Chapter- 3: Electrochemistry

1. Electrochemical cells and Electrode Potential:

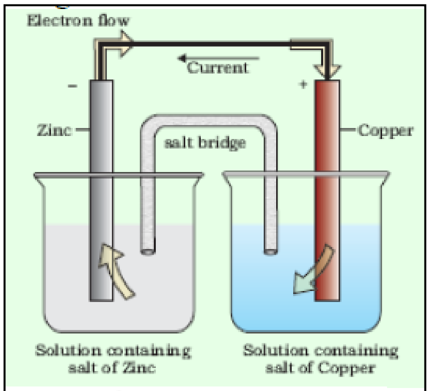
1) An electrochemical cell is a device in which chemical energy of a redox reaction is converted into electrical energy.

2) The simplest electrochemical cell is Daniel cell or Galvanic cell or voltaic cell in which a zinc rod is placed in a solution of Zn^{2+} ions (say $ZnSO_4$) in the left container and a bar of copper metal is immersed in a solution of Cu^{2+} ions (say $CuSO_4$) in the right container. The two metals which act as electrodes are connected by a metallic wire through a voltmeter.

3) The electrode at which oxidation occurs is called **anode** and is negatively charged. The electrode at which reduction takes place is called **cathode** and is positively charged.

Note: LOAN concept for understanding Electrochemical cell- Left Oxidation Anode Negative.

4) In an electrochemical cell the transfer of electrons takes place from anode to cathode so the flow of current is from cathode to anode.



Daniell cell having electrodes of zinc and copper dipping in the solutions of their respective salts.

$Zn \rightarrow Zn^{+2} + 2e^-$ (Oxidation) $Cu^{+2} + 2e^- \rightarrow Cu$ (Reduction)

5) Salt bridge: In the electrochemical cell, the electrical circuit is completed with a salt bridge. Salt bridge also maintains the electrical neutrality of the two half cells. A salt bridge is a U shaped tube filled with solution of inert electrolyte like sodium chloride or sodium sulphate which will not interfere in the redox reaction. The ions are set in a gel or agar agar jelly so that only ions flow when inverted.

6) Electrode potential: Electrical potential difference developed between the metal and its solution is called electrode potential. It can also be defined as tendency of an electrode in a half cell to gain or lose electrons.

7) Oxidation potential is the tendency of an electrode to lose electrons or to get oxidized and Reduction potential is the tendency of an electrode to gain electrons or get reduced.

8) The electrode (half cell) having a higher reduction potential has a higher tendency to gain electrons. So, it acts as a cathode while the electrode having a lower reduction potential acts as an anode and vice versa.

9) Redox couple: A redox couple is defined as having together oxidized and reduced forms of a substance taking part in an oxidation or reduction half reaction.

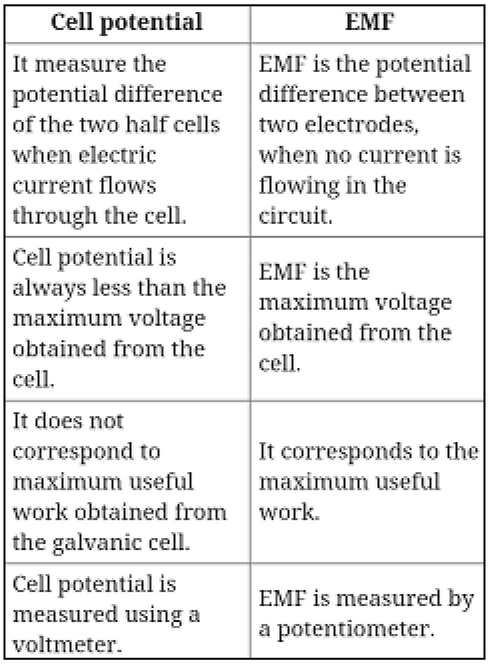
10) Cell potential (E_{cell}): The difference between the electrode potentials of two half cell is called cell potential and it measured in Volts.

$$E_{cell} = E_{cathode} - E_{anode}$$

$$E_{cell} = E_{right} - E_{left}$$

11) EMF (Electromotive force) of a cell: Cell potential is called the EMF of the cell when no current is drawn through the cell.

12) Difference b/w Cell potential (E_{cell}) and EMF:



Cell potential	EMF
It measure the potential difference of the two half cells when electric current flows through the cell.	EMF is the potential difference between two electrodes, when no current is flowing in the circuit.
Cell potential is always less than the maximum voltage obtained from the cell.	EMF is the maximum voltage obtained from the cell.
It does not correspond to maximum useful work obtained from the galvanic cell.	It corresponds to the maximum useful work.
Cell potential is measured using a voltmeter.	EMF is measured by a potentiometer.

