# Electro Chemistry

**1.** **Distinction between metallic and electrolytic conduction**

| Metallic conduction | Electrolytic conduction |
|---|---|
| **1.** Electric current flows by movement of electrons. | **1.** Electric current flows by movement of ions. |
| **2.** No chemical change occurs | **2.** Ions are oxidised or reduced at the electrodes. |
| **3.** It does not involve the transfer of any matter | **3.** It involves transfer of matter in the form of ions. |
| **4.** Ohm's law is followed | **4.** Ohm's law is followed |
| **5.** Resistance increases with increase of temperature | **5.** Resistance decreases with increase of temperature |
| **6.** Faraday law is not followed | **6.** Faraday law is followed |

**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 ions furnished by electrolyte called cation while the negative charged ion furnished by electrolyte is called anion.

☞ **Types of Electrolytes**

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

(b) Weak Electrolyte - Electrolytes which are decomposable into a very small extent in their dilute solutions are called weak electrolytes eg. Organic acids, inorganic acids and bases etc.

**3.** **Electrode**

(a) When the electric current pass 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.

☞ **Electrode potential -** The potential difference between the electrode and the electrolyte surrounding the electrode are called electrode potential.

☞ **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.

☞ **Type 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 are also bring a chemical change during 'the passage of electric current.

(ii) In this type of cells chemical energy is converted into electrical energy.

**5.** **Electrolysis**

**Faraday's laws of electrolysis**

**First Law :** The amount (W) of an ion oxidised or reduced at either electrode during the passage of current is proportional to the quantity of electricity passed.

$$\therefore W = Z \times i \times t$$

$$= \frac{E \times i \times t}{96500} = \frac{M \times i \times t}{n \times 96500}$$

Z = Electrochemical equivalent

i = Current in ampere

t = Time in sec.

E = Equivalent weight

M = Molecular weight or atomic weight as the case may be

n = Valency factor

**Second Law :** The passage of the same charge throgh different electrolytes brings in equal equivalents of ion to be oxidised or reduced at either electrodes as the case may be.

$$\therefore \frac{W_A}{E_A} = \frac{W_B}{E_B} = \frac{W_C}{E_C} \qquad \text{If Q the quantity of electricity (i} \times \text{t) is same.}$$

**Some important points.**

(i)      **1** Faraday is the quantity of one mole of electrons = 96500 coulombs.

(ii)     **1** Faraday current will deposit one gram equivalent of substance.

(iii)    During electrolysis of an aqueous solution of a electrolysis water also competes for oxidation at anode reduction at cathode according to following equations.

**at anode**      :  $2H_2O \longrightarrow 4H^+ + O_2 + 4e^-$  ;   SOP = – 1.23 V

**at cathode**   :  $2H_2O \longrightarrow 2OH^- + H_2$ ;       SRP = – 0.83 V

(iv)     Except overvoltage, that substance will be reduced first at cathode whose SRP is higher and similarly that will be oxidised at anode whose SOP is higher.

(v)      Lead storage battery.

Cell reactions during discharge :

**anode**      :  $Pb(s) + SO_4^{2-} (aq) \longrightarrow PbSO_4(s) + 2H_2O$

**cathode**    :  $PbO_2(s) + SO_4^{2-} (aq) + 4H^+(aq). 2e^- \longrightarrow PbSO_4(s) + 2H_2O$

over cell reaction :  $Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(\ell)$

(vi)     Fuel Cells

**Some more examples of electrolysis**

| Electrolyte | Electrode | Cathodic reaction | Anodic reaction |
| --- | --- | --- | --- |
| Aqueous acidified $CuCl_2$ Solution | Pt | $Cu^{2+} + 2e^- \longrightarrow Cu$ | $2Cl^- \longrightarrow Cl_2 + 2e^-$ |
| Molten $PbBr_2$ | Pt | $Pb^{2+} + 2e^- \longrightarrow Pb$ | $2Br^- \longrightarrow Br_2 + 2e^-$ |
| Sodium chloride Solution | Hg | $2Na^+ + 2e^- \longrightarrow 2Na$ | $2Cl^- \longrightarrow Cl_2 + 2e^-$ |
| Silver nitrate Solution | Pt | $Ag^+ + e^- \longrightarrow Ag$ | $2OH^- \longrightarrow \frac{1}{2}O_2 + H_2O + 2e^-$ |
| Sodium nitrate | Pt | $2H^+ + 2e^- \longrightarrow H_2$ | $2OH^- \longrightarrow \frac{1}{2}O_2 + H_2O + 2e^-$ |

