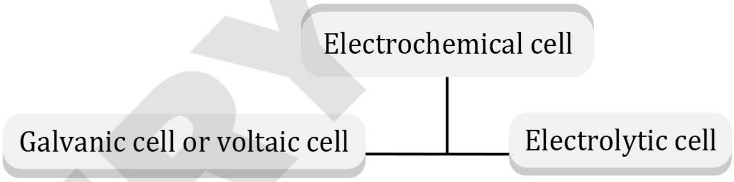
ELECTROCHEMISTRY

Introduction

Electrochemistry is the branch of physical chemistry which deals with the study of interconversion of chemical energy and electrical energy,


Electrochemical cell

Galvanic cell or voltaic cell

Electrolytic cell

Chemical energy → Electrical energy occurs through a Spontaneous redox reaction

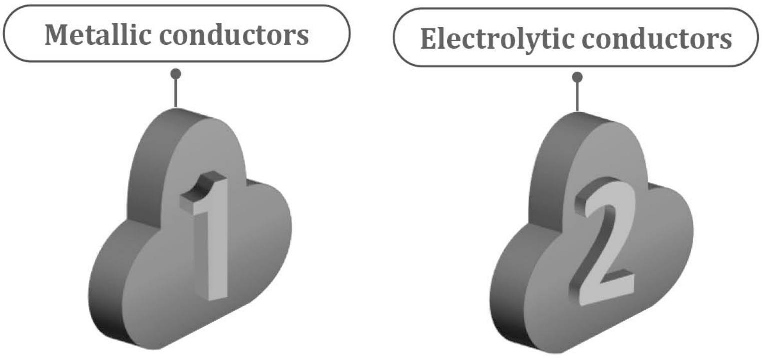
Electrical energy → Chemical energy occurs through a non-spontaneous redox reaction

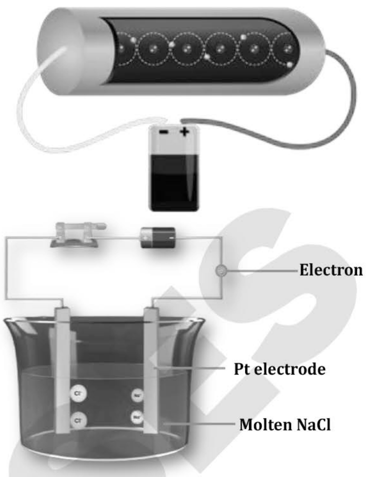
Conductors

Substances which allow electric current to flow through them are called conductors.

Examples - Metals, Aqueous solution of acids, bases and salts, fused salts, impure water etc.

Conductors are of two types – (1) Metallic conductors or electronic conductors
(2) Electrolytic conductors or ionic conductors





(1) **Metallic conductors:** The conductors which conduct electric current by the movement of electrons without undergoing any chemical change are known as metallic conductors.
Metals - Cu, Ag, Fe, Al etc, non metals - graphite

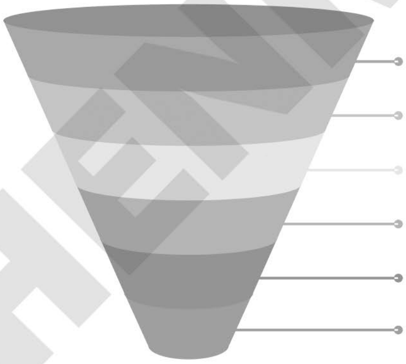
(2) **Electrolytic conductors:** Those substances which conduct the electric current through ions in aqueous solution or in molten state are called as electrolytic conductors.

- **Strong electrolytes:** Electrolytes which get ionized completely in an aqueous solution are called as strong electrolytes.
  Ex. : Salts, strong acids and strong bases in water.
- **Weak electrolytes:-** Electrolytes which do not get ionized completely in an aqueous solution are called as weak electrolytes.
  Ex. : CH_3COOH, HCN, NH_3, amine, etc.

Difference between metallic and electrolytic conductors

	Metallic conductor	Electrolytic conductor
(i)	Charge carriers are free electrons.	Charge carriers are free ions.
(ii)	Flow of electricity takes place without any chemical change.	Flow of electricity takes place by chemical changes at electrodes.
(iii)	No transfer of matter takes place.	Transfer of matter takes place in the form of ions.
(iv)	Resistance is due to vibration of Kernels.	Resistance is due to inter ionic attraction and viscosity of medium.
(v)	The resistance increases with the increase in temperature	The resistance decreases with the increase in temperature.
(vi)	Faraday's laws of electrolysis are not followed.	Faraday's laws of electrolysis are followed.

Electrolytic Conductance



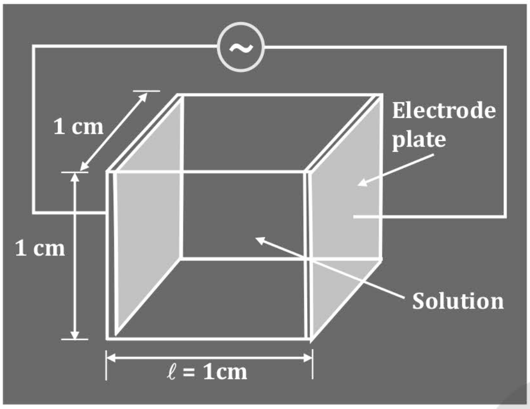
(a) Resistance (R)
(b) Conductance (G)
(c) Specific resistance/Resistivity (ρ)
(d) Specific conductance/ Conductivity (κ)
(e) Molar conductivity or Molar conductance (λ_m or Λ_m)
(f) Equivalent conductivity or Equivalent Conductance (λ_{eq} or Λ_{eq})

(a) **Resistance (R):-** Metallic and electrolytic conductors obey ohm's law according to which the resistance of a conductor is the ratio of the applied potential difference (V) to the follow of current (I). $\boxed{R=\frac{V}{I}}$ R is expressed in ohms.

(b) **Conductance (G):-** It is the property by virtue of which it favours flow of current. The conductance of a conductor is equal to reciprocal of resistance $\boxed{G=\frac{1}{R}}$ unit of G is **mho** or **ohm^{-1}** or **Siemens (S)**.

(c) **Specific resistance/Resistivity (ρ):-** The resistance (R) of a conductor is directly proportional to its length (ℓ) and inversely proportional to its area of cross section (A).

$$R \propto \frac{\ell}{A} \quad ; \quad R = \rho\frac{\ell}{A}$$



$$R = \rho\frac{\ell}{A} \quad ; \quad \rho = R.\frac{A}{\ell}$$

If ℓ = 1 cm, A = 1 cm^2, therefore ρ = R

∵ V = A × ℓ = 1 cm^3

Therefore, the resistance offered by 1 cm^3 electrolytic solution is known as resistivity.

Unit of ρ → ohm cm

(d) **Specific conductance/ Conductivity (κ) :-**

It is defined as the reciprocal of specific resistance, $\kappa = \frac{1}{\rho}$

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

$$\frac{1}{\rho} = \frac{1}{R}.\frac{\ell}{A}$$

$$\kappa = G \times G^*$$

Specific conductance = Conductance × Cell constant

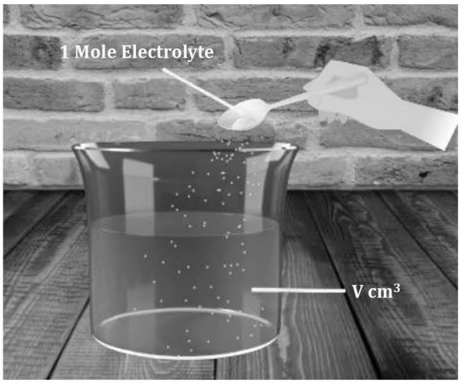
Hence specific conductivity of a solution is defined as the conductance offered by 1 cm^3 of electrolytic solution. Unit of κ is ohm^{-1} cm^{-1}

Cell constant: $G^* = \frac{\ell}{A}$; Its unit is cm^{-1}

(e) **Molar conductivity or Molar conductance (Λ_m or λ_m) :-** It is defined as the conductance of all the ions produced by one mole of electrolyte present in the given volume of solution.

$$\Lambda_m = \kappa \times V$$

V = Volume of solution containing 1 mol of electrolyte.

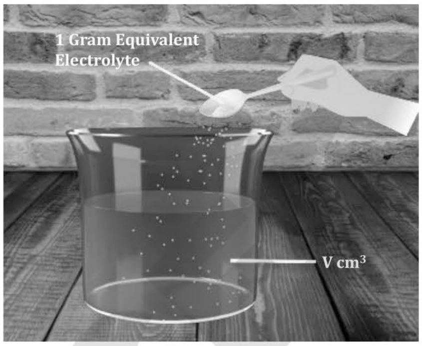


If concentration of solution is M - mol per litre then

$$\Lambda_m = \frac{\kappa \times 1000}{M}$$ Unit → ohm^{-1} cm^2 mol^{-1}

(f) Equivalent conductivity or Equivalent conductance (Λ_{eq} or λ_{eq}) :-

It is defined as the conductance of all the ions produced by one gram equivalent of the electrolyte in the given volume of solution.



$\therefore\ \Lambda_{eq} = \kappa \times V$

V = Volume of solution containing 1 g-eq of electrolyte.

If concentration of solution is N - gram equivalent per litre then

$\Lambda_{eq} = \dfrac{\kappa \times 1000}{N}$ Unit → $ohm^{-1}\,cm^2\,eq^{-1}$

Relation between $\Lambda_{eq.}$ and Λ_m

$$\Lambda_m = \frac{\kappa \times 1000}{M} \text{ and } \Lambda_{eq.} = \frac{\kappa \times 1000}{N}$$

We know that Normality = Valency Factor × Molarity. So $\Lambda_{eq} = \dfrac{\Lambda_m}{V.F.}$

Illustration 1:

The resistance of a 1N solution of salt is 50 Ω, Calculate the equivalent conductance of the solution, if the two platinum electrodes in solution are 2.1 cm apart and each having an area of 4.2 cm².

Solution:

$$\kappa = \frac{1}{\rho} = \frac{1}{R}\left(\frac{\ell}{A}\right) = \frac{1}{50} \times \frac{2.1}{4.2} = \frac{1}{100} \text{ and } \Lambda_{eq.} = \frac{\kappa \times 1000}{N} = \frac{1}{100} \times \frac{1000}{1} = 10\ ohm^{-1}\,cm^2\,eq^{-1}$$

Illustration 2:

Which of the following has maximum molar conductivity?

(i) 0.08 M solution and its specific conductivity is $2 \times 10^{-2}\ \Omega^{-1}\,cm^{-1}$.

(ii) 0.1 M solution and its resistivity is 50 Ω cm.

