

II PUC-CHEMISTRY ELECTROCHEMISTRY

Electrochemistry is the branch of physical chemistry which deals with the relationship between electrical energy and chemical changes taking place in redox reactions

Electrolyte: "The substances whose aqueous solution undergo decomposition into ions when electric current is passed through them are known as **electrolytes** and the whole process is known as **electrolysis** or **electrolytic decomposition**."

Solutions of acids, bases, salts in water and fused salts etc. are the examples of electrolytes. Electrolytes may be **weak** or **strong**. Solutions of cane sugar, glycerine, alcohol etc., are examples of **non-electrolytes**.

Electrolyte is a substance which conducts electricity either in aqueous solution or in molten state. Example: NaCl, KNO₃, CuSO₄, HCl, CH₃COONa etc.

Solid electrolyte does not conduct electricity since the ions are held to the lattice points by strong ionic bonds.

Non-electrolyte is a substance which does not conduct electricity in aqueous solution or in molten state.

Example: Rubber, sugar, glycerine, urea etc,

Strong electrolyte

Strong electrolyte is an electrolyte which undergoes complete ionization when dissolved in water at moderate concentration.

Examples:

Acids like HCl, HNO₃, H₂SO₄

Bases like NaOH, KOH

All salts like NaCl, Sodium acetate

Weak electrolyte

Weak electrolyte is an electrolyte which undergoes partial ionization when dissolved in water at moderate concentration.

Examples:

Organic acids like acetic acid, benzoic acid

Bases like ammonium hydroxide, aniline etc.

Electrolysis

A phenomenon where an electrolyte decomposes when current passes through its aqueous solution or through the molten electrolyte.

Solid electrolyte does not conduct current since the ions are bound to the lattice points in the crystal lattice. Hence the ions are not free to conduct current.

Terms connected with electrolysis

One coulomb = that quantity of current when one ampere flows for one second

Faraday = 96500 coulombs

Faraday's laws of electrolysis

First law: The amount of a substance deposited, dissolved or liberated at an electrode is directly proportional to the quantity of electricity passing through the electrolytic solution during electrolysis.

Mass of different substances discharged when a known quantity of electricity flows through their solutions can be calculated using Faraday's first law.

$$W \propto Q \text{ or } W = ZQ$$

$$W = Z.I.t \quad \text{where } Q = I.t.$$

$$\text{If } Q = 1$$

$$Z = W$$

I – current in Amp

t – time in seconds

Q - charge in coulombs

where 'Z' - Proportionality constant known as electrochemical equivalent

Unit of Z : g/C or kg/C

$$W = \frac{\text{Equivalent mass} \times \text{Number of coulombs flowing}}{96500}$$

$$\text{Equivalent mass} = \text{Electrochemical equivalent} \times 96,500$$

Ex:

(a) Atomic mass of silver = 108

Charge carried by 1 mole of Ag^+ = 1F

Charge needed to deposit 108g of Ag from Ag^+ = 96,500 C or 1F

\therefore Eq. mass of Ag = atomic mass = 108

(b) Atomic mass of copper = 63.5

Charge carried by 1 mole Cu^{2+} = 2F

Charge needed to deposit 63.5g of Cu from Cu^{2+} = 2F

\therefore Eq. mass of copper = $63.5/2 = 31.75$

(c) Charge needed to deposit 27g of Al from Al^{3+} = 3F

Eq. mass of Al = $27/3 = 9$

(d) 22.4L of oxygen at NTP = 1 mole = 32g = 4 equivalents

\therefore Charge needed to liberate 1 mole of oxygen = 4F

(e) 22.4L of Hydrogen at NTP = 1 mole = 2.016 = 2 equivalents

\therefore Charge needed to liberate one mole of hydrogen = 2F

Eq. mass = ECE \times 96500

Faraday's second law of electrolysis

When same quantity of electricity passes through solutions of different electrolytes the amounts of substances liberated at the electrodes are directly proportional to their chemical equivalents (equivalent masses)

The law can be illustrated by passing same quantity of electric current through three voltmeters containing solutions of H_2SO_4 , CuSO_4 and AgNO_3 respectively. In the first voltmeter, hydrogen and oxygen will be liberated; in the second, copper will be deposited and in the third, silver will be deposited.

$$\frac{\text{Mass of hydrogen}}{\text{Mass of copper}} = \frac{\text{Equivalent mass of hydrogen}}{\text{Equivalent mass of copper}}$$

$$\text{or } \frac{\text{Mass of copper}}{\text{Mass of silver}} = \frac{\text{Equivalent mass of copper}}{\text{Equivalent mass of silver}}$$

$$\text{or } \frac{\text{Mass of silver}}{\text{Mass of hydrogen}} = \frac{\text{Equivalent mass of silver}}{\text{Equivalent mass of hydrogen}}$$

it is observed that by passing one coulomb of electric charge,

Hydrogen evolved = 0.00001036 g

Copper deposited = 0.0003292 g

and silver deposited = 0.001118 g

These masses are in the ratio of their equivalent masses. From these masses, the amount of electric charge required to deposit one equivalent of hydrogen or copper or silver can be calculated.

