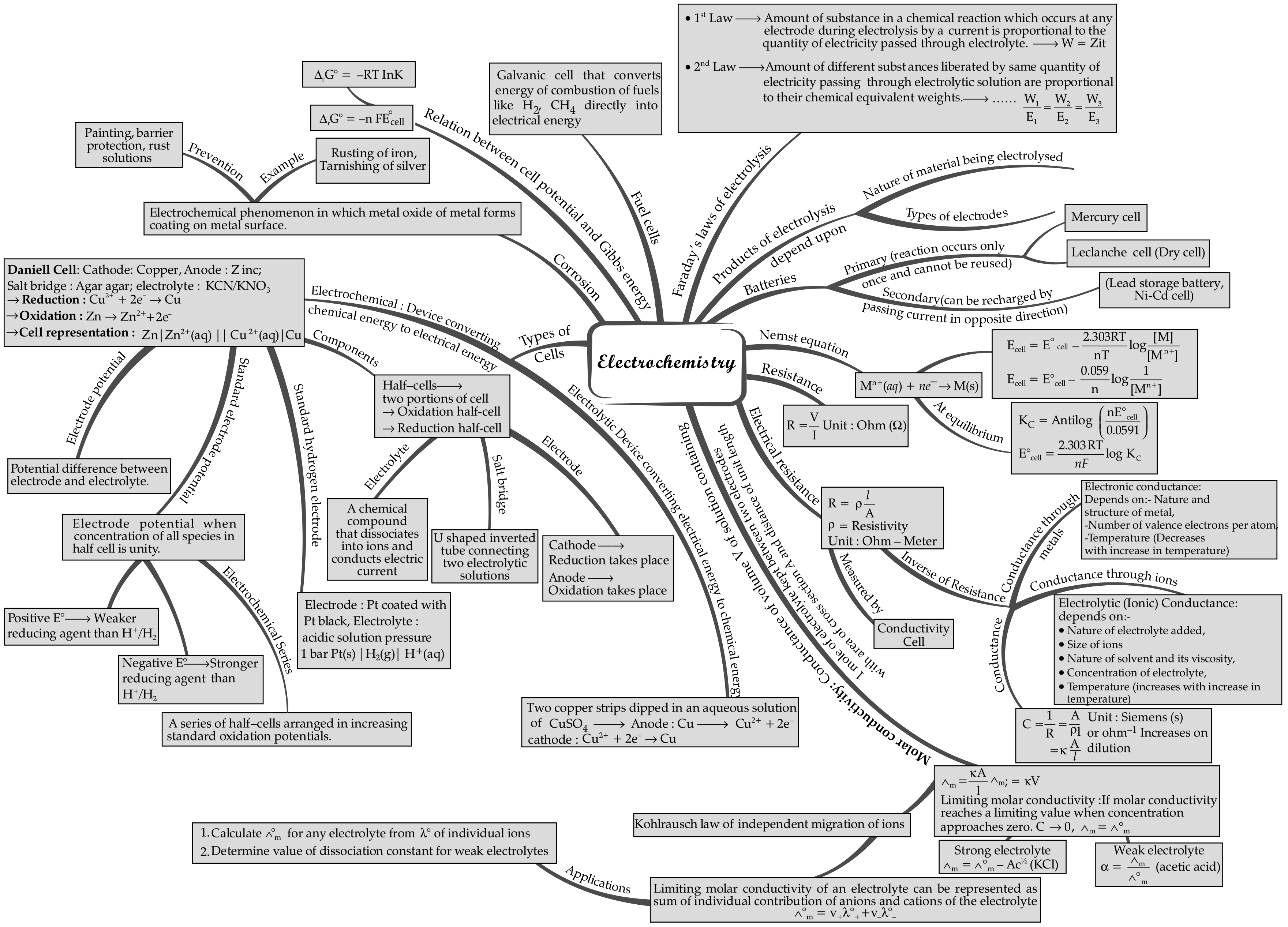


Electrochemistry

Faraday's laws of electrolysis

- 1st Law ⟶ Amount of substance in a chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through electrolyte. ⟶ W = Zit
- 2nd Law ⟶ Amount of different substances liberated by same quantity of electricity passing through electrolytic solution are proportional to their chemical equivalent weights. ⟶ …… $\frac{W_1}{E_1} = \frac{W_2}{E_2} = \frac{W_3}{E_3}$

Products of electrolysis depend upon

- Nature of material being electrolysed
- Types of electrodes

Batteries

- Primary (reaction occurs only once and cannot be reused): Mercury cell; Leclanche cell (Dry cell)
- Secondary (can be recharged by passing current in opposite direction): (Lead storage battery, Ni-Cd cell)

Nernst equation

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

$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nT}\log\frac{[M]}{[M^{n+}]}$

$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log\frac{1}{[M^{n+}]}$

At equilibrium

$K_C = \text{Antilog}\left(\frac{nE^\circ_{cell}}{0.0591}\right)$

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

Resistance

$R = \frac{V}{I}$ Unit : Ohm (Ω)

Electrical resistance

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

ρ = Resistivity

Unit : Ohm – Meter

Measured by: Conductivity Cell

Inverse of Resistance: **Conductance**

- Conductance through metals: Electronic conductance: Depends on:- Nature and structure of metal, -Number of valence electrons per atom, -Temperature (Decreases with increase in temperature)
- Conductance through ions: Electrolytic (Ionic) Conductance: depends on:-
  - Nature of electrolyte added,
  - Size of ions
  - Nature of solvent and its viscosity,
  - Concentration of electrolyte,
  - Temperature (increases with increase in temperature)

$C = \frac{1}{R} = \frac{A}{\rho l} = \kappa\frac{A}{l}$ Unit : Siemens (s) or ohm^{-1} Increases on dilution

Molar conductivity: Conductance of volume V of solution containing 1 mole of electrolyte kept between two electrodes with area of cross section A and distance of unit length

$\wedge_m = \frac{\kappa A}{l}$ $\wedge_m = \kappa V$

Limiting molar conductivity : If molar conductivity reaches a limiting value when concentration approaches zero. C → 0, $\wedge_m = \wedge^\circ_m$

Strong electrolyte $\wedge_m = \wedge^\circ_m - Ac^{½}$ (KCl)

Weak electrolyte $\alpha = \frac{\wedge_m}{\wedge^\circ_m}$ (acetic acid)

Kohlrausch law of independent migration of ions

Limiting molar conductivity of an electrolyte can be represented as sum of individual contribution of anions and cations of the electrolyte $\wedge^\circ_m = v_+\lambda^\circ_+ + v_-\lambda^\circ_-$

Applications

1. Calculate $\wedge^\circ_m$ for any electrolyte from λ° of individual ions
2. Determine value of dissociation constant for weak electrolytes

Electrolytic Device converting electrical energy to chemical energy

Two copper strips dipped in an aqueous solution of $CuSO_4$ ⟶ Anode : Cu ⟶ $Cu^{2+} + 2e^-$ cathode : $Cu^{2+} + 2e^- \rightarrow Cu$

Types of Cells

Electrochemical : Device converting chemical energy to electrical energy

Daniell Cell: Cathode: Copper, Anode : Zinc; Salt bridge : Agar agar; electrolyte : KCN/KNO_3

→ **Reduction :** $Cu^{2+} + 2e^- \rightarrow Cu$

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

→ **Cell representation :** $Zn|Zn^{2+}(aq)||Cu^{2+}(aq)|Cu$

Components

Half–cells ⟶ two portions of cell → Oxidation half-cell → Reduction half-cell

- Electrolyte: A chemical compound that dissociates into ions and conducts electric current
- Salt bridge: U shaped inverted tube connecting two electrolytic solutions
- Electrode: Cathode ⟶ Reduction takes place; Anode ⟶ Oxidation takes place

Standard hydrogen electrode: Electrode : Pt coated with Pt black, Electrolyte : acidic solution pressure 1 bar $Pt(s)|H_2(g)|H^+(aq)$

Standard electrode potential: Electrode potential when concentration of all species in half cell is unity.

- Positive E° ⟶ Weaker reducing agent than H^+/H_2
- Negative E° ⟶ Stronger reducing agent than H^+/H_2
- Electrochemical Series: A series of half–cells arranged in increasing standard oxidation potentials.

Electrode potential: Potential difference between electrode and electrolyte.

Corrosion

Electrochemical phenomenon in which metal oxide of metal forms coating on metal surface.

- Example: Rusting of iron, Tarnishing of silver
- Prevention: Painting, barrier protection, rust solutions

Relation between cell potential and Gibbs energy

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

$\Delta_r G^\circ = -RT\,\text{InK}$

Fuel cells

Galvanic cell that converts energy of combustion of fuels like H_2, CH_4 directly into electrical energy

CHAPTER

17

ELECTROCHEMISTRY

Chapter Objectives

- *Electrolytic and metallic conduction, Conductance in electrolytic solutions, Molar conductivities and their variation with concentration, Kohlrausch's law and its application, Farady's law of electrolysis.*
- *Electrochemical cells, Electrolytic and Galvanic cells, Electrode potential, Different types of electrodes, Half cell and cell reactions, Electromotive force (e.m.f.) of galvanic cell Electrochemical series, Nernst equation and its applications, Relationship between cell potential and Gibb's energy change, Concentration cell, Dry cell and lead accumulator, fuel cell, corrosion*

STUDY MATERIAL

I. Concept Clarified :

- **Electrochemistry** : The branch of chemistry which deals with the relationship between electrical energy and chemical energy and the inter conversion between them is known as electrochemistry.
  Electrochemistry may further be divided into main categories : **(a)** Electrolysis, and **(b)** Electromotive chemistry.
- **Fundamental definitions :**

  Conductor : A substance which allows electric current to pass through it. **For example;** Cu, Ag, Al etc.

