

# ELECTRO CHEMISTRY

## Preface

This chapter is of great importance in our daily life, because it relates energy with chemical changes. One must have clearcut knowledge of Redox and Thermodynamical concepts of chemical reactions before reading this chapter. In earlier part of this chapter you will study chemical changes due to electrical energy i.e. electrolysis which has great significance in electroplating, electrodeposition, electrorefining and metallurgy of metals. In later part you will come across energy libration due to chemical changes i.e. electrochemical cells. In this section we deal Galvanic and Concentration cells, Reference and other half electrodes, Nernst equation etc.

This book consists of theoretical & practical explanations of all the concepts involved in the chapter. Each article followed by a ladder of illustration. At the end of the theory part, there are miscellaneous solved examples which involve the application of multiple concepts of this chapter.

Students are advised to go through all these solved examples in order to develop better understanding of the chapter and to have better grasping level in the class.

Total No.of questions in **Electro Chemistry** are -

In chapter Examples .....	07
Solved Examples .....	10
<b>Total No. of questions .....</b>	<b>17</b>

## 1. CONDUCTORS & NONCONDUCTORS ::

Substances which allow the electric current to pass through them are called conductors and substances which do not allow any electric current to pass through them are called non conductors or insulators.

**1.1 Types of conductors :** Conductors are divided into following two types.

### (a) Metallic or Electronic conductors

- (i) Electric conduction is due to the free and mobile electrons.
- (ii) During the conduction no any physical and chemical changes occur except warming.
- (iii) It does not involve transfer of any matter during the passage of electric current.
- (iv) Ohm's law is followed.
- (v) Faraday's Law is not followed.
- (vi) Resistance increases with increase of temperature.
- (vii) Examples - Metals, alloys, graphite etc.

### (b) Solution or electrolytic conductors

- (i) Electric conduction is due to the free ions in molten state or in aqueous solution of electrolytes.
- (ii) During the conduction of electric current both physical and chemical changes take place because it involves transfer of matter in the form of ions.
- (iii) Ions are oxidized or reduced at the electrodes.
- (iv) Ohm's Law is followed.
- (v) Faraday's law is followed.
- (vi) Resistance decreases with increase of temperature.
- (vii) Examples –  $H_2O$ ,  $NaCl$ ,  $AgNO_3$ .

## 2. ELECTROLYTES ::

- (a) Substances whose aqueous solutions allow the conduction of electric current and are chemically decomposed are called as electrolytes.
- (b) The positive charged ion furnished by electrolyte is called cation while the negative charged ion furnished by electrolyte is called anion.

### 2.1 Types of Electrolytes

- (a) **Strong Electrolyte** - Electrolytes which are highly decomposable in aqueous solution and conduct electricity frequently are called strong electrolytes eg. Salts of strong acid and bases, mineral acid.

- (b) **Weak Electrolyte** - Electrolytes which are decomposable to a very small extent in their dilute solutions are called weak electrolytes eg. Organic acids, inorganic acids( $H_3PO_4$ ,  $HCN$ ) and) bases ( $Fe(OH)_3$ ,  $NH_4OH$ ) etc.

## 3. ELECTRODE ::

- (a) When the electric current is passed through an electrolytic conductor, two rods or plates are always needed, which are connected to the terminals of Battery to form a cell are called as electrodes. It is also called half cell.
- (b) Electrode through which the electric current enters into the electrolytic solution is called the anode which is also called positive electrode and anions are oxidised there.
- (c) Electrode through which the electric current leaves the electrolytic solution is called the cathode which is also called negative electrode and cations are reduced there.

**3.1 Electrode potential :** The potential difference between the electrode and the electrolyte surrounding the electrode is called electrode potential.

**3.1.1 Standard Electrode potential :** It is the potential which may be defined as the potential difference in volts developed in a cell consisting of two electrodes.

## 4. CELL ::

A combination of two electrodes or two half cells is called cell.

**4.1 Types of cells :** Cells are divided into following two types.

### (a) Electrolytic cells :

- (i) Cells which bring chemical changes during the passage of electric current are called electrolytic cells.
- (ii) In this type of cell electrical energy is converted into chemical energy.

### (b) Electrochemical cells :

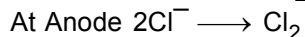
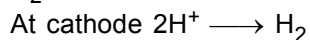
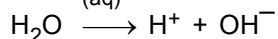
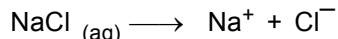
- (i) This type of cells also brings a chemical change during the passage of electric current.
- (ii) In this type of cells chemical energy is converted into electrical energy.

## 5. ELECTROLYSIS ::

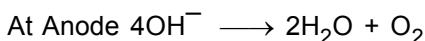
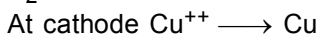
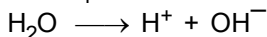
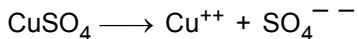
- (a) The process of chemical decomposition of an electrolyte on passing of electric current through its aqueous solution or in its molten state is known as electrolysis.
- (b) It involves oxidation process at the anode and reduction process at the cathode.

- (c) On electrolysis, If more than one type of cations are obtained then that cation is liberated at cathode which has higher reduction potential.
- (d) On electrolysis, If more than one type of anions are obtained then that anion is liberated at anode which has low reduction potential.
- (e) Electrolysis process appears only at electrodes at the time for which electricity is passed.