$$\text{For hydrogen} = \frac{1}{0.00001036} = 96500 \text{ coulomb}$$

$$\text{For copper} = \frac{31.78}{0.0003292} = 96500 \text{ coulomb}$$

$$\text{For silver} = \frac{107.88}{0.001118} \approx 96500 \text{ coulomb}$$

This follows that 96500 coulomb of electric charge will deposit 1 g equivalent of any substance. 96500 coulomb is termed as one faraday and is denoted by F.

Again according to first law,

$$W = Z \times Q$$

When Q = 96500 coulomb, W becomes gram equivalent mass (E).

$$\text{Thus, } E = Z \times 96500$$

$$\text{Or } Z = \frac{E}{96500}$$

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

Fundamental unit of charge:

As 1 g equivalent of an ion is liberated by 96500 coulomb, it follows that charge carried by 1 g equivalent of an ion is 96500 coulomb. If the valency of an ion is 'n', then 1 mole of these ions will carry a charge of nF coulomb. 1 g mole of an ion contains 6.02×10^{23} ions. Then

$$\text{The charge carried by an ion} = \frac{nF}{6.02 \times 10^{23}} \text{ coulomb}$$

$$\text{For } n = 1, \text{ the fundamental unit of charge} = \frac{F}{6.02 \times 10^{23}}$$

$$\text{i.e., } \frac{96500}{6.02 \times 10^{23}} \approx 1.6 \times 10^{-19} \text{ coulomb}$$

or 1 coulomb = 6.24×10^{18} electrons

The rate of flowing of electric charge through a conductor is called the electric current.

$$\text{Electric current} = \frac{\text{Electric charge}}{\text{Time}}$$

$$\mathbf{1 \text{ ampere}} = \frac{1 \text{ coulomb}}{1 \text{ second}}$$

volt is a unit of electrical potential difference. It is defined as potential energy per unit charge.

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}} = \frac{1 \text{ newton} \times 1 \text{ metre}}{1 \text{ ampere} \times 1 \text{ second}}$$

Electrical energy = Potential difference x Quantity of charge

$$= V \times Q$$

$$= V \times i \times t \quad (i = \text{ampere}; t = \text{second})$$

$$= \text{Watt-second}$$

Faraday's law for gaseous electrolytic product

We know that, $W = ZQ$

$$= Zit$$

$$W = \frac{itE}{96500} \text{ ----- (i)}$$

where, $Z = E/96500$

Equation (i) is used to calculate the mass of solid substance dissolved or deposited at an electrode.

For the gases, we use

$$V = \frac{itV_e}{96500}$$

Where, $V =$ Volume of gas evolved at STP at an electrode

$V_e =$ Equivalent volume.

Conductance:

It is the reciprocal of resistance, i.e., $G = \frac{1}{R}$. Its units are ohm^{-1} or Ω^{-1} or mhos or Siemens (S).

Specific conductance (k)

Specific conductivity (or simply called conductivity): It is the reciprocal of specific resistance, i.e., $k = \frac{1}{\rho}$. Hence, from $R = \rho \cdot \frac{\ell}{a}$, $\frac{1}{G} = \frac{1}{k} \cdot \frac{\ell}{a}$ or $k = G \times \frac{\ell}{a}$

If $\ell = 1 \text{ cm}$ and $a = 1 \text{ cm}^2$, $k = G$. Hence, conductivity is the conductance of 1 cm^3 of the conductor.

Units of $k = \text{ohm}^{-1} \text{ cm}^{-1}$ or SI units are $\Omega^{-1} \text{ m}^{-1}$ or S m^{-1}
 $(1 \text{ S cm}^{-1} = 100 \text{ S m}^{-1})$

It is the conductance of a material of length l metre and cross sectional area of 1 metre square.

It is also equal to the conductance of one metre cube of the electrolyte

Unit : Sm^{-1}

On diluting, the number of particles per unit volume decreases and hence specific conductance decreases

Specific resistance or Resistivity: If ' ℓ ' is the length of a conductor and ' a ' is its area of cross-section, $R \propto \frac{\ell}{a}$ or $R = \rho \frac{\ell}{a}$ where ρ is called **specific resistance** or **resistivity**.

The units of resistivity are $\Omega \text{ cm}$ or in SI units, these are $\Omega \text{ m}$.

Equivalent conductivity (Λ_{eq}): Equivalent conductivity of a solution at dilution V is the conductance of the all the ions produced when

(i) one gram equivalent of the electrolyte is dissolved in $V \text{ cm}^3$ of the solution.