  Insulator : A substance which does not allow the current to pass through it. **For example;** Glass, wool, wood, rubber etc.
- **Types of conductors :** Electrical conductors are of two types :
  (a) Metallic or electronic conductors
  (b) Electrolytic conductors
  (a) **Metallic or electronic conductors :** The substances which conduct electric current by transfer of electrons, without transfer of any matter are known as metallic or electronic conductors. These substances contain electrons which produce the relative mobility. The passage of current through these substances has no observable effect, but rise of temperature is observed (due to vibration of kernels which produce resistance in the flow of electrons).
  (b) **Electrolytic conductors :** The substances which ionize and conduct electricity with the decomposition of the substances either in molten state or in aqueous solution of acids, bases and salts are known as electrolytic conductors. With the rise in temperature, the resistance decreases. The resistance is due to ionic attractions and viscosity of the solvent.

  Non-electrolytes : The substances which do not conduct electric current either in their molten or aqueous state are known as non-electrolytes. **For example,** Solution of sugar, glycerine, alcohols, and naphthalene.

  Strong electrolytes : The electrolytes which are completely dissociated into ions in aqueous solution are known are strong electrolytes. **For example,** NaOH, NaCl, HCl, KNO_3 etc.

  Weak electrolytes : The electrolytes which are not completely dissociated in aqueous solution are known as weak electrolytes. **For example,** NH_4OH, CH_3COONH_4 etc.
- **Factors affecting electrolytic conductance :**
  (a) **Nature of electrolytes :** Ions conduct electric current. Since strong electrolytes produce a large extent of ions, they conduct electricity to large and reversely weak electrolytes produce electricity to a small extent.
  (b) **Concentration of solution :** Weak electrolytes dissociate to a small extent in concentrated solution but on dilution it increases the degree of ionisation which increases the conductance. In case of strong electrolyte on dilution, the interionic attraction is less and the conductance increases.
  (c) **Temperature :** On increasing the temperature the dissociation of electrolytes increases and hence, the conductance also increases.
  (d) **Nature of solvent :** Polar solvent ionises an electrolyte to a greater extent, thereby, increasing the conductance.
  (e) **Solvation of ions :** This depends on interaction between ions of solute and molecules of solvents. Greater the solvation of ions, lesser is the conductance.

- **Factors affecting metallic/electronic conductance :**
  - **(i)** Nature of the metal and its structure.
  - **(ii)** Number of valence electrons/atom.
  - **(iii)** Conductance decreases with the rise of temperature due to vibration of metallic kernels which produces resistance to the flow of electric current.
- **Ohm's law :** The current (I) flowing through a solution is directly proportional to the potential difference (V) applied between the electrodes dipping in it.

$$I \propto V$$

$$\Rightarrow \qquad V = IR \qquad [R = \text{Resistance of solution}]$$

'R' is the resistance (Ω) of the conductor and is expressed in ohms.

- **Resistance :** It measures the obstruction to the follow of current.

When components such as temperature, physical states etc., remain constant of a conductor, the resistance of the conductor is directly proportional to the length and inversely proportional to the cross section of the conductor.

$$R \propto \frac{l}{A} \text{ [where } l = \text{length, A = cross section]}$$

$$\Rightarrow \qquad R = \frac{\rho l}{A}$$

ρ = Proportionality constant and it is called specific resistance or resistivity.

$$\text{Units of } \rho = \frac{RA}{l} = \frac{\text{ohm} \times \text{cm}^2}{\text{cm}} = \text{ohm cm}$$

If $l = 1$ cm, $A = 1\text{cm}^2$, then $\rho = R$

Thus, it is the resistance between the two opposite sides having 1 cm length and cross section 1 cm^2 of the opposite sides of a cube is called specific resistance or resistivity.

- **Conductance :** Conductance of a conductor is the reciprocal of its resistance (R).

$$\text{Conductance (G)} = \frac{1}{\text{Resistance}} = \frac{1}{R} \qquad \ldots\text{(i)}$$

Unit : ohm^{-1} or mho or siemens (S).

- **Specific conductance :** The conductance offered by that portion of the solution which is enclosed between two parallel electrodes having 1 cm^2 area and 1 cm apart to each other is called specific conductance.

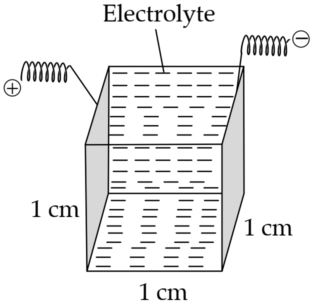


Fig 1. Specific conductance between two parallel electrodes

The reciprocal of the specific resistance is also called specific conductivity.

∴ Specific conductance = Conductance of the unit cube of a solution.

It is denoted by κ (kappa).

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \times \frac{l}{A} = \frac{\text{cm}}{\text{ohm cm}^2}$$

$$= \text{ohm}^{-1}\,\text{cm}^{-1}$$

$$\text{or S cm}^{-1}$$

Factors affecting Specific Conductance :

- **(i)** Concentration of the solution
- **(ii)** Temperature
- **(iii)** Valency of carrier ions
- **(iv)** Speed of ions

$$\text{Again } \kappa = \frac{1}{R} \times \frac{l}{A}$$

$$\Rightarrow \quad \kappa = \frac{1}{\text{R}} \times \text{G}^* \ \left[\ \frac{l}{\text{A}} = \text{cell constant denoted by G}^*\right]$$

$$\Rightarrow \quad \kappa = \text{G} \times \text{G}^*$$

$$\therefore \quad \text{G} = \frac{1}{R}$$

$\Rightarrow$ Specific conductance = Conductance (G) × cell constant (G^*)

- **Equivalent conductance ($\wedge$) :** It is the conductance of a solution containing 1g-equivalent of the dissolved electrolyte such that the entire solution is placed between two electrodes 1cm apart.

  If the resistance of the solution R, then according to the definition, $\wedge = \frac{1}{\text{R}}$

  Mathematically, equivalent conductance can be determined as follows : Let V mL or V cc solution contains 1 g-equivalent electrolyte then,

  1 mL solution contains $\frac{1}{\text{V}}$ g equivalent of electrolyte.

  $\therefore$ 1000 mL solution contains $\frac{1000}{\text{V}}$ g equivalent of electrolytes.

  If the concentration of the solution is expressed in normality, then concentration $C = \frac{1000}{\text{V}}$ g equiv/Litre.

  $$\therefore \qquad \text{V} = \frac{1000}{\text{C}} \text{ ml or } \frac{1000}{\text{C}} \text{ cc.}$$

  The two conductors are placed 1 cm apart , that is, the length of the conducting solution = 1cm

  $$\text{Cross section of solution (a)} = \frac{\text{Volume}}{\text{Length}}$$

  $$= \frac{\text{Vcm}^3}{1 \text{ cm}} = \text{V cm}^2$$

  Therefore, the conductance of this solution is known as equivalent conductance.

  $$\therefore \quad \wedge_e = \frac{1}{\text{R}} \text{ again}$$

  $$\Rightarrow \quad \wedge_e = \frac{1}{\frac{\rho l}{\text{A}}} = \frac{1}{\rho} \times \frac{\text{A}}{l}$$

  $$\Rightarrow \quad \wedge_e = \kappa \times \text{V} \quad \left[\text{As } \frac{1}{\rho} = \kappa \text{ and } \frac{\text{A}}{l} = \text{V cm}^2\right]$$

  $$\Rightarrow \quad \wedge_e = \kappa \times \frac{1000}{\text{C}}$$

  $$\therefore \quad \wedge_e = \frac{1000\ \kappa}{\text{C}}$$

  Unit of equivalent conductance :

  We know $\wedge_e = \frac{1000\kappa}{\text{C}}$

  $$\therefore \quad \wedge_e = \frac{\text{S cm}^{-1}}{\frac{\text{g-equiv}}{\text{cm}^3}} = \text{S cm}^2/\text{g equiv} = \text{ohm}^{-1}\,\text{cm}^2\,\text{g equiv}^{-1}$$

- **Molar conductivity or Molar conductance** (λ)

  It is defined as the conductance of all ions produced by ionisation of 1g mole of an electrolyte when present in V mL of solution .

  $$\therefore \quad \lambda_{\text{m}} = \kappa \times \text{V}$$

  $$= \frac{\kappa \times 1000}{\text{Molarity}} = \text{Scm}^2\,\text{mol}^{-1}$$

  Relation between equivalent conductance (λ_{eq}) and molar conductance (λ_m)

  $$\lambda_m = \lambda_{eq} \times n$$

Where n= equivalent factor of the electrolyte

$$n = \frac{\text{Molecular mass}}{\text{Equivalent mass}}$$

Experimental determination of conductance : The conductance is the reciprocal of resistance of solution. So the conductance of an unknown solution involves the measurement of its resistance. Measurement of all unknown resistance can be performed on Wheatstone bridge. In measuring the resistance of the solution (an ionic solution) we face the following two problems :

(a) Direct current (DC) changes the composition of the solution by electrolysis and polarisation. This problem can be solved by passing AC current.