For Example (i) Electrolysis of aq. NaCl



For Example (ii) Electrolysis of aq.  $\text{CuSO}_4$



## 6. ELECTROLYTIC CONDUCTANCE :::

- (a) **Ohm's Law** : According to this law the current (I) flowing through a conductor at a given standard temperature is directly proportional to the potential difference (V) and inversely proportional to the resistance (R). i.e.

$$I = \frac{V}{R} \quad \text{or} \quad V = IR$$

- (b) **Specific resistance ( $\rho$ )** : The resistance between two opposite faces of one cm cube of metal is called as specific resistance ( $\rho$ ). It is also called resistivity

$$\rho = \frac{R \cdot a}{l} = \frac{\text{ohms} \times \text{cm}^2}{\text{cm}} \\ = \text{ohms cm.}$$

- (c) **Specific conductivity ( $k$ )** : The reciprocal of specific resistance is called specific conductivity ( $k$ ). It is also called as conductance.

$$k = \frac{1}{\rho} \quad \text{or} \quad k = \frac{l}{a \times R}$$

$$\therefore \frac{l}{a} = \text{Cell constant}$$

$$\therefore k = \frac{\text{cell constant}}{\text{Resistance (R)}}$$

- (d) **Electrical conductivity (C)** :

- (i) It is the reciprocal of resistance (R), which is expressed in  $\text{ohm}^{-1}$  or mho.

$$C = \frac{1}{R}$$

- (ii) The unit of electrical conductivity is called siemens (s)

- (e) **Equivalent conductance ( $\wedge$ )** :

- (i) It is defined as the conductance of all the ions produced by the ionisation of one gram equivalent of an electrolyte in a given solution.

$$\wedge = k \times \frac{1000}{C}$$

$$\text{or} \quad \wedge = k \times \frac{1000}{N}$$

where N = normality C = concentration of the solution

- (ii) The unit of equivalent conductance is  $\text{ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}$  or  $\text{S cm}^2 \text{eq}^{-1}$ .

- (f) **Molar conductance ( $\mu$ )** : It is defined as the conductance of all the ions produced by the ionisation of 1 g of an electrolyte present in V ml of solution.

$$\mu = k \times \frac{1000}{C}$$

$$\mu = k \times \frac{1000}{M}$$

Its unit is  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$  or  $\text{S cm}^2 \text{mol}^{-1}$

Where M = Molarity and C = concentration of the solution.

**Note** : - On dilution the value of equivalent and molar conductance increases whereas the value of specific conductivity decreases because of no. of ions in per ml. of solution decreases.

Examples based on

### electrolytic conductance

- Ex.1** The resistance of a decinormal solution of a salt occupying a volume between two platinum electrodes 1.80 cm apart and 5.4  $\text{cm}^2$  in area was found to be 50 ohm. Calculate the equivalent conductance of the solution.

**Sol.** We know equivalent conductance

$$\Lambda_c = \frac{1000 \times \text{conductance} \times \text{cell constant}}{\text{normality}}$$

$$\text{given, conductance} = \frac{1}{\text{resistance}} \\ = \frac{1}{50} \text{ ohm}^{-1}$$

$$\text{cell constant} = \frac{l}{a} = \frac{\text{distance}}{\text{area}} \\ = \frac{1.80}{5.40} = \frac{1}{3} \text{ cm}^{-1}$$

$$\text{normality} = 0.1 \text{ N}$$

$$\therefore \Lambda_c = \frac{1000 \times \frac{1}{50} \times \frac{1}{3}}{0.1}$$

$$= 66.66 \text{ ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}$$

**Ex.2** What is molar conductivity, the conductivity and the resistance (in a cell with constant  $0.206 \text{ cm}^{-1}$ ) of an  $0.040 \text{ M}$  solution of acetic acid at  $25^\circ\text{C}$ ? Use  $K_a = 1.8 \times 10^{-5}$

**Sol.**  $[\lambda_m^\circ (\text{CH}_3\text{COOH}) = 390.5 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}]$

$$\lambda_m = \frac{1000 \times \text{conductivity}}{\text{molarity}}$$

but  $\frac{\lambda_m}{\lambda_m^\circ} = x$  (degree of ionisation)

$$\lambda_m = \lambda_m^\circ \times x$$

$$\therefore \lambda_m = \lambda_m^\circ \sqrt{\frac{K_a}{C}}$$

(by Ostwald dilution Law)

$$= 390.5 \sqrt{\frac{1.8 \times 10^{-5}}{0.04}}$$

$$= 8.28 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\therefore \text{conductivity} = \frac{\text{molarity} \times \lambda_m}{1000}$$

$$= 3.31 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$$

but conductivity (specific conductance)

$$= \text{cell constant} \times \frac{1}{\text{resistance}}$$

$$\therefore \text{resistance} = \frac{\text{cell constant}}{\text{conductivity}}$$

$$= \frac{0.206}{3.31 \times 10^{-4}} = 621.98 \text{ ohm}$$

**Ex.3** When a certain conductivity cell was filled with  $0.020 \text{ M}$   $\text{KCl}$  which has a specific conductivity of  $0.2768 \text{ ohm}^{-1} \text{ m}^{-1}$ , it had a resistance of  $82.40 \Omega$  at  $25^\circ\text{C}$ . With  $0.0025 \text{ M}$   $\text{K}_2\text{SO}_4$ . it has a resistance of  $326.0 \Omega$ . Calculate

- the cell constant
- conductivity of  $\text{K}_2\text{SO}_4$  solution
- equivalent conductance and molar conductance of  $\text{K}_2\text{SO}_4$  solution.