(ii) distance between the electrodes is 1 cm.

(iii) area of the electrodes is so large that the whole of solution is contained between them.

At large dilution the conductance reaches a limiting value corresponding to completion of ionization. This stage is called infinite dilution.

At infinite dilution equivalent conductance is equal to the sum of the ionic conductance of the constituent ions.

Units of equivalent conductivity = $\text{Ohm}^{-1} \text{cm}^2 \text{eq}^{-1}$ or SI units are $\text{S m}^2 \text{eq}^{-1}$

($1 \text{ S m}^2 \text{eq}^{-1} = 10^4 \text{ S cm}^2 \text{eq}^{-1}$ or $1 \text{ S cm}^2 \text{eq}^{-1} = 10^{-4} \text{ S m}^2 \text{eq}^{-1}$)

Relationship between equivalent conductivity (Λ_{eq}) and Specific conductivity (κ):

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

$$= \kappa \times \frac{1000}{\text{Normality}}$$

where V is the volume of the solution in cm^3 containing one gram equivalent of the electrolyte and C_{eq} represents the concentration of the solution in gram equivalents per litre (i.e., normality of the solution).

Molar conductance [μ]

It is the conductance due to all the ions present in a solution containing one gram molecular weight (mole) of the electrolyte

Molecular conductance increases with dilution since the total number of particles available from one mole of the electrolyte increase on dilution.

The molar conductance is related to specific conductance as $\mu = \kappa V$

V is the volume of the solution in m^3 containing one mole of the electrolyte

S. No.	Physical quantity	Unit (CGS)	Unit (SI)
1.	Conductance	Ohm^{-1}	S (siemen)
2.	Conductivity of specific conductance	$\text{Ohm}^{-1} \text{cm}^{-1}$	S m^{-1}
3.	Cell constant	cm^{-1}	m^{-1}
4.	Equivalent conductance	$\text{Ohm}^{-1} \text{cm}^2 \text{equiv}^{-1}$	$\text{Sm}^{-1} (\text{equiv L}^{-1})^{-1}$ or $\text{S m}^2 (\text{equiv}^{-1})$
5.	Molar conductance	$\text{Ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$	$\text{S m}^2 \text{mol}^{-1}$ or $\text{S m}^{-1} (\text{mol L}^{-1})^{-1}$

Mathematical relations of conductance are

$$C = \frac{1}{R} \text{ Where, } R = \text{Resistance, } C = \text{Conductance}$$

$$K = C \times \frac{\ell}{A} \quad \ell = \text{Distance between the two electrodes, } A = \text{Area of the electrodes,}$$

$$\frac{\ell}{A} = \text{Cell constant, } K = \text{Specific conductance,}$$

$$\Lambda_m = K \times \frac{1000}{M} \quad K = \text{Specific conductance, } \Lambda_m = \text{Molar conductance, } M = \text{Molarity}$$

$$\Lambda_e = K \times \frac{1000}{N} \quad \Lambda_e = \text{Equivalent conductance, } N = \text{Normality}$$

Physical quantity	Unit
-------------------	------

R	Ohm
C	Ohm ⁻¹ or mho or siemens
K	Ohm ⁻¹ cm ⁻¹ or S m ⁻¹
Λ _m	Ohm ⁻¹ cm ² mol ⁻¹
Λ _e	Ohm ⁻¹ cm ² eq ⁻¹
ℓ/A	cm ⁻¹ or m ⁻¹

Molar conductivity (Λ_m):

Molar conductivity (Λ_m) of a solution at dilution V is the conductance of all the ions produced when conductance of all the ions produced when

(i) one mole of the electrolyte is dissolved in V cm³ of the solution.

(ii) distance between the electrodes in 1 cm.

(iii) area of the electrodes is so large that the whole of the solution is contained between them.

Relationship between Molar conduction (Λ_m) and Specific conductivity (κ):

$$\Lambda_m \kappa \times V = \kappa \times \frac{1000}{C_m} = \kappa \times \frac{1000}{\text{Molarity}}$$

where V is volume of solution in cm³ containing one mole of the electrolyte and C_m is molar concentration (moles L⁻¹)

Units of molar conductivity:

= Ohm⁻¹ cm² mol⁻¹ or SI units are S m² mol⁻¹

(1 S m² mol⁻¹ = 10⁴ S cm² mol⁻¹ or 1 S cm² mol⁻¹ = 10⁻⁴ S m² mol⁻¹)

Expressions for Λ_{eq} and Λ_m in terms of SI units:

$$\Lambda_{eq} (\text{S m}^2 \text{ eq}^{-1}) = \frac{\kappa (\text{S m}^{-1})}{\text{Normality (g eq m}^{-3})} \text{ or } = \frac{\kappa (\text{S m}^{-1})}{1000 \text{ L m}^{-3} \times \text{Normality (g eq L}^{-1})}$$

$$\Lambda_m = \frac{\kappa (\text{S m}^{-1})}{\text{Molarity (mol m}^{-3})} \text{ or } = \frac{\kappa (\text{S m}^{-1})}{1000 \text{ L m}^{-3} \times \text{Molarity (mol L}^{-1})}$$

Conductivity cell:

A special type of glass vessel having two platinum electrodes at a fixed distance apart in which the experimental solution is taken is called conductivity cell.