(b) A solution control cannot be connected to the bridge like a metallic wire or any solid conduction. This problem can also be overcome by using a specially designed vessel called conductivity cells.

- **Determination of cell constant :** The quantity $\frac{l}{a}$ is known as cell constant and its value cannot be easily determined. However, it can be determined by actually measuring the conductance (Wheatstone bridge) of a solution whose conductivity is known at different concentration and temperature. Specific conductance of KCl solutions is as given below :

Concentration	**Specific conductance ($\Omega^{-1}cm^{-1}$)**		
	0°C	18°C	25°C
0.1M	0.007154	0.011192	0.012886
0.01M	0.0007751	0.0012227	0.0014114

Therefore, cell constant $(G) = \frac{\text{Specific conductance}}{\text{Measured conductance}}$

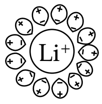
- **Factors Affecting the Conductance of Electrolytic Solutions :**

(1) Conductance $\propto$ extent of ionisation $\propto$ temperature

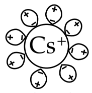
(2) **Nature of electrolyte :** Strong electrolytes undergo complete dissociation and furnish more number of ions, that is why strong electrolytes show greater conductivities, but weak electrolytes undergo dissociation to a lesser extent and most of the molecules remain undissociated, hence, they show comparatively low conductivities in solution.

(3) **Ionic size and mobility :** Conductivity $\propto$ ionic mobility $\propto \frac{1}{\text{Ionic size}}$.

But in aqueous state, the extent of hydration affects the mobility of the ion, hence, affects the conductivity of smaller ions which show lower conductance due to greater hydration.



Greater hydration
(moves slowly)



Lesser hydration
(moves rapidly)

(4) Conductivity depends upon the viscosity of the medium, conductivity decreases if viscosity increases in solution.

(5) **Concentration :**

(i) Electrolytic conductance increases on dilution as the number of ions increases on dilution.

(ii) The specific conductance (κ) increases with increase in concentration, because the number of ions per unit volume increases.

(iii) However, the equivalent and molar conductance increases with decrease in concentration (that is, upon dilution) because both λ_e and λ_m are the product of specific conductance and volume. Though on increasing volume, that is, decreasing concentration (κ) decreases but increasing volume of solution more compensated than K, consequently net effect increases equivalent/ molar conductivity.

At infinite dilution the equivalent conductance and molar conductance become constant since ionisation of electrolyte at infinity solution is complete. These maximum values are represented (equivalent and molar conductance) as λ_α or λ_σ and λ_m^α or λ_m^o.

- **Debye Huckel Onsager Equation :**

It is possible to determine the equivalent conductivity of electrolytes at constant temperature by using Debye – Huckel – Onsagar equation as follows :

$$\lambda_m = \lambda_m^\alpha - \left(A + B\lambda_m^o\right)\sqrt{C}$$

λ_m^α = molar conductivity at infinite dilution.

λ_m = molar conductivity at given concentration.

A, B are the constants that depend on temperature, charges of the ions, dielectric constant and viscosity of the solvent respectively.

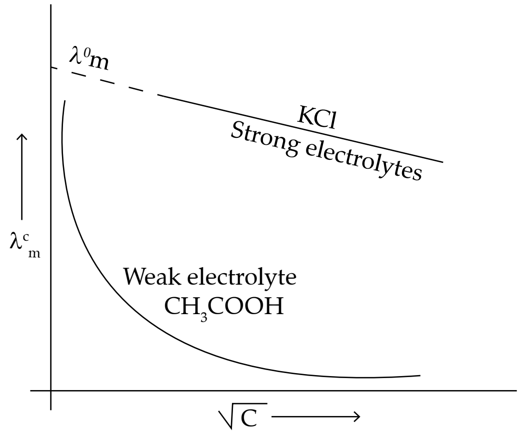


Fig 2. Plot of λ vs $\sqrt{C}$

It is obvious that the plot of λ vs $\sqrt{C}$ at low concentration would be a straight line. In dilute solutions, or a number of univalent electrolytes this can be justified. The slope of line in the curves gives the value of $A + B\ \lambda_m^o$ and intercept is λ_m^o. The equivalent conductance of weak electrolytes increases steeply at very low concentration and limiting value $\left(\lambda_m^o\right)$ cannot be determined by extrapolating the graph to zero concentration.

λ_m^0 values of weak electrolytes can be determined by using Kohlrausch Law of independent migration of ions.

Kohlrausch's Law of Independent Migration of Ions :

At infinite dilution when dissociation is complete, every ion makes some definite contribution towards molar conductance of the electrolyte irrespective of the nature of the other ion with which it is associated and molar conductance is the sum of the contributing two opposite ions.

$$\because \lambda_m^\infty = \lambda_{C^+}^\infty + \lambda_{A^-}^\infty$$

Where $\lambda_{C^+}^\infty$ and $\lambda_{A^-}^\infty$ are the contribution of cation and anion towards the molar conductance at infinite dilution. This law is also known as independent migration of ions. The above equation is applicable for binary electrolytes such as CH_3COONa, NaCl etc.

Applications of Kohlrausch's law :

(1) Determination of λ_m^o of weak electrolyte : For weak electrolytes by graphical method λ_m^∞ can not be determined. However, the values can be determined for strong electrolyte by applying graphical extrapolating method. By applying this law for strong electrolytes we can determine λ_m^∞ value for weak electrolytes as follows :

$$\therefore \lambda_{m\mathrm{CH_3COOH}}^\infty = \lambda_{(\mathrm{HCl})}^\infty + \lambda_{m(\mathrm{CH_3COONa})}^\infty - \lambda_{m(\mathrm{NaCl})}^\infty$$

$$= \lambda_{\mathrm{H^+}}^\infty + \lambda_{Cl^-}^\infty + \lambda_{mCH_3\ \mathrm{COO^-}}^\infty + \lambda_{\mathrm{Na^+}}^\infty - \lambda_{\mathrm{mNa^+}}^\infty - \lambda_{\mathrm{mCl^-}}^\infty$$

(2) Determination of degree of dissociation (α) :

(a) As the number of ions increases on dilution the molar conductivity increases and it reaches maximum at infinite dilution. If λ_m^c or λ_{eq}^c is the molar or equivalent conductivity at any concentration C and λ_m^o or λ_{eq}^o is the molar or equivalent conductivity at infinite dilution then for weak electrolytes,

$$\text{Degree of dissociation } (\alpha) = \frac{\lambda_m^c}{\lambda_m^\infty} = \frac{\lambda_{eq}^c}{\lambda_{eq}^\infty}$$

$$= \frac{\text{Conductance at concentration C}}{\text{Conductance at infinite dilution}}$$

(3) Calculation of dissociation constant of a weak electrolyte (K_a or K_b) :

Consider a reaction : $AB \rightleftharpoons A^+ + B^-$
At t = 0 $\quad$ C $\quad$ o $\quad$ o
At equilibrium $\quad$ $(C - C\alpha)$ $\quad$ $C\alpha$ $\quad$ $C\alpha$
Thus, dissociation constant,

$$K_a = \frac{[A^+][B^-]}{[AB]}$$

$$\Rightarrow \quad K_a = \frac{C\alpha \times C\alpha}{[1-\alpha]C}$$

$$\Rightarrow \quad K_a = \frac{\alpha^2 C}{1-\alpha} \qquad \ldots(i)$$

For weak electrolytes $\alpha << 1$

$$\therefore \quad K_a = \alpha^2 C$$

$$\Rightarrow \quad \alpha = \sqrt{\frac{K_a}{C}}$$

As concentration decreases, degree of dissociation increases,

$$\text{Now } \alpha = \frac{\lambda_C}{\lambda_O} \qquad \ldots(ii)$$

Putting in equation (i) we get

$$K_a = \frac{C\left(\frac{\lambda_C}{\lambda_O}\right)^2}{1-\frac{\lambda_C}{\lambda_O}} = \frac{C\lambda_C^2}{\lambda_O(\lambda_O - \lambda_C)}$$

(4) Determination of solubility product of sparingly soluble salt : Very small amount of sparingly soluble salt like AgCl, $BaSO_4$ or CaF_2 is present in a given solvent and in completely ionised form. Its molar or equivalent conductivity at same concentration 'C' is taken as its molar or equivalent conductivity at infinite dilution.

