

# ELECTROCHEMISTRY

## 1. ELECTROCHEMISTRY

Electrochemistry is the study of production of electricity from the energy released during a spontaneous chemical reaction and the use of electrical energy to bring about non-spontaneous chemical transformations.

## 2. ELECTROCHEMICAL CELLS

A spontaneous chemical process is the one which can take place on its own and in such a process the Gibb's energy of the system decreases. It is this energy that gets converted to electrical energy. The reverse process is also possible in which we can make non-spontaneous processes occur by supplying external energy in the form of electrical energy. These inter conversions are carried out in equipments called Electrochemical Cells.

## 3. TYPES

Electrochemical Cells are of two types:

### 3.1 Galvanic Cells

Converts chemical energy into electrical energy

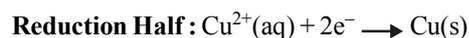
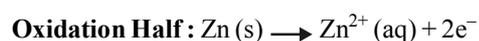
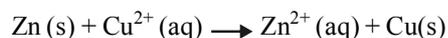
### 3.2 Electrolytic Cells

Converts electrical energy into chemical energy.

## 4. GALVANIC CELL

Cell energy is extracted from a spontaneous chemical process or reaction and it is converted to electric current.

For example, Daniell Cell is a Galvanic Cell in which Zinc and Copper are used for the redox reaction to take place.



Zn is the reducing agent and  $\text{Cu}^{2+}$  is the oxidising agent. The half cells are also known as **Electrodes**. The oxidation half is known as **Anode** and the reduction half is called **Cathode**. Electrons flow from anode to cathode in

the external circuit. Anode is assigned **negative polarity** and cathode is assigned **positive polarity**. In Daniell Cell, Zn acts as the anode and Cu acts as the cathode.

## 5. ELECTROLYTIC CELL

These electrodes are dipped in and electrolytic solution containing cations and anions. On supplying current the ions move towards electrodes of opposite polarity and simultaneous reduction and oxidation takes place.

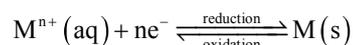
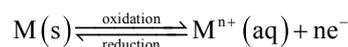
### 5.1 Preferential Discharge of ions

Where there are more than one cation or anion the process of discharge becomes competitive in nature. Discharge of any ion requires energy and in case of several ions being present the discharge of that ion will take place first which requires the energy.

## 6. ELECTRODE POTENTIAL

It may be defined as the tendency of an element, when it is placed in contact with its own ions to either lose or gain electrons and in turn become positively or negatively charged.

The electrode potential will be named as oxidation or reduction potential depending upon whether oxidation or reduction has taken place.



### 6.1 Characteristics

- (a) Both oxidation and reduction potentials are equal in magnitude but opposite in sign.
- (b) It is not a thermodynamic property, so values of E are not additive.

## 7. STANDARD ELECTRODE POTENTIAL ( $E^\ominus$ )

It may be defined as the electrode potential of an electrode determined relative to standard hydrogen electrode under standard conditions. The standard conditions taken are :

(i) 1M concentration of each ion in the solution.

(ii) A temperature of 298 K.

(iii) 1 bar pressure for each gas.

### 8. ELECTROCHEMICAL SERIES

The half cell potential values are standard values and are represented as the standard reduction potential values as shown in the table at the end which is also called Electrochemical Series.

### 9. CELL POTENTIAL OR EMF OF A CELL

The difference between the electrode potentials of two half cells is called cell potential. It is known as electromotive force (EMF) of the cell if no current is drawn from the cell.

$$E_{\text{cell}} = E_{\text{cathode}} + E_{\text{anode}}$$

For this equation we take oxidation potential of anode and reduction potential of cathode.