Cell constant of a conductivity cell:

As already explained, $\kappa = G \times \frac{\ell}{a}$. For a particular conductivity cell, ℓ = distance

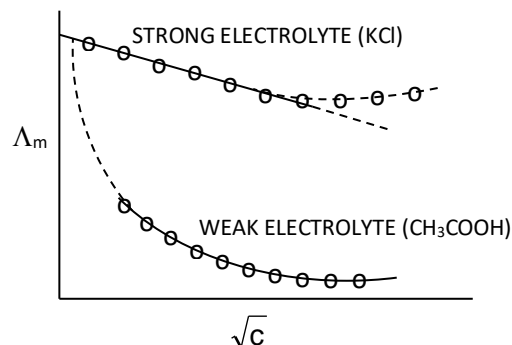
between the electrodes, and a = area of cross-section of the electrodes. Hence, $\frac{\ell}{a}$ is

constant, called **cell constant**. It is represented by G*. Thus, Specific conductivity = Conductance × Cell constant, i.e., $\kappa = G \times G^*$.

Units of cell constant: As $G^* = \frac{\ell}{a}$, therefore, $G^* = \frac{\text{cm}}{\text{cm}^2} = \text{cm}^{-1}$ or m⁻¹ in SI units.

Variation of Conductance, Conductivity, Equivalent and molar conductivities with dilution:

- Effect of dilution:** Conductance increases, specific conductivity decreases, equivalent and molar conductivity increase with dilution.
- Variation of molar conductivity with concentration:** For a strong electrolyte, it is given by **Debye-Huckel-Onsager equation**, viz, $\Lambda_m = \Lambda_m^0 - A\sqrt{c}$ where A is a constant depending upon the nature of the solvent and temperature, Λ_m^0 is the molar conductivity at infinite dilution (called **limiting molar conductivity**). Thus, a plot of Λ_m vs. \sqrt{c} will be linear with slope = -A. However, some deviation is observed at higher concentration as shown in the figure below. Further, for a weak electrolyte, Λ_m is much less and the increase with dilution is slow in the beginning and then steep at large dilutions.



- Reasons for increase of Λ_m with dilution:** Molar conductivity of a strong electrolyte increases with dilution because interionic attractions decrease with dilution. Small deviations at higher concentration are due to larger interionic attractions. Molar conductivity of a weak electrolyte increases with dilution because dissociation increases with dilution.
- Inability to determine Λ_m^0 experimentally for a weak electrolyte:** Molar conductivity at infinite dilution (Λ_m^0 or Λ_m^∞) for a strong electrolyte can be found by extrapolation to zero concentration but that of weak electrolyte cannot be thus found. Moreover, at infinite dilution, though the dissociation is complete, concentration of ions per unit volume is so low that conductivity cannot be measured accurately. The problem was solved by Kohlrausch.

Kohlrausch's law:

Definition: It states that "Equivalent conductivity of any electrolyte at infinite dilution is the sum of the equivalent conductivities of the cations and the anions",

$$\text{i.e., } \Lambda_{\text{eq}}^0 = \lambda_{\text{c}}^0 + \lambda_{\text{a}}^0$$

or molar conductivity of an electrolyte at infinite dilution is the sum of the ionic conductivities of the cations and the anions each multiplied by the number of ions present in one formula unit of the electrolyte", e.g., for A_xB_y .

$$\Lambda_m^0 = x \times \lambda_{A^y}^0 + y \times \lambda_{B^{x-}}^0$$

Application of Kohlrausch law

- In calculating λ^∞ of a weak electrolytes:** It is based on the fact that λ^∞ of an ion remains constant at constant temperature, no matter of which electrolyte it makes a part.

For example: λ^∞ of CH_3COOH can be calculated as follows

$$\begin{aligned} \lambda^\infty_{\text{CH}_3\text{COOH}} &= \lambda^\infty_{\text{CH}_3\text{COO}^-} + \lambda^\infty_{\text{H}^+} \\ &= \lambda^\infty_{\text{CH}_3\text{COOH}} + \lambda^\infty_{\text{Na}^+} - \lambda^\infty_{\text{Na}^+} + \lambda^\infty_{\text{H}^+} + \lambda^\infty_{\text{Cl}^-} - \lambda^\infty_{\text{Cl}^-} \end{aligned}$$

$$\therefore \lambda^\infty_{\text{CH}_3\text{COOH}} = \lambda^\infty_{\text{CH}_3\text{COONa}} + \lambda^\infty_{\text{HCl}} - \lambda^\infty_{\text{NaCl}}$$

where CH_3COONa , HCl and NaCl , all are strong electrolytes and their λ^∞ can be measured in laboratory.