Thus, $\lambda^\circ = \frac{1000 \times \text{Specific conductance}}{\rho}$

$$\Rightarrow \quad \lambda^\circ = \frac{1000 \times \kappa}{C}$$

$$\Rightarrow \quad C = \frac{1000 \times \kappa}{\lambda^\circ}$$

$$\therefore \quad \text{Solubility} = \frac{1000 \times \kappa}{\lambda^\circ_{C^+} + \lambda^\circ_{A^-}}$$

(5) Calculation of absolute ionic mobilities :

The ionic mobility (U_α) and ionic conductance (λ_α) at infinite dilution are related to each other as below;

$U_\alpha = \frac{\lambda_\alpha}{F} = \frac{\lambda_\alpha}{96500C}$ [ionic mobility (U) is defined as distance travelled by ion per second under a potential gradient of 1 volt per cm ionic molarity (U) = $\frac{\text{Speed}}{\text{Potential gradient}}$]

➢ Transport Number or Transference Number :

"The fraction of the total current carried by an ion is called as transport number.

$$t_+ + t_- = 1$$

Factors affecting transport number :

(i) Temperature

(ii) Concentration of electrolyte

➢ Faraday's Laws of Electrolysis (a quantitative analysis of electrolysis)

I law :

It states that, the amount of substance (expressed in g) liberated or deposited at or dissolved from an electrode during electrolysis is directly proportional to the quantity of electricity passing through the electrolytic cell.

Let W_g of substance be deposited at the electrode to the passage of Q coulomb of electricity through the electrolyte then according to Faraday's law,

$$W \propto Q$$

$$\Rightarrow \quad W = ZQ \qquad [Z = \text{Electrochemical equivalent of a substance}]$$

$$\Rightarrow \quad W = ZIt \qquad [\text{As } Q = \text{ampere} \times \text{time} = I \times t]$$

II law :

It states that, when the same quantity of electricity is passed through solution of different electrolytes, the weights of different substances (in g) produced at the electrodes are directly proportional to the respective equivalent weights.

Let W_A and W_B be weights of the two substances A and B having equivalent weight E_A and E_B respectively, liberated at the two electrodes connected in series by passing the same quantity of electricity Q coulomb, then according to II law,

$$\frac{W_A}{W_B} = \frac{E_A}{E_B}$$

$$W \propto E$$

Combination of I and II law of electrolysis :

Let E = Chemical equivalent of a substance.
W = Weight of substance deposited in g.
Q = Quantity of electricity in coulomb passed through the electrolyte.

From I law

$$W \propto Q \qquad \ldots\text{(i) when E is constant}$$

From II law

$$W \propto E \qquad \ldots\text{(ii) when Q is constant}$$

When the Q and E changes,

$$W \propto QE.$$

$$\Rightarrow \quad W = KQE \qquad \ldots\text{(iii) K = constant}$$

Experimentally, K is found to be $\frac{1}{F}$ where F = 1 Faraday = 96,500C

From equation (iii) we get $W = \frac{QE}{F}$

$$W = \frac{EIt}{F} \quad \text{[As Q = It, I = Current in ampere, t = Time in seconds]}$$

$$\Rightarrow \quad W = \frac{E.I.t}{96,500}$$

Electrochemical Cell :

The devices which convert electrical energy into chemical energy or vice versa is known as electrochemical cell.

Electrochemical cells are of two types :

(a) Electrolytic cell

(b) Galvanic or voltaic cell.

(a) **Electrolytic cell :** It is a device in which electrical energy is converted into chemical energy resulting in a chemical reaction.

(b) **Galvanic cell :** It is a device in which chemical energy or Gibbs' energy charge of a spontaneous redox reaction and there by electrical energy is produced with the help of redox reaction (oxidation and reduction part physically separated).

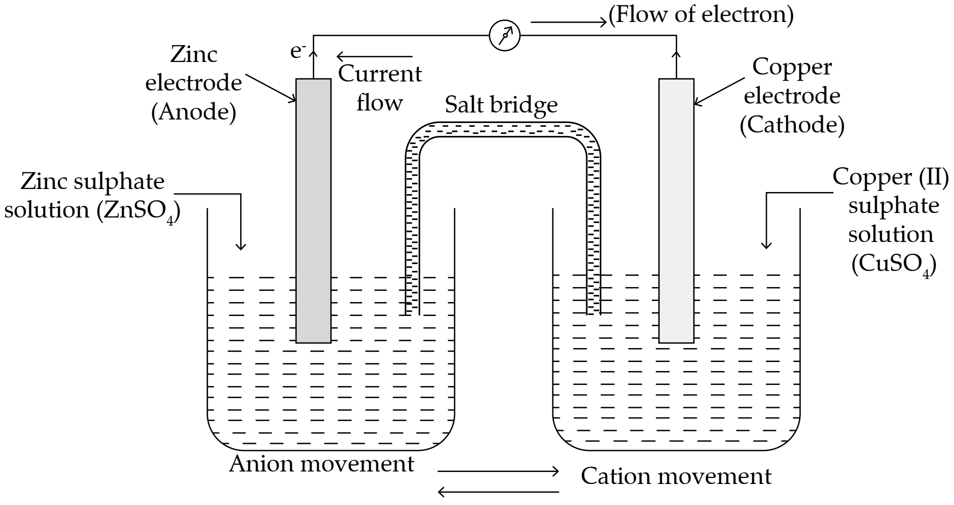


Fig 3. Daniel cell

Characteristics of Electrochemical cell :

(1) Electrochemical cell consists of two half cells, two electrodes, two electrolytic solutions and a salt bridge.

(2) In the two half cells two different electrodes (metals) are partly immersed in the solution.

(3) When metal (M) is present with its metallic ions (Mn^+) in the solution, it is called half cell.

(4) In the above figure, in one half cell zinc metal strip is dipped into a solution of zinc salt ($ZnSO_4$, 1M) and copper metal strip is dipped into a solution of copper salt ($CuSO_4$, 1M).

(5) At the Zn electrode, oxidation takes place and at Cu electrode reduction occurs.

(6) In this electrochemical cell, Zn^{2+} ions come to the solution and from the solution Cu^{2+} ions are liberated at the Cu electrode.

(7) The tendency of Zn atoms to pass into the solution in the form of positive ions, leaving behind electrons on the metal surface,

$$\left[\mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(aq) + 2e^-(\mathrm{metal})\right]$$

is known as solution pressure of the metal (P_s).

(8) The tendency of Cu^{2+} ions of the metal solution to get deposited on the metal by gaining electrons from metal surface,

$$\left[\mathrm{Cu}^{2+}(aq) + 2e^- \to \mathrm{Cu(s)}\right]$$

is called osmotic pressure (P_o) of ions in solution.

In first case $P_s > P_o$, Zn liberates as Zn^{2+} ions.

In second case $P_s > P_o$, Cu^{2+} ions move to the electrode.

(9) With the passage of time Zn rod goes on dissolving in one beaker and copper metal is precipitated. Thus, Zn rod loses in weight and copper rod gains in weight.

(10) The concentration of Zn^{2+} ions increases in Zn half cell and the concentration of Cu^{+2} ions decreases in Cu half cell.

(11) The solutions in both the beakers remain electrically neutral.

(12) No evolution of heat is observed during the reaction.

(13) The cell stops working after some time.

$$\mathrm{Zn(s) + CuSO_4(aq) \to ZnSO_4 + Cu(s)}$$
$$\mathrm{Zn(s) + Cu^{+2}(aq) \to Zn^{2+}(aq) + Cu(s)}$$

(14) As Zn rod is surrounded by the +ve ions, the release of Zn^{2+} ions becomes difficult. On the other hand Cu rod is surrounded by –ve ions. Electrical neutrality is hampered. To overcome this problem salt bridge is used which connects two half cells of the voltaic cell.

(15) A salt bridge is a inverted U shaped tube consisting of a inert electrolyte such as K_2SO_4, $NaNO_3$, NH_4NO_3, KNO_3, etc., mixing with semi solid paste obtained by adding gelatin or agar - agar algae.

It connects the two half cells and maintains electrical neutrality of two separate half cells.

(16) When in Zn half cell a bipositive Zn^{2+}comes to the solution, from salt bridge two negative ions or doubly charged negative ions come to the solution Zn(aq) of Cu half cell when one Cu^{2+} ion liberates at electrode, two positive ions come to the solution and maintains electrical neutrality.

(17) In Zn half cell oxidation takes place and Zn electrode acts as anode. But in Cu half cell reduction takes place and Cu electrode acts as cathode. When the two half cells are connected by a conducting wire, through outer circuit electrons flows from Zn rod to Cu rod and current flows from Cu rod to Zn rod.

(18) **Symbolic representation of a Galvanic cell :** The anode is written on the left hand side and the cathode is written on the right hand side. Salt bridge is present between anode and cathode as follows :

A	B	C
Anode	Bridge	Cathode

The cell can be represented as follows :

For A : Zn; Zn^{2+} or Zn | Zn^{2+} or Zn | $ZnSO_4$ (1M)

For C : Cu^{2+}, Cu or Cu^{2+} | Cu or $CuSO_4$ (1M) | Cu

The overall representation can be given as;

Zn | Zn^{2+} ||Cu^{2+}| Cu [Double lines represents salt bridge]

Z*n* | Z*n*SO_4 (1M) || $CuSO_4$ (1M) | Cu

(19) Standard EMF of a cell (E°)

E^o_{cell} = Difference in potential of two half cells.

$$= \{\text{Standard oxidation potential of anode} - \text{Standard oxidation potential of cathode}\}$$

$E^\circ_{cell} = \underset{ox}{E^\circ_a} - \underset{ox}{E^\circ_c}$ where a = anode

c = cathode

ox = oxidation

According to IUPAC, E°_{cell} is measured by using standard reduction potential.