13) Standard electrode potential (E°): It may be defined as the electrode potential of an electrode (half cell) determined relative to standard hydrogen electrode under standard conditions. It is denoted as E°. The standard electrode potential of hydrogen electrode is 0.00 volts. The standard conditions taken are:

- 1 M concentration of each ion in the solution.
- 298 K temperature and 1 bar pressure of each gas.

A negative E^o value means that the redox couple is a stronger reducing agent than the H^+/ H_2 couple and A positive E^o means that the redox couple is a weaker reducing agent than the H^+/ H_2 couple.

14) Standard Cell potential ($E°_{cell}$):

$$\overset{o}{E}_{cell} = \overset{o}{E}_{cathode} - \overset{o}{E}_{anode}$$

2. Cell Diagram or representation of an electrochemical cell: The Daniel cell is represented as follows:

$$Zn(s)\,|\,Zn^{2}(C_1)\,||\,Cu^{2+}(C_2)\,|\,Cu(s)$$

1) Anode half cell is written on the left hand side while cathode half cell on right hand side. A single vertical line separates the metal from aqueous solution of its own ions.

$$\underset{\text{Anodic chamber}}{Zn(s)\,|\,Zn^{2}(aq);} \qquad \underset{\text{Cathodic chamber}}{Cu^{2+}(aq)\,|\,Cu(s)}$$

2) A double vertical line represents salt bridge.

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

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

$$Zn(s)\,|\,Zn^{2+}(1M)\,||\,Cu^{2+}(1M)\,|\,Cu \qquad EMF = +1.1\ V$$

5) 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.

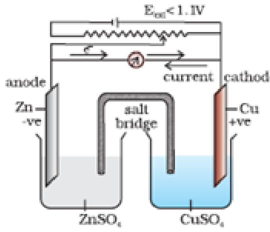
$$Zn(s)\,|\,Zn^{2+}(C_1)\,||\,H^{+}(C_2)\,|\,H_2(Pt)$$

3. Reversibility of Daniel Cell:

1) When external voltage is less than 1.10 V, electrons flow from Zn to Cu but current flows from Cu to Zn i.e., in opposite direction. Zinc dissolves at anode and copper deposits at cathode [see Fig (a)]

2) When external voltage applied is less than 1.10 V and is increased slowly, it is observed that the reaction continues to take place till the external voltage attains the value 1.10 V. When this is so, reaction stops altogether and no current flows [see Fig. (b)]

3) When the value of external voltage exceeds the voltage of Daniel cell (1.10 V), the reaction takes place in opposite direction, i.e., the cell functions like an electrolytic cell. [See Fig. (c)].

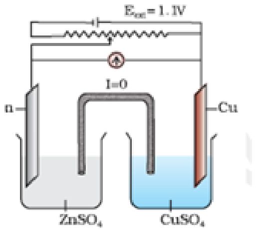


When $E_{ext} < 1.1$ V

(i) Electrons flow from Zn rod to Cu rod hence current flows from Cu to Zn.

(ii) Zn dissolves at anode and copper deposits at cathode.

(a)

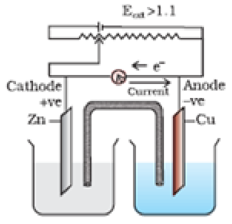


When $E_{ext}=1.1$V

(i) No flow of electrons or current

(ii) No chemical reaction.

(b)



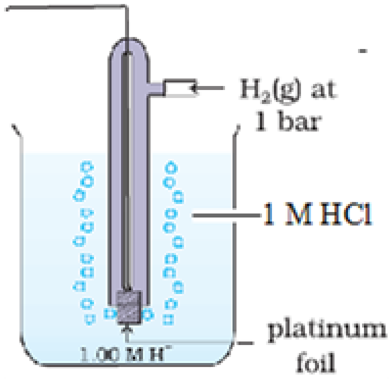
When $E_{ext}>1.1$V

(i) Electrons flow from Cu to Zn and current flows from Zn to Cu.

(ii) Zinc is deposited at the zinc electrode and copper dissolves at copper electrode.