**Sol.** (a) Calculation has been done using  $0.020 \text{ M}$   $\text{KCl}$  solution.

$$\text{specific conductance} = \frac{\text{cell constant}}{\text{resistance}(R)}$$

$$\therefore \text{Cell constant} = \text{specific conductance} \times \text{resistance}$$

$$= 0.2768 \times 82.4$$

$$= 22.81 \text{ m}^{-1}$$

(b) Thus specific conductance of  $\text{K}_2\text{SO}_4$  solution

$$= 22.81/326$$

$$= 0.07 \text{ ohm}^{-1} \text{ m}^{-1}$$

(c) molar conductance  $\Lambda_c$

$$= \frac{1000 \times 0.0007}{0.0025} = 280 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

from (b) specific conductance

$$= 0.07 \text{ ohm}^{-1} \text{ m}^{-1}$$

$$= 0.0007 \text{ ohm}^{-1} \text{ m}^{-1}$$

$$\text{normality} = 0.005 \text{ N ohm}^{-1} \text{ m}^{-1}$$

$\therefore$  Eq. conductance

$$\Lambda_{\text{eq}} = \frac{1000 \times 0.0007}{0.005}$$

$$= 140 \text{ ohm}^{-1} \text{ cm}^2 \text{ equiv.}^{-1}$$

## 7. FARADAY'S LAWS OF ELECTROLYSIS

**7.1 Faraday's First Law** - The amount of substance deposited during the passes of electric current is directly proportional to the quantity of electric charge passed through the electrolyte.

$$W \propto Q$$

$$\text{or } W \propto i t \quad \therefore Q = i \times t$$

$$\text{or } W = Z \cdot i \cdot t$$

where  $Q$  = total charge passed through the solution

$i$  = current in ampere

$t$  = time for which current flows in seconds.

$Z$  = Electrochemical equivalent (constant)

**7.2 Faraday's Second Law** - According to this law, when the same quantity of electric current is passed through different electrolytes, then the amount of deposited substance at the respective electrodes are in the ratio of their equivalent masses then suppose that  $W_1$  and  $W_2$  are the amount of the elements deposited by passing of electric current through their electrolytic solution and  $E_1$  and  $E_2$  are the respective equivalent weights.

$$\frac{W_1}{W_2} = \frac{E_1}{E_2}$$

$$\text{or } \frac{Z_1 i t}{Z_2 i t} = \frac{E_1}{E_2} \quad (\because W = Z i t)$$

$$\therefore \frac{Z_1}{Z_2} = \frac{E_1}{E_2}$$

Thus, the electrochemical equivalent ( $z$ ) of an element is directly proportional to its equivalent weight ( $E$ ), Means

$$E \propto Z$$

$$\text{or } E = FZ$$

where  $F$  = proportionality constant (Faraday)

If = 96540 C

$$\therefore E = 96540 Z$$

$$\text{or } E = 96500 Z$$

### Examples based on faraday's law of electrolysis

**Ex.4** An electric current of 0.25 ampere was passed through acidulated water for 2 hours. How much volume of hydrogen will be produced at NTP? (1 coulomb of electricity deposits  $1 \times 10^{-5}$  g of  $H_2$ ).

**Sol.**  $W = Z \times I \times t = 1 \times 10^{-5} \text{ g/c} \times 0.25 \text{ ampere} \times 2 \times 3600 \text{ s} = 0.018 \text{ g}$ .

Since 2 g of  $H_2$  at NTP occupies = 22.4 litres

$\therefore$  0.018 g of  $H_2$  at NTP will occupy

$$= \frac{22.4 \times 0.018}{2} \\ = 0.2016 \text{ litre}$$

**Ex.5** 0.15 amperes current is passed for 150 minutes in an electrolyte. The mass of metal deposited was 0.783 g. If atomic mass of the metal is 112, calculate equivalent mass and valency of metal in the salt.

**Sol.** Since,  $Q = I \times t = 0.15 \times 150 \times 60 \text{ C} = 1350$  coulombs

Now 1350 coulombs of electricity deposit = 0.783 g metal

$\therefore$  96500 coulombs of electricity will deposit

$$= \frac{0.783 \times 96500}{1350} = 55.97 \text{ g}$$

Thus equivalent mass of the metal = 55.97 g

Valency = Atomic mass/Eq. mass =  $112/55.97 = 2$

**Ex.6** A current of 5 amperes is passed through a solution of zinc sulphate for 40 minutes. What is the amount of zinc deposited on the cathode.

**Sol.**  $W = \frac{C \times t \times M}{Z \times F}$ ; Here  $t = 40 \times 60$  seconds,

$C = 5$  ampere,  $Z = 2$  (as two electrons are involved in the deposition of 1 atom of Zn at the cathode, i.e.,  $Zn^{2+} + 2e \rightarrow Zn$ ),  $M$ , the atomic weight of Zn = 65.38

$$W = \frac{5 \times 2400 \times 65.38}{2 \times 96500} \\ = 4.065 \text{ g}$$

## 8. KOHLRAUSCH'S LAW

For an infinite dilution, equivalent conductivity of a weak electrolyte is equal to the sum of conductivity of the two types of ion.

$$\lambda^\infty = a (\lambda_c^\infty) + b (\lambda_a^\infty)$$

where  $\lambda_c^\infty$  and  $\lambda_a^\infty$  are ionic conductances of cation and anion respectively at infinite dilution expressed in  $\text{ohm}^{-1} \text{ cm}^2 \text{ eq}^{-1}$ .