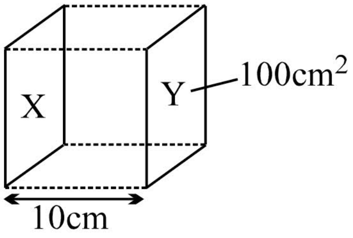
Solution:

(i) $\Lambda_m = \dfrac{\kappa \times 1000}{M} = 2 \times 10^{-2} \times \dfrac{1000}{0.08} = 250\ \Omega^{-1}\,cm^2\,mol^{-1}$

(ii) $\Lambda_m = \dfrac{\kappa \times 1000}{M}$, $\because \kappa = \dfrac{1}{\rho}$, $\therefore \Lambda_m = \dfrac{1}{50} \times \dfrac{1000}{0.1} = 200\ \Omega^{-1}\,cm^2\,mol^{-1}$

So, the molar conductivity of 0.08 M solution is greater than 0.1 M solution

Illustration 3:



The conductance of a salt solution (AB) measured by two parallel electrodes of area 100 cm² separated by 10 cm was found to be 0.0001 Ω^{-1}. If the volume enclosed between the two electrodes contain 0.5 mol of salt. What is the molar conductivity ($Scm^2\,mol^{-1}$) of the salt at same concentration?

(1) 0.01 (2) 0.02 (3) 2×10^{-5} (4) None of these

Solution:

$G^* = \dfrac{\ell}{A} = \dfrac{10}{100} = 0.1$; G = 0.0001 S; V = 100 × 10 = 1000 cm³ = 1 litre

$\kappa = G\,G^* = 0.1 \times 0.0001 = 10^{-5}$

$\Lambda_m = \dfrac{\kappa \times 1000}{M} = \dfrac{10^{-5} \times 1000}{0.5} = 0.02\ S\,cm^2\,mol^{-1}$

Factors Affecting Electrolytic Conductance

(a) **Inter ionic attraction :-** If the inter ionic attraction between ions of solute is more, then the conductance of solution will be less.

(b) **Polarity of solvent :-** If the solvent has a high-dielectric constant then the ionization and conductance of solution will be higher.

(c) **Viscosity of medium :-** On increasing the viscosity of medium, the conductance of solution decreases.

(d) **Temperature :-** As the temperature of electrolytic solution is increased, the conductance of Solution increases because K.E. of the ions increases and all the types of attraction forces decrease and the viscosity of the medium decreases.

(e) **Hydrated size :** Due to hydration of ions conductance decreases.

(f) **Dilution :-**

(i) On increasing the dilution conductance (G) increases.

For a strong electrolyte, on dilution, interionic force of attraction decreases, therefore, conductance increases.

For a weak electrolyte, on dilution, degree of dissociation (α) increases, therefore, conductance increases.

(ii) On dilution, specific conductance decreases because number of ions in 1 ml solution decreases.

(iii) On dilution, equivalent and molar conductance increases because normality and molarity decreases.

Determination of Molar Conductance of Electrolytes at Infinite Dilution (Λ_m^∞ or Λ_m^0)

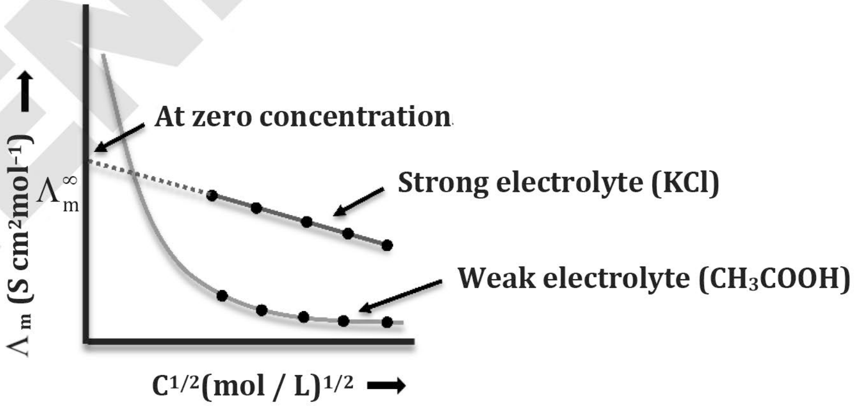
Debye Hucskel Onsäger equation –

$$\Lambda_m = \Lambda_m^\infty - b\sqrt{C} \quad \text{[only for strong electrolyte]}$$

Where Λ_m = molar conductance at concentration C,

Λ_m^∞ = molar conductance at infinite dilution,

b = constant and its value is same for a particular type of electrolyte.



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If a graph is plotted between Λ_m v/s $\sqrt{C}$ a straight line is obtained for a strong electrolyte. On extrapolation, this line touches the Λ_m axis. Therefore, Λ_m^∞ for strong electrolyte can be found out from intercept. For weak electrolyte the slope of curve is not constant. So, it cannot be extrapolated to obtain Λ_m^∞.

Kohlrausch’s Law of Independent Migration of Ions

At infinite dilution, when dissociation of electrolyte is complete; each ion makes a definite contribution towards equivalent conductivity of any electrolyte irrespective of the nature of other ion associated with it. This law states that the equivalent conductivity of any electrolyte at infinite dilution (Λ_{eq}^{∞}) is the sum of equivalent ionic conductivities of the cation and anion given by the electrolytes at infinite dilution.

$$\Lambda_{eq}^{\infty} = \Lambda_{c}^{\infty} + \Lambda_{a}^{\infty}$$

Where Λ_{c}^{∞} = equivalent conductance of cation at infinite dilution.

Λ_{a}^{∞} = equivalent conductance of anion at infinite dilution.

For $A_xB_y \rightarrow xA^{y+} + yB^{x-}$

In terms of molar conductance of cation and anion

$$\Lambda_{eq}^{\infty} = \frac{1}{y}\lambda_{m(c)}^{\infty} + \frac{1}{x}\lambda_{m(a)}^{\infty}$$

Where $\lambda_{m(c)}^{\infty}$ = Limiting molar conductance of cation.

$\lambda_{m(a)}^{\infty}$ = Limiting molar conductance of anion.

y = charge on cation

x = charge on anion

$$\Lambda_{m}^{\infty} = x\Lambda_{m(c)}^{\infty} + y\Lambda_{m(a)}^{\infty}$$

Where x = Stoichiometric coefficient of cation

y = Stoichiometric coefficient of anion

Illustration 4:

Calculate Λ_{m}^{∞} of oxalic acid, given that

Λ_{eq}^{∞} $Na_2C_2O_4$ = 400 S cm² eq⁻¹

Λ_{m}^{∞} H_2SO_4 = 700 S cm² mol⁻¹

Λ_{eq}^{∞} Na_2SO_4 = 450 S cm² eq⁻¹

Solution:

Λ_{m}^{∞} $H_2C_2O_4$ = 700 + 800 – 900 = 600 S cm² mol⁻¹

Applications of Kohlrausch's Law

(a) To calculate conductance of weak electrolyte.

(b) To calculate degree of dissociation :

$$\text{Degree of dissociation, } \alpha = \frac{\Lambda_{eq}}{\Lambda_{eq}^{\infty}} = \frac{\text{equivalent conductance at a given concentration}}{\text{equivalent conductance at infinite dilution}}$$

or

$$\alpha = \frac{\Lambda_{m}}{\Lambda_{m}^{\infty}} = \frac{\text{molar conductance at a given concentration}}{\text{molar conductance at infinite dilution}}$$

(c) To calculate dissociation constant of weak electrolyte

$$K_a = \frac{C\alpha^2}{(1-\alpha)}$$

If $\alpha \le 0.5$ then $K_a = C\alpha^2$

(d) To calculate Solubility (S) and K_{SP} of a sparingly soluble salt.

Sparingly soluble salt means salt with very less solubility

Saturated solution of a sparingly soluble salt can be considered as infinitely dilute solution.

In a saturated solution of a sparingly soluble salt, $\Lambda_m = \frac{\kappa \times 1000}{M}$

M = Solubility (S).

Λ_m (saturated) = $\Lambda_m^{\infty} = \frac{\kappa \times 1000}{\text{Solubility}}$; $S = \frac{\kappa \times 1000}{\Lambda_m^{\infty}}$

Illustration 5:

Equal volumes of 0.015 M CH_3COOH & 0.015 M NaOH are mixed together. What would be the molar conductivity of mixture if the conductivity of CH_3COONa is 6.3×10^{-4} S cm^{-1} ?

(1) 8.4 S cm^2 mol^{-1}
(2) 84 S cm^2 mol^{-1}
(3) 4.2 S cm^2 mol^{-1}
(4) 42 S cm^2 mol^{-1}

Solution:

[Salt] = $\frac{0.015}{2}$ M; $\Lambda_m = \frac{6.3 \times 10^{-4} \times 1000}{0.015/2}$ = 84 S cm^2 mol^{-1}

Illustration 6:

The dissociation constant of n-butyric acid is 1.6×10^{-5} and the molar conductivity at infinite dilution is 380×10^{-4} S $m^2 mol^{-1}$. The specific conductance of the 0.01 M acid solution is

(1) 1.52×10^{-5} S m^{-1}
(2) 1.52×10^{-2} S m^{-1}
(3) 1.52×10^{-3} S m^{-1}
(4) None

Solution:

$K_a = \frac{c\alpha^2}{1-\alpha} \Rightarrow 1.6 \times 10^{-5} = \frac{0.01 \times \alpha^2}{1-\alpha}$

Assuming $\alpha <<< 1$ So, $1 - \alpha \simeq 1$ and solving further we get

$\alpha = \sqrt{\frac{1.6 \times 10^{-5}}{0.01}} = \sqrt{1.6 \times 10^{-3}} = 0.04$; $\alpha = \frac{\Lambda_m}{\Lambda_m^{\infty}}$; $\Lambda_m = 0.04 \times 380 \times 10^{-4}$

$$\Lambda_m = \frac{\kappa \times 10^{-3}}{M}$$

$$\kappa = \frac{0.04 \times 380 \times 10^{-4} \times 0.01}{10^{-3}} = 1.52 \times 10^{-2}\ S\,m^{-1}$$

Illustration 7:

The conductivity of a saturated solution of Ag_3PO_4 is 9×10^{-6} Sm^{-1} and its equivalent conductivity is 1.50×10^{-4} S m^2 eq^{-1}. The K_{sp} of Ag_3PO_4 is

(1) 4.32×10^{-18}
(2) 1.8×10^{-9}
(3) 8.64×10^{-13}
(4) None of these

Solution:

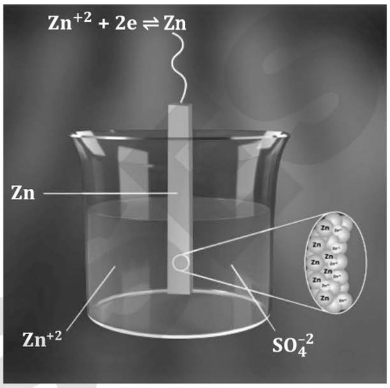
$\Lambda_{eq} = \kappa \times \frac{1000}{N}$; $1.50 \times 10^{-4} \times 10^{4} = 9 \times 10^{-6} \times 10^{-2} \times \frac{1000}{N}$; $N = 6 \times 10^{-5}$

$S = M = \frac{N}{n_f} = \frac{6 \times 10^{-5}}{3} = 2 \times 10^{-5}$ mol L^{-1}

$$Ag_3PO_{4(s)} \rightleftharpoons \underset{3S}{3Ag^+} + \underset{S}{PO_4^{3-}}$$

$K_{sp} = (3S)^3 . S = 27.S^4$
$= 27 \times (2 \times 10^{-5})^4 = 4.32 \times 10^{-18}$

Electrode Potential

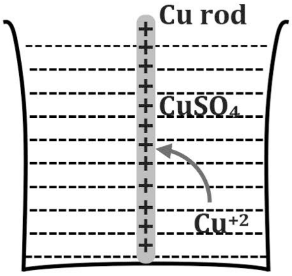


- The potential developed between metal electrode and its ions in solution is known as electrode potential.
- The potential developed between metal electrodes and the solution of its ions at 1 M concentration at 1 bar pressure and 298 K is known as **standard electrode potential.**
- There are two types of electrode potential :-

(a) Oxidation Potential (O.P.)