(c)

4. Standard Hydrogen Electrode (SHE): It is a reference electrode use for reference on all half-cell potential reactions. The value of the standard electrode potential is zero volt at all temperature. SHE is consists of a platinum electrode coated with platinum black. Platinum is used because it is inert and does not react much with hydrogen. The electrode is dipped in an acidic solution having 1.0 M concentration of H^+ ions. During the reaction, pure hydrogen gas at 1 bar pressure is continuously bubbled through the solution at a 298 K temperature. The hydrogen electrode can act both ways – as a anode or as a cathode.



Act as anode (oxidation take place): $H_2 (g) \rightarrow 2H^+ (aq) + 2e^-$

Act as cathode (reduction take place): $2H^+ (aq) + 2e^- \rightarrow H_2 (g)$

Representation of SHE: $Pt(s) \mid H_2(g,\ 1\ bar) \mid H^+ (aq,\ 1\ M)$

5. EMF and Gibbs free energy: The work done by an electrochemical cell is equal to decrease in Gibbs free energy.

$$\Delta G = - nFE_{cell}$$

If concentration of all the reacting species is unity, then

$$E_{cell} = E^\circ_{cell}$$

Where E_{cell} is Cell potential and E°_{cell} is the Standard cell potential.

$$\Delta G^\circ = - nFE^\circ_{cell}$$

Where n = number of electrons exchanged and F is faraday constant (96500 C mol^{-1})

From the fundamental thermodynamics equation

$$\Delta G^\circ = - RT \ln K$$

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

$$- nFE^\circ_{cell} = - 2.303\ RT \log K$$

$$E^\circ_{cell} = \frac{2.303\ RT}{nF} \log K$$

Where K is equilibrium constant, T is temp in Kelvin and R is a gas constant (8.314 JK^{-1} mol^{-1}).

6. Nernst Equation: Nernst studies the variations of electrode potential of an electrode with temperature and concentration of ions (electrolytes). Nernst formulates a relationship b/w standard electrode potential and electrode potential. For an electrode reaction,

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

Nernst equation can be written as

$$E_{(M^{n+}/M)} = E^0_{(M^{n+}/M)} - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

Where, $E_{(M^{n+}/M)}$ = Electrode potential and $E^0_{(M^{n+}/M)}$ = Standard electrode potential

But concentration of solid M is taken as unity so we have

$$E_{(M^{n+}/M)} = E^0_{(M^{n+}/M)} - \frac{RT}{nF}\ln\frac{1}{[M^{n+}]}$$

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

$$E_{(M^{n+}/M)} = E^0_{(M^{n+}/M)} - \frac{0.059}{n}\log\frac{1}{[M^{n^+}]}(At\ 298k)$$

Thus, the electrode potential increases with increases in the concentration of the electrolyte and decreases in temperature.

For a general electrochemical reaction, $aA + bB \xrightarrow{ne^-} cC + dD$

Nernst equation can be given as

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

$$E_{cell} = E^0_{cell} - \frac{0.059}{n}\log\frac{[C]^c[D]^d}{[A]^a[B]^b} \quad (At\ 298k)$$

Equilibrium constant Kc from Nernst Equation: For a Daniell cell, electrode reaction written as

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

While at equilibrium cell potential (E_{cell}) become zero so

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

$$E^0_{cell} = \frac{2.303RT}{2F}\log\frac{[Zn^{2+}]}{[Cu^{2+}]}$$

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

$$E^0_{cell} = \frac{2.303RT}{2F}\log Kc = \frac{0.059}{2}\log Kc$$

In general, $E^0_{cell} = \frac{0.059}{n}\log Kc$

7. Concentration Cell: If two electrodes of the same metal are dipped separately into two solution of the same electrolyte having different concentrations and the solutions are connected through salt bridge, such cell are known as concentration cells.

In these cells, oxidation takes place on the electrode with lower concentration (C_1) while reduction takes place on the electrode with higher concentration (C_2), for example

$$H_2(g) \,|\, H^+(C_1) \,||\, H^+(C_2) \,|\, H_2(g)$$

$$Zn(s) \,|\, Zn^{2+}(C_1) \,||\, Zn^{2+}(C_2) \,|\, Zn(s)$$

8. Characteristics of Electrolytic solutions:

1) Resistance (R): Every conducting material offers some obstruction to the flow of electricity which is called resistance. It is denoted by R and is measured in ohm.

The resistance of any object is directly proportional to its length l and inversely proportional to its area of cross section A.

$$R \propto \frac{l}{A} \text{ or } R = \rho \frac{l}{A}$$

Where, ρ (rho) is a constant called specific resistance or resistivity. Its SI unit is ohm cm.

2) Conductance (G): The inverse of resistance is known as conductance.