- (ii) **In calculating the degree of ionization of a weak electrolyte:** Degree of ionization of weak electrolyte (α) is by given by the following expression:

$$\alpha = \frac{\lambda_v}{\lambda^\infty}$$

Where $\lambda = \frac{\kappa \times 1000}{N}$. and λ^∞ is calculated from Kohlrausch law as explain in application (i).

- (iii) **In calculating the solubility (S) and solubility product (K_{sp}) of sparingly soluble salts:** suppose we want to measure solubility of BaSO_4 then we prepare a saturated solution of it and measure its conductivity (κ)

$$\text{Now, } \lambda_m^\infty = \lambda_m^v \text{ for a sparingly soluble salt} = \frac{\kappa \times 1000}{M}$$

Molar concentration = M = solubility of BaSO_4 can be calculated.

Then $K_{sp} = [\text{Ba}^{2+}] [\text{SO}_4^{2-}] = S^2$

Hence, K_{sp} can also be calculated.

Electrochemical cells:

It is a device which is used to convert the chemical energy of an indirect spontaneous redox reaction into electric energy, i.e, electricity.

Electrode potential

The potential developed when a metal is in equilibrium with the solution of its own ions is called electrode potential.

Standard Electrode Potential:

The potential developed when a metal is in equilibrium with one molar solution of its own ions at 298 K is called standard electrode potential.

Galvanic cell or Voltaic cell:

A device in which electricity is produced using a spontaneous chemical reaction involving oxidation and reduction is called galvanic cell or voltaic cell. Eg: Daniel cell.

Eg: **Daniel cell is represented as $\text{Zn} / \text{ZnSO}_4 (\text{aq}) // \text{CuSO}_4 (\text{aq}) / \text{Cu}$**

Negative electrode is called left hand electrode and the positive electrode is called right hand electrode.

Formation of a cell

1. When 2 electrodes are linked by a salt bridge a cell is formed.
2. A cell can be in general represented as $M_1 / M_1^{n+} // M_2^{n+} / M_2$.
3. During the operation of the cell oxidation takes place at the negative left hand electrode
It is called the anode. Reduction takes place at the positive right hand electrode. It is called the cathode
4. The electrons flow from anode to the cathode in the external circuit.

EMF of a cell

1. $E_{\text{cell}} = E_{\text{RHS}} - E_{\text{LHS}}$
(RHS electrode has higher electrode potential among the two electrode systems)
 $E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$

$$E_{\text{cell}} = E_{+\text{ve}} - E_{-\text{ve}}$$

Emf of Daniel cell is the sum of tendency of zinc to lose electrons + tendency of Cu^{+2} to gain electrons.

Emf = Reduction potential of Cu + Oxidation potential of

$$\text{Zn} = +0.34 + 0.76 = 1.10 \text{ V}$$

Note:

The latest convention is to express the electrode potential only in terms of reduction. Hence it is also called reduction potential.

E_{cell} = Reduction potential of Cu – Reduction potential of

$$\text{Zn} = 0.34 - (-0.76) = +1.10 \text{ V}$$

If copper and silver electrodes are combined then silver electrode with higher reduction potential forms the RHS electrode.

$$E_{\text{cell}} = E_{\text{Ag}} - E_{\text{Cu}}$$

2. Nernst equation for electrode potential is

$$E = E^{\circ} + \frac{2.303 RT}{nF} \log \frac{[\text{Oxidised state}]}{[\text{Reduced state}]}$$

Where,

E = electrode potential

E° = standard electrode potential

n = valency of the metal ion

F = one faraday = 96500 coulombs

T = temperature in Kelvin

R = gas constant = $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

Nernst equation for the EMF of a cell: $M_1 / M_1^{n+} // M_2^{n+} / M_2$.