- The electrode potential for oxidation half reaction

  $M(s) \rightarrow M^{+n}(aq) + ne^- \; ; \; E_{M/M^{n+}} = O.P.$
- Tendency to get oxidised.
- **Greater the O.P. greater will be the tendency to get oxidised.**



(b) Reduction Potential (R.P.)

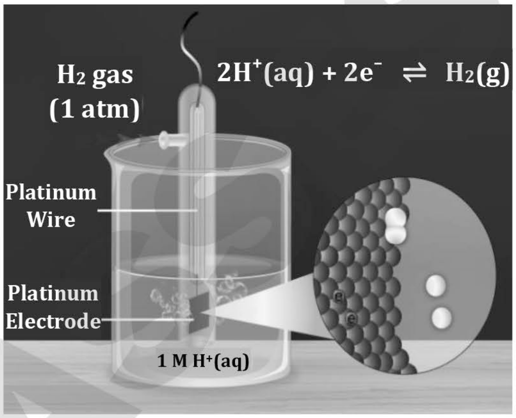
- The electrode potential for reduction half reaction

  $M^{+n}(aq) + ne^- \rightarrow M(s) \; ; \; E_{M^{n+}/M} = R.P.$
- Tendency to get reduced.
- **Greater the R.P., greater will be the tendency to get reduced.**

- Electrode potential depends upon :
  - Concentration of the solution.
  - Nature of the metal.
  - Pressure and temperature conditions.

Reference Electrode

- The potential of a single electrode cannot be determined but the potential difference between two electrodes can be accurately measured using a reference electrode.
- An electrode is chosen as a reference with respect to which all other electrodes are valued.



Standard Hydrogen Electrode (SHE):

Representation: Pt, $H_2(g)$ | H^+ (1M)

When it acts as an anode

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

$$E^0_{H_2(g)/H^+(aq.)} = SOP$$

When it acts as a cathode

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

$$E^0_{H^+_{(aq.)}/H_{2(g)}} = SRP$$

- For SHE electrode potential is arbitrarily assumed to be zero.

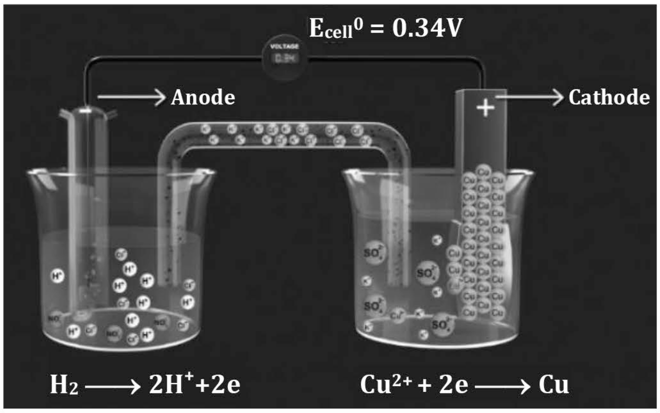
  SOP = –SRP = 0 for SHE.
- To calculate the standard potential of any other electrode a cell is coupled with standard hydrogen electrode (SHE) and it's potential is measured which gives the value of electrode potential of that electrode.

Cell Potential (E°_{Cell})

E°_{cell} = SRP of cathode – SRP of anode

E°_{cell} = SRP of cathode + SOP of anode

E°_{cell} = SOP of anode – SOP of cathode



Electrochemical Series

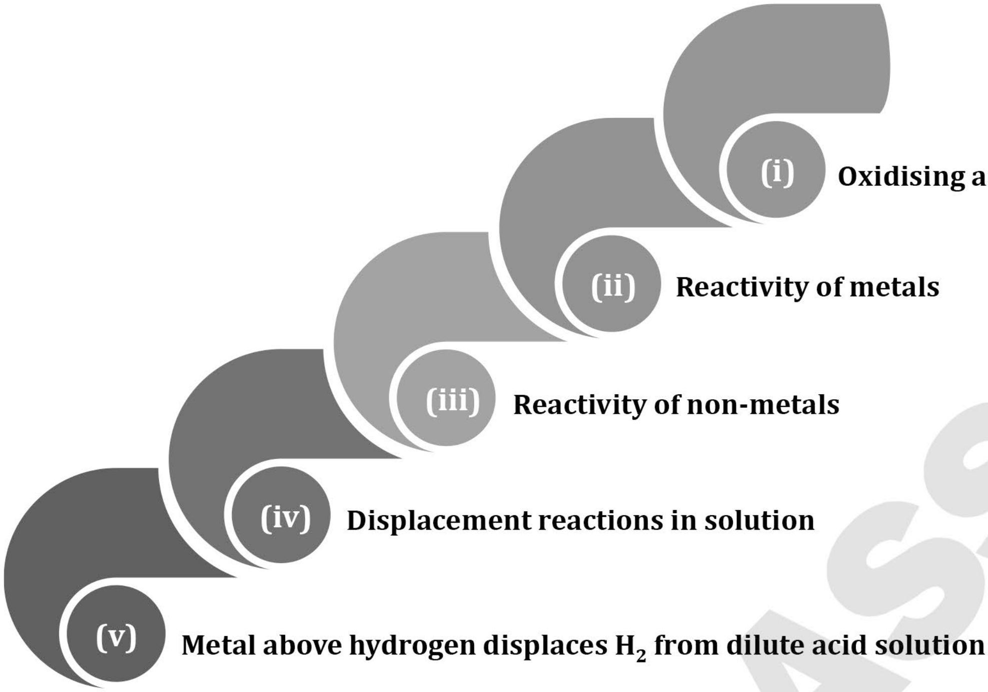
Arrangement of different elements on the basis of their SRP values is known as electrochemical series or activity series.

Electrode	Reaction	SRP (at 298 K)
Li	$Li^+ + e^- \rightarrow Li(s)$	– 3.05 V
K	$K^+ + e^- \rightarrow K(s)$	– 2.93 V
Ba	$Ba^{+2} + 2e^- \rightarrow Ba$	– 2.91 V
Ca	$Ca^{+2} + 2e^- \rightarrow Ca(s)$	– 2.87 V
Na	$Na^+ + e^- \rightarrow Na(s)$	– 2.71 V
Mg	$Mg^{+2} + 2e^- \rightarrow Mg(s)$	– 2.36 V
Al	$Al^{3+} + 3e^- \rightarrow Al$	– 1.66 V
Mn	$Mn^{+2} + 2e^- \rightarrow Mn$	– 1.18 V
H_2O	$H_2O(l) + e^- \rightarrow 1/2\ H_2 + OH^-$	– 0.828 V
Zn	$Zn^{+2} + 2e^- \rightarrow Zn(s)$	– 0.76 V
Cr	$Cr^{+3} + 3e^- \rightarrow Cr(s)$	– 0.74 V
Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	– 0.44 V
Cd	$Cd^{+2} + 2e^- \rightarrow Cd(s)$	– 0.40 V
Co	$Co^{2+} + 2e^- \rightarrow Co$	– 0.28 V
Ni	$Ni^{+2} + 2e^- \rightarrow Ni(s)$	– 0.25 V
Sn	$Sn^{+2} + 2e^- \rightarrow Sn(s)$	– 0.14 V
Pb	$Pb^{+2} + 2e^- \rightarrow Pb(s)$	– 0.13 V
H_2	$2H^+ + 2e^- \rightarrow H_2(g)$	0.00 V
Cu	$Cu^{2+} + 2e^- \rightarrow Cu(s)$	0.34 V
I_2	$I_2 + 2e^- \rightarrow 2I^-$	0.54 V
Fe	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77 V
Hg	$Hg_2^{2+} + 2e^- \rightarrow Hg(l)$	0.79 V
Ag	$Ag^+ + e^- \rightarrow Ag$	0.80 V
Hg	$Hg^{2+} + 2e^- \rightarrow Hg(l)$	0.85 V
Br_2	$Br_2 + 2e^- \rightarrow 2Br^-$	1.09 V
Pt	$Pt^{+2} + 2e^- \rightarrow Pt$	1.20 V
O_2	$\frac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O(\ell)$	1.23 V
Cl_2	$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36 V
Au	$Au^{+3} + 3e^- \rightarrow Au(s)$	1.40 V
F_2	$F_2 + 2e^- \rightarrow 2F^-$	2.87 V

↑ Increasing strength of reducing agent

↓ Increasing strength of oxidising agent

Applications of Electrochemical Series



(i) Oxidising and reducing power –

Oxidising power $\propto$ SRP $\propto \dfrac{1}{\text{SOP}}$

Reducing power $\propto$ SOP $\propto \dfrac{1}{\text{SRP}}$

(ii) Reactivity of metals –

Reactivity of metal $\propto$ SOP $\propto \dfrac{1}{\text{SRP}}$

- In ECS, reactivity of metal decreases from top to bottom.
- Li is the most reactive metal.

(iii) Reactivity of non-metals –

Reactivity of non-metal $\propto$ SRP $\propto \dfrac{1}{\text{SOP}}$

- In ECS, reactivity of non-metal increases from top to bottom.
- F_2 is the most reactive non-metal.