$\Lambda^\infty$  = eq. conductivity at infinite dilution.

$a$  = no of cations and

$b$  = no. of anions

eg.  $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$

$$\Lambda^\infty = \lambda_{\text{Na}^+}^\infty + \lambda_{\text{Cl}^-}^\infty$$

### 8.1 Applications of Kohlrausch's law -

(a) To evaluate equivalent and molar conductances at infinite dilution for weak electrolytes.

(b) To evaluate degree of dissociation of weak electrolyte.

$$\alpha = \frac{\Lambda^C}{\Lambda^\infty}$$

$\Lambda^C$  = Eq. conductance at a given concentration and

$\Lambda^\infty$  = Eq. conductance at  $\infty$  dilution

(c) To evaluate dissociation constant of weak electrolyses.

$$k = \frac{C\alpha^2}{1-\alpha}$$

(d) To evaluate absolute ionic mobilities.

(e) To evaluate solubility of sparingly soluble salts.

(f) To evaluate ionic product of water.

## 9. ELECTROCHEMICAL CELL ::

- (a) It is the device in which the decrease in free energy during the spontaneous redox reaction is made to convert chemical energy into electrical energy is called electrochemical cell.
- (b) Galvanic and voltaic developed such devices and therefore these cells are also known as Galvanic cells or voltaic cells or redox cells.
- (c) The Daniel cell is a typical galvanic cell. It is designed to make use of the spontaneous redox reaction between zinc and cupric ion to produce an electric current.
- (d) The Daniel cell reaction is represented as  

$$\text{Zn}_{(s)} + \text{Cu}^{+2}_{(aq)} \longrightarrow \text{Zn}^{+2}_{(aq)} + \text{Cu}_{(s)}$$
- (e) The Daniel cell can be conventionally represented as  

$$\text{Zn}_{(s)} | \text{Zn SO}_4 \text{ (aq)} | \text{salt bridge} | \text{CuSO}_4 \text{ (aq.)} | \text{Cu}_{(s)}$$

### 9.1 Salt Bridge

It is an inverted U-shaped glass tube filled with a gel like substance like agar-agar mixed with an inert electrolyte like, KCl, KNO<sub>3</sub> or K<sub>2</sub>SO<sub>4</sub> (which has equal mobility of cations and anions).

### 9.2 Functions of salt bridge

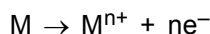
- It allows the flow of current by completing the electrical circuit.
- It maintains electrical neutrality of the two solutions in the two half cells.
- It prevents intermixing of solution as well as ions in the two half cells, which may lead to a precipitation reaction.

## 10. ELECTRODE POTENTIAL ::

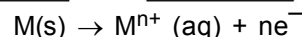
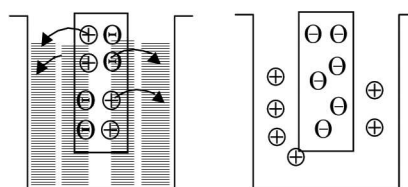
When a metal is placed in a solution of its ions, the metal acquires either a positive or negative charge with respect to the solution. On account of this a definite potential difference is developed between the metal and the solution. This potential difference is called electrode potential.

Example - If a Zn plate is placed in a solution having Zn<sup>+2</sup> ions, it becomes negatively charged with respect to solution and thus a potential difference is set up between Zn plate and the solution.

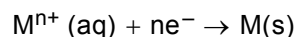
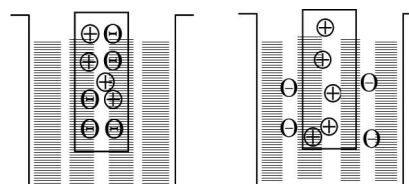
- (i) The conversion of metal atoms into metal ions take place by the attractive force of polar water molecules.



The metal ions go into the solution and electrons remain on the metal making it negatively charged. "The tendency of the metal to change into ions is known as electrolytic solution pressure"



- (ii) Metal ions start depositing on the metal surface leading to a positive charge on the metal. "This tendency of the ion is termed osmotic pressure"



- If first effect is greater than the second, the metal acquires a negative charge with respect to solution.
- If second is greater than the first it acquires positive charge with respect to solution.
- The magnitude of electrode potential of a metal is the measure of its relative tendency to lose or gain electrons
- The electrode potential depends upon the following factors-
  - Nature of the electrode
  - Concentration of the ions in solution
  - Temperature

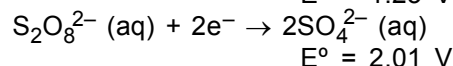
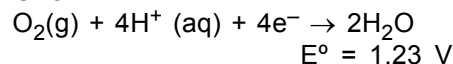
### 10.1 Types of electrode potential

- Oxidation potential** : The tendency of getting oxidised.
  - Reduction potential** : The tendency of getting reduced.
- ⇒ E<sub>oxi</sub> of an element is same in magnitude but opposite in sign to the E<sub>red</sub>. (i.e. E<sub>oxi</sub> = - E<sub>red</sub>)
- ⇒ By conventions, the electrode potential is represented by reduction potential (E<sub>red</sub>).