**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.

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

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

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

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

$$K = \frac{1}{\rho} \ \text{or} \ K = \frac{l}{a \times R} \qquad \therefore \ \frac{l}{a} = \text{Cell constant}$$

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

**(d)** **Electrical conductivity (C)**
(i) It is the reciprocal of resistance (R), which is expressed in ohm$^{-1}$ or mho.

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

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

**(e)** **Equivalent conductance (Λ)**
(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.

$$\Lambda = k \ x \ \frac{1000}{C}$$

or $\qquad \Lambda = k \ x \ \frac{1000}{N}$

where N = normality C = concentration of the solution
(ii) The unit of equivalent conductance is ohm$^{-1}$ cm$^2$ equivalent.

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

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

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

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

**7.** **Kohlrausch's law**
For an infinite dilution, equivalent conductivity of a weak electrolyte is equal to the sum of conductivity of the two types ion.

$$\bigwedge\nolimits_{AB}^{\infty} = \lambda_{A^+}^{\infty} + \lambda_{B^-}^{\infty}$$

☞ **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.

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

(c) To evaluate dissociation constant of weak electrolysis.

(d) To evaluate absolute ionic mobilities.

(e) To evaluate solubility of sparingly soluble salts.

(f) To evaluate ionic product of water.

## 8. Applications of Electrolysis

(a) In the extraction of metals

(b) Preparation of chemicals

(c) Preparation of organic compounds

(d) Corrosion and their prevention

## 9. ELECTROCHEMICAL CELL

A device which produce electricity as a result on chemical reaction.(Conversion of chemical energy into electrical energy)

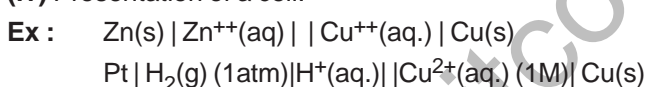**(i) Anode :** electrode of negative polarity at which oxidation occurs.

**Ex. :** $Zn \,|\, ZnSO_4(aq)$ ; $Zn(s) \longrightarrow Zn^{++}(aq.) + 2e^-$
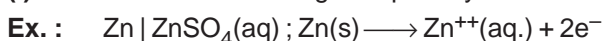
**(ii) Cathode :** Elecrode of positive polarity at which reduction occurs

**Ex. :** $Cu \,|\, CuSO_4(aq.)$ ; $Cu^{2+}(aq.) + 2e^- \longrightarrow Cu(s)$
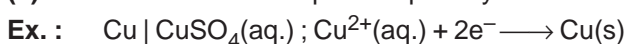
**(iii) Salt Bridge (II) :** Generally a U-tube containing a solution of KCl or $NH_4NO_3$ set with agar agar powder in the form of a jelly like structure. It provides an electric contact between anodic and cathodic compartments without allowing them to mix with each other.

**(iv)** Presentation of a cell.

**Ex :** $Zn(s) \,|\, Zn^{++}(aq) \,|\,| \, Cu^{++}(aq.) \,|\, Cu(s)$

$Pt \,|\, H_2(g) \,(1atm) | H^+(aq.)| \,|Cu^{2+}(aq.) \,(1M)| \, Cu(s)$

Here    Pt is an inert electrode.

**(v)**    $E_{cell}$ = Reduction potential of cathode – Reduction Potential of anode

$E^{o}_{cell}$ = Standard reduction potential of cathode – Standarde reduction potential of anode

A electrode is said to be under standard conditions if

(a)    Concentration of electrolytic solution is 1 molal (for preactical purpose 1.0 M)

(b)    Pressure of the gas/gases involved is 1 atm.

