolytic cells, the reaction is being driven in the non-spontaneous direction by external electrical force and free energy change is positive.

Power source

$+ve$ $-ve$

Anode   Cathode
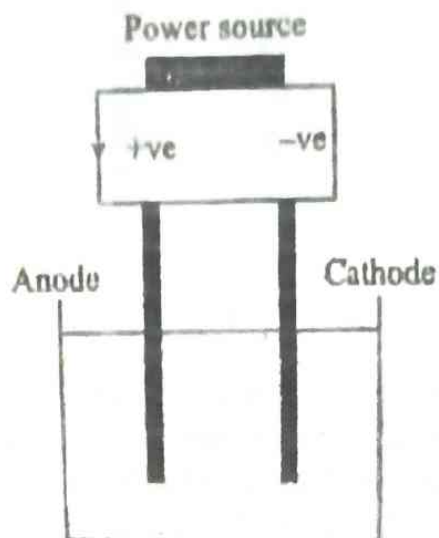
An electrolytic cell

(iii) Concentration cell :

A concentration cell is also an electrochemical device that generates electrical energy when two electrodes of the same metal are in contact with solutions of its ions at different concentrations. In a concentration cell, too, the free energy change of electrode reactions is converted into electric energy.

Similar metals

e

Anode   Cathode

$-ve$ $+ve$

C_1 C_2

$C_2 > C_1$
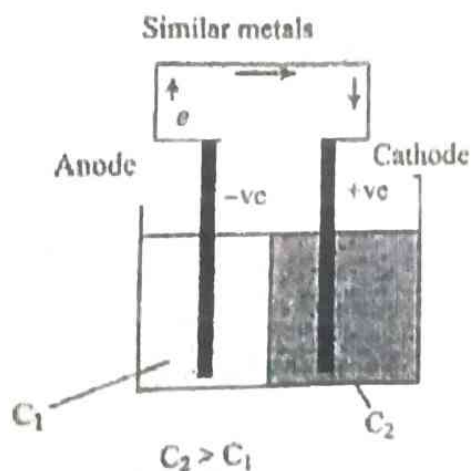
A concentration cell

(iv) Fuel cell :

A fuel cell is also an electrochemical device, which operates with continuous replenishment of the fuel at the electrode and no charging is required. In a fuel cell, the free energy change of electrode redox reactions is converted into electric energy.
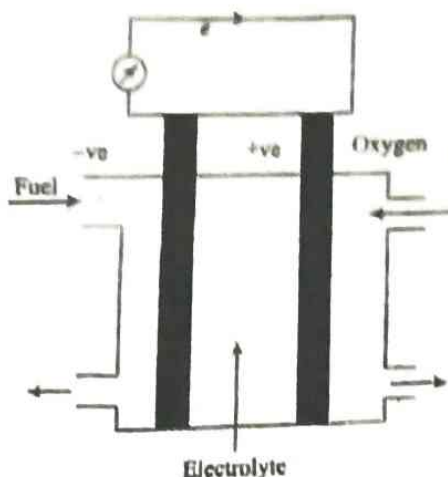
A fuel cell

Q.2 **Give applications of Electrochemical cells.**

Ans.: **Applications of Electrochemical cells :**
- They are used in electro-refining of many non-ferrous metals. They are used in electro-winning of these metals.
- The production of high purity lead, zinc, aluminium and copper involves their use.
- Metallic sodium can be extracted from molten sodium chloride by placing it in an electrolytic cell and passing an electric current through it.
- Many commercially important batteries are made up of galvanic cell.
- Fuel cells are an important class of electro chemical cells that serve as a source of clean energy in several remote locations.

**Q.3** **Distinguish between Galvanic Cell and Electrolytic Cell.**

Ans.:

	Galvanic Cell	Electrolytic Cell
1.	In these cells, chemical energy is converted into electrical energy.	In these cells, electrical energy is converted into chemical energy.
2.	The redox reactions that take place in these cells are spontaneous in nature.	The redox reactions that take place in these cells are non-spontaneous. An input of energy is required for redox reactions to proceed in these cells.
3.	In these cells the anode is negatively charged and cathode is positively charged.	These cells feature positively charged anode and negatively charged cathode.
4.	The electrons originate from the species that undergoes oxidation.	Electrons originate from an external source.
5.	Electrodes are of dissimilar metals.	Electrodes used may be of dissimilar or same metals.
6.	Electrode is immersed in its own ions and both have separate compartments.	Both the electrodes are immersed in the same electrolyte solution.
7.	The two electrolyte solutions are connected by a salt bridge.	No salt bridge is required.