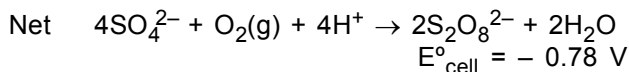
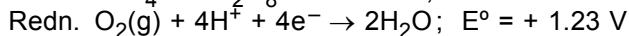
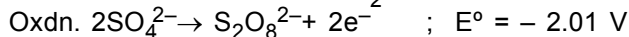
Examples based on

### electrode potential

- Ex.7** Peroxodisulphate salts (e.g. Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) are strong oxidising agents used as bleaching agents for fats, oils and fabrics. Can oxygen gas oxidise sulphate ion to peroxodisulphate ion (S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) in acidic solution, with the O<sub>2</sub> (g) being reduced to water-  
Given



**Sol.** We want oxidation of  $\text{SO}_4^{2-}$  by  $\text{O}_2(\text{g})$  which in turn is reduced to  $\text{H}_2\text{O}$  in acidic medium.



The large negative values of  $E^\circ_{\text{cell}}$  indicates that  $\text{O}_2(\text{g})$  will not oxidise  $\text{SO}_4^{2-}$  to  $\text{S}_2\text{O}_8^{2-}$  to any significant extent.

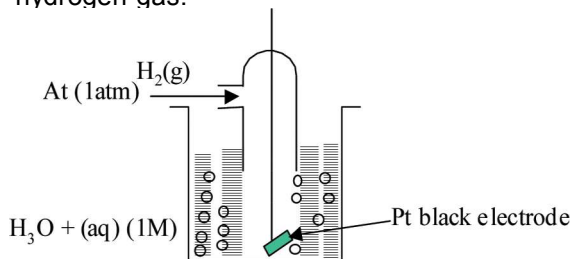
## 11. STANDARD ELECTRODE POTENTIAL ::

The potential difference developed between metal electrode and the solution of its ion of unit molarity (1M) at  $25^\circ\text{C}$  (298K) is called standard electrode potential) and is represented by  $E^\circ$ .

**Reference electrode :**

**(Standard Hydrogen Electrode, SHE or NHE)**

Hydrogen electrode is the primary standard electrode. It consists of a small platinum strip coated with platinum black so as to adsorb hydrogen gas.

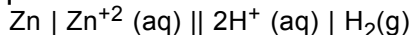


(Hydrogen electrode)

A platinum wire is welded to the Pt strip and sealed in a glass tube so as to make contact with outer circuit through mercury. The Pt strip is placed in an acid solution which has  $\text{H}^+$  ion concentration 1 M. Pure  $\text{H}_2$  gas is circulated through the solution at 1 atm and 298K,  $\text{H}_2 \rightleftharpoons 2\text{H}^+ + 2\text{e}^-$

- The SHE potential is fixed as zero
- SHE as cathode –  $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$   
SHE as anode –  $\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$
- Pt foil is used in SHE because it is a very good adsorber of  $\text{H}_2$  gas
- pH of acid solution in SHE is zero.

**Determination of standard electrode potential of Zn |  $\text{Zn}^{+2}$  electrode.**



Anode (-)                      cathode (+)

The e.m.f. of cell is 0.76 volt

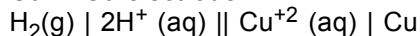
$E_{\text{cell}} = E^\circ_{\text{Anode}} + E^\circ_{\text{cathode}}$

$E^\circ_{\text{Anode}} = 0.76$

$E^\circ_{\text{oxidation}} = 0.76$

$E^\circ_{\text{Reduction}} = -0.76$

$\text{Cu}^{2+}/\text{Cu}$  electrode



anode (-)                      cathode (+)



e.m.f. of the cell is 0.34 volt.

$E^\circ_{\text{cell}} = E^\circ_{\text{anode}} + E^\circ_{\text{cathode}}$

$0.34 = 0 + E^\circ_{\text{cathode}}$

$E^\circ_{\text{Reduction}} = 0.34$

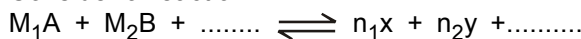
## 12. EMF OR CELL POTENTIAL ( $E_{\text{cell}}$ ); NERNST EQUATION ::

The difference between the electrode potentials of the two half cells is called electro motive force (EMF) of the cell. It is measured directly with a voltmeter and its value is expressed in volts. Due to the EMF, the electrons flow from an electrode of lower reduction potential (anode) to the electrode of higher reduction potential (cathode)

$$\text{EMF} = E_{\text{red}}(\text{cathode}) - E_{\text{red}}(\text{anode})$$

$\Rightarrow$  For a cell reaction to occur spontaneously, EMF = +ve;  $E_{\text{red}}(\text{cathode}) > E_{\text{red}}(\text{anode})$ .

