UNIT-3

ELECTROCHEMISTRY CONCEPTS

Electrochemistry may be defined as the branch of chemistry which deals with the quantitative study of interrelation ship between chemical energy and electrical energy and inter-conversion of one form into another.relationships between electrical energy taking place in redox reactions.
A cell is of two types:-

I. Galvanic Cell
II. Electrolytic cell.

In Galvanic cell the chemical energy of a spontaneous redox reaction is converted into electrical work.
In Electrolytic cell electrical energy is used to carry out a non-spontaneous redox reaction.

The Standard Electrode Potential for any electrode dipped in an appropriate solution is defined with respect to standard electrode potential of hydrogen electrode taken as zero. The standard potential of the cell can be obtained by taking the difference of the standard potentials of cathode and anode.

$E^0_{cell} = E^0$cathode-E^0anode
The standard potential of the cells are related of standard Gibbs energy.
$\Delta_r G = -nFE^0_{cell}$
The standard potential of the cells is related to equilibrium constant.
$\Delta_r G = -RT\ln k$
Concentration dependence of the potentials of the electrodes and the cells are given by Nernst equation.
$aA + bB \xrightarrow{ne^-} cC + dD$

Nernst equation can be written as

$$E_{cell} = E^0_{cell} - \frac{RT}{nF}\ln\frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The conductivity, K of an electrolytic solution depends on the concentration of the electrolyte, nature of solvent and temperature.
Molar Conductivity, Δm, is defined by K/C where C is the concentration in Mol L^{-1}

$$\Delta M = \frac{k*1000}{m}$$

the unit of molar conductivity is Ω^{-1} cm^2 $mol^{-}1$. Conductivity decrease but molar conductivity increases with decrease in concentration. It increases slowly with decrease in concentration for strong electrolyte while the increase is very dilute solutions.

Kohlrausch law of independent migration of ions. The law states that limiting conductivity of an electrolyte can be represented as the sum of the individual contribution to the anion and cation of the electrolyte.

Faraday's laws of Electrolysis

I. The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte.
II. The amount of different substances liberated by the same quantity of electricity passing through the electrolytic solution is proportional to their chemical equivalent weights.

Batteries and full cells are very useful forms of galvanic cells
There are mainly two types of batteries.

Corrosion of metals is an electrochemical phenomenon
In corrosion metal is oxidized by loss of electrons to oxygen and formation of oxides.
Anode (Oxidation): $2Fe(s) \rightarrow 2Fe^{2+} + 4e^-$
Cathode (Reduction): $O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2H_2O$

Atmospheric Oxidation:
$2Fe^{2+}(aq) + 2H_2O(l) + 1/2O_2(g) \rightarrow Fe_2O_3(s) + 4H^+(aq)$

QUESTION CARRING 1 MARK

1. What is the effect of temperature on molar conductivity?
Ans. Molar conductivity of an electrolyte increases with increase in temperature.
2. Why is it not possible to measure single electrode potential?
Ans. (It is not possible to measure single electrode potential because the half cell containing single electrode cannot exist independently, as charge cannot flow on its own in a single electrode.)
3. Name the factor on which emf of a cell depends:-
Ans. Emf of a cell depends on following factor-
   a. Nature of reactants.
   b. Concentration of solution in two half cells.
   c. Temperature

d. Pressure of gas.

4. What are the units of molar conductivity?
(cm^2 ohm^{-1} mol^{-1} or $Scm^2mol^{-1)}$

5. Write Nernst equation –
For the general cell reaction
$aA+bB \rightarrow cC+dD$

Ans. **$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}$**

6. What is the EMF of the cell when the cell reaction attains equilibrium?
Ans. Zero

7. What is the electrolyte used in a dry cell?
Ans. A paste of NH_4Cl, MnO_2 and C

8. How is cell constant calculated from conductance values?
Ans. Cell constant= specific conductance/ observed conductance.

9. What flows in the internal circuit of a galvanic cell.
Ans. Ions

10. Define electrochemical series.
Ans. The arrangement of various electrodes in the decreasing or increasing order of their standard reduction potentials is called electrochemical series.