(c)    Temp is constant usually 298 K.

**Ex.**    Standard Hydrogen Electrode (SHE)

$Pt \,|H_2(g), (1.0 \, atm)| \, H^+(1.0 \, M)$
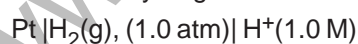
$E^{o}_{H^+/H_2}$ (SRP) = 0.00 V at all temperatures.

## 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 $Zn^{+2}$ 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 by the attractive force of polar water molecules.

$M \rightarrow M^{n+} + ne^-$
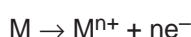
The metal ions go into the solution and electrons remains on the metal making it negatively charged.

"The tendency of the metal to change into ions is known as electrolytic solution pressure"



$$M(s) \rightarrow M^{n+} (aq) + ne^-$$
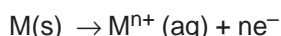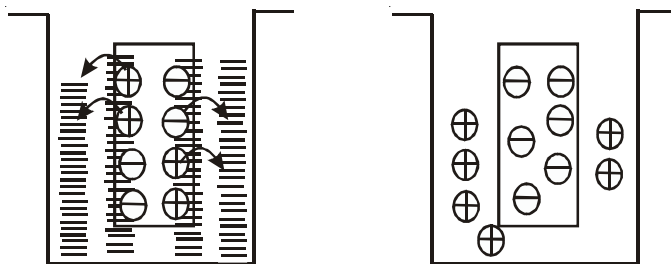
(ii) Metal ions start depositing on the metal surface leading to a positive charge on the metal.

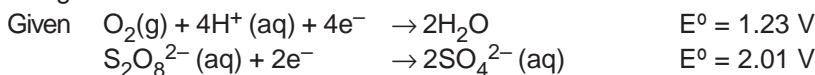"This tendency of the ion is termed osmotic pressure"



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

at equilibrium $M \rightleftharpoons M^{n+} + ne^-$
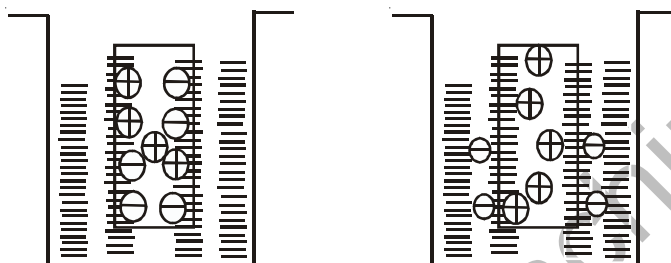
(i) If first effect is greater than the second.the metal acquires a negative charge with respect to solution.

(ii) If second is greater than the first it acquires positive charge with respect to solution

(iii) the magnitude of electrode potential of a metal is measure of its relative tendency to lose or gain electrons

(iv) The electrode potential depends upon the following factors -

    (a) Nature of the electrode

    (b) Concentration of the ions in sodium
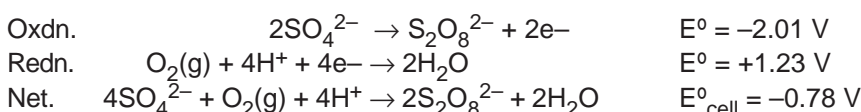
    (c) Temperature

**(i) Oxidation potential -** When electrode is negatively charged with respect to solution i.e. it acts as anode, oxidation occurs.

**(ii) Reduction potential -** When electrode is positively charged with respect to 'Solution i.e. it acts as cathode reduction occurs.

