ELECTROCHEMISTRY

Electrochemistry is that branch of chemistry which deals with the relationship between electrical energy and chemical changes taking place in redox reactions i.e., how chemical energy produced in a redox reaction can be converted into electrical energy or how electrical energy can be used to bring about a redox reaction which is otherwise non-spontaneous.

Under electrochemistry, we study two types of cells: electro chemical and electrolytic cell.

Difference Between Electrochemical and Electrolytic Cell:

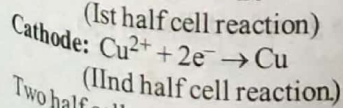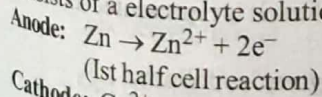| Electrochemical cell	Electrolytic cell
1. It converts chemical energy into electrical energy	i. It converts electrical energy into chemical energy.
2. It is based upon redox reaction which is spontaneous.	2. The redox reaction is non-spontaneous and takes place only when electrical energy is supplied.
3. The electrode on which oxidation takes place is called Anode (negative pole) and electrode on which reduction takes place is called cathode (positive pole).	3. The electrode which is connected to negative terminal of the battery is called cathode; the cations migrate to it, gain electrons and hence reduction takes place. The other electrode is called anode.
4. A salt bridge is used to set up the cell.	4. No salt bridge is used in this case.
5. Two electrolytes are used.	5. Only one electrolyte is taken.

GALVANIC CELL

It is also called voltaic cell. It converts chemical energy liberated during redox reaction to electrical energy.

For example reaction between Zn and $CuSO_4$.

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$$
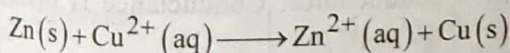
The chemical reaction responsible for production of electricity takes place in two separate compartments called half cells which consists of a electrolyte solution and a electrode.
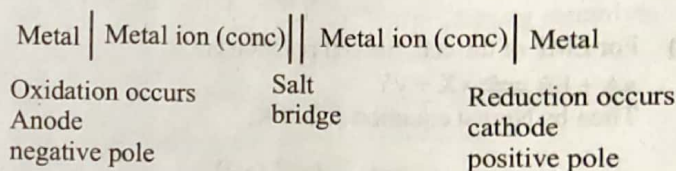
Anode: $Zn \rightarrow Zn^{2+} + 2e^-$

(Ist half cell reaction)

Cathode: $Cu^{2+} + 2e^- \rightarrow Cu$

(IInd half cell reaction)

Two half cells are connected by salt bridge.

Note:

(i) Electrode on which oxidation occurs is called anode (negative pole) while the electrode on which reduction occurs is called cathode (positive pole)

(ii) Electrons flow from anode to cathode in the external circuit.

(iii) Inner circuit is completed by flow of ions through the salt bridge.

(iv) Representation of electrochemical cell is like:

$$\text{Left electrode} \xrightarrow{\text{Electrons flow}} \text{Right electrode}$$

Metal | Metal ion (conc) || Metal ion (conc) | Metal

Oxidation occurs	Salt	Reduction occurs
Anode	bridge	cathode
negative pole		positive pole

Characteristics of Salt Bridge

(i) It allows the flow of current by completing the circuit.

(ii) It maintains electrical neutrality of electrolytes in two half cells.

ELECTROMOTIVE FORCE (EMF)

The difference in the electrode potentials of two electrodes of the cell is termed as electromotive force (EMF).

Cell potential or EMF of the cell is given by:

$$E_{cell} = E_{right} - E_{left} = E_R - E_L$$
$$= E_{cathode} - E_{anode} = E_{red} - E_{ox}$$

Conventionally, all electrode potentials are expressed at top as reduction potentials, and

Reduction potential $= -$ Oxidation potential

For a redox reaction to be spontaneous, EMF of the cell must be positive.

Reduction occurs at the electrode having higher reduction potential and oxidation occurs at the electrode having lower reduction potential.

Electrode potential is a fixed quantity and is not multiplied by 'n' i.e. number of e^-'s involved in a reaction.

Standard electrode potential for fluorine is the highest indicating that fluorine gas (F_2) has the maximum tendency to get reduced to F^- ions and thus, F_2 gas is the strongest oxidising agent. Lithium has lowest electrode potential indicating that Li^+ ion is the weakest oxidising agent while lithium metal is the most powerful reducing agent in an aqueous solution.

Note : Galvanic cell has an external voltage < 1.1.V when E_{ext} = 1.1V, the reaction stops and no current flows. And, if E_{ext} > 1.1V, the reaction occurs in opposite direction and the cell functions as an **electrolytic cell** where the electrons flow from Cu to Zn and current flows from Zn to Cu.

NERNST EQUATION

The relationship between the concentration of ions and electrode potential is given by Nernst equation.