(iv) Displacement reactions in solution –

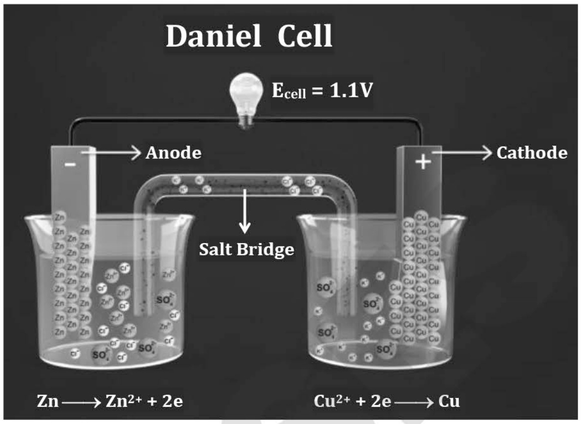
More reactive metal / non-metal displaces less reactive metal / non-metal from their solution.

- $Cu + 2\,AgNO_3 \rightarrow Cu(NO_3)_2 + 2\,Ag$
  $Ag + Cu(NO_3)_2 \rightarrow$ No reaction
- $2\,KI + Cl_2 \rightarrow 2\,KCl + I_2$
  $I_2 + 2\,KCl \rightarrow$ No reaction

(v) Metal above hydrogen displaces H_2 from dilute acid solution.

- $Zn + H_2SO_4(aq) \rightarrow ZnSO_4 + H_2(g)$
  $Cu + H_2SO_4(\text{dilute}) \rightarrow$ No reaction

Galvanic Cell



- It has two **half–cells**, each having a beaker containing a metal strip that dips in its aqueous salt solution.
- The metal strips are called **electrodes** and are connected by a conducting wire.
- Two solutions are connected by **salt bridge.**
- The oxidation and reduction half reactions occur at separate electrodes and electric current flows through the wire.

Salt Bridge and its functions:

Salt bridge is inverted U-tube containing solution of inert electrolyte with agar-agar or gelatin to convert into semi solid form.

Ions of inert electrolyte do not involve in any chemical change.

The electrolyte in salt bridge should be such that speed of it's cation is nearly equal to speed of it's anion. Ex. KCl, KNO_3, NH_4NO_3

If Ag^+, Hg_2^{+2}, Pb^{+2}, Tl^+ ions are present in a cell then KCl is not used because there can be formation of precipitate of AgCl, Hg_2Cl_2, $PbCl_2$ or TlCl.

Functions

- It connects the solution of two half cells to complete the circuit.
- It maintains the electrical neutrality of the solution in order to give continuous flow or generation of current.
- If the salt bridge is removed then voltage drops to zero.
- It prevents the liquid -liquid junction potential. The potential difference which arises between two solutions when they are brought in contact with each other.

Cell Representation:

We require two half cells to produce a galvanic cell, which can be represented by following few rules;

- The anode half-cell is always written on the left followed on the right by cathode half cell.
- The separation of two phases (state of matter) is shown by a vertical line.
- The various materials present in the same phase are shown together using commas.
- The salt bridge is represented by a double slash (||).
- The significant features of the substance like pressure of a gas, concentration of ions etc. are indicated in brackets immediately after writing the substance.

$Zn(s) \mid ZnSO_4(aq) \parallel CuSO_4(aq) \mid Cu(s)$

Nernst Equation

It gives relation between electrode potential/ EMF of cell and concentration of electrolytic solution.

Walther Nernst derived a relation between free energy change (ΔG) and Reaction quotient (Q).

$$\Delta G = \Delta G^\circ + RT \ln Q \qquad \text{...(1)}$$

where ΔG and ΔG° are free energy change and standard free energy change; ‘Q’ is reaction quotient.

$$\therefore\ -\Delta G = nFE \quad \text{and} \quad -\Delta G^\circ = nFE^\circ$$

Thus from Eq. (1), $-nFE = -nFE^\circ + RT \ln Q$

$$E = E^\circ - \frac{2.303\ RT}{nF}\log Q$$

Where - E° = Standard electrode potential,
R = Universal gas constant,
T = Temperature (in K)
F = Faraday (96500 coulomb mol^{-1}),
n = Number of moles of e^- gained, lost or transferred in balanced equation.

At 25°C, above equation may be written as $E = E^0 - \frac{0.0591}{n}\log Q$

$$E = E^0 - \frac{0.0591}{n}\log\frac{[P]}{[R]}$$

In general, for a redox cell reaction involving the transfer of n electrons

$$aA + bB \rightarrow cC + dD$$

$$E_{Cell} = E^\circ_{Cell} - \frac{0.0591}{n}\log\frac{[C]^c[D]^d}{[A]^a[B]^b} \text{ or } E_{cell} = E^o_{cell} - \frac{0.0591}{n}\log\frac{[\text{Product}]}{[\text{Reactant}]}$$

Applications of Nernst Equation

- a Calculation of electrode potential (E_{RP} or E_{OP})
- b Calculation of electrode potential and pH of hydrogen electrode
- c Calculation of EMF of cell (E_{cell})
- d Prediction and feasibility of a cell reaction
- e Calculation of equilibrium constant (K_{eq}) and ΔG°

(a) Calculation of electrode potential (E_{RP} or E_{OP}) –

$$M^{+n} + ne^- \xrightarrow{\text{Reduction}} M(s)$$

$$E_{RP} = E^0_{RP} - \frac{0.0591}{n}\log\frac{[M]}{[M^{+n}]}$$

$$E_{RP} = E^0_{RP} - \frac{0.0591}{n}\log\frac{1}{[M^{+n}]} \quad (\because \text{ active mass of } M_{(s)} = 1)$$

If $[M^{+n}]$ increases, then E_{RP} increases

(b) Calculation of electrode potential and pH of hydrogen electrode –

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

$$E_{RP} = E^0_{RP} - \frac{0.0591}{2}\log\frac{P_{H_2}}{[H^+]^2}$$

$$\because \quad E^0_{RP} = 0;\ E_{RP} = E^0_{RP} - \frac{0.0591}{2}\log\frac{1}{[H^+]^2} \qquad [P_{H_2} \text{ is taken to be 1 atm}]$$

$E_{RP} = 0.0591 \log [H^+]$

$\boxed{E_{RP} = -0.0591\ pH}$, $\boxed{E_{OP} = +0.0591\ pH}$

(c) Calculation of EMF of cell (E_{cell}) –

eg. $Zn(s) + Cu^{+2}(aq) \xrightarrow{n=2} Zn^{+2}(aq) + Cu(s)$

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

If $[Cu^{+2}]$ increases, then E_{cell} increases

If $[Zn^{+2}]$ increases, then E_{cell} decreases

(d) Prediction and feasibility of a cell reaction –

For a feasible cell reaction

$\Delta G = -ve$ ($\Delta G = -nFE_{cell}$)

$E_{cell} = +ve$

(e) Calculation of equilibrium constant (K_{eq}) and $\Delta G°$ –

From Nernst equation –

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n}\log\frac{[P]}{[R]}$$

At equilibrium, $E_{cell} = 0$ and $\frac{[P]}{[R]} = K_{eq}$

$$E^0_{cell} = \frac{0.0591}{n}\log K_{eq}$$

$$E^0_{cell} = \frac{2.303RT}{nF}\log K_{eq}$$

$$n\,F\,E^0_{cell} = 2.303\ RT\log K_{eq}$$

$$\Delta G^o = -2.303\ RT\log K_{eq}$$

★ Golden Key Points ★

- The value of electrode potential does not depend on stoichiometry of half reactions as it is an intensive property.
- Gibb's free energy is an extensive property.
- In an electrolytic cell, cathode is negative terminal whereas in Galvanic cell cathode is a positive terminal.
- Cell reaction is spontaneous, if

  $\Delta G = -ve$ or $E_{cell} = +ve$
- Cell reaction will be in equilibrium, if

  e.g. $\Delta G = 0$ or $-nFE_{cell;} = 0$ or $E_{cell} = 0$
- **Work done by a cell :**
  - (i) Let 'n' faraday charge be taken out of a cell of EMF ' E ' ; then work done by the cell will be calculated as:

    Work = Charge × Potential = nF × E
  - (ii) Work done by cell = Decrease in free energy

    so $-\Delta G = nFE$ or $W_{max} = +nFE°$, where E° is standard EMF of the cell.

Illustration 8:

Write cell representation for the following redox reaction,

$Sn^{2+}(aq) + 2Ag^{+}(aq) \rightarrow Sn^{4+}(aq) + 2Ag(s)$.

Solution:

The cell consists of a platinum wire anode dipped in Sn^{+2} solution and a silver cathode dipped in Ag^{+} solution, therefore, $Pt(s)|\ Sn^{2+}(aq), Sn^{4+}(aq)\ ||\ Ag^{+}(aq)\ |\ Ag(s)$.

Illustration 9:

Calculate the EMF of a Daniel cell when the concentration of $ZnSO_4$ and $CuSO_4$ are 0.001 M and 0.1 M respectively. The standard EMF of the cell is 1.1 V.

Solution:

$Zn(s) + CuSO_4 \rightarrow ZnSO_4 + Cu$

$$E_{cell} = E^0_{Cell} - \frac{0.0591}{2}\log\frac{\left[Zn^{2+}\right]}{\left[Cu^{2+}\right]}$$

$$= 1.1 - \frac{0.0591}{2}\log\frac{10^{-3}}{10^{-1}} = 1.159\ V$$

Illustration 10:

Calculate E^0 and E for the cell $Sn\ |\ Sn^{2+}(1M)\ ||\ Pb^{2+}(10^{-3}M)\ |\ Pb$, $E^0(Sn^{2+}|\ Sn) = -0.14V$, $E^0(Pb^{2+}|\ Pb) = -0.13\ V$. Is cell representation correct?

Solution:

$$E^0_{cell} = E^0_{Pb^{+2}/Pb} - E^0_{Sn^{+2}/Sn} = -0.13 - (-0.14) = +0.01\ V$$

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

$$= +0.01 - \frac{0.0591}{2}\log\left[\frac{1}{10^{-3}}\right] = -0.078\ V \text{ cell with not work}$$

So, cell representation is not correct.