**Ex.** Peroxod sulphate salts (e.g. $Na_2S_2O_8$) are strong oxidising agents used as bleaching agents for fats, oils and fabrics. Can oxygen gas oxidisesulphate ion to peroxodisulphate ion ($S_2O_8^{2-}$) in acidic solution, with the $O_2(g)$ being reduced to water

Given    $O_2(g) + 4H^+ (aq) + 4e^- \rightarrow 2H_2O$        $E^0 = 1.23$ V

           $S_2O_8^{2-} (aq) + 2e^- \rightarrow 2SO_4^{2-} (aq)$        $E^0 = 2.01$ V

**Sol.** We want oxidation of $SO_4^{2-}$ by $O_2(g)$ which in turn is reduced to $H_2O$ in acidic medium.

Oxdn.            $2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e-$        $E^0 = -2.01$ V

Redn.           $O_2(g) + 4H^+ + 4e- \rightarrow 2H_2O$      $E^0 = +1.23$ V

Net.            $4SO_4^{2-} + O_2(g) + 4H^+ \rightarrow 2S_2O_8^{2-} + 2H_2O$      $E^0_{cell} = -0.78$ V

The large negative values of $E^0_{cell}$ indicates that $O_2(g)$ will not oxidise $SO_4^{2-}$ to $S_2O_8^{2-}$ 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 25ºC (298 K) is called standard electrode potential .

According to IUPAC convention, the reduction potential along be called as the electrode potential ($E^0$) standard reduction potential = – (standard oxidation potential)

**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 as to adsorb hydrogen gas.



(Hydrogen electrode)
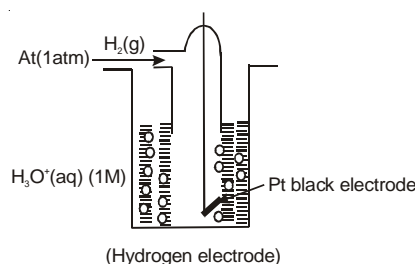
A platinum wire is welded to the Pt strip and sealed in a glass tube as to make contact with outer circuit through mercury. The Pt strip is placed in an acid solution which has $H^+$ ion concentration 1 M. Pure $H_2$ gas circulated at 1 atm, $H_2 = 2H^+ + 2e^-$.

(a) The SHE potential is fixed as zero

(b) Hydrogen electrode is difficult to maintain.

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

$Zn | Zn^{2+}$ (aq) || $2H^+$(aq)| $H_2$(g)

Anode (–)          Cathode (+)

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

$$E \text{ cell} = E^o_{Anode} + E^o_{Cathode}$$

$$E^o_{Anode} = 0.76$$

$$E^o_{Oxidation} = 0.76$$

$$E^o_{Reduction} = -0.76$$

$Cu^{2+}/Cu$ electrode

$H_2$(g) | $2H^+$(aq) || $Cu^{+2}$(aq) | Cu

anode (–)          Cathode (+)

$H_2 \rightarrow 2H^+ + 2e$   $Cu^{+2} + 2e \rightarrow Cu$
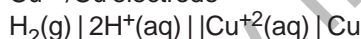
e.m.f. of the cell is 0.34 volt.

$$E^o_{cell} = E^o_{Anode} + E^o_{Cathode}$$

$$0.34 = 0 + E^o_{Cathode}$$

$$E^o_{Reduction} = 0.34$$

## 12. NERNST EQUATION

(a) For electroce say M | $M^{n+}$(aq.)

The half reaction is $M^{N+} + ne^- \longrightarrow M(s)$

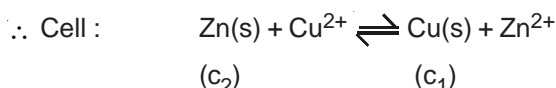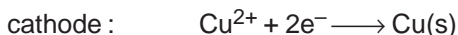$$\therefore E_{M^{n+}/M} = E^o_{M^{n+}/M} - \frac{2.303RT}{nF} \log \frac{[M(s)]}{[M^{n+}]}$$
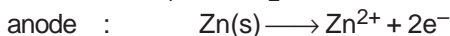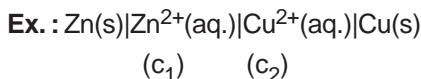
If T = 298 K than $\dfrac{2.303RT}{F} = \dfrac{2.303 \times 8.314 \times 298}{96500}$