Since anode is put on left and cathode on right, it follows therefore,

$$= E_R + E_L$$

For a Daniel cell, therefore

$$E_{\text{cell}}^{\circ} = E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} - E_{\text{Zn}/\text{Zn}^{2+}}^{\circ} = 0.34 + (0.76) = 1.10 \text{ V}$$

### 10. CELL DIAGRAM OR REPRESENTATION OF A CELL

The following conventions or notations are applied for writing the cell diagram in accordance with IUPAC recommendations. The Daniel cell is represented as follows :



(a) Anode half cell is written on the left hand side while cathode half cell on right hand side.

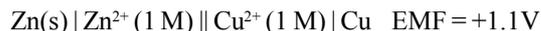
(b) A single vertical line separates the metal from aqueous solution of its own ions.



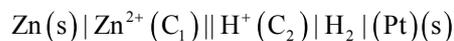
(c) A double vertical line represents salt bridge

(d) The molar concentration (C) is placed in brackets after the formula of the corresponding ion.

(e) The value of e.m.f. of the cell is written on the extreme right of the cell. For example,

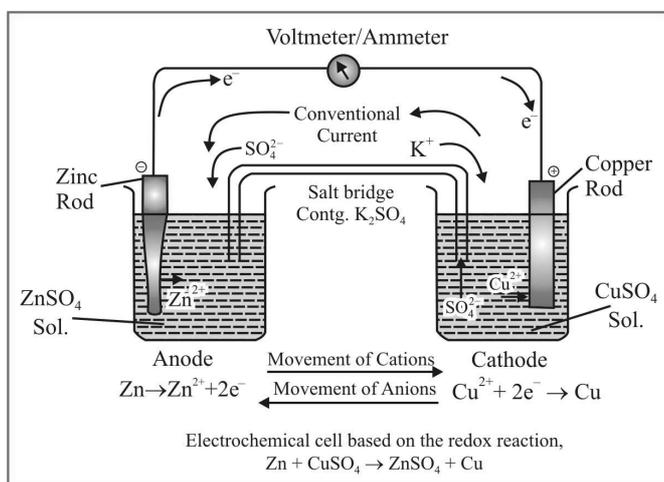


(f) If an inert electrode like platinum is involved in the construction of the cell, it may be written along with the working electrode in bracket say for example, when a zinc anode is connected to a hydrogen electrode.



### 11. SALT BRIDGE

Salt bridge is used to maintain the charge balance and to complete the circuit by facilitating the flow of ions through it. It contains a gel in which an inert electrolyte like  $\text{Na}_2\text{SO}_4$  or  $\text{KNO}_3$  etc are mixed. Negative ions flow to the anode and positive ions flow to the cathode through the salt bridge and charge balance is maintained and cell keeps on functioning.



### 12. SPONTANEITY OF A REACTION

$$\Delta G = - nFE_{\text{CELL}}$$

For a spontaneous cell reaction  $\Delta G$  should be negative and cell potential should be positive.

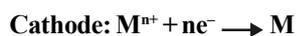
If we take standard value of cell potential in the above equation we will obtain standard value of  $\Delta G$  as well.

$$\Delta G^{\circ} = - nFE_{\text{CELL}}^{\circ}$$

### 13. TYPES OF ELECTRODES

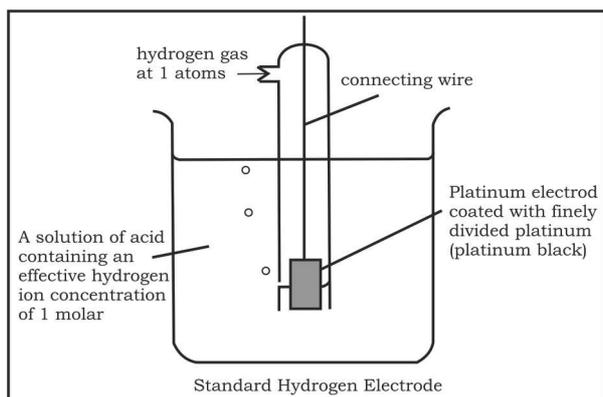
#### 13.1 Metal-Metal Ion electrodes

A metal rod/plate is dipped in an electrolyte solution containing metal ions. There is a potential difference between these two phases and this electrode can act as a cathode or anode both.