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

Unit of conductance is ohm^{-1} or mho. It is also expressed in Siemens denoted by S.

3) Conductivity or Specific Conductance (κ): The inverse of resistivity is known as conductivity. It is represented by the symbol κ. The SI unit of conductivity is S m^{-1}. But it is also expressed in S cm^{-1}

$$k = \frac{1}{\rho}$$

$$k = \frac{1}{R}\frac{l}{A}$$

Where $\frac{l}{A}$ is called cell constant and its denoted by G*

So, conductivity = Conductance x Cell constant

4) Conductivity cell: A conductivity cell consists of two Pt electrodes coated with Pt black. They have area of cross section A and are separated by a distance l. Resistance of such a column of solution is given by the equation:

$$R = \rho\frac{l}{A} = \frac{1}{k}\frac{l}{A}$$

5) Difference b/w Metallic and Electrolytic Conductance:

6) Molar conductivity ($\wedge_m$): Molar conductivity of a solution is defined as the conducting power of the ions produced by dissolving 1 mole of an electrolyte in solution.

$$\wedge_m = k \text{ x V}$$

$$\wedge_m = \frac{k \text{ x } 1000}{M}$$

Where k is conductivity, V is the volume of solution in cm^3 and M is the molarity (molar concentration) of solution.

Unit of Molar conductivity is ohm^{-1} cm^2 mol^{-1} or S cm^2 mol^{-1}

7) Limiting molar conductivity (Λ_m^0): The value of molar conductivity when the concentration approaches zero is known as limiting molar conductivity or molar conductivity at infinite dilution.

9. Variation of conductivity and molar conductivity with concentration (Effect of dilution):

1) Variation of conductivity (k) with concentration: Conductivity decreases with the decreases in concentration, this is because the numbers of ions per unit volume that carry the current in the solution decrease on dilution.

2) Variation of molar conductivity ($\wedge_m$) with concentration: Molar conductivity ($\wedge_m = k \text{ x } V$) is increases with the increases in dilution or decreases in concentration. This is because molarity is decreases with increases the total volume V of solution.

The trend of variation in molar conductivity ($\wedge_m$) with concentration for strong and weak electrolyte is show totally different.

For strong electrolytes, molar conductivity increases slowly (see curve for KCl) with dilution and can be represented by Debye, Huckle and Onsager equation:

$$\Lambda_m = \Lambda_m^\circ - A\, c^{½} \quad \text{(Applicable only for strong electrolyte)}$$

Where, A is a constant which depends on the nature of the solvent and temperature.

In case of strong electrolyte it is possible to determine the molar conductivity at infinite dilution (Λ_m^0) by extrapolation of curve of $\wedge_m$ vs $c^{1/2}$.

But in case of weak electrolyte, molar conductivity increases steeply with dilution (see curve for CH_3COOH). On contrary, the value of molar conductivity of weak electrolyte at infinite dilution cannot be determined by extrapolation of the curve becomes almost parallel to y-axis when concentration approaches to zero.

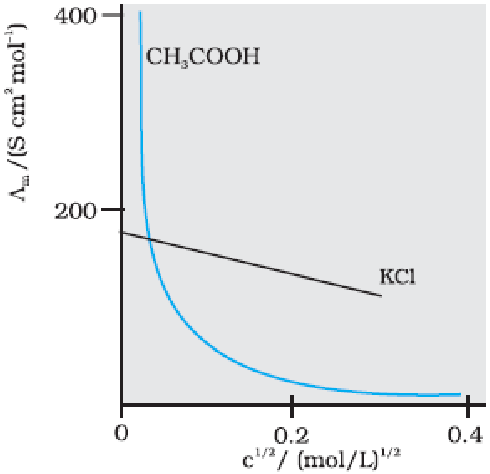


Figure: Molar conductivity Vs $c^{1/2}$ for weak and strong electrolytes in aqueous solution

10. Kohlrausch's Law of independent migration of ions: According to this law, limiting molar conductivity of an electrolyte, at infinite dilution, can be expressed as the sum of individual contributions of the anion and cation of the electrolytes.

If the limiting molar conductivity of the cation is denoted by $\lambda_+°$ and that of the anions by $\lambda_-°$ then the limiting molar conductivity of electrolyte:

$$\wedge_m^0 = v_+\lambda_+^0 + v_-\lambda_-^0$$

Where, v_+ and v_- are the number of cations and anions per formula of electrolyte.