$= 0.0591$ or simply $0.059$

By combining any electrode under standard conditions with SHE (for which SRP is always zero), SRP of that electrode is determined.These are then arranged in the increasing order which constitute a series known as Electro-chemical series. Some examples from that series are -

$$Li, K, Ca, Na, Mg, Zn, Fe, Pb, \quad H_2, \quad Cu, I_2, Ag, Br_2, O_2, Cl_2, F_2$$

$E^0$ (SRP)      (–3.05 V)                   (0.00 V)                     (+ 2.87 V)

(at 298 K)

**(b) For cell**

**Ex. :** $Zn(s)|Zn^{2+}(aq.)|Cu^{2+}(aq.)|Cu(s)$

               $(c_1)$         $(c_2)$

anode :          $Zn(s) \longrightarrow Zn^{2+} + 2e^-$

cathode :       $Cu^{2+} + 2e^- \longrightarrow Cu(s)$

_____

$\therefore$ Cell :         $Zn(s) + Cu^{2+} \rightleftharpoons Cu(s) + Zn^{2+}$

               $(c_2)$              $(c_1)$

$$E_{cell} = E^o_{cell} - \frac{2.303RT}{nF} \log \frac{[Product]}{[Reactants]}$$

$$= E^o_{cell} - \frac{2.303RT}{2F} \log \frac{C_1}{C_2} \quad [\text{ n = 2 in the above example}]$$

$$= E^o_{cell} - \frac{2.303RT}{2F} \log Q \quad [Q = \text{reaction quotient}]$$

$$= E^o_{cell} - \frac{0.059}{2} \log Q \quad [\text{at 298 K}]$$

$\because$ At equilibrium $E_{cell}$ = zero, then Q = k,

$$\therefore E^o_{cell} = \frac{0.059}{n} \log K$$

(vii) Thermodynamic Relations.

(a) For any electrode $\Delta G = - nEF$         or         $\Delta G^0 = - nE^oF$

                    (electrode)

**Note.** Construction of a new electrode with the help of two given electrodes must be done with the help of $\Delta G^0$ values.

(b) For a cell

      $\Delta G = - nFE_{cell}$ and $\Delta G^0 = - nE^oF$

    cell                  (cell)     (cell)

## 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 electrode (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 electro-chemical or electromotive or activity series, of the elements.

The electrochemical series

| Element | Electrode reaction (Reduction) | Standard electrode reduction potential E° volts |
|---------|-------------------------------|------------------------------------------------|
| Li | $Li^+ + e \rightarrow Li$ | - 3.05 |
| K | $K^+ + e \rightarrow K$ | - 2.925 |
| Ca | $Ca^{2+} + 2e \rightarrow Ca$ | - 2.87 |
| Na | $Na^+ + e \rightarrow Na$ | - 2.714 |
| Mg | $Mg^{+2} + 2e \rightarrow Mg$ | - 2.37 |
| Al | $Al^{+3} + 3e \rightarrow Al$ | - 1.66 |
| Zn | $Zn^{+2} + 2e \rightarrow Zn$ | - 0.7628 |
| Cr | $Cr^{+3} + 3e \rightarrow Cr$ | - 0.74 |
| Fe | $Fe^{+2} + 2e \rightarrow Fe$ | - 0.44 |
| Cd | $Cd^{+2} + 2e \rightarrow Ni$ | - 0.403 |
| Ni | $Ni^{+2} + 2e \rightarrow Sn$ | - 0.25 |
| Sn | $Sn^{+2} + 2e \rightarrow Sn$ | - 0.14 |
| $H_2$ | $2H^+ + 2e \rightarrow H_2$ | 0.00 |
| Cu | $Cu^{+2} + 2e \rightarrow Cu$ | + 0.337 |
| $I_2$ | $I_2 + 2e \rightarrow 2I^-$ | + 0.535 |
| Ag | $Ag^+ + e \rightarrow Ag$ | + 0.799 |
| Hg | $Hg^{+2} + 2e \rightarrow Hg$ | + 0.885 |
| $Br_2$ | $Br_2 + 2e^- \rightarrow 2Br$ | + 1.08 |
| $Cl_2$ | $Cl_2 + 2e^- \rightarrow 2Cl^-$ | + 1.36 |
| Au | $Au^{+3} + 3e \rightarrow Au$ | + 1.50 |
| $F_2$ | $F_2 + 2e \rightarrow 2F^-$ | + 2.87 |

*(left side of table: increasing tendency to accept electrons; right side of table: increasing tendency to loose electrons)*

☞ **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.