3.2 CONCEPT OF ELECTRODE POTENTIAL

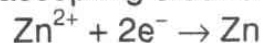**Q.1** **Explain Electrode Potential.**

Ans.: When a piece of metal is immersed in a solution of its own ions. a potential difference is created at the interface of the metal and the solution. The magnitude of the potential difference is a major of the tendency of the electrode to undergo oxidation or reduction or the tendency to loose or gain electrons. The immersed metal is an electrode and the potential due to reaction at the interface of the electrode and the solution is called the electrode potential.

In order to understand the origin of electrode potential, consider a zinc electrode consists of zinc strip dipped in $ZnSO_4$. Nernst proposed that in the electrode there will be two tendencies – oxidation and reduction. If oxidation tendency occurs then Zn atoms on the metal surface undergo oxidation, leaving behind electrons on the surface.
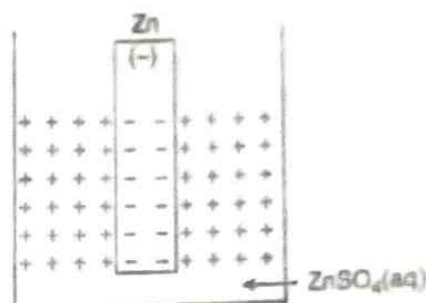
$$Zn \rightarrow Zn^{2+} + 2e^-$$
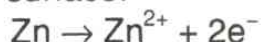
The Zn^{2+} ions pass into the solution and the metal strip becomes negatively charged. The positively charged metal ions accumulate around the metal as shown in the Figure.
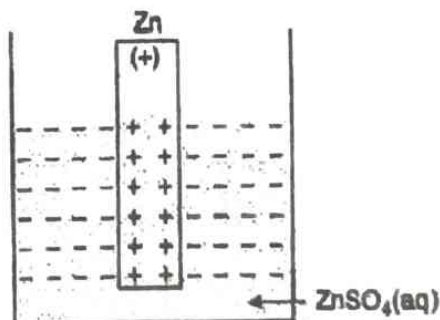
Origin of electrode potential (oxidation)

If the reduction tendency occurs, then Zn^{2+} ion in the solution undergo reduction by accepting electrons from the metallic surface.

$$Zn^{2+} + 2e^- \rightarrow Zn$$

Thus the metallic surface becomes positively charged and the negatively charged ions accumulate around the metal as shown in the figure.

Origin of electrode potential (reduction)

The two tendencies happen simultaneously on the same electrode. Hence, an electrical double layer called Helmboltz electrical double layer (HED)s established at the metal-aqueous solution interface. Across the HED layer. there is movement of charges. This results in the potential called electrode potential. It is defined as the potential that exists between the metal or the gas and it's ions in aqueous solution, at their equilibrium when they are in contact with each other. The electrode potential of a metal is thus a major of its tendency to loose or gain electrons when in contact with a solution of its own salt.

Q.2 **Define Standard Electrode Potential (E°).**

Ans.: It is defined as the potential that exists between the metal or the gas and its aqueous solution of unit concentration at 298°K when the sum of all partial

pressures of the gaseous reactants and products, if any, is equal to 1 atm pressure. This value is considered to compare the relative abilities of different electrodes to undergo oxidation or reduction.

3.3 REFERENCE ELECTRODE

The potential of an electrode cannot be accurately measured. It is not feasible to connect a measuring device to the solution of electrode, as it may lead to another equilibrium along with the existing one. This problem can be overcome if the electrode is connected to another electrode of known potential which can be termed as reference electrode. The criteria for an electrode to act as a reference electrode are :
1. The potential of such an electrode should be known, the conditions of utility.
2. The potential of the electrode should show minimum variation with temperature. In other words, the potential gradient with respect to temperature should be minimum.