$E^\circ_{cell} = \{$Standard reduction potential of cathode – Standard reduction potential of anode $\}$

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

[The value must be positive as $\Delta G = -nFE^\circ$]

(20) Cell reaction :

$$\text{Anode : } \overbrace{Zn \longrightarrow Zn^{2+} + 2e^-}^{ox}$$

$$\text{Cathode : } \underbrace{Cu^{\ +} + 2e^- \longrightarrow Cu}_{red}$$

$$\text{Overall cell reaction : } Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$$

➢ Electrode Potential :

When an electrode (metal) is in contact with its ions in solution in half cell, the potential difference between the metal and its ions in the solution is called electrode potential.

Or

The tendency of an electrode to lose or gain electrons is known as electrode potential. It is denoted by E.

Standard electrode potential : The potential difference developed between metal electrode and the solution of its ion having unit molarity (1M) at 25°C (298 K) is called standard electrode potential and it is denoted by E°.

Oxidation potential : The tendency of an electrode to lose electron or get oxidized is called oxidation potential.

Reduction potential : The tendency of an electrode to gain electron or get reduced is called reduction potential.

$$E^\circ_{red} = -E^\circ_{oxidation}$$

Reference electrode : The electrode of known potential at 298 K and which is used to find single electrode potential of different electrodes is known as reference electrode.

There are two types of reference electrodes :

(a) Primary reference electrode **(b)** Secondary reference electrode

(a) **Primary reference electrode :** Standard hydrogen electrode (SHE) or normal hydrogen electrode (NHE) is employed as primary reference electrode.

It has been observed that

(i) a half cell reaction can not take place independently.

(ii) loss or gain of electrons is a relative tendency.

(iii) Objectives of measurement, as soon as another metal conductor is placed into the solution, will set up its own potential.

For the above difficulties the electrode potential has to be against a reference electrode like Standard hydrogen electrode (SHE) or Normal hydrogen electrode(NHE).

It consists of Pt wire carrying Pt foil coated with finely divided Pt block. The wire is sealed into a glass tube, placed in a beaker containing 1M HCl. At 1 atm pressure hydrogen gas is bubbled through the solution at 298K. Thus, in solution quantity equilibrium between H_2 gas, H^+ is attained.

When it is used as anode, oxidation takes place as follows ;

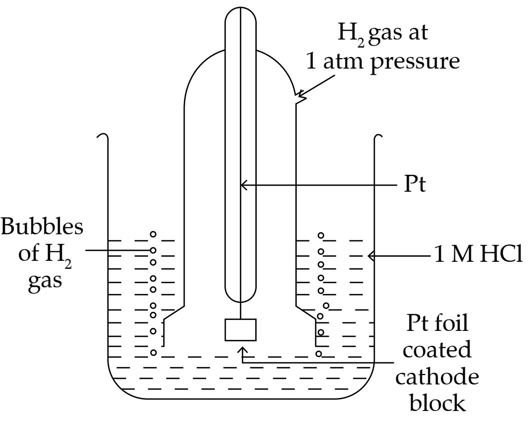


Fig 4. Standard hydrogen electrode

$$H_2(g) \rightarrow 2H^+(aq) + 2e^-$$

When this electrode is used as cathode, the following cell reaction takes place;

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

Depending upon whether SHE acts as anode or cathode in a given cell, it is represented as;

Pt, H_2(1 atm) | H^+(1M) or H^+(1M) | H_2 (1 atm) Pt respectively.

The electrode potential of the SHE is taken as zero.

Drawbacks of SHE :

(i) It is not possible to maintain H_2 at 1 atm pressure.

(ii) It is not easy to maintain H^+ion concentration at 1M.

(iii) It is impossible to protect Pt electrode from poison in presence of traces impurities.

To overcome above difficulties calomel and silver chloride electrodes are conveniently used as reference electrodes.

- **Calomel Electrode :** Calomel electrode consists of a thin layer of pure mercury at the bottom of the container. A paste of Hg, Hg_2, Cl_2 and KCl of known concentration is taken above the paste. The rest of the container is filled KCl solution of a known concentration and standard Hg_2Cl_2.

The electrode may be represented as Pt, Hg (*l*), Hg_2Cl_2 (s) | KCl (*x*M) (saturated with Hg_2Cl_2. when electrode reaction involves reduction, the reaction can be represented as;

At the anode : $Hg_2Cl_2(s) \rightleftharpoons Hg_2{}^{2+}(aq) + 2Cl^-(aq)$

At the cathode : $Hg_2{}^{2+} + 2e^- \rightleftharpoons 2Hg(l)$

Overall reaction $Hg_2Cl_2 + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-(aq)$

Concentration of KCl solution	$E^\circ_{(\text{Red. pot})}$
0.1M	+0.3335
1.0M	+0.2802
Saturated	+0.2415

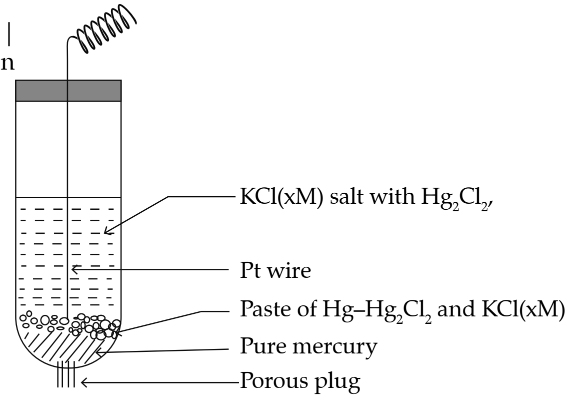


Fig 5. Calomel electrode

Advantages of Calomel Electrode :

(i) It is easy to construct and to transport.

(ii) With change of temperature it supplies a steady potential.

(iii) It can be used in laboratories for measuring potential.

(iv) It may be used in corrosion studies.

When the electrode involves oxidation, the reaction can be represented as;

At the anode : $2Hg \rightarrow Hg_2^{2+} + 2e^-$

At the cathode $2Hg_2^{2+}(aq) + 2Cl^- \rightleftharpoons Hg_2Cl_2$

Overall reation, $2Hg + 2Cl^- \rightleftharpoons Hg_2Cl_2$

So, this electrode is reversible with respect to Cl^- ions.

- **Electromotive Force (EMF) of a Cell :**

It is the difference of potential between the electrodes of a cell which causes the flow of current from electrode higher potential to another lower potential is known as electromotive force or EMF of a cell or cell potential.

EMF depends upon

(i) nature of reactants.

(ii) concentration of solution of two half cells.

(iii) temperature.

- **Electrochemical series :** It is the arrangement of elements in order of increasing reduction potential values.

Table : Standard reduction potentials at 25°C

Half reaction	**E°(V)**
Stronger oxidising agent	
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$S_2O_8^{2-}(aq) + 2e^- \rightleftharpoons 2SO_4^{2-}(aq)$	+2.01
$PbO_2 + HSO_4^-(aq) + 3H^+(aq) + 2e^- \rightleftharpoons PbSO_4 + 2H_2O$	+1.69
$2HOCl + 2H^+(aq) + 2e^- \rightleftharpoons Cl_2(g) + 2H_2O$	+1.63

	$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{1+}(aq) + 4H_2O.$	+1.51
	$PbO_2 + 4H^+(aq) + 2e^- \rightleftharpoons Pb^{2+}(aq) + 2H_2O$	+1.46
	$BrO_3^-(aq) + 6H^+(aq) + 6e^- \rightleftharpoons Br^-(aq) + 3H_2O$	+1.44
	$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.42
↑	$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
	$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O$	+1.23
	$Br_2(aq) + 2e^- \rightleftharpoons 2Br^-$	+1.07
	$NO_3^-(aq) + 4H^+(aq) + 4e^- \rightleftharpoons NO + 2H_2O$	+0.96
	$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
	$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
	$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
Oxidising power, Reactivity of metal	$NiO_2(s) + 2H_2O + 2e^- \rightleftharpoons Ni(OH)_2(s) + 2OH^-(aq)$	+0.49
	$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
	$SO_4^{2-}(aq) + 4H^+(aq) + 2e^- \rightleftharpoons H_2SO_3(aq) + H_2O$	+0.17
	$AgBr(s) + e^- \rightleftharpoons Ag(s) + Br^-(aq)$	+0.07
	$2H^+(aq) + 2e^- \rightleftharpoons H_2(s)$	0
	$Sn^{2+}(aq) + 2e^- \rightleftharpoons Sn(s)$	–0.14
↓	$Ni^{2+}(aq) + 2e^- \rightleftharpoons Ni(s)$	–0.25
	$CO^{2+}(aq) + 2e^- \rightleftharpoons CO(s)$	–0.28
	$PbSO_4(s) + H^+(aq) + 2e^- \rightleftharpoons Pb(s) + HSO_4^-(aq)$	–0.36
	$Cd^{2+}(aq) + 2e^- \rightleftharpoons Cd(s)$	–0.40
	$Fe^{2+}(aq) + 2e^- \rightleftharpoons Fe(s)$	–0.44
	$Cr^{3+}(aq) + 3e^- \rightleftharpoons Cr(s)$	–0.74
	$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	–0.76
	$2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^-$	–0.83
	$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	–1.66
	$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	–2.37

$Na^+(aq) + e^- \rightleftharpoons Na(s)$	–2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	–2.76
$K^+(aq) + e^- \rightleftharpoons K(s)$	–2.92
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	–3.05
Stronger reducing agent	

Applications of Electrochemical series :

(i) Oxidizing power

Oxidizing power $\propto$ SRP (Standard reduction potential)

Maximum SRP of F_2 (+2.87V)

(ii) Reducing power

Reducing power $\propto \frac{1}{\text{SRP}}$ [Minimum SRP Li(− 3.05V)]

(iii) A metal placed higher in series is anode. Metals which are placed above in series can easily displace the metal ion from their aqueous solution which are placed below in series.

$$Zn + CuSO_4 \rightleftharpoons ZnSO_4 + Cu\downarrow$$

$$\text{But } Cu + ZnSO_4 \rightleftharpoons \text{No reaction}$$

(iv) A non-metal which is placed higher in series can displace anion of non-metal which is below in series.

$$2Cl^- + F_2 \rightarrow 2F^- + Cl_2$$

The following displacement reactions take place on the basis of relative position of metals.