(b) The substances which are stronger reducing agents than hydrogen are placed above hydrogen in the series.

(c) The substances which are stronger oxidising agents than $H^+$ ion are placed below hydrogen in the series.

(d) The metals on the top are called active metals and activity decreases from top to bottom.

☞ **Application of electro-chemical series**

**(i) Reactivity of metals**

(a) 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.

(b) Metals like Fe; Pb, Sn, Ni, Co, etc. do not react with cold water but react with steam to evolve hydrogen.

(c) Metals U, l3e, Cu, Ag, and Au which lie below hydrogen are less reactive and donot 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

$-\Delta G = n\, FE_{cell}$        $\Delta G^o = n\, FE^o_{cell}$

free energy and equilibrium constant        $\Delta G^o = -2.303\, RT \log K$
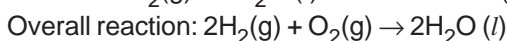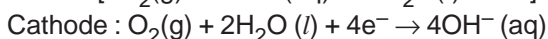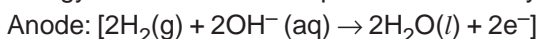
## 15.   SOME COMMERCIAL CELLS

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 occuring in this cell are.

Anode: $[2H_2(g) + 2OH^-(aq) \rightarrow 2H_2O(l) + 2e^-]$

Cathode : $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

Overall reaction: $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

## 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 $Fe_2O_3. xH_2O$. 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). Galvinisation (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 $ZnCO_3.Zn(OH)_2$

(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.

## 17.   SOME IMPORTANT POINTS

(1) Conductivity of 1 cm$^3$ substance is called specific conductivity. Its unit is ohm$^{-1}$ cm$^{-1}$ and 1 cm$^3$ resistance of substance is specific resistance. Its unit is ohm cm.

(2) When 1 gram equivalent of a solute is dissolved in the solution present between two parallel electrodes situated at 1 cm distance, then the conductivity of this solution is called equivalent conductivity.

$$\lambda_N = \frac{1000 \times \kappa_v}{N} \text{ ohm}^{-1} \text{ cm}^2 \text{ equivalent}^{-1}$$

(3) Conductivity of the solution present between two parallel electrodes in which one mole solute is dissolved can be expressed as fallows.        $\lambda_M = \dfrac{1000 \times \kappa_v}{M}$ ohm$^{-1}$ cm$^2$ mole$^{-1}$

(4) Measurement of conductivity is done by Wheatstone bridge using the following expression $\dfrac{P}{Q} = \dfrac{R}{S}$

(5) Cell constant $\dfrac{\ell}{a}$. Its unit is $cm^{-1}$.

(6) Specific conductivity = Observed conductivity × Cell constant.

(7) Cell in which chemical change occurs due to passage of electric current is called electrolytic cell.

(8) The cell from which electricity is produced by chemical reactions is called electrochemical cell.

(9) The electrode at which oxidation occurs is called anode and the electrode at which reduction occurs is called cathode.

(10) Hydrogen gas is filled on platinum electrode in 1M acidic solution at 1 atmospheric pressure and 25ºC. Second electrode potential is zero.

(11) Total potential of cell, i.e., difference of the two half-cells is called electromotive force.