Consider a reaction



$$\Delta G = \Delta G^\circ + 2.303 RT \log_{10} \frac{a_x^{n_1} \times a_y^{n_2} \dots}{a_A^{M_1} \times a_B^{M_2} \dots}$$

$$-nFE_{\text{cell}} = -nFE^\circ_{\text{cell}} + 2.303RT \log_{10} \frac{a_x^{n_1} \times a_y^{n_2} \dots}{a_A^{M_1} \times a_B^{M_2} \dots}$$

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{2.303}{nF} RT \log_{10} \frac{a_x^{n_1} \times a_y^{n_2}}{a_A^{M_1} \times a_B^{M_2}}$$

or

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{n} \log_{10} \frac{[\text{Products}]}{[\text{Reactants}]}$$

The above relation is known as Nernst equation.

$\Rightarrow$   $E_{\text{red}}$  of a metal generally decreases with decrease in the concentration of its ions and increases with increase in the concentration of its ions in the solution.

$\Rightarrow$   $E_{\text{red}}$  of a non metal (except H) decreases with increase in concentration of its ions (anions) in the solution.

## 13. ELECTROCHEMICAL SERIES ::

By measuring the potential of various electrode versus hydrogen electrode (SHE) a series of standard electrode potentials has been established.

When the electrodes (metal and non-metal) in contact with their ions are arranged on the basis of the values of their standard reduction potentials or standard oxidation potentials, the resulting series is called the electrochemical or electromotive or activity series, of the elements.

### The electrochemical series

Element	Electrode reaction (Reduction)	Standard electrode reduction potential $E^\circ$ volts
Li	$\text{Li}^+ + e \rightarrow \text{Li}$	-3.05
K	$\text{K}^+ + e \rightarrow \text{K}$	-2.925
Ca	$\text{Ca}^{2+} + 2e \rightarrow \text{Ca}$	-2.87
Na	$\text{Na}^+ + e \rightarrow \text{Na}$	-2.714
Mg	$\text{Mg}^{+2} + 2e \rightarrow \text{Mg}$	-2.37
Al	$\text{Al}^{+3} + 3e \rightarrow \text{Al}$	-1.66
Zn	$\text{Zn}^{+2} + 2e \rightarrow \text{Zn}$	-0.7628
Cr	$\text{Cr}^{+3} + 3e \rightarrow \text{Cr}$	-0.74
Fe	$\text{Fe}^{+2} + 2e \rightarrow \text{Fe}$	-0.44
Cd	$\text{Cd}^{+2} + 2e \rightarrow \text{Ni}$	-0.403
Ni	$\text{Ni}^{+2} + 2e \rightarrow \text{Sn}$	-0.25
Sn	$\text{Sn}^{+2} + 2e \rightarrow \text{Sn}$	-0.14
$\text{H}_2$	$2\text{H}^+ + 2e \rightarrow \text{H}_2$	0.00
Cu	$\text{Cu}^{+2} + 2e \rightarrow \text{Cu}$	+0.337
$\text{I}_2$	$\text{I}_2 + 2e \rightarrow 2\text{I}^-$	+0.535
Ag	$\text{Ag}^+ + e \rightarrow \text{Ag}$	+0.799
Hg	$\text{Hg}^{+2} + 2e \rightarrow \text{Hg}$	+0.885
$\text{Br}_2$	$\text{Br}_2 + 2e^- \rightarrow 2\text{Br}$	+1.08
$\text{Cl}_2$	$\text{Cl}_2 + 2e^- \rightarrow 2\text{Cl}^-$	+1.36
Au	$\text{Au}^{+3} + 3e \rightarrow \text{Au}$	+1.50
$\text{F}_2$	$\text{F}_2 + 2e \rightarrow 2\text{F}^-$	+2.87

increasing tendency to accept electrons

increasing tendency to lose electrons

#### 13.1 Characteristics of electrochemical series

- Negative sign of SRP (standard reduction potential) indicates that an electrode when joined with SHE acts as anode and oxidation occurs on this electrode. Similarly positive sign of SRP indicates that an electrode when joined with SHE acts as cathode and reduction occurs on this electrode.
- The substances which are stronger reducing agents than hydrogen are placed above hydrogen in the series.
- The substances which are stronger oxidising agents than  $\text{H}^+$  ion are placed below hydrogen in the series.
- The metals on the top are called active metals and activity decreases from top to bottom.

#### 13.2 Application of electro-chemical series

##### (i) Reactivity of metals

- Alkali metals and alkaline earth metals having high -ve values of SRP which are chemically active. These react with cold water and evolve hydrogen and readily dissolve in acids.
- Metals like Fe, Pb, Sn, Ni, Co, etc. do not react with cold water but react with steam to evolve hydrogen.
- Metals Li, Be, Cu, Ag, and Au which lie below hydrogen are less reactive and do not evolve hydrogen from water.

##### (ii) Electropositive character of metals

Electropositive character of metals decreases from top to bottom.

### (iii) Displacement reactions

To predict whether a given metal will displace another, from its salt solution.

The metal having low SRP will displace the metal from its salt's solution which has higher value of SRP.

### (iv) Reducing power of metals

Reducing nature decreases from top to bottom in the electrochemical series.

### (v) Oxidizing nature of non-metals

Oxidizing nature increases from top to bottom in the electrochemical series.

### (vi) Thermal stability of metallic oxides

The thermal stability of the metal oxide decreases from top to bottom.

### (vii) Products of electrolysis

The ion which is stronger oxidizing agent is discharged first at cathode.