The most commonly used reference electrode is the hydrogen electrode. The potential of all other electrodes are measured with respect to the hydrogen electrode which is also called a primary reference electrode. There are few more reference electrodes which are standardized using standard hydrogen electrodes and then can be used as reference electrodes. They are called as secondary reference electrodes. Calomel electrode and Silver-Silver Chloride electrode are the examples of secondary reference electrodes.
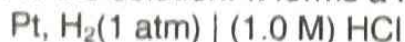
3.3.1 Standard Hydrogen Electrode (SHE) :
Q.1 **Explain Standard Hydrogen Electrode with neat diagram.**
Ans.: It consists of a platinum foil dipped in 1.0 M HCl. The platinum foil is enclosed in a thick walled glass tube and connected to an external contact wire. Pure hydrogen is passed into the container at 1 atm pressure through the inlet at the top. Excess hydrogen leaves the electrode through the outlet at the bottom as shown in the Figure.
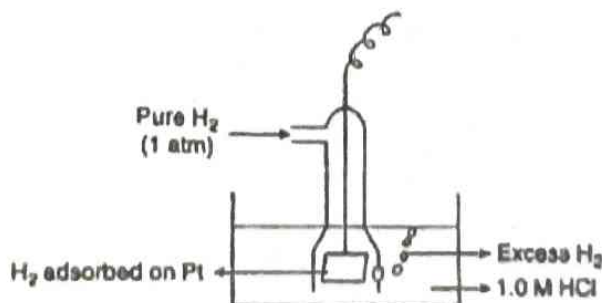
Standard Hydrogen Electrode

Pure hydrogen gets adsorbed on the platinum surface and is in contact with H^+ ions in the solution. It forms a reversible electrode and can be represented as :
    Pt, H_2(1 atm) | (1.0 M) HCl
If reduction occurs at the electrode, the reaction with be :
    $2H^+ + 2e^- \leftrightarrow H_2$
As the potential cannot be measured directly, it is assumed to be zero at 298 K. Since E° of SHE is assumed to be zero, the potential of the second electrode can be obtained. The potential of an electrode measured at standard condition is known as standard electrode potential. The electrode potential is a measure of reduction potential of an electrode with respect to SHE.

Limitations of SHE :
1. SHE cannot be used in presence of strong oxidizing and reducing agents.
2. It is difficult to maintain unit molar concentration of hydrogen throughout and to pass hydrogen at 1 atm pressure.
3. Presence of arsenic compounds would get adsorbed on platinum foil and poisons the surface thereby affecting equilibrium of the reaction.
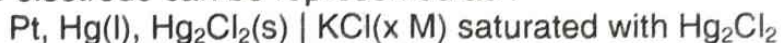
3.3.2 Calomel Electrode

Q.2 Explain Calomel Electrode with neat diagram.

Ans.: It consists of a thin layer of pure mercury at the bottom of the container. It is covered with a paste of Hg, Hg_2Cl_2 and KCl of known concentration. The rest of the container is filled with KCl solution of known concentration, saturated with $Hg_2 Cl_2$ as shown in the Figure.
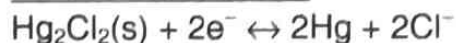

KCl(xM) sat. with Hg_2Cl_2
Pt wire
Paste of Hg, Hg_2Cl_2 and KCl(xM)
Pure mercury
Porous plug
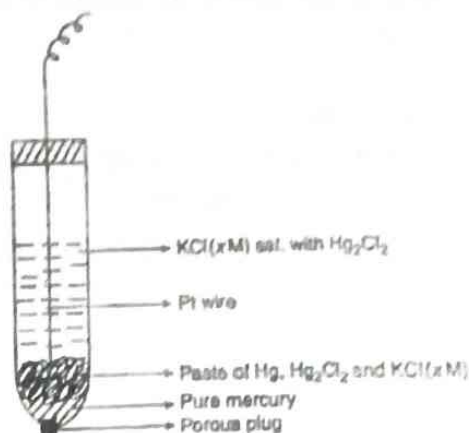
Calomel Electrode

The electrode can be represented as :

Pt, Hg(l), Hg_2Cl_2(s) | KCl(x M) saturated with Hg_2Cl_2

The potential of this electrode depends on the concentration of KCl. It is a reversible electrode.