(12) Calculation of potential at different concentrations and at different temperatures is done by the following formula.

$$E_{Cell} = E^{0}_{Cell} + \frac{2.303RT}{nF} \log \frac{[A]^a [B]^b}{[C]^c [D]^d}$$

(13) Relation between cell potential and equilibrium constant is as fallows :

$$E^{0}_{Cell} = \frac{2.303 \times RT}{nF} \log K_c$$

(14) Relation between free energy and cell potential is as fallows :
$$\Delta G^0 = -nFE^{0}_{Cell}$$

(15) Faraday's law : In electrolysis, amount of substance deposited on an electrode is proportional to the electricity passed through it.

$$W \propto Q$$

$$W = ZQ \qquad (Q = It) \qquad Z = \frac{M}{nF} \qquad ; \qquad Z = \text{Electrochemical equivalent}$$

Therefore, $\qquad W = \dfrac{M}{nF} \times IT$

(16) 1 Faraday = 96500 Coulomb $\qquad ; \qquad$ Charge = Current × Time

(17) Amounts of substances released on electrodes on passing 1 faraday of electricity through the electrolytes are equal to their equivalent weights. $\qquad \dfrac{W_1}{E_1} = \dfrac{W_2}{E_2}$

(18) The battery which cannot be reused on getting discharged, is called primary battery.

(19) The battery which can be recharged after getting discharged, is called secondary battery.

(20) Rusting of metals by atmospheric gases is called corrosion process and electro protection is done to prevent this.

(21) Reaction involved in resulting of iron are as fallows :

$$Fe \rightarrow Fe^{+2} + 2e^{-} \qquad ; \qquad 2F^{+2} + 2O_2 + 2H_2O \rightarrow Fe_2O_3 + 4H^{+}$$
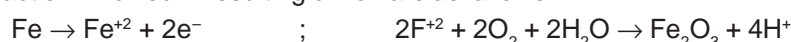
**Ex.1** Resistance of a cell (cell constant = 1.1), in which $\dfrac{N}{50}$ KCl is there, is found to be 400 ohm. Determine the specific conductivity and equivalent conductivity of KCl at this dilution.

**Sol.** Specific conductivity = Observed conductivity x Cell constant

$$= \frac{1}{400} \text{ x } 1.1 = \frac{1.1}{400} \text{ ohm}^{-1} \text{ cm}^{-1}$$

Equivalent conductivity $\lambda_N = K_V$ x V

$$\text{or } \lambda_N = \frac{1000 \times \kappa_v}{N} = \frac{1000 \times \dfrac{1.1}{400}}{\dfrac{N}{50}}$$

$$= 50000 \text{ x } \frac{1.1}{400} = 137.5 \text{ ohm}^{-1}\text{cm}^{-1}$$

**Ex.2** Equivalent conductivity of $H_2SO_4$ at infiinte dilution is 384 ohm$^{-1}$. If 49 gm per litre $H_2SO_4$ is present in the solution and its specific resistance is 18.4 ohm, then what would be the amount of dissociation of the solute?

**Sol.** Equivalent of $H_2SO_4 = \dfrac{49}{49} = 1N$

Specific conductivity $= \dfrac{1}{\text{Specifi resistance}} = \dfrac{1}{18.4}$

$$\lambda_N = \frac{1000 \times K_V}{N} = \frac{1000 \times 1}{18.4} \text{ x } 1$$

$$= 55 \text{ ohm}$$

$$\alpha = \frac{55}{384} = 0.14$$

i.e.　$a = 14\%$

**Ex.3** Equivalent conductivity of $NH_4Cl$ at infinite dilution is 150 cm$^3$ ohm$^{-1}$ cm$^{-1}$ and ionic mobilities of OH$^-$ and Cl$^-$ are 198 and 76.5, then what should be the equivalent conductivity of $NH_4OH$ at infinite dilute?

**Sol.** $\lambda_{NH_4} + \lambda_{OH^-} = (\lambda_{NH_4} + \lambda_{Cl^-}) + \lambda_{OH^-} - \lambda_{Cl^-}$
$$= 150 + 198 - 76.5$$
$$= 271.5$$

**Ex.4** A current of 0.2 ampere is passed for 15 minutes through a copper sulphate solution. If atomic weight of Cu is 63.5, then calculate the amount of Cu deposited on cathode.