11. Application of Kohlrausch's Law:

1) Calculation of molar conductivities of weak electrolyte at infinite dilution

2) Determination of Degree of dissociation: It is ratio of molar conductivity at a specific concentration 'c' to the molar conductivity at infinite dilution, it is denoted by α.

$$a = \frac{\wedge_m}{\wedge_m^0}$$

3) Determination of dissociation constant (K) of weak electrolyte:

$$K = \frac{ca^2}{1-a}$$

$$K = \frac{c\Lambda_m^2}{\Lambda_m^{o2}\left(1 - \frac{\Lambda_m}{\Lambda_m^o}\right)} = \frac{c\Lambda_m^2}{\Lambda_m^o\left(\Lambda_m^o - \Lambda_m\right)}$$

Where, K is dissociation constant, 'c' is concentration of Electrolyte and α is degree of ionization.

4) Determination of solubility of sparingly soluble salts:

$$\wedge_m^o = \frac{k \text{ x } 1000}{\text{molarity}} = \frac{k \text{ x } 1000}{\text{solubility}}$$

$$\text{Solubility} = \frac{k \text{ x } 1000}{\wedge_m^o}$$

12. Electrolysis: The process of decomposition of an electrolyte when electric current is passed through its aqueous solution or fused state is called electrolysis. The process of a substance is governed by Faraday's laws of electrolysis.

1) Faraday's first law of electrolysis: The weights of substances deposited or liberated at an electrode during electrolysis are directly proportional to the quantity of electricity that passes through the electrolyte.

If w gm of the substance deposited on passing Q coulombs of electricity, then

$w \alpha Q$

$w = Z \text{ x } Q$

$w = Z \text{ x } I \text{ x } t$ (while $Q = I \text{ x } t$)

Where, Z is a proportionality constant known as electrochemical equivalent of the substance deposited.

- **Electrochemical equivalent (Z):** If I = 1 ampere and t = 1 second, then w = Z
  So, the electrochemical equivalence may be defined as the amount of the substance deposited by passing one ampere of current for one second or by passing one coulomb of charge through the electrolyte.
- 1 Faraday = Quantity of electricity (charge) carried by 1 mole of electrons. So
  1 Faraday = 6.023×10^{23} mol^{-1} x 1.6×10^{-19} C = 96472 C mol^{-1} = 96500 C mol^{-1}
- If n mol of electrons are involved in an electrode reaction, then
  n x 96500 C of charge will deposit = M gm of the element
  $$1 \text{ C of charge will deposit} = \frac{M}{n \times 96500} \text{ gm of the element}$$
  But 1 C of charge deposit mass of element = Z gm, so
  $$Z = \frac{M}{n \times 96500} \text{ gm} = \frac{E}{96500} \text{ gm}$$
  Where M is atomic mass and E is equivalent mass of element

2) Faraday's second law of electrolysis: When same quantity of electricity is passed through different electrolytes, the amount of different substances deposited at the electrodes is directly proportional to their equivalent masses (E).

$$\frac{w_1}{w_2} = \frac{E_1}{E_2}$$

13. Commercial Cells (Batteries): Any battery consists of two or more than two galvanic cells connected in series where the chemical energy is converted in to electrical energy through redox reaction. There are mainly two types of batteries:

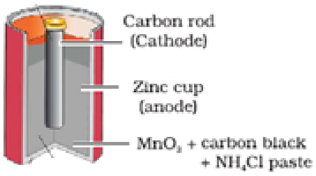
1) Primary cells (Batteries): These cells are not chargeable b/c the electrode reaction occurs only once and after the use over a period of time the cells become dead and cannot be used. Example Dry cell (Leclanche cell), Mercury cell

a) Dry cell: Dry cell is constructed with a zinc shell that serves as the anode a graphite rod which serves as the cathode; and a space b/w the electrodes is filled by a moist mixture of ammonium chloride {NH4Cl}, zinc chloride {ZnCl2}, and manganese dioxide {MnO2}. The cell has potential nearly 1.5 V. The electrode reactions are:

At anode $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

At cathode $MnO_2(s) + NH_4^+(aq) + e^- \rightarrow MnO(OH) + NH_3$

The net reaction: $Zn + NH_4^+(aq) + MnO_2(s) \rightarrow Zn^{2+} + MnO(OH) + NH_3$



The role of $ZnCl_2$ in dry cell is to combines with the NH_3 produced to form the complex salt otherwise the pressure developed due to NH_3 would crack the seal of the cell.

$$2\,NH_3\,(g) + ZnCl_2\,(aq) \rightarrow [Zn(NH_3)_2]Cl_2$$

In this reaction, zinc ion, primarily from ZnCl2, is acting as a Lewis acid; the complex formed solubilizes the gas.