If reduction occurs at this electrode, the reaction can be shown as :

$$Hg_2Cl_2(s) \leftrightarrow Hg_2^{2+} + 2Cl$$
$$Hg_2^{2+} + 2e^- \leftrightarrow 2Hg$$
$$\overline{}$$
$$Hg_2Cl_2(s) + 2e^- \leftrightarrow 2Hg + 2Cl^-$$
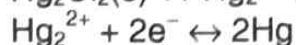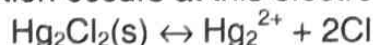
Nernst's equation for the Calomel electrode is :

$$E_{Hg/Hg_2Cl_2} = E^\circ_{Hg/Hg_2Cl_2} - \frac{2.303\,RT}{nF} \log [Cl^-]^2$$

Calomel electrode with saturated KCl and 1.0 M KCl have potential values of 0.2412 V and 0.28 V respectively.

Advantages of Calomel Electrode :
1. It is used in corrosion studies.
2. It is easy to construct and easy to transport.
3. It provides constant potential value with varying temperature.
4. It finds application in laboratories for measuring potential of an electrode.

3.4 ELECTRODE CHEMICAL SERIES

The elements arranged in the increasing order of their standard electrode potential constitute a series called electrochemical series. These values are measured with respect to standard hydrogen electrode at 25°C. The greater the negative value of the ...ential, the greater is the tendency of the metal to pass into solution in the ionic state ...nents occupying higher position in the series have a greater negative potential are d to be highly electronegative and those placed lower in the series are said to be highly electronegative. Metals occupying top positions in the series hold their valence electrons rather loosely and hence exhibit greater tendency to lose electrons. Consequently such metals are highly electropositive and readily oxidized and corroded. On the other hand metals occupying lower positions in the series do not easily lose electrons and hence not corroded easily. All metals standing above in the electrochemical series will have a tendency to displace all metals standing below from dilute solutions containing their ions.

Standard electrode potentials of metals.

(The values given refer to the normal activity of ions at a standard temperature of 25°C)

Metal ion electrode system	Electrode reaction (Acid solution)	Standard electrode potential (E_0) in volts	
Li/Li$^+$	Li$^+$ + e$^-$ = Li	−3.045 (Reactive metals)	
K/K$^+$	K$^+$ + e$^-$ = K	−2.925	
Ca/Ca^{++}	Ca^{+2} + 2e$^-$ = Ca	−2.866	
Na/Na$^+$	Na$^+$ + e$^-$ = Na	−2.714	
Mg/Mg^{++}	Mg^{+2} + 2e$^-$ = Mg	−2.363	
Al/Al^{+++}	Al^{+3} + 3e$^-$ = Al	−1.662	
Mn/Mn^{++}	Mn^{+2} + 2e$^-$ = Mn	−1.180	
Zn/Zn^{++}	Zn^{+2} + 2e$^-$ = Zn	−0.763	
Cr/Cr^{+++}	Cr^{+3} + 3e$^-$ = Cr	−0.744	
Fe/Fe^{++}	Fe^{+2} + 2e$^-$ = Fe	−0.0441	
Cd/Cd^{++}	Cd^{+2} + 2e$^-$ = Cd	−0.441	
Co / Co^{++}	Co^{+2} + 2e$^-$ = Co	−0.277	
Ni/Ni^{++}	Ni^{+2} + 2e$^-$ = Ni	−0.25	
Sn/Sn^{++}	Sn^{2+} + 2e$^-$ = Sn	−0.136	
Pb / Pb^{++}	Pb^{2+} + 2e$^-$ = Pb	−0.126	
H$_2$/2H$^+$	2H^{+2} + 2e$^-$ = H$_2$	0.00	Reference
Cu/Cu^{++}	Cu^{+2} + 2e$^-$ = Cu	0.337	
Cu/Cu$^+$	Cu$^+$ + e$^-$ = Cu	0.522	
Hg/Hg$^+$	Hg$^+$ + e$^-$ = Hg	0.799	
Ag/Ag$^+$	Ag$^+$ + e$^-$ = Ag	0.80	
Hg/Hg^{++}	Hg^{++} + 2e$^-$ = Hg	0.854	
Pd/Pd^{++}	Pd^{++} + 2e$^-$ = Pd	0.987	
Pt / Pt^{++}	Pt^{++} + 2e$^-$ = Pt	1.2	
Au/Au^{+++}	Au^{+++} + 3e$^-$ = Au	1.42	(Noble metals)

All metals standing above hydrogen tend to displace hydrogen from acid solutions. In a coupling of two metals, the metals having higher negative potential becomes anode and gets corroded and the other metal having positive potential becomes cathode and gets protected. The corrosion is more rapid, if a more active metal is placed far away from the less active metal.