Illustration 11:

Calculate the equilibrium constant for the reaction $Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$,

[Given: $E^0_{Ce^{4+}/Ce^{3+}} = 1.44\ V$; $E^0_{Fe^{3+}/Fe^{2+}} = 0.68\ V$]

Take $\frac{2.303\ RT}{F} = 0.06$ at 25 °C, $\log 4.68 = 0.67$

Solution:

$Fe^{2+} + Ce^{4+} \rightleftharpoons Fe^{3+} + Ce^{3+}$

$$E^\circ = 1.44 - 0.68 = 0.76V = \frac{0.06}{1}\log K_C;\ K_C = 4.64 \times 10^{12}$$

Illustration 12:

The 0.1 M copper sulphate solution in which copper electrode is dipped at 25^0C. Calculate the electrode potential of copper electrode [Given $E^0_{Cu^{+2}/Cu}$ = 0.34V]

Solution:

$Cu^{+2} + 2e^- \rightarrow Cu(s)$

$$E_{red} = E^0_{red} - \frac{0.059}{n}\log\frac{[Product]}{[Reactant]}$$

Here, n = 2 so $E = 0.34 - \frac{0.059}{2}\log 10$

$E = 0.34 - 0.03 = 0.31$ V

Illustration 13:

Calculate the EMF of the cell Cr $|Cr^{+3}$ (0.1M) || Fe^{+2} (0.01M) | Fe

(Given $E^\circ_{Cr^{+3}/Cr} = -0.75V$, $E^\circ_{Fe^{+2}/Fe} = -0.45$ V)

Solution:

Half cell reactions are –

At Anode $[Cr \rightarrow Cr^{+3} + 3e^-] \times 2$

At Cathode $[Fe^{+2} + 2e^- \rightarrow Fe] \times 3$

Cell reaction $2Cr + 3Fe^{+2} \rightarrow 2Cr^{+3} + 3Fe$

$E^\circ_{cell} = (SRP)_C - (SRP)_A = (-0.45) + (-0.75) = 0.30$ V

$$E_{cell} = E^0 - \frac{0.059}{n}\log\frac{[Product]}{[Reactant]} = 0.30 - \frac{0.059}{6}\log\frac{[0.1]^2}{[0.01]^3} = 0.30 + \frac{0.24}{6} = 0.34 \text{ V}$$

Illustration 14:

For the cell Pt(s) | H_2(0.4 atm) | H^+(pH=1) || H^+(pH = 2) | H_2 (0.1 atm) | Pt

The measured potential at 25°C is

(1) –0.1 V (2) –0.5 V (3) –0.041 V (4) –0.030 V

Solution:

Anode reaction : $H_2(0.4 \text{ atm}) \rightarrow 2H^+ (10^{-1} M) + 2e^-$

Cathode reaction : $2H^+ (10^{-2} M) + 2e^- \rightarrow H_2 (0.1 \text{ atm})$

Cell reaction $H_2(0.4 \text{ atm}) + 2H^+ (10^{-2} M) \rightarrow 2H^+ (10^{-1} M) + H_2 (0.1 \text{ atm})$

$$E = 0 - \frac{0.059}{2}\log\frac{(10^{-1})^2(0.1)}{(0.4)(10^{-4})} = -0.041V$$

Illustration 15:

If $E^o_{Au^+/Au}$ is 1.69 V & $E^o_{Au^{3+}/Au}$ is 1.40 V, then $E^o_{Au^{3+}/Au^+}$ will be

(1) 0.19 V (2) 2.945 V (3) 1.255 V (4) none

Solution:

$Au^+ + e^- \rightarrow Au(s)$ $E° = 1.69$ V ...(1) ; ΔG^o_1

$Au^{3+} + 3e^- \rightarrow Au(s)$ $E° = 1.40$ V ...(2) ; ΔG^o_2

From (2) – (1)

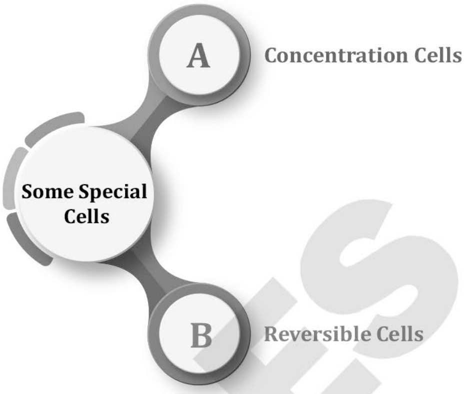
$Au^{3+} + 2e^- \rightarrow Au^+$ ...(3) ; ΔG^o_3

$\Rightarrow \Delta G^o_3 = \Delta G^o_2 - \Delta G^o_1$

$-2 \times F \times E° = -3 \times F \times 1.40 + 1 \times 1.69 \times F$

$E° = 1.255$ V

(A) Concentration Cells



A concentration cell is a form of galvanic cell that has two equivalent half cells of the same material having difference only in concentrations. For such cells anode and cathode are same so $E^\circ_{cell} = 0$.

eg. Pt, $H_2(g)$ (P_1 atm)|$H^+(C_1)$ || $H^+(C_2)$|$H_2(g)$ (P_2 atm), Pt

Anode Reaction : $H_2(P_1) \rightarrow 2H^+(C_1) + 2e^-$

Cathode Reaction : $2H^+(C_2) + 2e^- \rightarrow H_2(P_2)$

Cell Reaction : $H_2(P_1) + 2H^+(C_2) \rightarrow 2H^+(C_1) + H_2(P_2)$

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n}\log\frac{[P]}{[R]}$$

$$\text{So, } E_{cell} = 0 - \frac{0.0591}{2}\log\left[\frac{C_1}{C_2}\right]^2\frac{P_2}{P_1}$$

Case 1 : If $P_1 = P_2 = 1$ atm ;

$$E_{cell} = -\frac{0.059}{2}\log\left[\frac{C_1}{C_2}\right]^2$$

$$E_{cell} = -0.0591\log\left[\frac{C_1}{C_2}\right]$$

If $C_2 > C_1$ then $E_{cell} > 0$ and cell will be spontaneous.

Case 2 : If $C_1 = C_2$

$$E_{cell} = -\frac{0.0591}{2}\log\left[\frac{P_2}{P_1}\right]$$

$P_1 \neq P_2$

If $P_1 > P_2$ then $E_{cell} > 0$ and cell will be spontaneous.

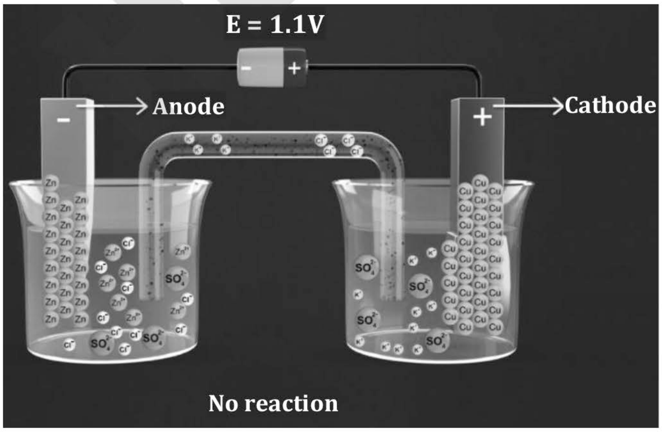
(B) Reversible Cells :

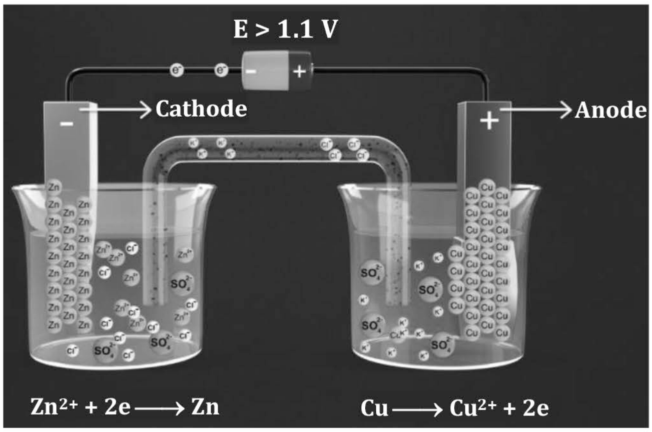
Those cell in which chemical reactions are reversed by applying external emf in opposite direction is known as reversible cells. A daniel cell is said to be reversible if it follows two conditions:

(i) When $E_{ext} > 1.1$ V (emf of daniel cell) : cell reactions are reversed

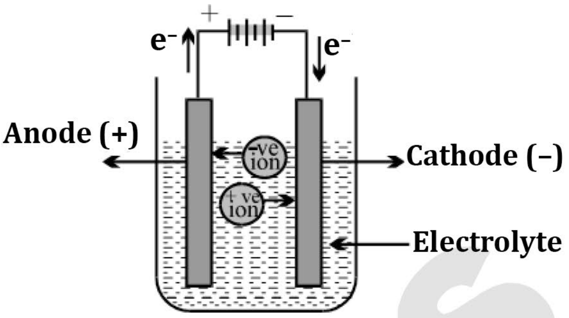
(ii) When $E_{ext} = 1.1$ V (emf of daniel cell) ; equilibrium is established.

In general, secondary cells are reversible in nature.





Electrolysis



Electrolytic cell

The process of chemical decomposition of an electrolyte by the passage of electricity is called as electrolysis or electrolytic dissociation. It is carried out in an **electrolytic cell** where electrical energy is converted into chemical energy. For electrolysis two suitable electrodes are immersed in the solution of an electrolyte. When an electric potential is applied between the electrodes, the positive ions move towards the cathode and negative ions move towards the anode. The gain of electrons (decrease in oxidation number) means reduction takes place at the cathode and loss of electrons (increase in oxidation number) means oxidation takes place at anode.

There are two aspects of electrolysis

- **(A) Qualitative aspects of electrolysis**
  - **Examples of electrolysis:**
    - **(a) Electrolysis of Molten Sodium Chloride**
    - **(b) Electrolysis of Sodium Chloride Solution**
    - **(c) Electrolysis of Molten lead bromide using inert (Pt/graphite) electrodes.**
    - **(d) Electrolysis of aq $CuSO_4$ using inert (Pt/graphite) electrode**
    - **(e) Electrolysis of aq. $CuSO_4$ using Cu electrode**
    - **(f) Electrolysis of dilute H_2SO_4**
    - **(G) Electrolysis of concentrated H_2SO_4**
- **(B) Quantitative Aspects of Electrolysis**

(A) Qualitative aspects of electrolysis :-

In qualitative aspect, products formed at electrode are identified. At electrode product formation depends on the following:

(i) Nature of electrolyte

(ii) Nature of electrodes: The metal strip at which current enters is called **anode**; anode is positively charged in an electrolytic cell. On the other hand, the electrode at which current leaves is called **cathode**. Cathode is negatively charged. There are two types of electrodes

(a) Attackable: The attackable electrodes participate in the electrode reaction. They are made up of reactive metals like Zn, Cu, Ag etc in their respective solutions. In such electrodes, atom of the metal gets oxidised into the corresponding cation, which is passed into the solution. Thus, such anode gets dissolved and their mass decreases.

- If electrode is active at cathode, metal goes on depositing and at anode metal is dissolved. The process is called electroplating.

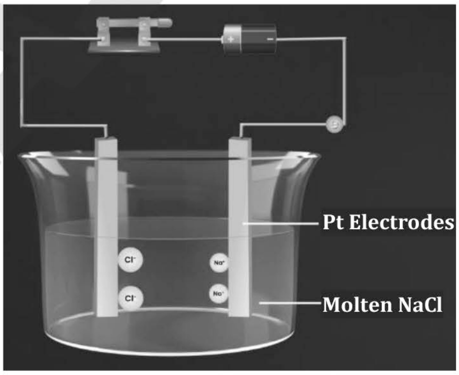
(b) Non - attackable: Non-attackable electrodes do not participate in the electrode reaction as they are made up of unreactive elements like Pt, graphite etc. Such electrodes do not dissolve and their mass remain same.