QUESTIONS CARRYING TWO MARKS

1. How can you increase the reduction potential of an electrode.?
For the reaction

$M^{n+}(aq) + ne^- \rightarrow M(s)$

Ans. Nernst equation is:

$$E^0_{M^{n+}/M} = E_{M^{n+}/M} - \frac{2.303RT}{nF} \log \frac{1}{[Mn^+]}$$

$E_{M^{n+}/M}$ can be increased by

a. increase in concentration of M^{n+} ions in solution
b. by increasing the temperature.

2. Calculate emf of the following cell at 298K

Zn/Zn^{2+} (10^{-4} M) || Cu^{2+} (10^{-2}M)/Cu

Given E^0 Zn^{2+}/Zn=-0.76V

E^0Cu^{2+}/Cu=+0.34V

Ans. Cell reaction is as follows.

$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

N=2

T=298K

$$Ecell=(E^0Cu^{2+}/Cu-E0Zn^{2+}/Zn)-0.0591V \log\frac{[Zn^{2+}(aq)]}{[Cu^{+}(aq)]}$$

$$= 0.34V-(-0.76)-0.02955V\log\frac{10^{-4}}{10^{-2}}$$

= 1.10V-0.02955V log 10-2

= 1.10V+2 X 0.02955V

= 1.10V + 0.0591 V

= 1.1591V

Q 3. Electrolysis of KBr(aq) gives Br_2 at anode but KF(aq) does not give $F^{2.}$ Give reason.

Ans. Oxidation takes place at anode. Now higher the oxidation Potential, easier to oxidize. Oxidation potential of Br^-, H2O,F^- are in the following order.

Br->H_2O>F-

Therefore in aq. Solution of KBr. Br^- ions are oxidized to Br_2 in preference to H_2O. On the other hand, in aq. Solution of KF, H_2O is oxidized in preference to F^-. Thus in this case oxidation of H_2O at anode gives O_2 and no F_2 is produced.

3. What happens when a piece of copper is added to (a) an aq solution of $FeSO_4$(b) an Aq solution of $FeCl_3$?

a. Nothing will happen when the piece of copper is added to FeSo4 because reduction potential E0 Cu2/Cu(0.34) is more than the reduction potential E0(Fe2+/Fe) (0.44V).

b. Copper will dissolve in an aq solution of $FeCl_3$ because reduction potential E^0Fe^{3+}/Fe^{2+}(0.77V) is more than the reduction potential of E^0Cu_2/Cu(0.34)

$Cu(s)+ 2FeCl_3(aq) \rightarrow Cu_2(aq) + 2 FeCl_2(aq)$

4. Define corrosion. Write chemical formula of rust.
   Corrosion is a process of determination of metal as a result of its reaction with air and water, surrounding it. It is due to formulation of sulphides, oxides, carbonates, hydroxides, etc.
   Formula of rust- $Fe_2O.XH_2O$
5. Write short notes on reduction and oxidation potentials.
6. How are standard electrode potentials measured?
7. What is cell constant? How it is determined?
8. what is conductivity water

9. Why it is necessary to platinize the electrodes of a conductivity cell before it is used for conductance measurement?
10. Why mercury cell gives the constant voltage.
11. What is fuel cell, write reaction involved in h_2-o_2 fuel cel.

QUESTION CARRYING THREE MARKS

1. Write any three differences between potential difference and e.m.f.

E.M.F	POTENTIAL DIFFERENCE
1.It is difference between electrode potential of two electrodes when no current is flowing through circuit.	1.it is difference of potential between electrode in a closed circuit.
2. it is the maximum voltage obtained From a cell.	2.it is less than maximum voltage Obtained from a cell.
3. it is responsible for steady flow of Current.	3.it is not responsible for steady Flow of current.

2. Why an electrochemical cell stops working after sometime?
   The reduction potential of an electrode depends upon the concentration of solution with which it is in contact.

   As the cell works, the concentration of reactants decrease. Then according to Le chatelier's principle it will shift the equilibrium in backward direction. On the other hand if the concentration is more on the reactant side then it will shift the equilibrium in forward direction. When cell works concentration in anodic compartment in cathodic compartment decrease and hence E^0 cathode will decrease. Now EMF of cell is
   $E^0_{cell} = E^0_{cathode} - E^0_{anode}$

   A decrease in $E^0_{cathode}$ **and a corresponding increase in** E^0 anode wil mean that EMF of the cell will decrease and will ultimately become zero i.e., cell stops working after some time.