b) Mercury cell: Her zinc-mercury amalgam act as anode and a paste of HgO and carbon as the cathode. The electrolyte is a paste of KOH and ZnO. The cell potential is approximately 1.35 V and remains constant as the ionic concentration of the solution is not change during its life. The electrode reactions are:

$$\text{At Anode: } Zn(Hg) + 2OH^- \rightarrow ZnO(s) + H_2O + 2e^-$$

$$\text{At cathode: } HgO(s) + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$$

$$\text{The net reaction: } Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$$

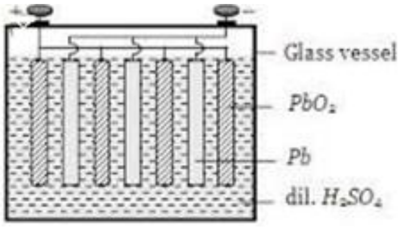
2) Secondary cells (Batteries): A secondary cell is rechargeable and can be used again and again. It is recharged by passing current through it from an external source. Examples Lead storage cell, Nickel-cadmium cell

a) Lead Storage Cell (Battery): It consists of a lead as anode and a grid of lead packed with lead dioxide as cathode. A 38% solution of H_2SO_4 is used as an electrolyte. The cell reaction when battery is in use, are:

$$\text{Anode: } Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$$

$$\text{Cathode: } PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$$

$$\text{Net Reaction: } Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \rightarrow 2PbSO_4(s) + 2H_2O(l)$$



On recharging the battery, the reaction is reversed.

b) Nickel-cadmium cell (Battery): It is another type of secondary cell which has longer life than lead storage cell but more expensive to manufacture. Here Cd act as anode, Ni act as cathode and sodium or potassium hydroxide is used as an electrolyte. The overall reaction during discharge is

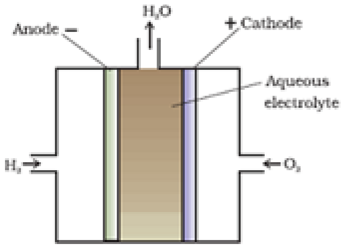
$$Cd(s) + 2Ni(OH)_3(s) \rightarrow CdO(s) + 2Ni(OH)_2(s) + H_2O(l)$$

13. Fuel Cells: Fuel cells are those cells which produce electrical energy directly from the combustion of fuels such as hydrogen, carbon monoxide or methane. The most successful fuel cell, H_2-O_2 cell utilizes the reaction b/w H_2 and O_2 to produce water. H_2 and O_2 are bubbled through a porous carbon electrode in the cell into concentrated aqueous NaOH. Catalysts are incorporated into the electrode. The electrode reactions are:

$$\text{Cathode: } O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$$

$$\text{Anode: } 2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$$

$$\text{Overall reaction being: } 2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$



Advantage of Fuel Cells:

- It is a pollution free device.
- Its efficiency is about 75% which is higher than conventional cells.

- It is a continuous source of energy if the supply of gases is maintained.
- These cells are light in weight as compared to electrical generators to produce corresponding quantity of power.

16. Corrosion: Gradual loss of metal from its surface in presence of air and moisture is known as Corrosion. Chemically, rust is hydrated ferric oxide ($Fe_2O_3.xH_2O$). Corrosion may be considered as an electrochemical phenomenon. According to electrochemical theory of rusting, the impure iron surface behaves like a small electrochemical cell in the presence of moisture containing O_2 or CO_2. Such a cell is called corrosion cell or corrosion couple. In these miniature corrosion cells, pure iron act as anode, surface area act as cathode and moisture having dissolved CO_2 or O_2 act as electrolyte. We can write the reaction as

At anode: Oxidation of iron takes place:

$$2\ Fe\ (s) \longrightarrow 2\ Fe^{2+} + 4\ e^- \qquad E^{\ominus}_{(Fe^{2+}/Fe)} = -\ 0.44\ V$$

The electrons are picked up by the H^+ ions which are produced from H_2CO_3, while H_2CO_3 is formed due to dissolution of CO_2 in moisture or water ($H_2CO_3 \rightarrow 2H^+ + CO_3^{2-}$)

At cathode: $O_2(g) + 4\ H^+(aq) + 4\ e^- \longrightarrow 2\ H_2O\ (l) \qquad E^{\ominus}_{H^+|O_2|H_2O} = 1.23\ V$

Net Reaction: $2Fe(s) + O_2(g) + 4H^+(aq) \longrightarrow 2Fe^{2+}(aq) + 2\ H_2O\ (l) \qquad E^{\ominus}_{(cell)} = 1.67\ V$

The ferrous ions so formed move through water and come at the surface where these are further oxidised by atmospheric oxygen to ferric ions ad form rust which is hydrated ferric oxide ($Fe_2O_3.xH_2O$).