Metals placed above H_2 $\xrightarrow{\text{Displace}}$ From aqueous solution of acid $\longrightarrow H_2\uparrow$

Metals placed above Mg $\xrightarrow{\text{Displace}}$ From cold H_2O $\longrightarrow H_2\uparrow$

Metals from Mg to Cr $\xrightarrow{\text{Displace}}$ From hot H_2O $\longrightarrow H_2\uparrow$

Metal Fe $\xrightarrow{\text{Displace}}$ From steam H_2O $\longrightarrow H_2\uparrow$

(v) Oxides of metals which occupy position below Cu metal, their oxides are mainly unstable and easily reduced to metal.

$$Ag_2CO_3 \overset{\Delta}{\rightleftharpoons} Ag_2O + CO_2$$
$$\downarrow\Delta$$
$$2Ag + \frac{1}{2}O_2$$

(vi) Spontaneity and feasibility of the cell can easily be predicted.

➢ Nernst equation :

If the electrode concentration is not normal (1M) or the temperature is not standard (298 K), the electrode potential has a different value. Then value is obtained by using Nernst equation. Nernst equation is a relationship between electrode potential and the concentration of electrolyte solution. Consider a general reduction as follows :

$$M^{n+}(aq) + ne^- \rightarrow M(s)(\text{Example: } Cu^{2+} + 2e \rightarrow Cu)$$

The Nernst equation is applied as follows :

$$E_{(M^{n+}/M)} = E^\circ_{(M^{n+}/M)} - \frac{2.303RT}{nF}\log\frac{[M(s)]}{[M^{n+}(aq)]}$$

Where, E = Electrode potential under given concentration of M^{n+} ions and temperature T

E° = Standard electrode potential

R = Gas constant (8.314 J K^{-1} mol^{-1})

T = Temperature in K

F = 1 Faraday (1F = 96500 C)

n = Number of electrons involved in the electrode reaction

Substituting the values of R (8.314 J K^{-1} mol^{-1}), T = 298K, F = 96500C, the Nernst equation becomes

$$E_{(M^{n+}/M)} = E^\circ_{(M^{n+}/M)} - \frac{0.0591}{n}\log\frac{[M(s)]}{[M^{n+}(aq)]}$$

The above equation may also be written as :

$$E = E^\circ - \frac{0.0591}{n}\log\frac{1}{[M^{n+}(aq)]}[\because [M(s) = 1)]$$

Applications of Nernst equation :

(1) Determination of equilibrium constant :

In general,

$$aA + bB \xrightarrow{ne^-} xX + yY$$

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n} \log \frac{[X]^x [Y]^y}{[A]^a [B]^b}$$

At equilibrium, $E_{cell} = 0$

Therefore, $0 = E^0_{cell} = \frac{0.0591}{n} \log \frac{[\text{Products}]}{[\text{Reactants}]}$

$$\Rightarrow E^0_{cell} = \frac{0.0591}{n} \log K_c \quad \text{at } 298\text{K}$$

If E^0_{cell} and *n* are known, K_c can be calculated.

(2) Calculation of pH of solution :

Pt H_2 (g) | H^+(pH=?) | | Cl^- (1M) | Hg_2Cl_2, Hg

[Calomel electrode]

Cell reaction :

Anode: $H_2 \rightleftharpoons 2H^+(aq) + 2e^- \quad E^0_H = 0.0V$

Cathode : $Hg_2Cl_2(s) + 2e^- \rightleftharpoons 2Hg(l) + 2Cl^-(aq) \quad E^0_{\frac{Hg^{2+}}{Hg}} = 0.2676V$

Overall cell reaction :

$H_2 + Hg_2Cl_2 \rightleftharpoons 2H^+(aq) + 2Hg(l) + 2Cl^-(aq) \quad E^0_{cell} = 0.2676V$

$$\Rightarrow E_{cell} = E^0_{cell} - \frac{0.0591}{2} \log[H^+]^2$$

[Activities of all other reagents and products can be taken]

$$\Rightarrow E_{cell} = E^0_{cell} - 0.0591 \log[H^+]$$

$$\boxed{\Rightarrow pH = \frac{E_{cell} - E^\circ_{cell}}{0.0591}}$$

(3) Determination of solubility of sparingly soluble salts.

Consider a general electrode,

Ag | Ag_2CrO_4 | | AgCl (saturated solution) | Ag (saturated solution)

$$\therefore E_{(\text{cell at } 298K)} = E^\circ - \frac{0.0591}{1} \log \frac{[Ag^+_C]}{[Ag^+_A]}$$

$$= -0.0591 \log \frac{[Ag^+_C]}{[Ag^+_A]} \left[\text{Since } E^\sigma_{cell} = 0\right] \quad \ldots(1)$$

Ag^+ in anode and cathode half cells is written in terms of K_{sp} as;

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+ + CrO_4^{2-}$$

$$K_{sp} = [\underset{2x}{Ag^+}]^2 [\underset{x}{CrO_4^{2-}}]$$

$$K_{sp} = [Ag^+]^2 [CrO_4^{2-}] = (2x)^2 \times x = 4x^3$$

$$\therefore \quad x = \sqrt[3]{\frac{(K_{sp})_3}{4}}$$

$$\Rightarrow [Ag^+_A] = 2x = 2 \times \sqrt[3]{\frac{(K_{sp})_3}{4}} \quad \ldots(2)$$

Similarly, let the solubility of AgCl be *y* moles/ litre

$$AgCl(s) \rightleftharpoons \underset{y}{Ag^+} + \underset{y}{Cl^-}$$

$$\therefore (K_{sp})_2 = [Ag^+][Cl^-] = y^2$$

$$\Rightarrow y = \sqrt{(K_{sp})_2}$$

$$\Rightarrow [Ag^+_c] = \sqrt{(K_{sp})_2} \quad \ldots(3)$$

From equations, (1), (2) & (3) we get,

$$E_{cell} = 0.0591 \log \frac{\sqrt{(K_{sp})_2}}{2 \times \sqrt[3]{\frac{(K_{sp})_3}{4}}} \quad \ldots(4)$$

(4) Determination of ionisation constant of weak acid or weak base : For a cell , Pt $(H_{2)|}H^+$, HA (C_1) | | Cu^{z+} (C_2) | Cu

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{[H^+]^2}{[Cu^{2+}]} \Rightarrow E_{cell}$$

$$= E^\circ_{cell} - \frac{0.059}{2} \log \frac{\left(\sqrt{K_a C_1}\right)^2}{C_2}$$

- **Relationship between Cell potential and Gibb's energy change :** In a galvanic cell, reduction takes place at cathode and oxidation at anode. These two electrodes have different cell potentials. The difference in potential of electrodes is the electromotive force (emf). It is called vigor with which the cell works and also measure of chemical reactions occurring in the cell. In a spontaneous process, Gibb's energy (ΔG) decreases. The electrical work of a cell is the decrease in free energy.

$\therefore$ Electrical work = Decrease in free energy

$\Rightarrow$ $-\Delta G$ = Electrical work done …(1)

Electrical work done = Electrical energy produced

= Quantity of electricity × EMF

For 1 mole of electrons, quantity of electricity =1F

For *n* moles of electrons, quantity of electricity = *n*F

Now E_{cell} is the EMF of the cell

$\therefore$ Electrical work done = nFE_{cell} …(2)

Comparing (1) and (2) we get

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

$$\therefore \quad \Delta G = -nFE_{cell} \qquad \ldots(3)$$

At standard condition,

$$\Delta G^\circ = -nF\,E^o_{cell} \qquad \ldots(4)$$

The value of Gibb's energy can be used to calculate the equilibrium constant of reaction.