3.5 GALVANIC SERIES

Galvanic series (on the basis of relative oxidation potentials in sea water)

More Anodic or Active	(or Corroded end)	
Magnesium		↑
Magnesium alloys		
Zinc		
Aluminium		
Aluminium alloys		
Low carbon steel		
Cast iron		
Stainless steel (active)		
Lead-tin alloys		
Lead		
Tin		
Brass		
Copper		
Bronze		
Copper-Nickel alloys		
Inconel		
Silver		
Stainless steel		
Monel		
Graphite		
Titanium	Noble (cathodic)	
Gold		
Platinum		↓

Although electrochemical series gives very useful information regarding chemical reactivity of metals, it may not be able to provide sufficient information in predicting the corrosion behavior in a particular set of environmental conditions. However, in practical situations many side reactions may take place which influence the corrosion reactions. In view of this, oxidation potential measurements of various metals and alloys in common use have been made using standard calomel electrode as the reference electrode and immersing the metals and alloys in sea water. These are arranged in decreasing order of their activity and this series is known as 'galvanic series'. (above Table)

Whereas in the electrochemical series, metals are arranged from top to bottom in increasing order of their reduction potential. A metal high in the series is more anodic and undergoes corrosion faster than metal below it. However, some exceptions to this generalisation are known. For example, in Zn - Al couple, Zn (below than Al) corrodes as Al develops oxide layer and resists corrosion. Such a behavior is well explained by

considering the positions of these metals in galvanic series. The galvanic series provide more accurate information regarding the relative tendency of common metals and alloys to undeigo corrosion and is more reliable than those based on electrochemical series. In the galvanic series more active metals are given higher place and corrode readily. The metals at the lower end do not easily react and therefore do not corrode so easily under atmospheric condition. When two metals are in electrical contact and an electrolyte is present, the one higher up in the galvanic series corrodes and the other is protected. The greater the difference in their positions in the galvanic series the faster will be the corrosion. Metals close to each other in the galvanic series show less tendency to corrode when in contact with each other.

Q.1 **Distinguish between Electrochemical series and Galvanic series.**

Ans.:

	Electrochemical series	Galvanic series
1.	Electrode potentials are measured by dipping pure metals in their salt solution of 1M concentration, without any oxide film on them.	This series was developed by studying corrosion of metals and alloys in unpolluted sea water, without their oxide films, if any removed.
2.	The position of a given metal in electrochemical series is fixed.	The positions of given metal may shift in galvanic series.
3.	It gives no information regarding positions of alloys.	Since alloys are included in galvanic series so their corrosion can be studied from this series.
4.	The position of a metal in this series is permanently fixed.	The position of a metal when present in the form of an alloy, is different from pure metal.
5.	This series comprises of metals and non-metals.	This series comprises of metals and alloys
6.	It predicts the relative displacement tendencies.	It predicts the relative corrosion tendencies.

3.6 NERNST EQUATION

Q.1 **Explain Nernst Equation.**

Ans.: In an electrochemical cell, the electrode potential depends on the nature of the electrode, concentration of the electrolyte and temperature. Nernst derived a fundamental equation relating the free energy change of any electrode processes to the potential developed at the electrode along with the concentration of ions in the solutions and its temperature.

Derivation :

Consider an electrode assembly undergoing a spontaneous reaction.

$$M^{n+} + ne^- \leftrightarrow M$$

The equilibrium constant (K) for this system in equilibrium can be evaluated as

$$K = \frac{[M]}{[M^{++}]}$$

Some amount of electrical work is done and is maximum at equilibrium referred to as W_{max}.

W_{max} = (Number of Coulombs of charge flowing across the HED) × (Energy available per Coulombs of charge)

$$W_{max} = nEF$$

As the reaction is spontaneous, there is decrease in the free energy. Also the decrease in free energy appears as work done (W_{max}).

Therefore,

$$-\Delta G = W_{max} = nEF$$

Under standard conditions, $-\Delta G^0 = nE^0F$.