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} + \frac{0.059}{n} \log \frac{[M_2^{n+}]}{[M_1^{n+}]} \quad \text{where } E^{\circ}_{\text{cell}} = E^{\circ}_{M_2} - E^{\circ}_{M_1}$$

3. The EMF of a cell increases when the concentration of the solution of RHS electrode increases or the concentration of the solution of LHS electrode is decreased.
4. To evaluate E°
- a) For Daniel cell

$$E_{\text{cell}} (\text{Daniel}) = (E^{\circ}_{\text{Cu}} - E^{\circ}_{\text{Zn}}) = 0.34 - (-0.76) = 1.1 \text{ volt.}$$

b) The EMF of Daniel cell constructed with 0.1 M CuSO_4 and 0.01 M ZnSO_4 is

$$\begin{aligned} E_{\text{cell}} &= E^{\circ}_{\text{cell}} + \frac{0.059}{n} \log \frac{[M_2^{n+}]}{[M_1^{n+}]} = 1.1 + \frac{0.059}{2} \log \frac{[\text{Cu}^{2+}]}{[\text{Zn}^{2+}]} \\ &= 1.1 + \log \frac{0.1}{0.01} = 1.1295 \text{ V.} \end{aligned}$$

5. Nernst equation for metal-metal ion electrode system

$E = E^{\circ} + 0.59 \log [M^{n+}]$ where $[M^{n+}]$ is the molar concentration of the solution.

Application of Nernst equation

- (i) In calculation of E_{cell} and E°_{cell} (as explained above).

- (ii) In calculating the equilibrium constant of the cell reaction: When the cell reaction is at equilibrium, $\Delta G = 0$ and hence, $E_{\text{cell}} = 0$ and $Q = K_C$.

$$\text{So, } 0 = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log K_C \text{ at } 25^{\circ}\text{C}$$

$$\therefore E_{\text{cell}}^{\circ} = \frac{0.0591}{n} \log K_C \text{ (iii)}$$

K_C can be calculated from equation (iii)

- (iii) In calculating the free energy change (ΔG) of the cell reaction. It is calculated by the following equation.

$$\Delta G = -n F E_{\text{cell}}$$

$$\text{and } \Delta G = -n F E_{\text{cell}}^{\circ}$$

Note: EMF or E_{cell} is not a state function but ΔG is a state function.

- (iv) In calculating ΔH and ΔS of the cell reaction: From Gibb's Helmholtz equation.

$$\Delta G = \Delta H + T \left(\frac{d(\Delta G)}{dT} \right)_P \text{ but } \Delta G = -n F E_{\text{cell}}$$

$$\therefore -n F E_{\text{cell}} = \Delta H - n F T \frac{dE_{\text{cell}}}{dT} \quad \text{or, } E_{\text{cell}} = -\frac{\Delta H}{nF} + T \left(\frac{dE_{\text{cell}}}{dT} \right)$$

$$\text{or, } \Delta H = nF \left[T \left(\frac{dE_{\text{cell}}}{dT} \right) - E \right] \text{ (iv)}$$

$\frac{dE_{\text{cell}}}{dT}$ is called temperature coefficient of EMF hence ΔH can be calculated from

equation (iv)

$$\text{Also } \Delta G = \Delta H = -T \Delta S \text{ (v)}$$

So, ΔS can also be calculated from (v)

- (v) In predicting the spontaneity of cell reaction

If $\Delta G < 0$, i.e. $E_{\text{cell}} > 0$ then the cell reaction is spontaneous.

If $\Delta G = 0$, i.e. $E_{\text{cell}} = 0$ then the cell reaction is at equilibrium.

+ If $\Delta G > 0$, i.e. $E_{\text{cell}} < 0$ then the cell reaction is not spontaneous.

- (vi) In calculating the solubility and solubility product of a sparingly soluble salt.



sat. solution

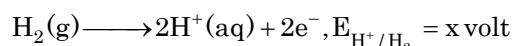
$$E_{\text{cell}} = 0.00 - \frac{0.0591}{n} \log \frac{[\text{Ag}^+]_{\text{anode}}}{[\text{Ag}^+]_{\text{cathode}}} \text{ (vi)}$$

But $[\text{Ag}^+]_{\text{anode}} = \text{solubility of AgCl} = S$ and $[\text{Ag}^+]_{\text{cathode}} = C$

So 'S' can be calculated from equation (vi)

And then, $K_{\text{sp}} (\text{AgCl}) = [\text{Ag}] [\text{Cl}^-] = S \times S = S^2$

- (vii) In calculating the pH of a solution in the cell. For example, consider the following half cell,



1.0 atm

$$\therefore \text{pH} = \frac{E_{\text{H}^+/\text{H}_2}}{0.0591} \text{ (viii)}$$

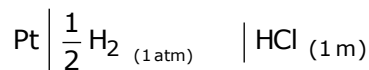
So, pH of solution can be calculated from the above equation (viii) for this half cell.

Factors affecting electrode potential

1. the nature of the electrode material(E^0)
2. valency (n)
3. temperature(T)
4. molar concentration of the solution (c)

Standard hydrogen electrode

A standard hydrogen electrode is obtained by passing pure hydrogen gas through 1 molar HCl solution in the presence of an inert metal like platinum at 25° C & 101.3 KPa pressure.