3. for the standard cell
   $Cu(s)/Cu^+(aq)||\ Ag^+(aq)/Ag(s)$
   $E^0_{cell}\ ^{2+/}Cu = +0.34$ V
   $E^0_{cell}\ ^{2+} = +0.34$ V

   $E^0\ Ag^+/Ag = +0.80$ V

i. identify the cathode and the anode as the current is drawn from the cell.
ii. Write the reaction taking place at the electrodes.
iii. Calculate the standard cell potential.

Ans. 1.From the cell representation

Ag/Ag^+ electrode is cathode and Cu/Cu^+ electrode is anode .

1. At anode :

$Cu(s) \rightarrow$
Cu^{2+} (aq)+$2e^- \rightarrow$Ag(s)
$E^0_{cell} = E^0_{cathode} - E^0_{anode}$
$= E^0_{Ag+/Ag} - E^0_{Cu2+/Cu}$
= +.80 V – (+0.34V)
= +0.80V-0.34V
= 0.46V

2. Can we store copper sulphate in (i)Zinc vessel (ii) Silver vessel? Give reasons.
Given E^0 Cu^{2+}/Cu = +0.34V, E^0Zn^{2+}/Zn= -0.76V) , $E0Ag^+/Ag$ = +0.80V

Ans. A metal having lower reduction potential can displace a metal having higher reduction potential from solution of its salt.of Cu^{2+}(E^0Cu^{2+}/C

I. Since standard reduction potential of Zn^{2+}(E^0Zn^{2+}/Zn = -0.76V) is less than the standard reduction potentialof Cu^{2+} (E^0Cu^{2+}/Cu=+0.34V), Zn can displace copper from copper sulphate solution. Thus, $CuSo_4$ solution can be stored in silver vessel.

3. How many grams of chlorine can be produced by the electrolysis of matters NaCl with a current of 1.02 A for 15 min?
$2NaCl(l) \rightarrow 2Na^+(l)+2Cl^-(l)$
$2\ Cl^- \rightarrow Cl_2(g) + 2e^-$
2 mole 1mol
Q= nf
Q= 2 x 96500 C/mol= 1.93 x 10^5C

Quantity of electricity used = IT
= 1.02 A X (15 X 60)sec
= 900C
Molar mass of Cl2 = 2 X 35.5 = 71 $gmol^{-1}$ X 10^5 C of charge produce chlorine = 71g
1.93 X 10^5 C of charge produce chlorine = 71gm
900 C of charge produce chlorine $\frac{71 \text{ X } 900}{1.93 \text{ X } 10^5}$
= 0.331 gm

4. What is understood by a normal hydrogen electrode? Give its significance.
5. Define electrode potential. Why absolute value of reduction potential of electrode cannot be determined?
6. Write the equation showing the effect of concentration on the electrode potential.

7. Derive the relationship between Gibb's free energy change and the cell potential.
8. How Nernst equation can be applied in the calculation of equilibrium constant of any cell reaction.?
9. The cell reaction as written is spontaneous if the overall EMF of the cell is positive. Comment on this statement.

QUESTIONS CARRYING 5 MARKS

1. Explain the term electrolysis. Discuss briefly the electrolysis of (i) molten NaCl (ii) aqueous sodium chloride solution (iii) molten lead bromide (iv) water.
2. state and explain Faraday's laws of electrolysis. What is Electrochemical equivalent?
3. What do you understand by 'electrolytic conduction'? what are the factors on which electrolyte conduction depends.? What is the effect of temperature on electrolytic conduction?
4. How is electrolytic conductance measured experimentally?
5. Describe normal hydrogen electrode and its applications.

HOT QUESTIONS

<u>1 Mark questions</u>:-

1. Why in a concentrated solution, a strong electrolyte shows deviations from Debye-Huckle- Onsagar equation?
Ans:- Because interionic forces of attractions are large.

2. What is the use of Platinum foil in the hydrogen electrode?
A: It is used for inflow and outflow of electrons.
3. Corrosion of motor cars is of greater problem in winter when salts are spread on roads to melt ice and snow. Why?