$2Fe^{+2} + 1/2\ O_2 + H_2O \rightarrow Fe_2O_3 + 4H^+$

$Fe_2O_3 + xH_2O \rightarrow Fe_2O_3.xH_2O$

17. Prevention of Corrosion:

1) Barrier protection: A thin film is introduced b/w iron and atmospheric gases and moisture like-

i) By covering the surface with paint or thin film of grease.

ii) By electroplating iron with some non corrosive metals such as Cu, Ni, Cr etc

2) Sacrificial protection: In this method iron surface is covered with a more electropositive metal than iron which gets oxidised in preference to iron. More electropositive metal loses electrons instead of iron and thus this metal is sacrificed at the cost of iron. Iron is generally coated with zinc and this process is called galvanization.

3) Electrical protection (Cathodic protection): This method is used for the protection of underground water pipes or iron tanks. In this method, the exposed surface of iron is protected with connected more reactive metal (act as anode) with the help of a wire. Here iron surface act as cathode, so this method is also called cathodic protection.

Chapter 3: Electrochemistry (Some Important Formulas)

1. Cell potential (E_{cell}): The difference between the electrode potentials of two half cell is called cell potential and it measured in Volts. It is measured by voltmeter.

$$E_{cell} = E_{cathode} - E_{anode}$$

2. EMF (Electromotive force) of a cell: Cell potential is called the EMF of the cell when no current is drawn through the cell. It is measured by potentiometer.

3. Cell Diagram or representation of an electrochemical cell:

$$Zn(s) \mid Zn^{2+}(C_1) \| H^+(C_2) \mid H_2(Pt)$$

4. LOAN Concept: Left Oxidation Anode Negative

5. EMF and Gibbs free energy: $\Delta G° = -nFE°_{cell}$; Where n = number of electrons exchanged and F is faraday constant (96500 C mol^{-1})

$$\Delta G° = -2.303\ RT \log K$$

$$nFE°_{cell} = 2.303\ RT \log K$$

$$E°_{cell} = \frac{0.0591}{n} \log K$$

Where K is equilibrium constant, T is temp in Kelvin and R is a gas constant (8.314 $JK^{-1}\ mol^{-1}$).

6. Nernst Equation for a general electrode reaction:

$$E_{(M^{n+}/M)} = E^0_{(M^{n+}/M)} - \frac{0.059}{n} \log \frac{1}{[M^{n+}]} \quad (At\ 298k)$$

Where, $E_{(M^{n+}/M)}$ = Electrode potential and $E^0_{(M^{n+}/M)}$ = Standard electrode potential

7. Nernst Equation for a general electrochemical reaction:

$$E_{cell} = E^0_{cell} - \frac{0.059}{n} \log \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad (At\ 298k)$$

While at equilibrium cell potential (E_{cell}) become zero so $E^0_{cell} = \frac{0.059}{n} \log Kc$

8. Resistance (R):

$$R \propto \frac{l}{A} \text{ or } R = \rho \frac{l}{A}$$

Where, ρ (rho) is a constant called specific resistance or resistivity. Its SI unit is ohm cm.

9. Conductance (G): The inverse of resistance is known as conductance.

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

Unit: ohm^{-1} or mho. It is also expressed in Siemens denoted by S.

10. Conductivity or Specific Conductance (κ): The inverse of resistivity is known as conductivity. The SI unit of conductivity is S m^{-1}. But it is also expressed in S cm^{-1}

$$k = \frac{1}{\rho}$$

$$k = \frac{1}{R}\frac{l}{A}$$ Where $\frac{l}{A}$ is called cell constant and its denoted by G*

So, conductivity = Conductance x Cell constant

11. Molar conductivity ($\wedge_m$):

$$\wedge_m = k \text{ x } V$$

$$\wedge_m = \frac{k \text{ x } 1000}{M}$$

Where k is conductivity, V is the volume of solution in cm^3 and M is the molarity of solution.
Unit of Molar conductivity is ohm^{-1} cm^2 mol^{-1} or S cm^2 mol^{-1}

12. Limiting molar conductivity (Λ_m^0): The value of molar conductivity when the concentration approaches zero is known as limiting molar conductivity or molar conductivity at infinite dilution.