$K^+$ ,  $Ca^{2+}$ ,  $Na^+$ ,  $Mg^{+2}$ ,  $Al^{+3}$ ,  $Zn^{+2}$ ,  $Fe^{+2}$ ,  $H^+$ ,  $Cu^{+2}$ ,  $Ag^+$ ,  $Au^{+3}$

increasing order of deposition

### (viii) Corrosion of metals

Corrosion is defined as the deterioration of a substance because of its reaction with its environment. The corrosion tendency decreases from top to bottom.

### (ix) Extraction of metals

Ag and Au extracted by cyanide process.

## 14. EMF OF CELL AND FREE ENERGY ::

$$-\Delta G = n FE_{\text{cell}}$$

$$-\Delta G^0 = n FE_{\text{cell}}^0$$

free energy and equilibrium constant

$$\Delta G^0 = -2.303 RT \log K$$

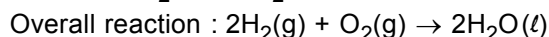
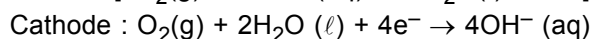
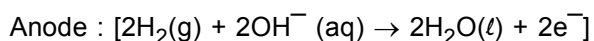
## 15. SOME COMMERCIAL CELLS ::

An electrochemical cells can be used to generate electricity. Such cells are called battery. The word battery is generally used for two or more galvanic cells connected in series. There are two types of commercial cells.

(i) **Primary cells** : in which electrode reactions cannot be reversed by external energy source. These are not chargeable. Examples of this type of cell is dry cell or Leclanche cell, mercury cell.

(ii) **Secondary cells** : are those cells which are rechargeable. For example, lead storage battery, nickel cadmium cell.

(iii) **Fuel cells** : These are voltaic cells in which the reactants are continuously supplied to the electrodes. These are designed to convert the energy from combustion of fuel such as  $H_2$ ,  $CO$ ,  $CH_4$ , etc. directly into electrical energy. The common example of fuel cell is Hydrogen - Oxygen fuel cell. The reactions occurring in this cell are.



## 16. CORROSION ::

It is the deterioration of a metal as result of its reaction with air or water (environment) surrounding it. Corrosion of iron is called rusting. The electrochemical theory is proposed to explain the phenomenon of rusting. Rust is  $Fe_2O_3 \cdot xH_2O$ . Pure iron does not rust. Also iron does not rust in vacuum because air is necessary for rusting. Rust is faster in sea water because of dissolved salts. In it the rusting of iron can be prevented by a number of methods.

(i) Barrier protection through coating of paints or electroplating.

(ii) Through galvanisation or coating of surface with tin metal (sacrificial protection). Galvanisation (with Zn) is better than tinning (with Sn) of iron. The galvanised iron has lustre due to the coating of layer of basic zinc carbonate  $ZnCO_3 \cdot Zn(OH)_2$

(iii) By the use of anti rust solution, etc.

(iv) Electrical protection by connecting the iron pipe to a more electropositive metal with a wire.

## SOLVED EXAMPLES

- Ex.1** The reaction : $\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$  has an electrode potential of  $-0.76\text{ V}$ . This means-
- (A) Zn cannot replace hydrogen from acids  
 (B) Zn is reducing agent  
 (C) Zn is oxidizing agent  
 (D)  $\text{Zn}^{2+}$  is a reducing agent

**Sol. (B)** Negative electrode potential shows that  $\text{Zn}^{2+}$  is difficult to be reduced and therefore, Zn acts as reducing agent.

- Ex.2** Other things being the same, the  $E_{\text{cell}}$  of the Daniel cell may be increased by-
- (A) Keeping low temperature  
 (B) Using large copper electrode  
 (C) Using small zinc electrode  
 (D) Decreasing the conc. of  $\text{Cu}^{2+}$

**Sol. (A)**  $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$

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

Decrease in temperature makes the value of

$\frac{2.303 RT}{nF}$  smaller. Smaller the value of this factor, greater is  $E_{\text{cell}}$ .

- Ex.3** The equivalent conductivities at infinite dilution of the cation and the anion of a salt  $\text{A}_2\text{B}$  are 140 and 80  $\text{ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$  respectively. The equivalent conductivity of the salt at infinite dilution is-

- (A) 160  $\text{ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$   
 (B) 220  $\text{ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$   
 (C) 60  $\text{ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$   
 (D) 360  $\text{ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$

**Sol.(D)**  $\Lambda_{\text{eq}}^{\infty}(\text{A}_2\text{B}) = 2 \times \lambda_{\text{eq}}^{\infty}(\text{A}^+) + \lambda_{\text{eq}}^{\infty}(\text{B}^{2-}) = 2 \times 140 + 80 = 360 \text{ ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$

- Ex.4** The specific conductance of a 0.20 mol  $\text{L}^{-1}$  solution of an electrolyte at  $20^{\circ}\text{C}$  is  $2.48 \times 10^{-4} \text{ ohm}^{-1} \text{cm}^{-1}$ . The molar conductivity of the solution is -

- (A) 1.24  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$   
 (B) 4.96  $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$   
 (C) 1.24  $\text{ohm}^{-1} \text{cm}^2$   
 (D) 4.96  $\text{ohm}^{-1} \text{cm}^2$

**Sol. (A)**  $\Lambda_m = \frac{\kappa}{M} = \frac{2.48 \times 10^{-4} \text{ ohm}^{-1} \text{cm}^{-1}}{0.20 \text{ mol L}^{-1}}$