(i) For electrode potential, the reaction is,

$$M^{n+} + ne^- \longrightarrow M$$
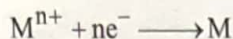
Then Nernst equation, is applied as

$$E = E° - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

for pure solids liquids or gases at 1 atm pressure [M] = 1

$$E = E° - \frac{RT}{nF} \ln \frac{[M]}{[M^{n+}]}$$

putting R = 8.314 Jk^{-1} mol^{-1}
F = 96500 C
T = 298 K

$$E_{Red} = E°_{Red} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

(ii) For EMF of the cell, the cell reaction is:

$$aA + bB \rightleftharpoons xX + yY$$

Then by Nernst equation at 298 K,

$$E_{cell} = E°_{cell} - \frac{0.0591}{n} \log \frac{[X]^x [Y]^y}{[A]^a [B]^b}$$

Where n is the number of electrons involved in the cell reaction.

(iii) For a cell reaction in equilibrium,

$$E_{cell} = 0$$

$$K_C = \frac{[X]^x [Y]^y}{[A]^a [B]^b}$$

$$E°_{cell} = \frac{0.0591}{n} \log K_c \text{ at } 298 \text{ K}$$

where n = no. of electrons involved in the cell reaction
K_C = equilibrium constant for the cell reaction.

Gibb's Free Energy and Cell Potential

$$\Delta G° = -nFE°_{cell}$$

as $\quad E°_{cell} = \frac{RT}{nF} \ln K_C$

$$\Delta G° = -2.303 RT \log K_C$$

where $\Delta G°$ = standard free energy change of the reaction
F = Faraday's constant = 96500 C
R = 8.314 JK^{-1}mol^{-1}

ELECTROLYSIS

It is a process of decomposition of an electrolyte by the passage of electricity through its aqueous solution of molten state.

On passing electric current, positively charged ions move towards cathode and negatively charged ions move towards anode; where they loose their charge and become neutral species. **Oxidation occurs at anode while reduction takes place at cathode.**

Faraday's Laws

The quantitative aspects of electrolysis were studied by Faraday. He put forward two laws as follows:

(i) **Faraday's First law of Electrolysis:**
According to this law, the amount of chemical reaction and hence the mass of any substance deposited at any electrode during electrolysis by a current is directly proportional to the quantity of electricity passed through the electrolyte i.e.,

$$m \propto Q$$
$$m = ZQ$$
as, Q = It
$$\therefore m = ZIt$$

where m → amount of subs. deposited
Q → quantity of electricity in 'C'
Z → Constant called Electrochemical equivalent
I → Current in ampere
t → time in seconds

Electrochemical equivalent can be defined as the mass of the substance deposited by one coulomb of charge or by one ampere of current passed for one second.

$$\text{Electro-chemical equivalent (Z)} = \frac{\text{equivalent wt.of element}}{96500}$$

(ii) **Faraday's second law of electrolysis**
When same amount of electricity is passed through solutions of different electrolytes connected in series, the weight of the substances produced at the electrodes are directly proportional to their equivalent weights.
Ex: for $AgNO_3$ and $CuSO_4$ solutions connected in series, if same quantity of electricity is passed, then

$$\frac{\text{wt. of Ag deposited}}{\text{Wt. of Cu deposited}} = \frac{\text{Eq. wt. of Ag}}{\text{Eq. wt. of Cu}}$$

Note:

(i) If n electrons are involved in the electrode reaction, the passage of n faradays (i.e., nF = n × 96500 C) of electricity will liberate one mole of the substance.

(ii) Equivalent weight of a substance can be calculated as:

$$\text{Eq. wt.} = \frac{m}{Q} \times 96500 \begin{bmatrix} m \rightarrow \text{amount of substance deposited} \\ Q \rightarrow \text{Quantity of electricity} \end{bmatrix}$$

CONDUCTANCE OF ELECTROLYTIC SOLUTIONS

Conductance (G)

The amount of electric current that can be passed through the solution is called conductance. Conductance is inverse of resistance.

$$\text{Conductance} = \frac{1}{\text{Resistance}} \quad \text{or} \quad G = \frac{1}{R}$$

Unit of conductance is inverse of ohm. It is represented as mho or ohm^{-1} or siemens (s).

(i) Resistance of a conductor is given as follows:

$$R = \rho \frac{\ell}{A}$$

R = resistance; ρ = resistivity; l = length,
A = area of cross-section.