### 13.2 Gas Electrodes

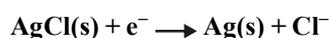
Electrode gases like  $H_2$ ,  $Cl_2$  etc are used with their respective ions. For example,  $H_2$  gas is used with a dilute solution of HCl ( $H^+$  ions). The metal should be inert so that it does not react with the acid.



The hydrogen electrode is also used as the standard to measure other electrode potentials. Its own potential is set to 0 V as a reference. When it is used as a reference the concentration of dil HCl is taken as 1 M and the electrode is called "Standard Hydrogen Electrode (SHE)".

### 13.3 Metal-Insoluble salt electrode

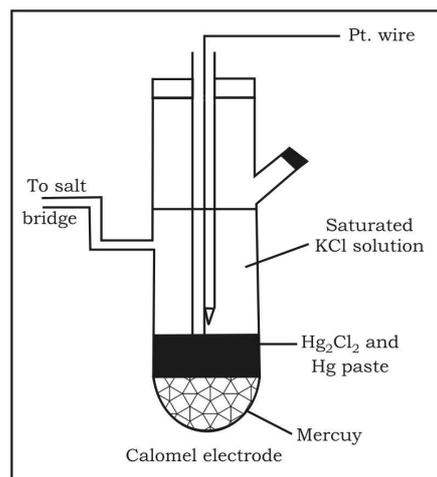
We use salts of some metals which are sparingly soluble with the metal itself as electrodes. For example, if we use AgCl with Ag there is a potential gap between these two phases which can be identified in the following reaction:



This electrode is made by dipping a silver rod in a solution containing  $AgCl(s)$  and  $Cl^{-}$  ions.

### 13.4 Calomel Electrode

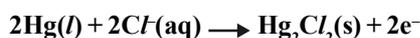
Mercury is used with two other phases, one is a calomel paste ( $Hg_2Cl_2$ ) and electrolyte containing  $Cl^{-}$  ions.



**Cathode :**



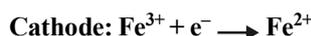
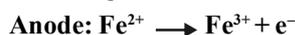
**Anode :**



This electrode is also used as another standard to measure other potentials. Its standard form is also called **Standard Calomel Electrode (SCE)**.

### 13.5 Redox Electrode

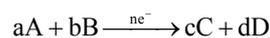
In these electrodes two different oxidation states of the same metal are used in the same half cell. For example,  $Fe^{2+}$  and  $Fe^{3+}$  are dissolved in the same container and an inert electrode of platinum is used for the electron transfer. Following reactions can take place:



## 14. NERNST EQUATION

It relates electrode potential with the concentration of ions.

Thus, the reduction potential increases with the increase in the concentration of ions. For a general electrochemical reaction of the type.



Nernst equation can be given as

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

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2303}{nF} RT \log \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Substituting the values of R and F we get

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[C]^c [D]^d}{[A]^a [B]^b}, \text{ at } 298 \text{ K}$$

## 15. APPLICATIONS OF NERNST EQUATION

### 15.1 Equilibrium Constant from Nernst Equation

For a Daniel cell, at equilibrium

$$E_{\text{cell}} = 0 = E_{\text{cell}}^{\circ} - \frac{2.303 RT}{2F} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

or 
$$E_{\text{cell}}^{\circ} = \frac{2.303 RT}{2F} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

But at equilibrium, 
$$\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = K_c$$

$$E_{\text{cell}}^{\circ} = \frac{2.303 RT}{2F} \log K_c$$

$$E_{\text{cell}}^{\circ} = \frac{2.303 \times 8.314 \times 298}{2 \times 96500} \log K_c$$

$$= \frac{0.0591}{2} \log K_c$$

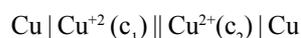
In general, 
$$E_{\text{cell}}^{\circ} = \frac{0.0591}{n} \log K_c$$

or, 
$$\log K_c = \frac{n E_{\text{cell}}^{\circ}}{0.0591}$$

## 16. CONCENTRATION CELLS

If two electrodes of the same metal are dipped separately into two solutions of the same electrolyte having different

concentrations and the solutions are connected through salt bridge, such cells are known as concentration cells. For example