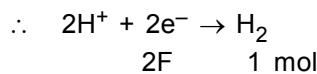
$$= \frac{2.48 \times 10^{-4} \times 1000 \text{ ohm}^{-1} \text{mol}^{-1} \text{cm}^2}{0.20} \quad (1\text{L} = 1,000 \text{ cm}^3)$$

$$= 1.24 \text{ ohm}^{-1} \text{mol}^{-1} \text{cm}^2$$

- Ex.5** When an electric current is passed through acidulated water, 112 mL of hydrogen gas at N.T.P. collects at the cathode in 965 seconds. The current passed, in amperes, is-
- (A) 1.0  
 (B) 0.5  
 (C) 0.1  
 (D) 2.0

**Sol. (A)** 22,400 mL of hydrogen at STP(or NTP) = 2g  
 $\therefore$  12 mL of hydrogen at

$$\text{STP} = \frac{2\text{g} \times 112\text{mL}}{22,400\text{mL}} = 10^{-2} \text{ g}$$



$$= 2 \times 96,500 \text{ C} = 2 \text{ g}$$

2 g hydrogen is deposited by  $2 \times 96,500 \text{ C}$

$\therefore 10^{-2} \text{ g}$  hydrogen will be deposited by

$$= \frac{2 \times 96,500 \times 10^{-2} \text{ g}}{2\text{g}} = 965 \text{ C}$$

- Ex.6** The charge required to deposit 40.5 g of Al (atomic mass = 27.0 g) from the fused  $\text{Al}_2(\text{SO}_4)_3$  is-
- (A)  $4.34 \times 10^5 \text{ C}$   
 (B)  $43.4 \times 10^5 \text{ C}$   
 (C)  $1.44 \times 10^5$   
 (D) None of these

**Sol. (A)**  $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$

$$\frac{3F}{1 \text{ mol}} = 27.0 \text{ g}$$

$$= 3 \times 96,500 \text{ C}$$

to deposit 27g required charge

$\therefore$  to deposit 40.4g required charge

$$= \frac{40.5\text{g} \times 3\text{mol} \times 96,500\text{C mol}^{-1}}{27.0\text{g}}$$

$$= 4.34 \times 10^5 \text{ C}$$

**Ex.7** The same amount of electricity was passed through two separate electrolytic cells containing solutions of nickel nitrate and chromium nitrate respectively. If 0.3 g of nickel was deposited in the first cell, the amount of chromium deposited is (At. wt. Ni = 59, Cr = 52)

- (A) 0.1 g                      (B) 0.176 g  
(C) 0.3 g                      (D) 0.6 g

**Sol. (B)** 
$$\frac{m_{\text{Ni}}}{m_{\text{Cr}}} = \frac{\text{Eq. mass of Ni}}{\text{Eq. mass of Cr}}$$

For  $\text{Ni}^{2+}$  and  $\text{Cr}^{3+}$ , we have :

$$\frac{0.3 \text{ g}}{m_{\text{Cr}}} = \frac{59/2}{52/3}$$

$$m_{\text{Cr}} = \frac{0.3 \text{ g} \times \frac{52}{3}}{(59/2)} = 0.176 \text{ g}$$

**Ex.8** Electrolytic conduction differs from metallic conduction. In case of metallic conduction -

- (A) The resistance increases with increasing temperature  
(B) The resistance decreases with increasing temperature  
(C) The flow of current does not generate heat  
(D) The resistance is independent of the length of electrolytic conductor

**Sol. (A)** With the increase in temperature, the ions start moving faster and therefore, conduction increases and hence, resistance of the electrolytic conductor decreases.

**Ex.9** Three faraday of electricity is passed through aqueous solutions of  $\text{AgNO}_3$ ,  $\text{NiSO}_4$  and  $\text{CrCl}_3$  kept in three vessels using inert electrodes. The ratio in mol in which the metals Ag, Ni and Cr will be deposited is-

- (A) 1 : 2 : 3                      (B) 3 : 2 : 1  
(C) 6 : 3 : 2                      (D) 2 : 3 : 6

**Sol (C)** (i)  $\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$

$$1 \text{ mol} = 1\text{F} \quad 1 \text{ mol}$$

$$3 \text{ F} \quad 3 \text{ mol}$$

(ii)  $\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Ni}(\text{s})$

$$2 \text{ mol} = 2 \text{ F} \quad 1 \text{ mol}$$

$$3 \text{ F} \quad 3/2 \text{ mol}$$

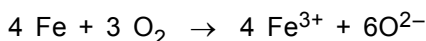
(iii)  $\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Cr}(\text{s})$

$$3 \text{ mol} = 3 \text{ F} \quad 1 \text{ mol}$$

The required ratio of moles of Ag, Ni and Cr is :

3 mol Ag : 3/2 mol Ni : 1 mol Cr or **6 mol Ag : 3 mol Ni : 2 mol Cr.**

**Ex.10** In the reaction :



which of the following statements is correct

- (A) A redox reaction  
(B) Fe is reducing agent  
(C)  $\text{Fe}^{3+}$  is an oxidizing agent  
(D) Fe is reduced to  $\text{Fe}^{3+}$

**Sol. (A)** In this reaction, Fe is oxidized to  $\text{Fe}^{3+}$  and  $\text{O}_2$  is reduced to  $\text{O}^{2-}$ .