Working:

Standard hydrogen electrode is connected to an experimental electrode to form a cell. The emf of the cell is determined by experiment

$$\text{emf} = E_{\text{exp}} - E_{\text{H}_2}^0 \quad \text{emf} = E_{\text{exp}} - 0 \quad \therefore \text{emf} = E_{\text{exp}}$$

Demerits:

- 1) It is very difficult to pass hydrogen gas always at 101.3 KPa pressure.
- 2) The platinum foil can be damaged by the impurities in the hydrochloric acid and the gas.
- 3) This electrode cannot be used in the presence of an oxidising agent because hydrogen is a reducing agent.
- 4) It is difficult to maintain concentration of HCl at 1 molar throughout the experiment.
- 5) Equilibrium is attained very slowly. Therefore hydrogen gas should be passed for a long time.

Uses:

- 1) Standard hydrogen electrode is used as a primary standard electrode. The electrode potential of other electrodes can be determined using SHE.
- 2) It is used to determine the pH of the solution.

Note: Potential of hydrogen electrode is $E_{\text{H}_2} = E_{\text{H}_2}^0 + \log [\text{H}^+] = 0.05915 \log [\text{H}^+]$

$E_{\text{H}_2}^0$ which is the potential of standard hydrogen electrode

(Constructed with 1 M HCl and H_2 gas passed under a pressure of 101.3k Pa at 298 K) is taken as zero.

Since $-\log [\text{H}^+] = \text{pH}$, $E_{\text{H}_2} = -0.059 \text{ pH}$

Electrochemical series

1. A series of electrode systems arranged in the increasing order of reduction potential is called electrochemical series.

Li^+ / Li	-3.05 V	It is a series of electrode systems arranged in the increasing order of their standard reduction potential from top to bottom
K^+ / K	-2.97 V	
Na^+ / Na	-2.71 V	
$\text{Al}^{+3} / \text{Al}$	-1.66 V	
$\text{Zn}^{+2} / \text{Zn}$	-0.76 V	
$\text{H}^+ / \text{H}_2, \text{Pt}$	0.0 V	
$\text{Cu}^{+2} / \text{Cu}$	+ 0.34 V	
Ag^+ / Ag	+ 0.8 V	
$\text{Au}^{+3} / \text{Au}$	+1.5 V	

2. Applications of electrochemical series
 - i) The reducing power of elements decreases from top to bottom.

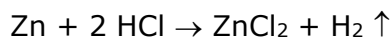
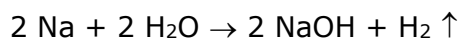
- ii) Reduction potential increases from top to bottom
- iii) The ease of reduction increases with the increase in the reduction potential.

Illustration:

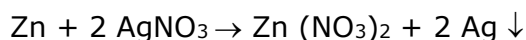
Reduction potential of Zn = - 0.76 V and Cu = + 0.34 V

Hence Cu⁺⁺ ions are easily reduced to Cu by Zn, but copper cannot reduce Zn⁺² to Zn

3. A metal found above hydrogen in the series displaces hydrogen from an acid and water.



4. A metal found above in the series displaces another found below.



5. Any two electrode systems can be combined to form a cell.

The electrode system with more negative potential (found above in the series) forms the left hand electrode.

When silver and aluminium electrodes are connected the emf of cell is $E_{\text{Ag}}^0 - E_{\text{Al}}^0$

$$E_{\text{Ag}}^0 = 0.80, E_{\text{Al}}^0 = -1.66 \text{ V}$$

$$\text{emf} = 0.80 - (-1.66) = 0.80 + 1.66 = + 2.46 \text{ V}$$

Some Commercial Cells:

Difference between a cell and a battery: An electrochemical cell which can be used to produce electric current for practical use is known as a commercial cell or simply a cell. If a number of cells are connected in series, the arrangement is called a battery.

Types of Commercial Cells/Batteries:

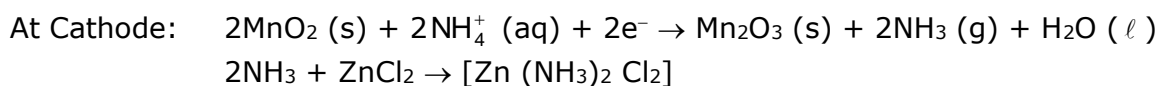
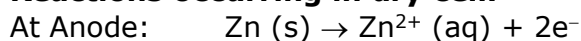
- (i) **Primary cells** are those which cannot be recharged, e.g., dry cell and mercury cell.
- (ii) **Secondary cells** are those which can be recharged, e.g., lead storage battery and Ni - Cd cell.
- (iii) **Fuel cells** are those in which energy produced from the combustion of fuels can be converted into electrical energy, e.g., H₂ - O₂ fuel cell.