- Among the two cations, that cation is discharged at the cathode which has higher reduction potential. Among the two anions, that anion will be discharged at the anode which has lower reduction potential or higher oxidation potential.
- The discharge of NO_3^-, PO_4^{3-} and SO_4^{2-} ions at anode does not commonly take place from aqueous solution.

(iii) Concentration of electrolytic solution.

Examples of electrolysis:

(a) Electrolysis of Molten Sodium Chloride



$NaCl_{(molten)} \rightarrow Na^+ + Cl^-$

Reaction at anode (oxidation) : $2Cl^- \rightarrow Cl_2(g) + 2e^-$

Reaction at cathode (reduction) : $2Na^+ + 2e^- \rightarrow 2Na(s)$

(b) Electrolysis of Sodium Chloride Solution

On electrolysis of aqueous solution of NaCl, the possible species involved in half-reactions are Na^+, Cl^- and H_2O.

The possible cathode half-reactions are

$Na^+(aq) + e^- \rightarrow Na(s)$ $E° = -2.71V$

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E° = -0.83V$

Under the standard conditions, H_2O is to be reduced in preference to Na^+ and Hydrogen is evolved at the cathode.

The possible anode half-reactions are

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ $E° = -1.36V$

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

Under the standard-state conditions, H_2O is to be oxidized in preference to Cl^-. But since electrode potentials, depend on concentrations it turns out that when the solution is concentrated enough in Cl^-, Cl_2 is the product; but in dilute solution, O_2 is the product.

Starting with very dilute NaCl solutions, the oxidation potential of Cl^- is very negative, so H_2O is oxidised in preference to Cl^-. But as the NaCl concentration increase, the oxidation potential of Cl^- increases until eventually Cl^- is oxidized in preference to H_2O. The product changes from O_2 to Cl_2.

The half-reactions and cell reaction for the electrolysis of aqueous sodium chloride to chlorine and hydroxide ion are as follows:

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ (cathode)

$2\,Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ (anode)

––

$2H_2O(l) + 2Cl^-(aq) \rightarrow H_2(g) + Cl_2(g) + 2OH^-(aq)$

Because the electrolysis started with sodium chloride, the cation in the electrolyte solution is Na^+. On evaporation of the electrolyte solution, sodium hydroxide NaOH is obtained.

(c) Electrolysis of Molten lead bromide using inert (Pt/graphite) electrodes.

Cathode (reduction) : $Pb^{2+} + 2e^- \rightarrow Pb(s)$ $E^0 = -0.13$ V

Anode (oxidation) : $2Br^- \rightarrow Br_2(g) + 2e^-$ $E^0 = -1.09$ V

Overall reaction $Pb^{+2} + 2Br^- \rightarrow Pb(s) + Br_2(g)$

$E_{cell} = -0.13 - 1.09 = -1.22$ V

$E_{ext} > 1.22$ V

(d) Electrolysis of aq $CuSO_4$ using inert (Pt/graphite) electrode

Cathode (reduction) : $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$ $E^0 = 0.34$ V

$2H_2O(\ell) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E^0 = -0.83$V

At cathode reduction of Cu^{2+} (aq) will be preferred over reduction of water as its standard reduction potential is more, than that of water.

Thus reaction at cathode : $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Anode (oxidation) : $2\,SO_4^{2-}(aq) \rightarrow S_2O_8^{2-}(aq) + 2e^-$ $E^0 = -1.96$ V

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

At anode oxidation of water is preferred over oxidation of sulphate ion as its standard oxidation potential is more, than that of sulphate ion.

Thus reaction at anode : $2H_2O(\ell) \rightarrow O_2(g) + 4H^+ + 4e^-$

After electrolysis solution will become acidic (pH < 7)

(e) Electrolysis of aq. $CuSO_4$ using Cu electrode.

Cathode (reduction) : $Cu^{2+}(aq) + 2e^- \rightarrow Cu$ $E^0 = +0.34$ V

$2H_2O(\ell) + 2e^- \rightarrow H_2(g) + 2OH^-$ $E^0 = -0.83$ V

At cathode reduction of Cu^{2+} (aq) will be preferred over reduction of water as its standard reduction potential is more, than that of water.

Thus reaction at cathode :

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

Anode (oxidation) : $SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^-$ $E^0 = -1.96$ V

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

$Cu(s) \rightarrow Cu^{2+}(aq) + 2e-$ $E^0 = -0.34$ V

At anode oxidation of copper solid is preferred over oxidation of water and sulphate ion, as its standard oxidation potential is more than that of water and sulphate ion.

Thus reaction at anode :

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

It is an example of electrolytic refining and there will be no change in the pH and concentration of electrolyte.

(f) Electrolysis of dilute H_2SO_4 :

Cathode (reduction) $2H^+ + 2e^- \rightarrow H_2(g)$ E° = 0

$2H_2O(\ell) + 2e^- \rightarrow H_2(g) + 2OH^-$ E° = –0.83 V

due to less availability of H^+ ions, it will not participate in formation of H_2 gas therefore reduction of water will take place.

Anode (oxidation) $SO_4^{-2} \rightarrow S_2O_8^{-2} + 2e^-$ E° = –1.96 V

$2H_2O(l) \rightarrow O_2(g) + 2H^+ + 4e^-$ E° = –1.23 V

oxidation of water is preferred over oxidation of sulphate ion as its standard oxidation potential is more, than that of sulphate ion.

(g) Electrolysis of concentrated H_2SO_4

Cathode (reduction) $2H^+ + 2e^- \rightarrow H_2(g)$ E° = 0

$2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-$ E° = –0.83 V

due to reduction of H^+ ions, formation of H_2 gas takes place.

Anode (oxidation) $SO_4^{-2} \rightarrow S_2O_8^{-2} + 2e^-$ E° = –1.96 V

$2H_2O(l) \rightarrow O_2(g) + 2H^+ + 4e^-$ E° = –1.23 V

due to oxidation of SO_4^{2-} ions, formation of peroxydisulphate ion ($S_2O_8^{-2}$) takes place.

(B) Quantitative Aspects of Electrolysis

1 mole electrons = N_A number of electrons = 96500 Coulomb = 1 Faraday

$$\underset{1\,mol}{Na^+}(aq) + \underset{1\,F}{e^-} \rightarrow \underset{1\,mol}{Na}(s)$$

$$\underset{1\,mol}{Cu^{+2}}(aq) + \underset{2F}{2e^-} \rightarrow \underset{1\,mol}{Cu}(s)$$

Therefore, $$\underset{1\,mol}{M^{+n}}(aq) + \underset{nF}{ne^-} \rightarrow \underset{1\,mol}{M}(s)$$

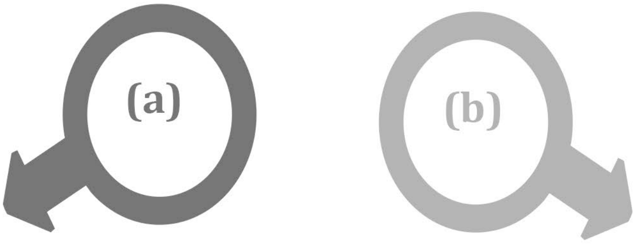
nF charge discharges = 1 mol of M^{+n} ion

$\therefore$ 1 F charge discharges = $\frac{1}{n}$ mol of M^{+n} ion

$= \frac{1}{n} \times n$ = 1 g equivalent of M^{+n} ion

Hence 1 mole e^- = 1F = 1g equivalent

Faraday's Laws of Electrolysis



First law of electrolysis Second law of electrolysis

(a) First law of electrolysis :

Amount of substance deposited or liberated at an electrode is directly proportional to amount of charge passed through the solution.

$W \propto Q$

W = amount of substance deposited, Q = charge in coulomb

$W = ZQ$

Z = electrochemical equivalent

when Q = 1 coulomb, then W = Z

Thus, amount of substance deposited or liberated by 1 coulomb charge is called **electrochemical equivalent.**

Let I ampere current is passed till 't' seconds .

Then, $Q = I\,t \qquad \therefore\ W = Z\,I\,t$

1 Faraday = 96500 coulomb = Charge on one mole electrons

One faraday is the charge required to liberate or deposit one gram equivalent of a substance at corresponding electrode.

Let 'E' is equivalent weight then 'E' gram will be liberated by 96500 coulomb.

$\therefore$ 1 Coulomb will liberate $\dfrac{E}{96500}$ gram;

By definition, $Z = \dfrac{E}{96500} \quad \therefore\ W = \dfrac{E\,I\,t}{96500}$ $\quad \dfrac{W}{E} = \dfrac{It}{96500}$ = number of g eq = number of faraday

(b) Second law of electrolysis:

When same amount of charge is passed through different electrolyte solutions connected in series then weight of substances deposited or liberated at electrodes are in ratio of their respective equivalent weights. i.e. $\dfrac{W_1}{W_2} = \dfrac{E_1}{E_2}$

Golden Key Points

Products of Electrolysis of Some Electrolytes

S.No.	Electrolyte	Electrode	Product obtained at anode	Product obtained at cathode
(i)	Aqueous NaCl	Pt or Graphite	Cl_2	H_2
(ii)	Fused NaCl	Pt or Graphite	Cl_2	Na
(iii)	Aqueous NaOH	Pt or Graphite	O_2	H_2
(iv)	Fused NaOH	Pt or Graphite	O_2	Na
(v)	Aqueous $CuSO_4$	Pt or Graphite	O_2	Cu
(vi)	Aqueous $CuSO_4$	Copper	Cu oxidises to Cu^{+2} Ions	Cu
(vii)	Aqueous $CuCl_2$	Copper	Cu oxidises to Cu^{+2} ions	Cu
(viii)	Aqueous HCl	Pt or Graphite	Cl_2	H_2
(ix)	Dilute H_2SO_4	Pt or Graphite	O_2	H_2
(x)	Conc. H_2SO_4	Pt or Graphite	$S_2O_8^{-2}$	H_2
(xi)	Aqueous $AgNO_3$	Pt of Graphite	O_2	Ag
(xii)	Dilute NaCl	Pt or Graphite	O_2	H_2

- For electrolysis, ΔG = +ve, So it is non-spontaneous process.
- In an electrolytic cell D.C. current is used.

Illustration 16:

How much electric charge is required to oxidise

(a) 1 mol of H_2O to O_2 ? (b) 1 mol of FeO to Fe_2O_3?