These are of two types :

### 16.1 Electrode concentration cells



$$E_{\text{cell}} = 0 - \frac{0.059}{n} \log \frac{P_2}{P_1}$$

where  $p_2 < p_1$  for spontaneous reaction

### 16.2 Electrolyte concentration cell

The EMF of concentration cell at 298 K is given by  $\text{Zn} | \text{Zn}^{2+}(c_1) || \text{Zn}^{2+}(c_2) | \text{Zn}$

$$E_{\text{cell}} = \frac{0.0591}{n_1} \log \frac{c_2}{c_1},$$

where  $c_2 > c_1$  for spontaneous reaction

## 17. CASES OF ELECTROLYSIS

### 17.1 Electrolysis of molten sodium chloride



The reactions occurring at the two electrodes may be shown as follows :

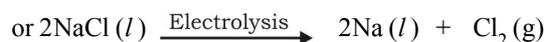
At cathode :



At anode :



Overall reaction :



At cathode    At anode

## Chapter - 3

# Electro Chemistry

### 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-

- Nature of reactants.
- Concentration of solution in two half cells.
- Temperature
- Pressure of gas.

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

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

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

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  $\text{NH}_4\text{Cl}$ ,  $\text{MnO}_2$  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



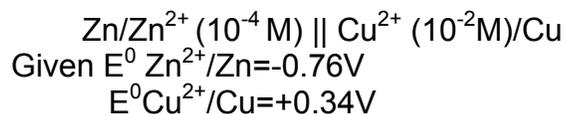
Ans. Nernst equation is:

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

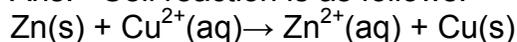
$E_{\text{M}^{n+}/\text{M}}$  can be increased by

- increase in concentration of  $\text{M}^{n+}$  ions in solution
- by increasing the temperature.

2. Calculate emf of the following cell at 298K



Ans. Cell reaction is as follows.



$N=2$

$T=298 \text{ K}$

$$E_{\text{cell}} = (E^{\circ} \text{Cu}^{2+}/\text{Cu} - E^{\circ} \text{Zn}^{2+}/\text{Zn}) - 0.0591 \text{ V} \log \frac{[\text{Zn}^{2+}(\text{aq})]}{[\text{Cu}^{2+}(\text{aq})]}$$

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

$$= 1.10 \text{ V} - 0.02955 \text{ V} \log 10^{-2}$$

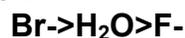
$$= 1.10 \text{ V} + 2 \times 0.02955 \text{ V}$$

$$= 1.10 \text{ V} + 0.0591 \text{ V}$$

$$= 1.1591 \text{ V}$$

Q 3. Electrolysis of  $\text{KBr(aq)}$  gives  $\text{Br}_2$  at anode but  $\text{KF(aq)}$  does not give  $\text{F}_2$ . Give reason.

Ans. Oxidation takes place at anode. Now higher the oxidation Potential, easier to oxidize. Oxidation potential of  $\text{Br}^-$ ,  $\text{H}_2\text{O}$ ,  $\text{F}^-$  are in the following order.

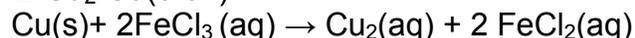


Therefore in aq. Solution of  $\text{KBr}$ .  $\text{Br}^-$  ions are oxidized to  $\text{Br}_2$  in preference to  $\text{H}_2\text{O}$ . On the other hand, in aq. Solution of  $\text{KF}$ ,  $\text{H}_2\text{O}$  is oxidized in preference to  $\text{F}^-$ . Thus in this case oxidation of  $\text{H}_2\text{O}$  at anode gives  $\text{O}_2$  and no  $\text{F}_2$  is produced.