Main Features of Different Cells / Batteries:

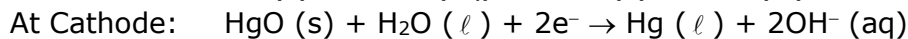
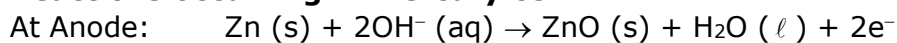
	Name of the cell/battery	Anode	Cathode	Electrolyte
(i)	Dry cell	Zinc	Graphite	MnO ₂ + C (touching cathode) NH ₄ Cl + ZnCl ₂ (touching anode)
(ii)	Mercury cell	Zinc	Graphite	HgO + KOH (moist)
(iii)	Lead storage battery	Lead	Lead dioxide	H ₂ SO ₄ (38%)
(iv)	Ni-Cd cell	Cadmium	Nickel dioxide	KOH sol.
(v)	H ₂ - O ₂ fuel cell	Porous carbon contg catalysts (H ₂ passed)	Porous carbon contg catalysts (O ₂ passed)	Conc. aq. KOH sol

Reactions occurring in different cells:

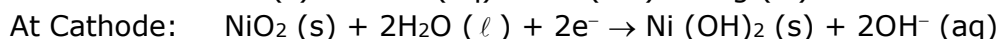
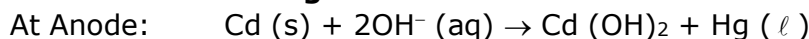
(i) Reactions occurring in dry cell:



(ii) Reactions occurring in mercury cell:

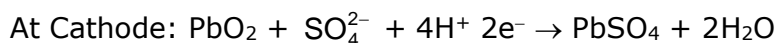


(iii) Reactions occurring in Ni – Cd cell:

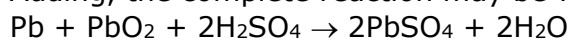


(iv) Reactions occurring in lead storage battery:

(a) Reactions occurring during discharge:



Adding, the complete reaction may be written as

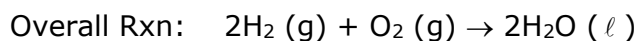
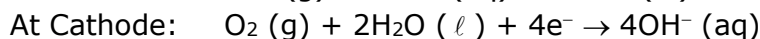


As H_2SO_4 is consumed, the voltage of the battery drops.

(b) Reactions occurring during charging:

Now the cell acts as an electrolytic cell as electrical energy is supplied to it. Reactions occurring are the reverse of the above reactions, i.e., PbSO_4 is reduced to Pb at cathode and PbSO_4 is oxidized to PbO_2 at the anode.

(v) Reactions occurring in $\text{H}_2 - \text{O}_2$ fuel cell:



Advantages of Fuel Cells:

- (i) They never become dead so long as H_2 and O_2 are supplied.
- (ii) They do not cause any pollution problem.
- (iii) They have high efficiency.

Efficiency of a Fuel cell:

$$\eta = \frac{\text{Useful work done (electrical energy produced)}}{\text{Enthalpy of combustion (chemical energy produced)}}$$

i.e., $\eta = \frac{\Delta G}{\Delta H} = \frac{-n FE_{\text{cell}}}{\Delta H}$ (ΔG = free energy change)

It is generally 60 – 70% which is much better than thermal power plants.

Corrosion:

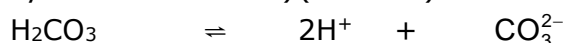
Corrosion is the process of change of metal surface into salts like oxides, sulphides, carbonates etc. due to attack of atmospheric gases.

Rust: Chemically, it is hydrated ferric oxide, $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$

Theory of Rusting: Rusting of iron can be explained on the basis of **electrochemical theory** as follows:

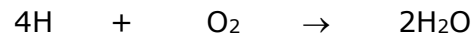


(layer on the surface)(from air)



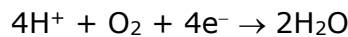
At anodic sites: $\text{Fe} \rightarrow 2\text{Fe}^{2+} + 2\text{e}^-$

At cathodic sites: $\text{H}^+ + \text{e}^- \rightarrow \text{H}$

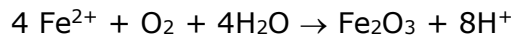


(Dissolved)

We can write the reaction at the cathodic sites directly as

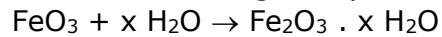


Further, ferrous ions formed at the anodic sites react with the dissolved O_2 to form Fe_2O_3 .



(Dissolved)

Fe_2O_3 then undergoes hydration to form hydrated ferric oxide (rust)



Factors which enhance corrosion:

- (i) Presence of impurities in the metal (pure metals do not corrode)
- (ii) Presence of moisture (e.g., in rainy season)
- (iii) Presence of electrolytes (e.g., saline water)

Prevention of corrosion: Corrosion can be prevented by the following methods:

- (i) Barrier protection by oil/grease layer, paints or electroplating.
- (ii) Sacrificial protection by coating the metal with more electropositive metal (e.g., Zn called galvanization).