Solution:

(a) The oxidation reaction is :

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$$

1 mol 2 mol

$Q = 2F = 2 \times 96500 = 1.93 \times 10^5$ C

(b) The oxidation reaction is :

$$FeO + \frac{1}{2}H_2O \rightarrow \frac{1}{2}Fe_2O_3 + H^+ + e^-$$

Q = F = 96500 C

Illustration 17:

One mole of electron passes through each of the solution of $AgNO_3$, $CuSO_4$ and $AlCl_3$ when Ag, Cu and Al are deposited at cathode. The molar ratio of Ag, Cu and Al deposited are

(1) 1 : 1 : 1 (2) 6 : 3 : 2 (3) 6 : 3 : 1 (4) 1 : 3 : 6

Solution:

Deposited equivalent will be same

1 eq.Ag = 1 mol Ag

1 eq.Cu = 1/2 mol Cu

1 eq.Al = 1/3 mol Al

$\Rightarrow$ ratio $1 : \frac{1}{2} : \frac{1}{3} \Rightarrow 6 : 3 : 2$

Illustration 18:

Exactly 0.4 F electric charge is passed through three electrolytic cells connected in a series. First cell containing $AgNO_3$, second cell containing $CuSO_4$ and third cell containing $FeCl_3$ solution. How many grams of each metal will be deposited assuming only cathodic reaction in each cell ?

Solution:

The cathodic reaction in the cell are respectively,

$Ag^+ + e^- \rightarrow Ag$

1 mol 1 mol

108 g 1 F

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

1 mol 2 mol

63.5 g 2 F

and $Fe^{3+} + 3e^- \rightarrow Fe$

1 mol 3 mol

56 g 3 F

Hence, Ag deposited = 108 × 0.4 = 43.2 g

Cu deposited $= \frac{63.5}{2} \times 0.4 = 12.7$ g

and Fe deposited $= \frac{56}{3} \times 0.4 = 7.47$ g

Illustration 19:

An electric current of 100 A is passed through a molten liquid of sodium chloride for 5 hours. Calculate the volume of chlorine gas liberated at the electrode at NTP.

Solution:

The reaction taking place at anode is

$2Cl^- \rightarrow Cl_2 + 2e^-$

71.0 g   71.0 g   2 × 96500 C

= 1 mol

$Q = i \times t = 100 \times 5 \times 60 \times 60$ C

The amount of chlorine liberted by passing 100 × 5 × 60 × 60 C of electric charge.

$= \frac{1}{2\times96500} \times 100 \times 5 \times 60 \times 60 = 9.3264$ mole

Volume of Cl_2 liberated at NTP = 9.3264 × 22.4 = 208.91 L

Illustration 20:

How long a current of 2 A has to be passed through a solution of $AgNO_3$ to coat a metal surface of 80 cm^2 with 5 μm thick layer? Density of silver = 10.8 g/cm^3.

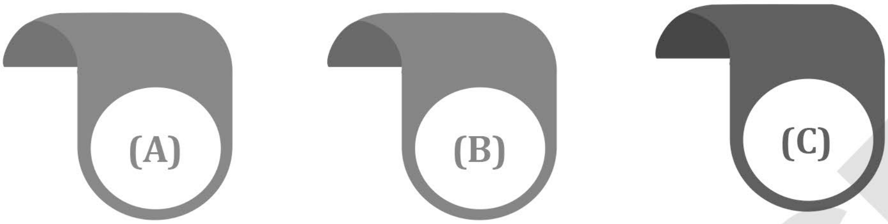
Solution:

$d = \frac{M}{V} \Rightarrow 10.8 = \frac{M}{80\times5\times10^{-4}} \Rightarrow M = 10.8 \times 400 \times 10^{-4}$

$W = \frac{E\times I\times t}{96500} \Rightarrow 10.8 \times 400 \times 10^{-4} = \frac{108\times2\times t}{96500} \Rightarrow t = 193$ s

Commercial Voltaic Cells

Batteries can be classified as primary and secondary. Primary batteries can not be returned to their original state by recharging, so when the reactants are consumed, the battery is "dead" and must be discarded. Secondary batteries are often called storage batteries or rechargeable batteries. The reactions in these batteries can be reversed; thus, the batteries can be recharged.



Primary cells: Dry cells and mercury cells — Secondary or Rechargeable Batteries — Fuel Cells

(A) Primary cells : Dry cells and mercury cells

The most familiar type of battery is the dry cell which is a compact of Leclanche cell known after its discoverer Leclanche (fig.). In this cell, the anode consists of a zinc container and the cathode is a graphite rod surrounded by powdered MnO_2 and carbon. The space between the electrodes is filled with a moist paste of NH_4Cl and $ZnCl_2$. The electrode reactions are complex, but they can be written approximately as follows.

Anode $Zn(s) \rightarrow Zn^{+2} + 2e^-$

Cathode $MnO_2 + NH_4^+ + e^- \rightarrow MnO(OH) + NH_3$

In the cathode reaction, manganese is reduced from the 4+ oxidation state to the 3+ state. Ammonia is not liberated as a gas but combines with Zn^{2+} to form $Zn(NH_3)_4^{2+}$ ion. Dry cells do not have an indenfinite life as acidic NH_4Cl corrodes the zinc container even when not in use. **Dry cells have a potential of approximately 1.25 to 1.5V.**

(B) Secondary or Rechargeable Batteries

The most important secondary cell is the lead storage battery. It consists of a **lead anode** and a grid of lead packed with **lead dioxide as cathode.** A solution of sulphuric acid (38 percent by mass or having density 1.30 gm cm^{-3}) is used as an electrolyte.

When the cell discharges, it operates as a voltaic cell. The lead is oxidised to Pb^{+2} ion and lead plates acquire a negative charge.

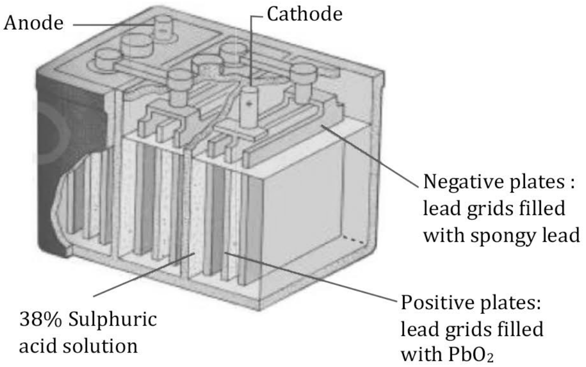


Fig: The Lead storage battery

At Anode : $Pb(s) \rightarrow Pb^{+2} + 2e^-$ ...(i)

Pb^{+2} ions combine with sulphate ions of solution to form insoluble $PbSO_4$

$Pb^{+2} + SO_4^{2-} \rightarrow PbSO_4$ (Precipitation) ...(ii)

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

The electrons given by Pb are used at cathode (PbO_2 electrode)

At Cathode : $PbO_2(s) + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$ ...(iii)

$Pb^{+2} + SO_4^{-2} \rightarrow PbSO_4$ (Precipitation) ...(iv)

$PbO_2(s) + 4H^+ + SO_4^{-2} + 2e^- \rightarrow PbSO_4(s) + 2H_2O$

Therefore the overall cell reaction during discharging

$$Pb(s) + SO_4^{2-} \rightarrow PbSO_4(s) + 2e^-$$
$$PbO_2(s) + 4H^+ + SO_4^{-2} + 2e^- \rightarrow PbSO_4(s) + 2H_2O$$
$$\overline{\hspace{10cm}}$$
$$Pb(s) + PbO_2(s) + 2H_2SO_4 \rightarrow 2PbSO_4(s) + 2H_2O$$

When a potential slightly greater than the potential of battery is applied, the battery can be recharged. During recharging the cell is operated like an **electrolytic cell** i.e. now electrical energy is supplied to it from an external source. The electrode reactions are reverse of those that occur during discharging:

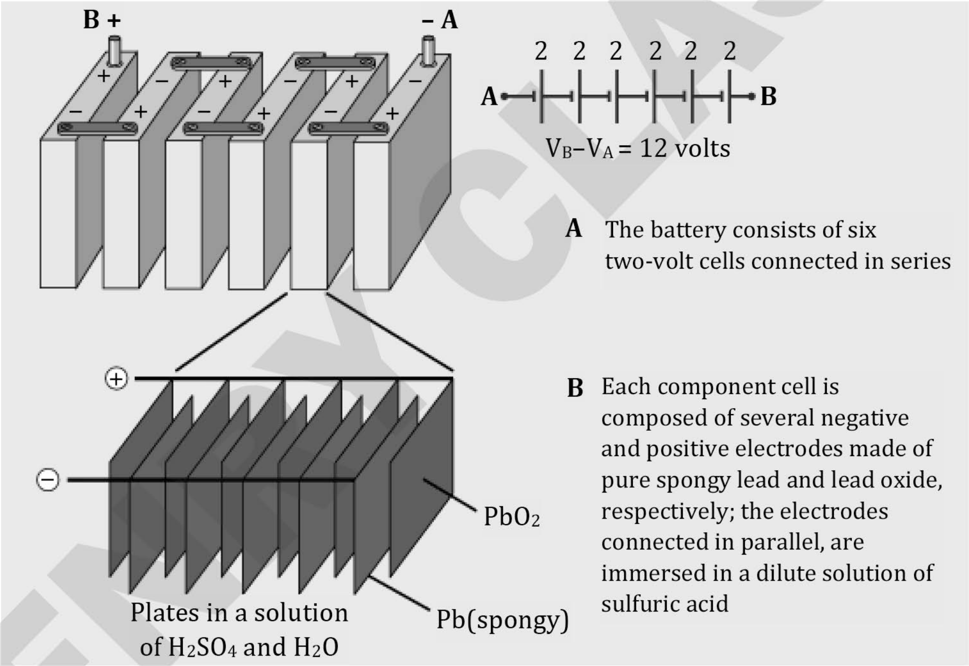
At Cathode : $PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}$

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

$$\overline{\hspace{10cm}}$$
$$2PbSO_4(s) + 2H_2O \rightarrow Pb(s) + PbO_2(s) + 2H_2SO_4$$

It is clear that H_2SO_4 is used up during the discharge & produced during reacharging reaction of cell.

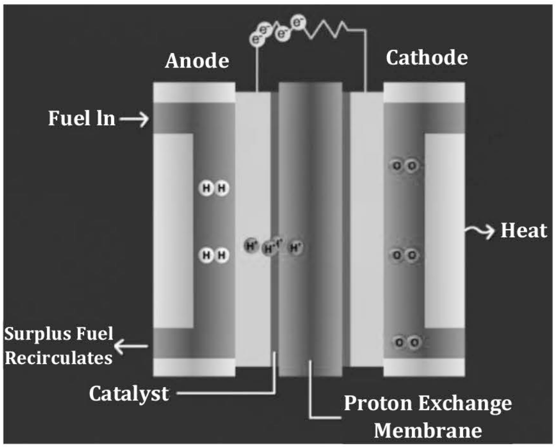
The discharging process of the storage cell is based on the principles of electrochemical cell, whereas the charging process is based upon the principles of electrolytic cells.