3. What happens when a piece of copper is added to (a) an aq solution of  $\text{FeSO}_4$  (b) an Aq solution of  $\text{FeCl}_3$ ?

a. Nothing will happen when the piece of copper is added to  $\text{FeSO}_4$  because reduction potential  $E^{\circ} \text{Cu}^{2+}/\text{Cu}$  (0.34) is more than the reduction potential  $E^{\circ}(\text{Fe}^{2+}/\text{Fe})$  (0.44V).

b. Copper will dissolve in an aq solution of  $\text{FeCl}_3$  because reduction potential  $E^{\circ} \text{Fe}^{3+}/\text{Fe}^{2+}$  (0.77V) is more than the reduction potential of  $E^{\circ} \text{Cu}^{2+}/\text{Cu}$  (0.34)



4. Define corrosion. Write chemical formula of rust.

Corrosion is a process of deterioration of metal as a result of its reaction with air and water, surrounding it. It is due to formation of sulphides, oxides, carbonates, hydroxides, etc.

Formula of rust-  $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$

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 cell.

### QUESTION CARRYING THREE MARKS

- |   |  |
|---|--|
| <p>1. Write any three differences between potential difference and e.m.f.</p> <p><b>E.M.F</b></p> <ol style="list-style-type: none"> <li>1. It is difference between electrode potential of two electrodes when no current is flowing through circuit.</li> <li>2. it is the maximum voltage obtained From a cell.</li> <li>3. it is responsible for steady flow of Current.</li> </ol> | <p><b>POTENTIAL DIFFERENCE</b></p> <ol style="list-style-type: none"> <li>1. it is difference of potential between electrode in a closed circuit.</li> <li>2. it is less than maximum voltage Obtained from a cell.</li> <li>3. it is not responsible for steady Flow of current.</li> </ol> |
|---|--|

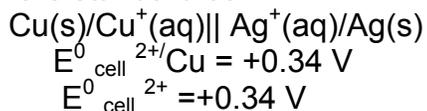
2. Why an electrochemical cell stops working after sometime?  
The reduction potential of an electrode depends upon the concentration of solution with which it is in contact.

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

$$E^0_{\text{cell}} = E^0_{\text{cathode}} - E^0_{\text{anode}}$$

A decrease in  $E^0_{\text{cathode}}$  **and a corresponding increase in  $E^0$  anode** will 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



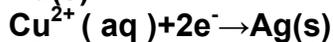
$$E^0 \text{ Ag}^+/\text{Ag} = +0.80 \text{ V}$$

- 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<sup>+</sup> electrode is cathode and Cu/Cu<sup>+</sup> electrode is anode .

1. At anode :



$$\begin{aligned} E^{\circ}_{\text{cell}} &= E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}} \\ &= E^{\circ}_{\text{Ag}^{+}/\text{Ag}} - E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} \\ &= +0.80 \text{ V} - (+0.34 \text{ V}) \\ &= +0.80 \text{ V} - 0.34 \text{ V} \\ &= 0.46 \text{ V} \end{aligned}$$

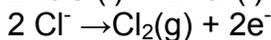
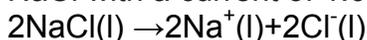
2. Can we store copper sulphate in (i) Zinc vessel (ii) Silver vessel? Give reasons.

Given  $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$ ,  $E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$ ,  $E^{\circ}_{\text{Ag}^{+}/\text{Ag}} = +0.80 \text{ V}$

Ans. A metal having lower reduction potential can displace a metal having higher reduction potential from solution of its salt. of Cu<sup>2+</sup> ( $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}}$ )

i. Since standard reduction potential of Zn<sup>2+</sup> ( $E^{\circ}_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$ ) is less than the standard reduction potential of Cu<sup>2+</sup> ( $E^{\circ}_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$ ), Zn can displace copper from copper sulphate solution. Thus, CuSO<sub>4</sub> 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?