**Sol.** $W = \dfrac{M}{nF}$ x It

M = 63.5g .　　　　　n = 2, F = 96500 coulomb

I = 0.2 ampere,　　　t = 15 minute (15 x 60 = 900 second)

$W = \dfrac{63.5}{2 \times 96500}$ x 0.2 x 900

W = 0.05 g

**Ex.5** What should be the amount of Al deposited on the cathode, when 0.1 farady of electricity is passed through $AlCl_3$ (Al = 27)?

**Sol.** $W = \dfrac{M}{n \times F} \times Q$

$= \dfrac{27}{3 \times 96500} = 96500 = 0.9g$

**Ex.6** Standard reduction potential of $Ag^{+1} \rightarrow Ag$ in $2Ag^+ + Cd \rightarrow 2Ag + Cd^{+2}$ reaction is 0.80 V and standard reduction potential of $Cd^{+2} \rightarrow Cd$ is –0.40 V. What should be the electromotive force of the cell?

**Sol.** EMF = Cathode (reduction) – Anode (reduction)

Cd has higher electropositive character than Ag. Therefore, Cd acts an an anode (oxidation) and Ag act as a cathode.

Therefore, EMF = 0.80 – (–0.40)

EMF of cell + 1.20 V

**Ex.7** Calculate the electromotive force of a cell for the following reaction, if the reduction potentoal of $Cu^{+2} \rightarrow Cu$ is +0.35 V and the reduction potential of $Zn^{+2} \rightarrow Zn$ is –0.76 V.

$Zn \mid Zn^{+2} \| Cu^{+2} \mid Cu$ where Zn is anode and Cu is cathode.

      1M    1M

**Sol.** EMF = E(Cathode) – E (Anode)

where E is reduction potential

$+ 0.35 - (0.76) = + 1.11V$

**Ex.8** Standard reduction potentials for $Fe^{+2} \mid Fe$ and $Sn^{+2} \mid Sn$ are –0.44V and –0.14V, respectively, then what should be the standard electromvtive force for $Fe^{+2} + Sn \rightarrow Fe + Sn^{+2}$ cell reaction?

**Sol.** Oxidation of Sn is taking place. Therefore, Sn acts an an anode and Fe as a cathode.

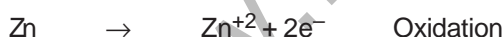Thus, EMF = $E_{(Cathode)} - E_{(Anode)} = -0.44 - (-0.14) = -0.30$

**Ex.9** $Zn(s) + Co^{+2} \rightarrow Co(s) + Zn^{+2}$

Find out the standard EMF of the above cell if

        $E^o Zn \rightarrow Zn^{+2}$         = 0.76 volt

        $E^o Co \rightarrow Co^{+2}$         = 0.28 volt

**Sol.** Reduction potential of Zn = –0.76 volt

$Co^{+2}$    $\rightarrow$    Co       reduction

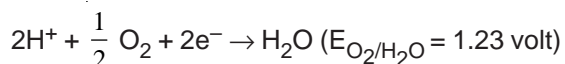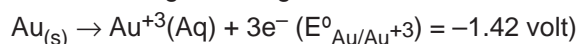Zn       $\rightarrow$    $Zn^{+2} + 2e^-$    Oxidation

Standard EMF of cell = $E_{(Cathode)} - E_{(Anode)}$

                $- 0.28 - (-0.76)$

                = + 0.48 volt

**Ex.10** Why does gold not get rusted in the atmosphere?

**Sol.** If it is presumed that gold also gets oxidised in the atmosphere, then

$Au_{(s)} \rightarrow Au^{+3}(Aq) + 3e^-$ $(E^0_{Au/Au+3})$ = –1.42 volt)

$2H^+ + \dfrac{1}{2} O_2 + 2e^- \rightarrow H_2O$ $(E_{O_2/H_2O}$ = 1.23 volt)

Potential of the cell = –1.42 + 1.23 = –0.19 volt

This potential is negative, therefore reaction does not get completed.