(ii) The reciprocal of resistivity is called conductivity

$$\kappa = \frac{1}{\rho} = \frac{1}{R}\frac{l}{A} \qquad \kappa \rightarrow \text{specific conductivity or conductivity.}$$

or $\kappa = G \times \dfrac{l}{A}$ = observed conductance × cell constant

$= G \times G^*$ (where cell constant = l/A)

$\therefore$ Cell constant $(G^*) = \dfrac{\kappa}{G} = \dfrac{\text{Conductivity}}{\text{Conductance}}$

Equivalent Conductivity

If one equivalent of an electrolyte is dissolved in a solution, then the conductivity of two parallel electrodes situated 1 cm apart is called equivalent conductivity. It is denoted by Λ_{eq}.

$$\Lambda_{eq} = \kappa \times V \text{ (where V = volume)}$$

In terms of concentration,

$$\Lambda_{eq} = \frac{\kappa \times 1000}{C_{eq}} = \frac{\kappa \times 1000}{\text{Normality}}$$

Where C_{eq} = Concentration

Unit of Λ_{eq} = cm^2 ohm^{-1} gm eq^{-1}

Molar Conductivity

If one mole of an electrolyte is dissolved in a solution, then the conductivity of that solution between two parallel electrodes situated 1 cm apart, is called molar conductivity. It is represented by λ_m.

$$\lambda_m = \kappa \times V_m$$

where V_m = Volume of the solution in which 1 mole solute is dissolved. $\left(V_m = \dfrac{1}{C}\right)$

κ = specific conductivity

$$\lambda_m = \frac{1000 \text{ cm}^3}{M} \times \kappa$$

or Unit = cm^2 mol^{-1} ohm^{-1} = S cm^2 mol^{-1}

Unit of Different Quantities

Physical Quantity	Commonly used units	SI units
1. Resistance(R)	ohm (Ω)	ohm (Ω)
2. Resistivity(ρ)	ohm cm $(\Omega\,cm)$	ohm m $(\Omega\,m)$
3. Conductance(G)	Ω^{-1}	siemen(S)
4. Conductivity(κ)	$\Omega^{-1}cm^{-1}$	$S\,m^{-1}$
5. Equivalent Conductivity(Λ_{eq})	$\Omega^{-1}cm^2eq^{-1}$	$S\,m^2eq^{-1}$
6. Molar Conductivity(Λ_m)	$\Omega^{-1}cm^2mol^{-1}$	$S\,cm^2mol^{-1}$
7. Cell constant(G^*)	cm^{-1}	m^{-1}

Effect of Dilution on Conductance, Specific Conductivity and Λ_m

(i) Conductance increases with increase in dilution due to increase in number of ions in solution.

(ii) Conductivity decreases with the decrease in concentration. This is because conductivity is the conductance of one unit volume of solution. As the number of ions per unit volume decrease on dilution, hence conductivity decreases with decrease in concentration.

(iii) Molar conductivity and equivalent conductivity increases with decrease in concentration. This is because $\Lambda_m = \kappa\,V$ and $\Lambda_{eq} = \kappa\,V$. Though 'κ' decreases with decrease in concentration but it is compensated by increase in volume and hence Λ_m and Λ_{eq} increase with dilution.

The variation of Λ_m for strong and weak electrolytes with concentration is as follows:
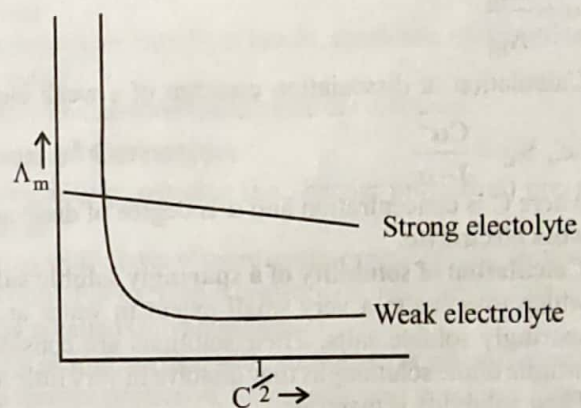
The increase in Λ_m for strong electrolyte with dilution is not very sharp. This is because strong electrolyte is already completely dissociated into ions. On dilution, ions get separated and their movement becomes easier and hence, Λ_m increases but not sharply.

On the other hand, weak electrolyte has lower degree of dissociation at higher concentrations. On dilution, the degree of dissociation increases and number of ions in the solution increases. Thus, Λ_m increases sharply.

KOHLRAUSCH'S LAW

According to this law, limiting molar conductivity of an electrolyte is the sum of the limiting ionic conductivities of the cation and the anion each multiplied with the number of ions present in one formula unit of the electrolyte.

Mathematically, Λ_m° for $A_xB_y = x\lambda^{\circ y+}_{(A)} + y\lambda^{\circ x-}_{(B)}$

where,

Λ_m° = Limiting molar conductivity of the electrolyte

$\lambda^{\circ y+}_{(A)}$ and $\lambda^{\circ x-}_{(B)}$ = Limiting molar conductivities of cation and anion respectively.