For any reaction.

$$\Delta G = \Delta G^\circ + RT\ln Q \qquad \ldots(5)$$

$$\Rightarrow -nFE_{cell} = -nF\,E^o_{cell} + RT\ln Q$$

$$\Rightarrow E_{cell} = E^o_{cell} - \frac{RT\ln Q}{nF} \qquad \ldots(6)$$

At equilibrium when $E_{cell} = 0$, then $Q = K$ putting in above (6) equation we get.

$$\boxed{E^o_{cell} = -\frac{RT}{nF}\ln K = -\frac{2.303RT}{nF}\log K}$$

Determination of Thermodynamic data : From Gibb's – Helmholtz equation we get,

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P \qquad \ldots\textbf{(1)}$$

$$\text{Applying } \Delta G = -nFE \qquad \ldots\textbf{(2)}$$

$$\therefore \quad \left(\frac{\partial \Delta G}{\partial T}\right)_P = -nF\left(\frac{\partial E}{\partial T}\right)_P \qquad \ldots\textbf{(3)}$$

Therefore, from (1), (2), (3) we get.

$$-nFE = \Delta H - nFT\left(\frac{\partial E}{\partial T}\right)_P$$

$$\Rightarrow \quad \Delta H = -nF\boxed{\left[E - T\left(\frac{\partial E}{\partial T}\right)_P\right]}$$

$$\text{Again } \Delta G = \Delta H - T\Delta S,$$

$$\therefore \quad \Delta S = \boxed{\frac{\Delta H - \Delta G}{T} = nF\left(\frac{\partial E}{\partial T}\right)_P}$$

- **Concentration cell :** A cell in which electrical energy is formed by the transference of a substance from a system of high concentration to one at low concentration is called concentration cell.
  Let us take an electrode M/M^{n+} having two different concentrations as;

$$M^{n+}/M(C_1) \text{ and } M/M^{n+}(C_2)$$

This type of cell can be represented as;

$$M/Mn^{+}(C_1) \,||\, M^{n+}(C_2) \,|\, M$$

The two half cell reactions are written as;

Anode : $M \rightarrow M^{n+}(C_1) + ne^-$

Cathode $M^{n+} + ne^- \rightarrow M$

Overall cell reaction is $M^{n+}(C_2) \rightarrow M^{n+}(C_1)$

$$\therefore \quad E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{\left[M^{n+}(C_1)\right]}{\left[M^{n+}(C_2)\right]}$$

Now, $E^\circ_{cell} = 0$

$$\therefore \quad E_{cell} = -\frac{0.0591}{n}\log\frac{\left[M^{n+}(C_1)\right]}{\left[M^{n+}(C_2)\right]}$$

[Similarly H_2 electrode in aqueous solution]

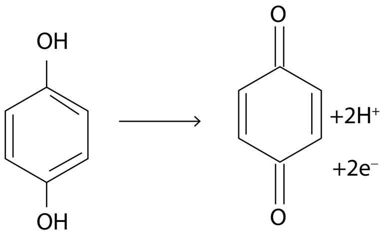
H_2(g) (P atm) | HCl (aq) (C_1) || HCl(aq)(C_2) | H_2(g) (P atm)

$$E_{cell} = -\frac{0.0591}{1}\log\frac{[H^+]_A}{[H^+]_C}$$

$$= 0.0591\,[\text{pH (anode)} - \text{pH(cathode)}]$$

Types of Half Cells :

Sl. No	Type	Example	Half cell reaction
1.	Metal – metal ion half cell	Ag/ Ag^+ (*aq*)	$Ag(s) \rightarrow Ag^+ + e^-$
2.	Gas - ion half cell	Pt (H_2) | H^+(*aq*)	$H_2 \rightarrow 2H^+ + 2e^-$

3.	Metal insoluble salt anion half cell	Hg, $HgCl_2$ | Cl^- (*aq*) Calomel electrode	$2Hg(l) + 2Cl^-(aq)$ ↓ $Hg_2Cl_2 + 2e^-$
4.	Oxidation / Reduction half cell	Pt | Fe^{2+}, Fe^{3+}	$Fe^{2+} \rightarrow Fe^{3+} + e^-$
5.	Quinohydrone	Pt |Quinohydrone| H^+ (*aq*)	
6.	Metal, metal oxide – hydroxide half cell	Hg / HgO | OH^- (*aq*)	$Hg(l) + 2OH^- \rightarrow HgO + H_2O + 2e^-$

- **Some Commercial Cells (Batteries and Fuel Cells) :**

There are two types of batteries :

(1) Primary batteries

(2) Secondary batteries

(1) **Primary battery (Dry cell) :** In this kind of battery , the reaction occurs only once and the battery then becomes dead after use over a period of time and can not be recharged again. Examples : Dry cell, mercury cell, Daniel cell and an Alkaline dry cell. It is also called as primary voltaic cell.

Characterstics of primary battery :

(i) It has a cathode consisting of carbon (graphite) rod .

(ii) Carbon rod is surrounded by a paste consisting of MnO_2 and powdered graphite.

(iii) Zinc rod serves as the anode.

(iv) The electrolyte is a moist paste of NH_4Cl, $ZnCl_2$ and MnO_2 (this type of cells are often called dry cells because there is no visible liquid phase).

(v) The reactions at the electrodes are ;

Anode : $Zn \rightarrow Zn^{2+} + 2e^-$

Cathode: $2MnO_2 + 2\overset{+}{N}H_4 + 4H_2O + 2e^- \rightarrow 2Mn(OH)_3 + 2NH_4OH$

Overall cell reaction : $Zn + 2MnO_2 + 2\overset{+}{N}H_4 + 4H_2O \rightarrow 2Mn(OH)_3 + Zn^{2+} + 2NH_4OH$

The cell generates a potential of 1.5V.

Another type of dry cell is mercury cell (Ruben Mallory cell) :

(i) It is suitable for low current devices like hearing aids, watches etc.

(ii) Zn – Hg amalgam is used as anode.

(iii) Carbon plus HgO is used as cathode.

(iv) The electrolyte is a paste of KOH and Zn.

(v) The reactions at the electrode are;

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

Cathode: $HgO + H_2O + 2e^- \rightarrow Hg(l) + 2OH^-$

Overall cell reaction: $Zn(Hg) + HgO(s) \rightarrow ZnO(s) + Hg(l)$

(vi) The cell generates a potential of 1.35 V and this voltage remains constant as the overall reaction does not involve any ion in solution whose concentration can change during its life time.

Alkaline dry cell :

It is similar to an ordinary dry cell. The reaction in alkaline dry cell are as follows:

Anode : $Zn + 2OH^- \rightarrow Zn(OH)_2 + 2e^-$

Cathode : $2MnO_2 + 2H_2O + 2e^- \rightarrow 2MnO(OH) + 2OH^-$

Overall cell reaction : $Zn + 2MnO_2 + 2H_2O \rightarrow Zn(OH)_2 + 2MnO(OH)$

The cell potential is 1.5 V.

(2) **Secondary batteries :** In the secondary cells, the reactions can be reversed for the respective cell reactions, that is, anode becomes cathode and cathode becomes anode by imposing a higher voltage than E.M.F of cell (external voltage). These are also called storage cells.

Examples : Lead storage battery and nickel cadmium cell.

(a) Lead storage battery :

Anode : spongy lead.

Cathode : grid of lead packed with PbO_2.

Electrolyte : 38 % H_2SO_4 by mass

When the battery is being used up half cell reactions are :

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

Cathode : $PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$

Overall cell reaction :

$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \rightarrow 2PbSO_4 + 2H_2O$

Ecell = 2.041 V

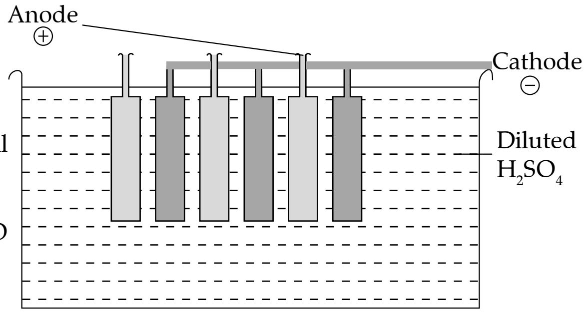


Fig 6. Lead storage battery of 6V

The battery is reversible (chargeable) since $PbSO_4$ (product of both anode and cathode reactions) sticks to the plates. When the concentration of battery falls in the cell, the cell is required to be charged. When the density of solution falls between 1.20 g/mL and 1.30 g/mL the cell is considered as fully charged. When the value falls to 1.20 g/ml, the battery is required to be charged. By imposing higher voltage from external source we can charge the battery again.

During recharging the cell reactions are reversed;

Anode: $PbSO_4 + 2H_2O \rightarrow PbO_2 + SO_4^{2-} + 4H^+ + 2e^-$

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

Overall cell reaction : $2PbSO_4 + 2H_2O \rightarrow Pb + PbO_2 + 2H_2SO_4$

(b) Nickel cadmium storage cell :

Another important secondary cell is nickel cadmium cell which has longer life than lead storage cell but more expensive and is popularly used in calculators. Cadmium is used as anode and nickel (IV) oxide is used as cathode. KOH solution is used as electrolyte. During discharge the following reactions take place :

At anode : $Cd\ (s) + 2OH^-(aq) \rightarrow Cd\ (OH_2)\ (s) + 2e^-$

At cathode : $NiO_2\ (s) + 2H_2O + 2e^- \rightarrow Ni(OH)_2\ (s) + 2OH^-\ (aq)$

Overall cell reaction is : $Cd\ (s) + NiO_2\ (s) + 2H_2O \rightarrow Cd(OH)_2\ (s) + Ni\ (OH)_2$

The cell Ni – Cd generates a potential of 1.4 V.

- **Fuel Cell :** Galvanic cells that are designed to convert energy evolved during the combination of fuels such as H_2, CH_4, CH_3OH, etc., directly into electrical energy are known as fuel cells. To avoid the main disadvantage of primary cell that is delivery of current for a short period only due to quantity of oxidizing , use of reducing agents are limited . $H_2 – O_2$ fuel cell can be used indefinitely as long as the outside supply of fuel is maintained.