(C) Fuel Cells

It is possible to make batteries in which the reactants are fed continuously to the electrodes. Electrical cells that are designated to convert the free energy from the combustion of fuels such as hydrogen, carbon monoxide or methane directly into electrical energy are called **fuel cells**.

One of the most successful fuel cells uses the reaction of hydrogen with oxygen to form water (fig.). This cell has been used for electric power in the Appollo space programme.



The water vapours produced were condensed and added to the drinking water supply for the astronauts.

In the cell shown in figure hydrogen and oxygen are bubbled through a porous carbon electrode into concentrated aqueous sodium hydroxide. Catalysts are incorporated in the electrode. The electrode reactions are:

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

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

Net cell reaction : $2H_2(g) + O_2(g) \rightarrow 2H_2O(\ell)$

This cells runs continuously as long as the reactants are supplied. Since fuel cells convert the energy of a fuel directly to electricity, they are potentially more efficient than the conventional method of generating electricity on a large scale by burning hydrogen, carbon fuels or by using nuclear reactor. Although **theoretically we expect 100 percent efficiency in fuel cells, so far an efficiency of only 60-70 per cent has been attained**. Since fuel cells are efficient and free from pollution, efforts are being made to produce better commercially practical fuel cells.

Efficiency of a Fuel Cell : $\eta = \frac{(\Delta G)}{(\Delta H)} \times 100$

Main features of different cells:

S.No.	Name of the cell/Battery	Anode	Cathode	Electrolyte
(i)	Dry cell	Zinc	Graphite surrounded by MnO_2 & C.	$NH_4Cl + ZnCl_2$ (touching anode)
(iii)	Lead storage battery	Lead	Lead dioxide	H_2SO_4 (38%)
(v)	$H_2 - O_2$ fuel cell	Porous carbon containing catalysts (H_2 passed)	Porous carbon containing catalysts (O_2 passed)	Conc. aq. NaOH sol.

Corrosion

Corrosion is basically an electrochemical phenomenon. The rusting of iron, the tarnishing of silver, development of a green coating on copper and bronze are some of the examples of corrosion. Corrosion causes enormous damage to building, bridges, ships and to many other articles made of iron.

In corrosion, a metal is oxidised by loss of electrons to oxygen and forms metal oxide. Corrosion of iron(which is commonly known as rusting) occurs in presence of water and oxygen (air). Although the chemistry of corrosion is complex but it is understood that at one spot of an iron object oxidation occurs and that spot behaves as an anode.

Anode : $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$; ($E^0_{Fe^{2+}/Fe} = -0.44V$)

Electrons released at anode move through the metal and go to another spot on the metal and reduce the oxygen in presence of H^+ ions (which is believed to be available from H_2CO_3 formed due to dissolution of CO_2 in water). This spot works as a cathode :

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

Here Fe^{2+} ions move through water on the surface of the iron object. (If water present is saline, it will help more in carrying the current in the miniature cell thus formed and will enhance corrosion). The overall reaction of the miniature cell is the sum of the cathode and anode reactions as follows :

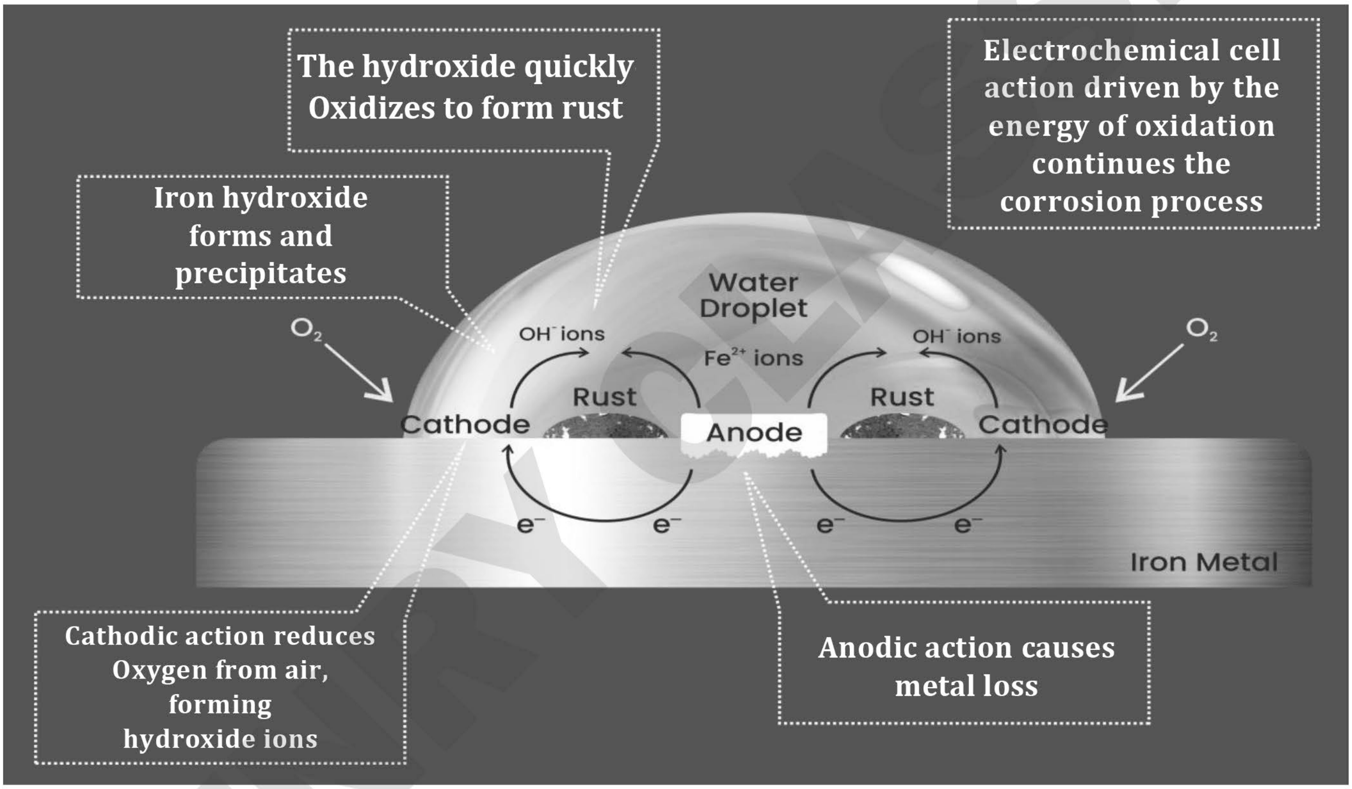
$2Fe(s) + O_2(g) + 4H^+(aq) \rightarrow 2Fe^{2+}(aq) + 2H_2O(\ell)$; $E^0_{Cell} = 1.67$ V)

The Fe^{2+} ions are further oxidised by atmospheric oxygen to Fe^{3+} (as Fe_2O_3) and comes out as rust in the form of a hydrated iron (III) oxide expressed as $Fe_2O_3 . xH_2O$

$4Fe^{2+}(aq) + O_2(g) + 4H_2O(\ell) \rightarrow 2Fe_2O_3(s) + 8H^+$

H^+ ions produced in the above reaction help further in rusting.

Impurities present in iron also enhance rusting by setting a number of miniature cells. Very pure iron does not rust quickly.



Prevention From Corrosion

Corrosion of a metal is prevented by applying protective coating (such as grease, paint, bisphenol or metal coatings) on metal surface. In case of iron this coating is done in two ways : (i) electrolysis (Cr, Ni and Cd coating) (ii) dipping iron objects in a molten metal (Zn and Sn coating). Use of zinc coating to protect iron is called Galvanisation. In galvanising iron, zinc being more reactive than iron serves as an anode and is oxidised

($E^0_{Zn^{2+}/Zn} = -0.76$V and $E^0_{Fe^{2+}/Fe} = -0.44$V).

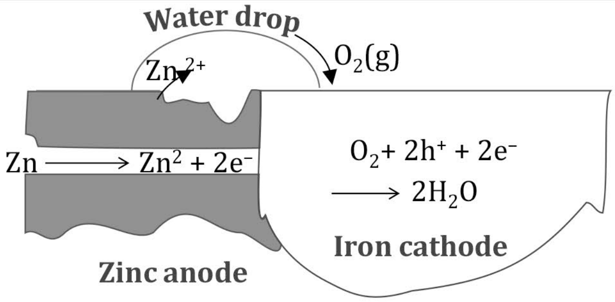


Fig. : Galvanised iron. Cathodic protection of iron in contact with zinc is provided by galvanization

Here it is important to note that iron does not rust even after zinc coating is broken which is not true in case of tin coating over iron ($E^0_{Sn^{2+}/Sn} = -0.14V$). Now if the coating is broken, iron is exposed and iron being more active than both copper and tin, is corroded. Here iron corrodes more rapidly than it does in the absence of tin. But tin protects copper in the same way as zinc protects iron ($E^0_{Cu^{2+}/Cu} = 0.34V$).

Instead of coating more reactive metal on iron, the use of such metals is made as sacrificial anode. This method of preventing iron from corrosion is called CATHODIC PROTECTION.

In this method, a plate of reactive metal (Zn or Mg) is burried beside the iron pipe or tank and connected to it by wires.

Here iron becomes **cathode** and more reactive metal becomes **anode**. The reactive metal anode is sacrificed to protect the iron. Since these reactive metal plates are oxidised quickly, they are replaced from time to time which is easy to do.

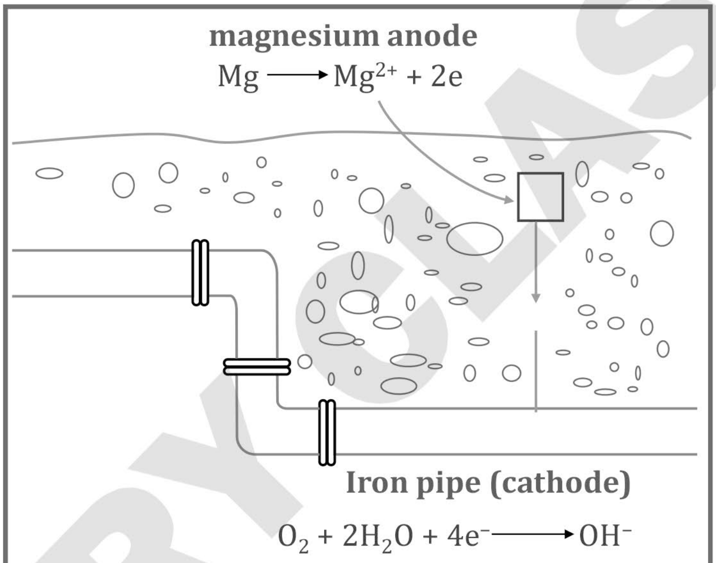


Fig. : Cathodic protection by connecting a block of magnesium to an iron pipe buried underground.