2 mole    1mol

$$Q = nf$$

$$Q = 2 \times 96500 \text{ C/mol} = 1.93 \times 10^5 \text{ C}$$

Quantity of electricity used =  $IT$

$$= 1.02 \text{ A} \times (15 \times 60) \text{ sec}$$

$$= 900 \text{ C}$$

Molar mass of Cl<sub>2</sub> =  $2 \times 35.5 = 71 \text{ gmol}^{-1}$  X  $10^5 \text{ C}$  of charge produce chlorine = 71g

$1.93 \times 10^5 \text{ C}$  of charge produce chlorine = 71gm

$$\begin{aligned} 900 \text{ C of charge produce chlorine } & \frac{71 \times 900}{1.93 \times 10^5} \\ & = 0.331 \text{ gm} \end{aligned}$$

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.

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

### QUESTIONS CARRYING 5 MARKS

- Explain the term electrolysis. Discuss briefly the electrolysis of (i) molten NaCl (ii) aqueous sodium chloride solution (iii) molten lead bromide (iv) water.
- state and explain Faraday's laws of electrolysis. What is Electrochemical equivalent?
- 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?
- How is electrolytic conductance measured experimentally?
- Describe normal hydrogen electrode and its applications.

### VERY IMPORTANT QUESTIONS

#### 1 Mark questions:-

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  $\text{AgNO}_3$  solution with copper spoon? ( $E^0_{\text{Ag}^+/\text{Ag}} = 0.80$  Volt;  $E^0_{\text{Cu}^+/\text{Cu}} = 0.34$  Volt)

Ans: No it is not safe because reacts with  $\text{AgNO}_3$  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.

#### 2 mark questions:-

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

2. Equilibrium constant is related to  $E^\theta$  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  $\text{Cu}^{2+}$  was found to be 0.8 M. What is the molarity of  $\text{SO}_4^{-2}$  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 galvanised iron pipe but rusting occurs much faster if tin coating over iron is broken. Explain.
4. ' Corrosion is an electrochemical phenomenon', explain.
5. Calculate the pH of following cell: Pt,  $\text{H}_2/\text{H}_2\text{SO}_4$ , if its electrode potential is 0.03V.
- 6 . A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of  $10^{-5}$  M  $\text{H}^+$  ions. The emf of the cell is 0.118 V at 298 K. Calculate the concentration of the  $\text{H}^+$  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  $E^\theta_{\text{Zn}^{2+}/\text{Zn}} = - 0.76$  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  $\text{MnSO}_4$  in aq sulphuric acid is a method for the preparation of  $\text{MnO}_2$  as per the chemical reaction  

$$\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow \text{MnO}_2 + 2\text{H}^+ + \text{H}_2$$
 Passing a current of 27 A for 24 Hrs gives 1 kg of  $\text{MnO}_2$ . What is the current efficiency ? What are the reactions occurring at anode and cathode ?

## Electrochemistry

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

$$\Delta m^\infty \text{Ba(OH)}_2 = 457.6 \, \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$$

$$\Delta m^\infty \text{BaCl}_2 = 240.6 \, \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$$

$$\Delta m^\infty \text{NH}_4\text{Cl} = 129.8 \, \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$$

Calculate  $\Delta m^\infty$  for  $\text{NH}_4\text{OH}$

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

Q2. Calculate the equilibrium constant for the reaction



If  $E^0 \text{Cd}^{2+}/\text{Cd} = -0.403 \text{ V}$

$E^0 \text{Zn}^{2+}/\text{Zn} = -0.763 \text{ V}$

Antilog 12.1827

Ans.  $1.52 \times 10^{12}$

Q3. Predict the products of electrolyzing of the following

(a) a dil. solution of  $\text{H}_2\text{SO}_4$  with Pt. electrode

(b). An aqueous solution of  $\text{AgNO}_3$  with silver electrode