4. Is it safe to stir $AgNO_3$ solution with copper spoon? ($E^0_{Ag+/Ag}$ = 0.80 Volt; $E^0_{Cu+/Cu}$ = 0.34 Volt)
Ans: No it is not safe because reacts with $AgNO_3$ Solution (Emf will be positive.)
5. Why is it necessary to use salt bridge in A galvanic cell?
Ans: To complete inner circuit and to maintain electrical neutrality of the solution.

<u>2 mark questions</u>:-

1. Why is Li best reducing agent where as Fluorine is best oxidizing agent ?

2. Equilibrium constant is related to Eθ cell but not to Ecell. Explain.
3. Why sodium metal is not obtained at cathode when aq NaCl is electrolysed with Pt electrodes but obtained when molten NaCl is electrolysed ? 2
4. Zn rod weighing 25 g was kept in 100 mL of 1M copper sulphate solution. After certain time interval, the molarity of Cu^{2+} was found to be 0.8 M. What is the molarity of SO_4^{-2} in the resulting solution and what should be the mass of Zn rod after
cleaning and drying ?
5. Which will have greater molar conductivity and why? Sol A. 1mol KCl dissolved in 200cc of the solution or Sol B. 1 mol KCl dissolved in 500cc of the solution.

3/ 5 mark questions:-
1. What do you mean by (i) negative standard electrode potential and
(ii) positive standard electrode potential ?
2. Which cell is generally used in hearing aids?Name the material of the anode, cathode and the electrolyte. Write the reactions involved.
3. Iron does not rust even if Zinc coating is broken in agalvanised iron pipe but rusting occurs much faster if tin coating over iron is broken.Explain.
4. ‘ Corrosion is an electrochemical phenomenan’, explain.

5. Calculate the pH of following cell: Pt, H_2/ H_2SO_4, if its electrode potential is0.03V.
6 . A cell contains two hydrogen electrodes. The negative electrode is in contact witha solution of 10^{-5} M H+ ions. The emf of the cell is 0.118 V at 298 K. Calculate theconcentration of the H+ ions at the positive electrode.

7. Crude copper containing Fe and Ag as contaminations was subjected to electro refining by using a current of 175 A for 6.434 min. The mass of anode was found to decrease by 22.260 g, while that of cathode was increased by 22.011 g. Estimate the % of copper, iron and silver in crude copper.

8 Zinc electrode is constituted at 298 K by placing Zn rod in 0.1 M aq solution of zinc sulphate which is 95 % dissociated at this concentration. What will be the electrode potential of the electrode given that EθZn2+/Zn= - 0.76 V. 3

9. At what pH will hydrogen electrode at 298 K show an electrode potential of -0.118 V, when Hydrogen gas is bubbled at 1 atm pressure ? 3

10 Electrolysis of the solution of MnSO4 in aq sulphuric acid is a method for the preparation of MnO2 as per the chemical reaction
$Mn^{2+} + 2H_2O \rightarrow MnO_2 + 2H^+ + H_2$
Passing a current of 27 A for 24 Hrs gives 1 kg of MnO2. What is the current efficiency ? What are the reactions occurring at anode and cathode ?

Electrochemistry

Q 1.What do you mean by kohlrauch's law: from the following molar conductivities at infinite dilution

Δm^{∞} $Ba(OH)_2$ =457.6 Ω^{-1} cm^2 mol^{-1}

Δm^{∞} Ba Cl_2 = 240.6 Ω^{-1} cm^2 mol^{-1}

Δm^{∞} NH_4Cl= 129.8 Ω^{-1} cm^2 mol^{-1}

Calculate Δm^{∞} for NH_4OH

Ans. 238.3 $\Omega^{-1}cm^2$ mol^{-1}

Q2. Calculate the equilibrium constant for the reaction

$Zn + Cd^{2+} \longleftrightarrow Zn^{2+} + Cd$

If E^0 Cd^{++}/Cd =-.403 v

E^0 Zn^{++}/Zn= -0.763 v

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Ans.$1.52*10^{12}$

Q3. Predict the products of electrolyzing of the following

(a) a dil. Solution of h^2So^4 with Pt. electrode

(b). An aqueous solution of AgNO3 with silver electrode