The decrease in free energy change for the above mentioned reaction can be expressed as,

$$\Delta G = \Delta G^0 + 2.303 \, RT \log_{10} \frac{[M]}{[M^{++}]}$$

Substituting the value of ΔG and ΔG^0,

$$-nEF = nE^0F + 2.303 \, RT \log_{10} \frac{[M]}{[M^{++}]}$$

Dividing by $-nF$ we get,

$$E = E^0 - \frac{2.303 \, RT}{nF} \log_{10} \frac{[M]}{[M^{++}]}$$

For a Galvanic cell the EMF is given as,

$$E_{cell} = E^0_{cell} - \frac{2.303 \, RT}{nF} \log_{10} K$$

Where, K is the equilibrium constant for the reaction.

Applications of Nernst Equation

1. The potential of an electrode and EMF of a cell can be calculated at any temperature and concentration.
2. The concentration of the reactants can be calculated by knowing the potential of an electrode.
3. The pH of a solution can be calculated by measuring the EMF.
4. The concentration of a solution in the ganvanic cell can be determined.

3.7   SOLVED EXAMPLES (On Nernst Equation)

Ex.1   Calculate the electrode potential of copper, if the concentration of $CuSO_4$ is 0.206 M at 23.1°C. Given that $E° \, Cu^{2+}/Cu = +0.34V$.

Ans.:   Given that

$[CuSO_4] = 0.206$; $T = 296.1°K$

The reaction taking place is

$$Cu^{2+} + 2e^- \leftrightarrow Cu; \; n = 2$$

According to Nernst's equation,

$$E_{Cu^{2+}/Cu} = E^0_{Cu^{2+}/Cu} - \frac{2.303 \, RT}{nF} \log_{10} \frac{1}{[Cu^{2+}]}$$

$$= +0.34 - \frac{2.303 \times 8.314 \times 296.1}{2 \times 96500} \times \log_{10} \frac{1}{0.206}$$

$$= 0.31984 \, V$$

$$E_{Cu^{2+}/Cu} = 0.31984 \, V$$

Ex.2 Calculate the concentration of $NiCl_2$ in the nickel electrode having a potential of –0.16942 V at 24.9°C. Given that $E^0_{Ni^{2+}/Ni} = -0.14V$.

Ans.: According to Nernst's equation,

$$E_{Ni^2/Ni} = E^0_{Ni^{2+}/Ni} - \frac{2.303\,RT}{nF}\log_{10}\frac{1}{[Ni^{2+}]};$$

Here n = 2. So,

$$-0.16942 = -0.14 + \frac{2.303 \times 8.134 \times 297.9}{2 \times 96500} \times \log_{10}(x);$$

Where x = $[Ni^{2+}]$. So,

$$-0.16942 = -0.14 + (0.02955) \times \log_{10}x$$
$$-0.02942 = 0.02955 \times \log_{10}x$$

We get x = $[NiCl_2]$ = 0.1010 M

Concentration of $NiCl_2$ = 0.1010 M

Ex.3 Calculate the standard electrode potential of lead electrode, if the electrode potential is – 0.18025 V at 301 K and a concentration of Pb^{2+} solution is 0.0096 M.

Ans.: Given $[Pb^{2+}]$ = 0.0096 M; $E_{Pb^{2+}/Pb}$ = –0.18025 V; T = 301 K

According to Nernst's equation,

$$E_{Pb^{2+}/Pb} = E^0_{Pb^{2+}/Pb} - \frac{2.303\,RT}{nF}\log_{10}\frac{1}{\left[Pb^{2+}\right]}$$

$$E^0_{Pb^{2+}/Pb} = E_{Pb^{2+}/Pb} - \frac{2.303\,RT}{nF}\log_{10}[Pb^{2+}]$$

$$= -0.18025 - \frac{2.303 \times 8.314 \times 301}{2 \times 96500} \times \log_{10}(0.0096)$$

$$= -0.18025 - 0.02986 \times (-2.0177) = 0.1200\ V$$

$$E^0_{Pb^{2+}/Pb} = 0.1200\ V$$

GRADED QUESTIONS

1. Classify various types of electrochemical cells with neat diagram.
2. Give applications of Electrochemical cells.
3. Distinguish between Galvanic Cell and Electrolytic Cell.
4. Explain Electrode Potential.
5. Define Standard Electrode Potential.
6. Explain Standard Hydrogen Electrode with neat diagram.
7. Explain Calomel Electrode with neat diagram.
8. Distinguish between Electrochemical series and Galvanic series.
9. Explain Nernst Equation.

EXAMINATION QUESTIONS

Topic newly introduced in revised syllabus.

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