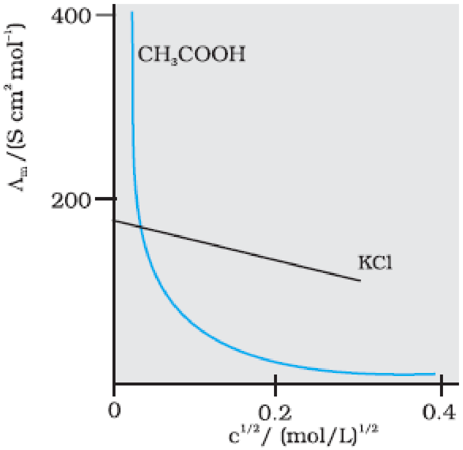
13. Variation of conductivity (k) with concentration: Conductivity decreases with the decreases in concentration.

14. Variation of molar conductivity with concentration: Molar conductivity ($\wedge_m = k \text{ x } V$) is increases with the increases in dilution or decreases in concentration.

For strong electrolytes, molar conductivity increases slowly (see curve for KCl) with dilution and can be represented by Debye, Huckle and Onsager equation:

$\Lambda_m = \Lambda_m^\circ - A\, c^{½}$ (Applicable only for strong electrolyte)

In case of strong electrolyte it is possible to determine the molar conductivity at infinite dilution by extrapolation of curve of $\wedge_m$ vs $c^{1/2}$. But in case of weak electrolyte, molar conductivity increases steeply with dilution (see curve for CH_3COOH). On contrary, the value of molar conductivity of weak electrolyte at infinite dilution cannot be determined by extrapolation of the curve becomes almost parallel to y-axis when concentration approaches to zero.



15. Kohlrausch's Law of independent migration of ions: If the limiting molar conductivity of the cation is denoted by λ_+° and that of the anions by λ_-° then the limiting molar conductivity of electrolyte:

$$\wedge_m^0 = \nu_+\lambda_+^0 + \nu_-\lambda_-^0$$

Where, ν_+ and ν_- are the number of cations and anions per formula of electrolyte.

16. Application of Kohlrausch's Law:

1) Calculation of molar conductivities of weak electrolyte at infinite dilution

2) Determination of Degree of dissociation:

$$a = \frac{\Lambda_m}{\Lambda_m^0}$$

3) Determination of dissociation constant (K) of weak electrolyte:

$$K = \frac{ca^2}{1-a}$$

$$K = \frac{c\Lambda_m^2}{\Lambda_m^{o2}\left(1 - \frac{\Lambda_m}{\Lambda_m^o}\right)} = \frac{c\Lambda_m^2}{\Lambda_m^o\left(\Lambda_m^o - \Lambda_m\right)}$$

4) Determination of solubility of sparingly soluble salts:

$$\Lambda_m^o = \frac{k \text{ x } 1000}{\text{molarity}} = \frac{k \text{ x } 1000}{\text{solubility}}$$

$$\text{Solubility} = \frac{k \text{ x } 1000}{\Lambda_m^o}$$

17. Faraday’s first law of electrolysis: w = Z x I x t (while Q = I x t)

Z is a proportionality constant known as electrochemical equivalent of the substance deposited.

Electrochemical equivalent (Z): If I = 1 ampere and t = 1 second, then w = Z So, the electrochemical equivalence may be defined as the amt of the substance deposited by passing 1 ampere of current for 1 sec or by passing 1 coulomb of charge through the electrolyte.

- 1 Faraday = Quantity of electricity (charge) carried by 1 mole of electrons. So 1 Faraday = 6.023×10^{23} mol^{-1} x 1.6×10^{-19} C = 96472 C mol^{-1} = 96500 C mol^{-1}
- If n mol of electrons are involved in an electrode reaction, then n x 96500 C of charge will deposit = M gm of the element

  $$1 \text{ C of charge will deposit} = \frac{M}{n \text{ x } 96500} \text{ gm of the element}$$

  But 1 C of charge deposit mass of element = Z gm, so

  $$Z = \frac{M}{n \text{ x } 96500} \text{ gm} = \frac{E}{96500} \text{ gm}$$

  Where M is atomic mass and E is equivalent mass of element

18. Faraday’s second law of electrolysis: When same quantity of electricity is passed through different electrolytes, the amount of different substances deposited at the electrodes is directly proportional to their equivalent masses (E).

$$\frac{w_1}{w_2} = \frac{E_1}{E_2}$$