In this cell there are three compartments which are separated by a porous electrode.

Hydrogen and oxygen gases are introduced into two separate compartments. Here, the resin containing concentrated aqueous solution of NaOH is used as electrolyte . Hydrogen is oxidized at anode and oxygen is reduced at cathode. The reactions at the electrodes are :

At anode : $2H_2\ (g) + 4OH^-\ (aq) \rightarrow 4H_2O + 4e^-$

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

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

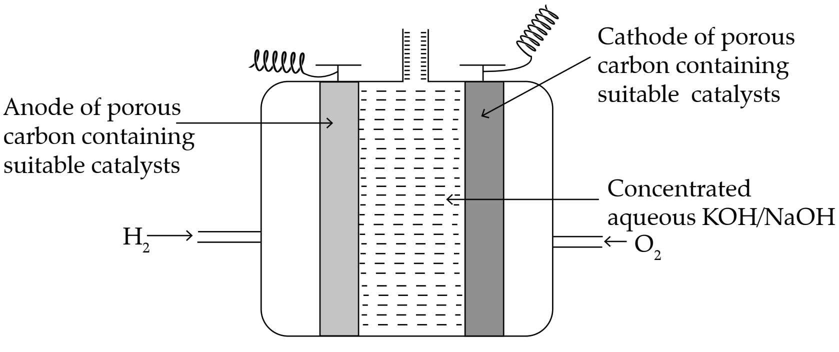


Fig 7. H_2-O_2 fuel cell

Advantages :

(i) Gaseous materials are consumed and continuously supplied and hence, such cells never become dead.

(ii) Such cells can be operated at higher temperature of 70° - 140°C and fuel cell can generate potential of 0.9 V.

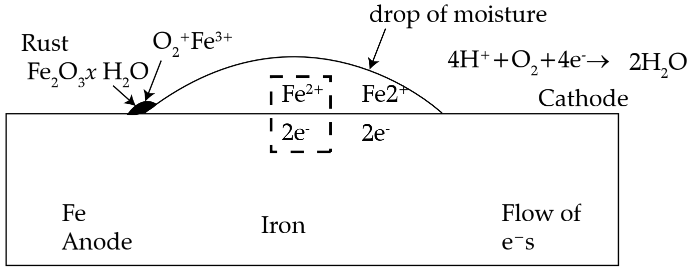
(iii) Theoretically, these cells have efficiency of 100%, but in practical use they have efficiency of about 70%. This can be compared with thermal plants whose efficiency is about 40%.

(iv) It is completely environment friendly, i.e., pollution free.

- **Corrosion :** The atmospheric gases attacking on the surface of the metal resulting in slow formation of undesirable compounds such oxides, sulphates, carbonates, sulphates, etc., causing decomposing of metal is known as corrosion.

Example : Rusting of iron (hydrated ferric oxide $Fe_2O_3 . xH_2O$ is the chemical formula of Rust)

Mechanism of corrosion :



Overall reaction :

$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(l)$ $E^o_{cell} = 1.67$ V
$4Fe^{2+} + O_2(O) + 4H_2O \rightarrow 2Fe_2O_3 + 8H^+(aq)$
$Fe_2O_3 + x\,H_2O \rightarrow 2Fe_2O_3 . xH_2O$ (Rust)

Factors which promote corrosion :

(i) Reactivity of metal : More active metals are readily corroded.
(ii) Presence of air and moisture : Air, moisture and gases like SO_2, CO_2 catalyse the corrosion process.
(iii) Presence of impurity : Impure metals are readily corroded but pure metals do not corrode.
(iv) Presence of electrolyte : Presence of electrolytes dissolving chloride, sulphate, carbonates, in water accelerates the corrosion.
(v) Strains in metals : Corrosion occurs rapidly at bends, scratches, nicks and cuts in the metal.

Prevention of Corrosion :

(a) Barrier protection by oil/ grease layer, paints or electroplating.
(b) Sacrificial protection : Coating the metal with more electropositive metal. Example : Galvanization.
(c) Electrical protection : Connecting the iron pipe to a more electropositive metal with a wire (cathode protection).

II. Important Formulae :

(1) Resistance $(R) = \frac{V}{I}$

(2) Conductance $(G) = \frac{1}{R}$

(3) Cell constant $(G^*) = \frac{l}{A}$

(4) Resistivity or specific resistance $R = \rho\frac{l}{A}$

(5) Specific conductance / Conductivity

κ(Kappa) $= \frac{l}{\rho} = \frac{l}{A \times R} = G \times G^*$

(6) Debye Huckel Onsager's equation

For strong electrolyte $\lambda_m = \lambda_m - b\sqrt{c}$
b = Debye Huckel onsager constant

(7) Molar conductance

$\lambda_m = \kappa \times V$

$= \frac{\kappa \times 100}{M}$ [M=Molarity]

$\lambda_{eq} = \kappa \times V = \frac{\kappa \times 1000}{N}$ [N=Normality]

(8) Kohlrausch Law

$\lambda^\infty_m = \lambda^\infty_{C^+} + \lambda^\infty_{A^-}$

(9) (a) Degree of dissociation $\alpha = \frac{\lambda^C_n}{\lambda^C_m} = \frac{\lambda^C_{eq}}{\lambda^C_{eq}}$

(b) $K_a = \frac{\alpha^2 C}{1-\alpha} = \frac{C\lambda_c^2}{\lambda_\sigma(\lambda_\sigma - \lambda_C)}$

(c) Solubility $= \frac{1000\kappa}{\lambda^0_C + \lambda^0_A}$

(10) Transport number(t_+) =

$$\frac{\text{Current carried by cations}}{\text{Total current carried by ions}}$$

$$t_+ = \frac{\text{Current carried by anions}}{\text{Total current carried by ions}}$$

(a) $t_+ + t_- = 1$

(b) $t_+ \propto Q_+ m_+ V_+$

(c) $t_- \propto Q_- m_- V_-$

(d) $t_+ = \frac{V_+}{V_+ + V_-}$ Q, m, v → change, moral concentration, speed of ions.

(e) $t_- = \frac{V_-}{V_+ + V_-}$

(f) $\frac{t_+}{t_1} = \frac{V_+}{V_-} = \frac{\lambda_+}{\lambda_-}$

(11) Ionic mobility = $\dfrac{\text{Ionic velocity}}{\text{Potential gradient}} = \dfrac{V}{dV/dt} =$ $m^2\,V^-\,s^{-1}$.

(12) Daniel cell

$$\mathrm{Zn}(s)\,|\,\underset{C_1M}{\mathrm{ZnSO_4}(aq)}\,||\,\underset{C_2M}{\mathrm{CuSO_4}(aq)}\,|\,\mathrm{Cu}(s)$$

(13) $E^\circ_{cell} = E^\circ_{athode} - E^\circ_{anode}$

(14) **Nernst equation :** For a general reaction.

$aA + bB \rightarrow cC + dD$

Reaction quotient $K = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$

(a) $\Delta G = \Delta G^0 + 2.303\,RT \log K$

(b) $\Delta G = -nF\,E_{cell}$

(c) $\Delta G^0 = -nF\,E^o_{cell}$

(d) $E_{cell} = E^o_{cell} - \dfrac{2.303RT}{nF}\log K$

$\Rightarrow$ $E_{cell} = E^o_{cell} - \dfrac{0.0591}{n}\log K$ [at 298K]

(15) Concentration cell

(a) $M\,|\,M^{n+}(C_1)\,||\,M^{n+}(C_2)\,|\,M$

$$E_{cell} = E^\circ_{Cell} - \frac{0.0591}{n}\log\frac{C_1}{C_2}$$

(b) Pt, $H_2(g)(P_1)$ |HCl (1M) | $H_2(g)$ (P_2), Pt

$$E_{cell} = E^0_{cell} - \frac{0.0591}{2}\log\frac{P_2}{P_1}$$
$$= 0 - \frac{0.0591}{2}\log\frac{P_2}{P_1}$$

E_{cell} = +ve if $P_1 > P_2$; cell is spontaneous (ΔG = –ve)

(c) Pt, $H_2(g)$(1atm) | H^+ (C_1) || $H^+(C_1)$ || $H^+(C_2)|H_2(G)$ (1atm), Pt

$$E_{cell} = -\frac{0.0591}{2}\log\left[\frac{H^+(C_1)}{H^+(C_2)}\right]$$

$= 0.0591\,[pH_{(anode)} - pH_{(cathode)}]$

(16) $E^\circ_{Cell} = \dfrac{0.0591}{n_{cell}}\log K_{eq}$

$= \log K_{eq} = \dfrac{n_{cell} \times E^0_{cell}}{0.0591}$

(17) Thermodynamic data

(a) $\left(\dfrac{\partial E_{cell}}{\partial T}\right)_p = \dfrac{\Delta H}{nRT} + \dfrac{E_{cell}}{T}$

(b) $\Delta H = -nF\left[E_{cell} - T\left(\dfrac{\partial E_{cell}}{\partial T}\right)_p\right]$

(c) $\Delta S = nF\left(\dfrac{\partial E_{cell}}{\partial T}\right)_p$